PROCESS SIMULATION OF THE CO-GASIFICATION OF BIOMASS AND POLYETHYLENE

by

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Process simulation of the co-gasification of biomass and polyethylene

I declare that the above dissertation is my own work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

I further declare that I submitted the dissertation to originality checking software and that it falls within the accepted requirements for originality.

I further declare that I have not previously submitted this work, or part of it, for examination at Unisa for another qualification or at any other higher education institution.

SIGNATURE DATE: 01 December 2021

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ABSTRACT

The aim of this study was to determine the effects of the feedstock composition, such as biomass, polyethylene and their respective blend ratios, -gasifying agents and operating conditions on the product gas composition, H_2/CO ratio of the syngas and on the Lower Heating Value (LHV) of the syngas. The synergistic interaction between the polyethylene and biomass was also evaluated.

The co- gasification of biomass (pine sawdust) and polyethylene (low- density polyethylene) was conducted using an equilibrium model in Aspen Plus. The co- gasification of biomass and polyethylene (75% PE + 25% biomass) showed that a H_2 composition of 56% was achieved at equivalence ratio (ER) equals to 0.1 from the use of oxygen, and a H_2 composition of 54.5% was achieved at ER equals to 0.34 and steam to fuel ratio (SFR) equals to 0.6 from the use of oxygen – steam mixture. High CO of 54% was achieved at ER equals to 0.22 from the use of oxygen as a gasifying agent and 52% was achieved at ER equals to 0.22 and carbon dioxide – to- carbon ratio (CO_2/C) ratio of 0.6 for the use of oxygen – carbon dioxide mixture as a gasifying agent. The recommended H_2/CO ratio of 2 was attained from the use of various gasifying agents and a Lower Heating Value of 10.7 MJ/Nm^3 was achieved at ER equals to 0.2 and Steam to Fuel Ratio (SFR) equals to 0.6 was attained from the use of oxygen – steam mixture and for an oxygen – carbon dioxide mixture as a gasifying agent, a Lower Heating Value (LHV) of the syngas of 9.2 MJ/Nm^3 was attained at ER equal to 0.1 and CO_2/C ratio of 0.6.

The co- gasification of biomass and polyethylene results indicated that an increase in the polyethylene percentage in the blended mixtures also has shown positive influence on the H_2 composition in the product gas, the H_2/CO ratio of the syngas and also on the Lower Heating Value (LHV) of the syngas. The blend ratio of (75% PE + 25% biomass) produced a high H_2 composition in the product gas and a blend ratio of (25% PE + 75% biomass) produced a high CO composition in the product gas. An increase in the polyethylene percentage in the blend mixture, using oxygen-steam mixture as a gasifying agent, increases the gas yield (GY), cold gas efficiency (CGE) and the extent of the synergistic effect. The results from this study have shown that the co- gasification of biomass and polyethylene can be a feasible study that can be used to alleviate challenges associated with a syngas of biomass with low H_2 composition, and low energy content.

Key terms: co- gasification, polyethylene, syngas, gasifying agents, biomass, blend ratio, equivalence ratio; synergistic effect.

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CHAPTER 1: INTRODUCTION

1.1. BACKGROUND

1.1.1. Dependency on the fossil fuels

The world energy demand has shown a tremendous increase due to the population growth, society urbanization and industrialization (Wang et al. 2021)**.** Fossil fuels such as coal, natural gas, and oil account for about 79.4% of world's total primary energy (Figure 1.1). However, the high consumption of the fossil fuels serves as a threat to the sustainability of the future energy supply. The risk of fossil fuels depleting in the near future, as fossil fuels, are non – renewable resource is a concern. Bhatia et al. (2021) reported that due to the tremendous rate of depletion of fossil fuels, the major exporters of oil will not be able to meet the energy demand by the next 50 years. The depletion of the fossil fuels negatively affects energy supply and energy security. Fossil fuels are also unevenly distributed across the globe, which also impacts on energy security. Furthermore, fossil fuels have a detrimental effect on the environment. The use of non- renewable fossil resources has led to a substantial amount of carbon dioxide and other greenhouse gas emissions, which has contributed to global warming and climate change.

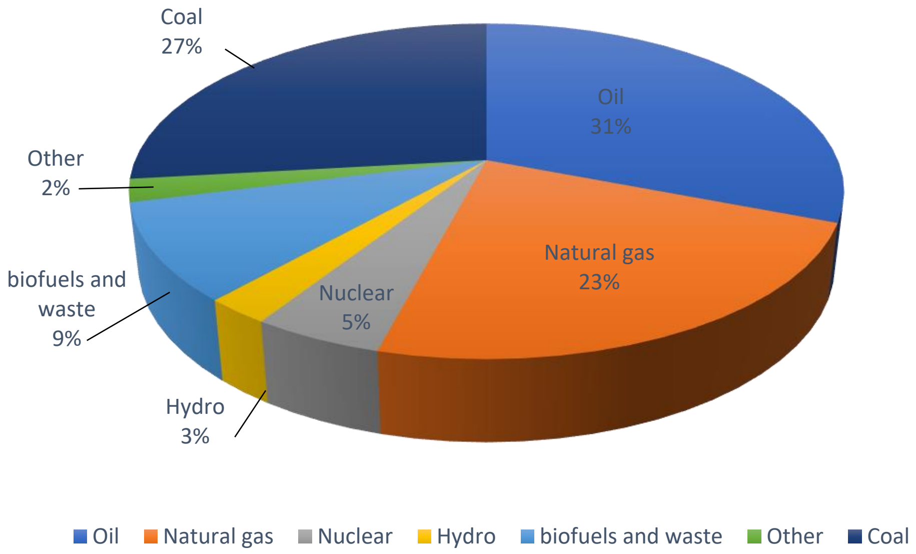


Figure. 1.1. World total primary energy supply classified according to the source of energy (Source: World Energy Outlook, IEA, 2021).

1.1.2. Consumption of fossil fuels in South Africa

South Africa is heavily reliant on fossil fuels, with close to 90% of the country's energy supply being produced from fossil fuels (Akinbami et al. 2021). In particular, coal has been the dominant energy source in South Africa for the past century. South Africa is regarded as one of the world's largest coal producers. In 2020, about 71% of the primary energy demand in South Africa was provided by coal (Figure 1.2). Furthermore, 53% of the coal in South Africa was used for electricity generation (U.S. Energy Information Administration (EIA), 2022), providing over 80% of power generation (CSIR, 2021). South Africa is also regarded as one of the leading emitters of greenhouse gases and its fossil fuel-based emissions have increased significantly with coal accounting for about 90% of the emissions (Oladipupo et al. 2022)

The issues mentioned above have resulted in an unsustainable energy system and there is urgent need for alternative solutions that will address the sustainability of energy systems in terms of economic, social, and environmental impact.

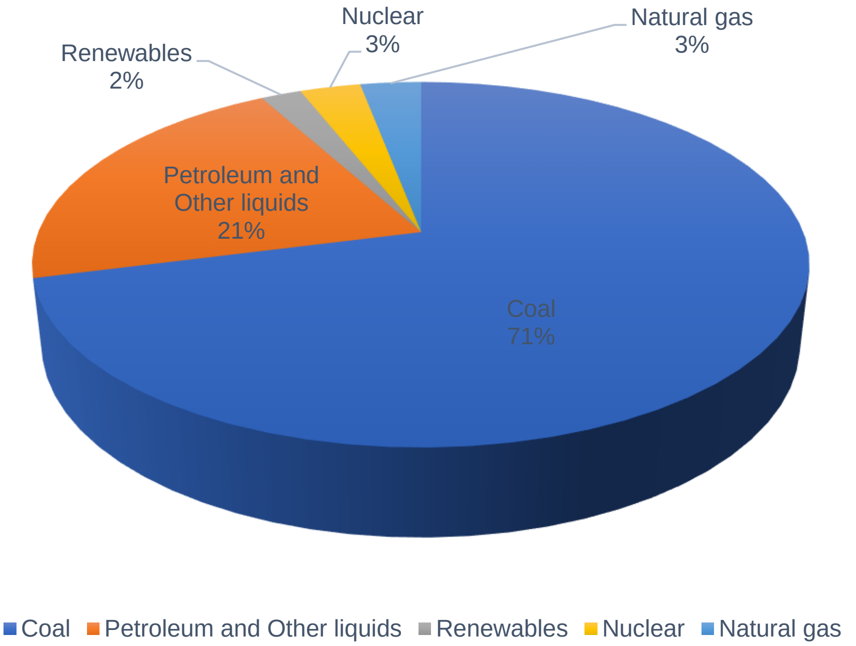


Figure 1.2. Primary energy consumption in South Africa in 2020 (U.S. Energy Information Administration (EIA), 2022).

1.1.3. Biomass as a renewable energy source

To mitigate these challenges alternative renewable energy sources have been identified such as solar, wind, biomass, hydro, geothermal etc. However, among the identified energy sources, biomass is potentially an attractive energy source since it is the only renewable source of carbon, that can be used to generate carbon- based fuels and chemicals.

The utilisation of biomass as an alternative energy source has various benefits. Biomass is abundantly available in most parts of the world, and it is available in different forms, such as forestry, agricultural residues, organic waste, energy crops, woody plants etc. Wang et al. (2021) has reported that globally, more than 100 billion metric tons of forestry residue along with agricultural waste are produced every year, thus indicating that the lignocellulosic biomass is highly abundant. Biomass as a renewable energy source is environmentally friendly, unlike fossil fuels, as it is considered a carbon-neutral fuel source since biomass is formed through the photosynthesis process, absorbing carbon dioxide from the atmosphere, and during combustion the same carbon dioxide that it has absorbed from the atmosphere is released (Kartal et al. 2021).The extensive utilization of biomass as a renewable energy source can contribute positively by reducing the dependency on the fossil fuels and assist in achieving the energy sustainability (Tavares et al. 2020).

Another interesting factor that makes biomass a preferred renewable source of energy is that, it can be utilized as a feedstock material to produce various types of products such as the liquid biofuels, syngas, chemicals or charcoal etc. Biomass can be converted into densified solid biofuels such as pellets and briquettes, which further increases the utilization of its applications. Biomass when converted into a solid form, storage and transportation challenges may be alleviated, and this increases its utilization efficiency. Biomass can also be used as a feedstock material to produce electric energy.

1.1.4. Biomass conversion methods

The biomass material can be converted using two main conversion routes, namely; the biochemical and thermochemical conversion routes. The biochemical conversion route includes the fermentation and digestive methods. Whereas, the thermochemical conversion, includes several conversion technologies, such as torrefaction, combustion, pyrolysis and gasification technologies. The thermochemical conversion technologies are efficient in converting the biomass material or any other feedstock types into an energy source that can be utilized in order to produce high value products and eliminate challenges of unsustainable energy supply.

The preferred method of biomass conversion is the thermochemical conversion route, since it is versatile route, it consists of various conversion technologies that allows various products to be produced. For instance, in the pyrolysis technology, the main product is the bio- oil, while in the gasification technology the main product is the syngas. The thermochemical conversion methods have an advantage of being a faster route of conversion as compared to the biochemical conversion route. For instance, the fermentation process, takes a longer duration to produce the desired product.

The gasification technology is a thermochemical process at which the carbonaceous materials such as biomass and other types of materials such as coal, waste plastics etc , are converted into syngas, at high temperatures, which is typically between 800 – 1100°C (Alli et al. 2018). The gasification technology employs the different types of the gasifiying agents such as air, steam, oxygen, carbon dioxide, or their combination. The main product produced from the gasification technology is the syngas product, which consists of several gases such as H_2, CO_2, CO, CH_4 and H_2O.

The gasification technology is mostly preferred due to it being a very versatile conversion technology as it can accommodate various types of feedstocks, provides better conversion efficiency as compared to the other technologies and can be applied over a wide range of capacities, the product composition can be manipulated to suit a range of downstream applications using different gasifier types and different operating conditions. Gasification is also regarded as a cleaner alternative (in terms of emissions) for waste treatment than incineration and other feedstock conversion methods.

1.1.5. Drawbacks of biomass feedstock

However, the biomass feedstock has various drawbacks., When biomass is gasified it produces a gas with a high oxygen content and low thermal stability, and this inhibits the gas from being utilized in the downstream applications to manufacture high value products. It is therefore crucial that the gas produced from the biomass gasification be of high quality and has high heating value, so that it can be utilised for downstream applications, such as the production of the high value products. Secondly, biomass feedstocks have disadvantages such as low bulk density which results in challenges in terms of storage, handling and transportation. Biomass has certain unfavourable physical properties such as high moisture content, low carbon content and varying particle size. These can negatively affect the performance of the biomass conversion technology utilised.

Furthermore, maintaining and supplying of biomass at large scale is a challenge due to its seasonal availability which might have detrimental effect on the constant supply of energy. These drawbacks of usage of biomass as a main feedstock material for energy supply, indicates that there is a need for an alternative energy source that can be used to solve the challenges that occurs during the individual biomass conversion process and which can also assist in the reduction of the dependency on the fossil fuels. Recently co- gasification technology has been identified as a feasible and effective method to improve the quality of the product gas and eliminate the operational challenges that occurs during individual gasification of feedstocks.

1.1.6. Waste Plastic as an energy source

Plastic waste could be a suitable co- feed with biomass during the co- gasification (Alvarez et al. 2014) because of its great abundance and its physical properties such as high hydrogen content, low oxygen content and high carbon content that can compensate the physical properties of biomass, which contributes towards the low conversion efficiency and overall performance of the biomass gasification.

The high volume of the waste plastics mainly in the landfills has shown a tremendous increase in the recent years. This is due to factors such as modernization of societies, industrialization and population growth. As a result, the plastic usage has become a basic necessity for most applications of the modern lifestyle. This is due to their low density; durability and they are resistance to corrosion, and they can be sourced at low cost, depending on the type of plastic package used. This has led to a high consumption of plastics, for instance Lopez et al. (2018) reported that, the plastic global production has increased in the recent years, thus reaching a global annual production of 322 million tons (Mt) in 2015. The high consumption of plastic has become a major problem due to the high generation of waste plastics.

The increase in waste plastic has resulted in serious challenges in terms of waste management at landfills, due to limited landfill space available. Plastics are non- degradable by nature, and as a result leads to serious environmental challenges. Park et al. (2016) has reported that in 2012 it was estimated that 1.3 billion tons per year of municipal solid waste was generated, and it is expected that this waste will increase exponentially to 2.2 billion tons per year in 2025. Therefore, there is a need to solve these challenges, as this may have a detrimental effect on human and aquatic life, as the mismanagement of waste in landfills has resulted to be an hazard in the oceans, since a huge number of animals have died due to suffocation caused to high pollution of plastic waste in the oceans.

During the plastic waste conversion, there are several operational challenges such as challenges in feeding of the plastic waste conversion process of plastic alone, The challenges that typically occur are that it is difficult to feed waste plastic to the gasifier due to its nature, secondly, during the gasification process, when temperature in the gasifier increases, the waste plastics tends to change its structure, and become viscous and sticky, causing agglomeration in the gasifier which results in operational challenges of the gasifier. The gasification of plastic produces a high tar content, which is an undesired product of the gasification process.

1.2. MOTIVATION

The co- gasification process is a process whereby two different feedstock materials, with different physical and chemical properties, such as biomass and plastic waste are combined and mixed at specific blend ratios, and then undergo gasification with the aim of obtaining a synergistic effect between the different feedstocks, increase the heating value of the syngas and improve the quality of a syngas product (Ahmed et al. 2011). The syngas product produced from the co- gasification is also hydrogen – rich (Moghadam et al. 2014). The use of the co- gasification allows an additional freedom of the adjustment of the feedstock composition, depending on the feed blend ratios. This technique may assist in reducing the challenges experienced during individual feedstock gasification, such as low gasification performance, low carbon conversion efficiency, and low-quality syngas product (Pinto et al. 2002).

During the co- gasification process suitable operating parameters, feedstock blend ratio and gasifying agents, are obtained and this conversion technique allows the optimisation of the conversion process which leads to a yield of a good quality syngas, which can be used for various downstream applications to produce high quality and high value products such as for the liquid synthesis, chemical production, and also for the power and energy production applications, can be produced. Furthermore, the physical characteristics of biomass can be improved when biomass is combined with plastic waste, thus, providing better handling and storage.

Co- gasification of fuels may benefit the environment by reducing greenhouse gases (GHG) (Kamble et al. 2018) emissions from individual feedstocks. Also, the co-gasification of biomass and waste plastics can potentially alleviate the issue of high volumes of plastic waste in landfills, providing the municipalities and government at large and opportunity of adequate control of waste (improved waste management). This conversion technology reduces the high dependency on fossil fuels, thus ultimately has the potential of reducing the risk of shortage of energy supply.

1.3. PURPOSE OF THE STUDY

The purpose of this study is to investigate the co- gasification of biomass (sawdust) and plastic waste (polyethylene) by evaluating the synergistic effect between the two co- gasified feedstocks using different gasifying agents such as oxygen, air-, carbon dioxide, steam and their relative mixtures. Therefore, the co- gasification of biomass and plastic waste was conducted by initially developing the simulation model using the Aspen Plus software. Although some simulation work has been done on biomass gasification, there has limited work on co- gasification of biomass and plastic waste (Ramos et al. 2018).

However, in recent years, there has been a rise in the number of studies on the co-gasification of biomass and plastic waste (Tavares et al. (2020), Singh et al. (2022), Wang et al. (2021), Rosha et al. (2021), Tian et al. (2022)). Most studies of the co-gasification of biomass and plastic waste, either compare the effect of one gasifying agent at a time. Thus, the novelty of this study is that mixed gasifying agents, such as oxygen and carbon dioxide mixture, and oxygen and steam mixture, will be considered.

Mathematical modelling of the co- gasification process is very important in determining the suitable operating parameters, predicting the product quality and its yield. Modelling also allows optimisation of the process without wasting time and money, as compared to laboratory experiments, which it is costly to achieve results due to the consumables, and procurement of other equipment required to conduct the experiment. However, the experiment results are still regarded as valuable source of information since they are used to validate the results obtained from the simulation model.

Therefore, this study is beneficial to the research community, since it will bridge a gap in the literature, as there is a lack of process simulation models utilizing multiple feedstocks at different blend ratios in the gasification process.

1.4. AIMS AND OBJECTIVES

The aim of this study is to determine the effect of the feedstock composition such as biomass, polyethylene and their respective blend ratios, gasifying agents and operating conditions on the product gas composition, H_2/CO ratio of the syngas and on the Lower Heating Value (LHV) of the syngas. The synergistic interaction between the polyethylene and biomass will be evaluated. Therefore, following specific objectives will be undertaken to achieve the aims of the study:

- Analyse the effect of the individual feedstock, such as biomass or polyethylene, and their respective blend ratio on the product gas composition, H_2/CO ratio of the syngas and on the Lower Heating Value (LHV) of the syngas.
- Determine the effect of the operating parameters (such as gasifying agents, equivalence ratio, steam to biomass ratio) on the equilibrium product gas composition, H_2/CO ratio of the syngas and on the Lower Heating Value (LHV) of the syngas.
- Determine the effect of the equivalence ratio on gas yield (GY) and cold gas efficiency (CGE), and extent of the synergistic effect of the co-gasification of biomass and plastic waste when individual or combined gasifying agents are used.

1.5. DISSERTATION STRUCTURE

This section presents an overview of the structure of the dissertation. The dissertation is divided into five chapters: Chapter 1 - Introduction, 2 - Literature Review, 3 - Methodology, 4 – Results and Discussion and 5 – Conclusion. A brief description of each chapter is provided below:

Chapter 1: Introduction

This chapter provides a brief background on the challenges related to the over reliance on fossil fuels and their depletion as well as greenhouse emissions resulting from fossil fuel usage and the negative impact of these emissions on the environment and the application of biomass as an alternative energy source. The motivation for using the co- gasification process, as a possible solution that can address the challenges arising from the use of fossil fuels are also discussed in this chapter. The purpose of the study is explained in detail in this chapter. The aims and objectives of the dissertation are elaborated.

Chapter 2: Literature Review

This chapter extensively describes biomass and plastic waste in terms of its structure, formation, different types, and conversion routes. The chapter will also focus on the thermochemical route for biomass and plastic conversion. Within the thermochemical conversion route, gasification technology will be described in detail. The fundamentals of biomass and plastic waste gasification such as the different stages of gasification and the chemical reactions involved, will be presented. The concept of co-gasification of different feedstock material is discussed.

The chapter will also elaborate on the classification of the different types of gasifiers and the advantages and disadvantages of each type of gasifier. The effect of the operating parameters on the product gas composition, H_2/CO ratio of the syngas and lower heating value of the syngas are discussed. These factors are discussed with the aim of highlighting all the factors that require attention when designing or optimizing the co-gasification system. Lastly the chapter discusses the modelling of the gasification systems.

Chapter 3: Methodology

This chapter provides an overview of the approach used in the development of a simulation model for the co- gasification of biomass and polyethylene in Aspen Plus software. The chapter describes all the processing units that were used for the development of the model and the streams connecting process units. The thermodynamic property methods, operating parameters and operating conditions are also specified in the chapter. The manner in which the model was validated is also outlined in this chapter.

Chapter 4: Results and Discussion

This chapter presents and discusses the findings from the process simulation. The effect of different factors such as feedstock input, operating conditions, and operating parameters, on product gas composition are interpreted.

Chapter 5: Conclusions

This chapter summarises the key findings obtained from the results and recommendations for future work will be discussed.

REFERENCES

Ahmed. I.I, Nipattummakul. N, Gupta. A.K, (2011), Characteristics of Syngas from Co-gasification of Polyethylene and Wood – Chips. *Applied Energy*, 88,165 – 174.

Akinbami. O.M, Oke. S. R, Bodunrin. M.O, (2021), The State of Renewable Energy Development in South Africa: An Overview, Alexandria Engineering Journal, 60,5077 – 5093.

Alli. R.D, Kannan. P, Shoaibi. A. A, Srinivasakannan. C, (2018), Performance Prediction of Waste Polyethylene Gasification using CO_2 in a Bubbling Fluidized Bed: A modelling Study, Chemical. *Biochemical Engineering*, 32 (3), 349 – 358.

Alvarez. J, Kumagai. S, Wu. C, Yoshioka. T, Bilbao. J, Olazar. M, Williams. P. T, (2014), Hydrogen Production from Biomass and Plastic Mixtures by Pyrolysis – Gasification, *International Journal of hydrogen Energy*,39,10883 – 10891.

Bhatia. S.K, Palai. A.K, Kumar. A, Bhatia. R.K, Patel. A.K, Thakur. V.K, Yang. Y, (2021), Trends in Renewable Energy Production Employing Biomass – Based Biochar. *Bioresource Technology*, 340, 125644.

International Energy Agency (IEA), (2021), World Energy Outlook, https://www.iea.org/reports/world-energy-outlook-2021, 17 June 2022.

Independent Statistics & Analysis, U.S. Energy Information Administration (EIA),(2022), https://www.eia.gov/international/analysis/country/ZAF, August 2022

Kamble A.D, Saxena V.K, Chavan P. D, Mendhe V. A, (2019), Co- gasification of Coal and Biomass an Emerging Clean Energy Technology; Status and Prospects of development in India Context. *International Journal of Mining Science and Technology*, 29,171–186.

Lopez. G, Artetxte. M, Alvarez. J, Bilbao. J, Olazar. M, (2018), Recent Advances in the Gasification of Waste Plastics: A Critical Overview. *Renewable and Sustainable Energy Reviews*, 82, 576 – 596.

Menyah. K, Wolde-Rufael. Y, (2010), Energy Consumption Pollutant Emissions and Economic Growth in South Africa, *Energy Economics*,32, 1374 – 1382.

Moghadam. R.A, Yusup. S, Uemura. Y, Chin. B.L.F, Lam. H.L, Al Shoaibi. A, (2014), Syngas Production from Palm Kernel Shell and Polyethylene Waste Blend in Fluidized Bed Catalytic Steam Co-gasification Process. *Energy*, 75,40 – 44.

Oladipupo. S. D, Rjoub.H, Kirikkaleli.D, Adebayo. T. S, (2022), Impact of Globalization and Renewable Energy Consumption on Environmental Degradation: A Lesson for South Africa, International Journal of Renewable Energy Development, 11, 145 – 155.

Park. J. H, Park. H, Choi. S, Park. D, (2016), Effects of Blend Ratio Between High Density Polyethylene and Biomass on Co- gasification Behaviour in a Two – Stage Gasification System. *International Journal of Hydrogen Energy*, 41,16813 – 16822.

Pinto. F, Franco. C, Andre. R. N, Miranda. M, Gulyurtlu. I, Cabrita. I, (2002), Co-gasification Study of Biomass mixed with Plastic Wastes. *Fuel*, 81,291 – 297.

Ramos. A, Monteiro. E, Silva. V, Rouboa. A, (2018), Co- gasification and Recent Developments on Waste – to- Energy Conversion: A Review. *Renewable and Sustainable Energy Reviews*, 81, 380 – 398.

Rosha. P, Kumar. S, Vikram. S, Ibrahim. H, Al-Muhtaseb. A.H, (2021), H_2 – enriched Gaseous Fuel Production Via Co-gasification of an Algae-Plastic Wate mixture using Aspen Plus, International Journal of Hydrogen Energy, 1-9.

Singh. M, Salaudeen. S.A, Gilroyed. B.H, Dutta. A, (2022), Simulation of Biomass-Plastic Co-gasification in a Fluidized Bed Reactor Using Aspen Plus, Fuel, 319, 123708.

Tavares. R, Monteiro. E, Tabet. F, Rouboa. A, (2020), Numerical Investigation of Optimal Operating Conditions for Syngas and Hydrogen Production from Biomass Gasification Using Aspen Plus, Renewable Energy,146,1309 – 1314.

Tian. Y, Luo. Z, He. D, Yang, Y, Liang. S, Liu. W, Yuan. L, (2022), Co-gasification of Biomass and Polyethylene: A Simulation Study by Considering Tar Formation, Biomass Conversion and Biorefinery.

The Council for Scientific and Industrial Research (CSIR),(2021), CSIR Releases its Annual Statistics on Power Generation in South Africa in 2021,https://www.csir.co.za/csir-statistics-on-power-generation-south-africa-2021, 29 August 2022.

Wang. Z, Li. J, Burra. K.G, Liu. X, Li. X. Zhang. M, Lei. T, (2021), Synergetic Effect of CO_2 – Assisted Co- gasification of Biomass and Plastics, *Journal of Energy Resources Technology*, 143, 031901 – 9.

CHAPTER 2: LITERATURE REVIEW

2.1. Biomass feedstock material

2.1.1. Introduction

This chapter will focus on the literature related to the following factors: properties of both biomass and plastic waste feedstock materials, types and their structure, composition, pre-treatment and conversion routes to product gas. The conversion technology that will be used in this study is predominantly the co - gasification technology, which will be discussed in depth. The aspects of co-gasification that will be discussed are as follows: the stages of gasification, the chemical reactions that takes place during the gasification process, the types of gasifiers, the factors that affects the gasification performance and quality of the product gas (syngas) and finally, the cleaning process of syngas.

2.1.2. Biomass feedstock

Biomass is formed from living species like plants and animals, that is anything that is alive or was a short while ago (Puig -Arnavat et al. 2010). Biomass is produced through photosynthesis process as shown in Figure 2.1 (a) and whereby the sun’s energy is captured, converting carbon dioxide from air into complex organic compounds, using chlorophyll and water.

This process is represented by equation 2.1.

$$\text{Living plant} + CO_2 + H_2O + \text{sunlight} \rightarrow (CH_mO_n) + O_2 \qquad (2.1)$$

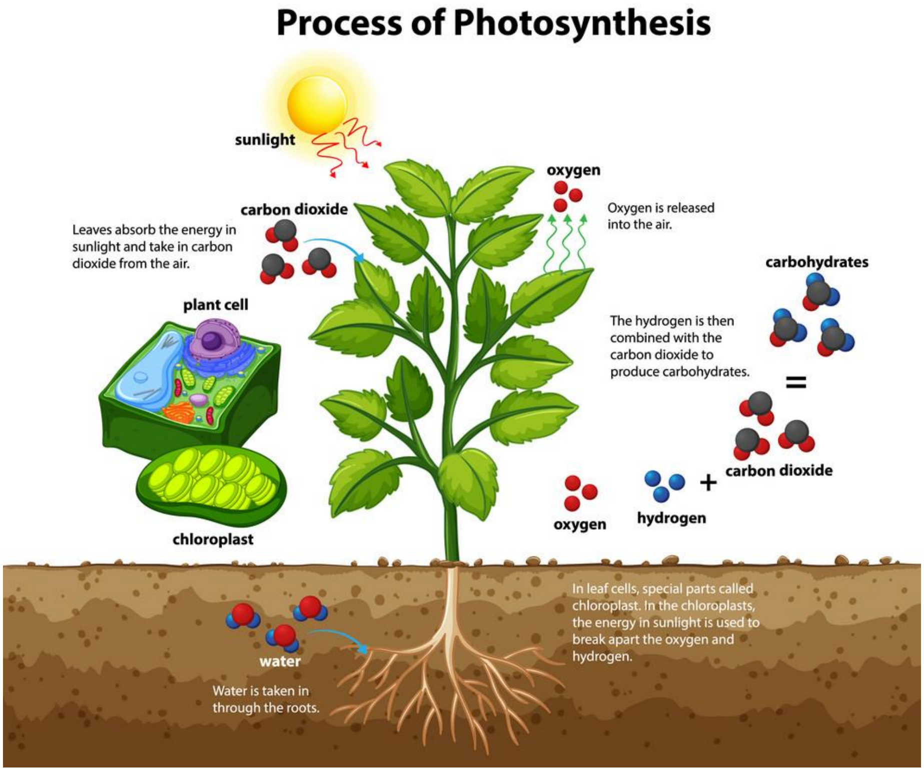


Figure 2.1 (a) Photosynthesis process used to produce biomass feedstock (https://en.wikimedia.org/wiki/Photosynthesis,2022).

Biomass feedstock is one of the preferred sources of renewable energy as compared to the other types of renewable sources such as, wind, solar etc. Amongst the various renewable sources, biomass is the only energy source that comprises of carbonaceous material. It is converted through the thermochemical and biological routes, and different products such as syngas are produced from its conversion. The produced syngas is further used to produce to different high value products such as electricity, dimethyl ether, methanol etc, (Ramzan et al. 2011). It is abundant, can be obtained easily from different sources as shown in Table 2.1. Biomass can be obtained in most parts of the world, at very low costs. It is estimated that energy of 7.7 EJ/year is produced from biomass material. Furthermore, it is estimated that by 2050, the production of energy from the biomass would have risen to 10 EJ/year (Arregi et al. 2018).

Table 2.1. Biomass classifications based on their origin (rural and urban), (Ren et al. 2020).

Main categories	Sub- categories	Representatives
Rural waste	Agricultural resources	- Straw, shell, grass, wood, seeds etc.
	Energy crops	- Soghurm, maize, soybean, wheat, oil, Palm, sugarcane, etc.
	Forest resources	
	Animal wastes	- Fat, oil, grease, chicken litter, bones, meat manure etc.
Urban wastes	Municipal solid waste (MSW),	Wastewater, sewage, waste papers, wood pallets and boxes, bio- solids etc.
	Food industry waste,	
	Industrial wastes	

2.1.3. Biomass structure

The structure of lignocellulosic biomass, typically originating from the forestry and agricultural residues, consists of three main components, namely, cellulose, hemi- cellulose and lignin, and minor non-structural components (Figure 2.2). Figure 2.3 - 2.5 shows the different cell structures of biomass components and their specific functions. The cell wall of biomass consists of 40 – 60% cellulose, 15 – 30% hemicellulose and approximately 10 – 25% of lignin (Kumar et al. 2008).

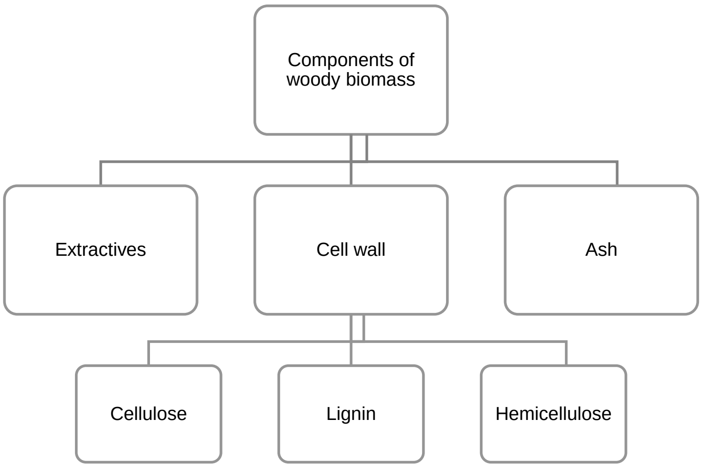


Figure 2.2. Major constituents of woody biomass (Basu et al. 2013).

The structural components of the biomass cell wall are discussed as follows:

(i) Cellulose

Cellulose structure consists of a linear mono-molecular polysaccharide, that consists of long unbranched chains of glucose units, linked by β – 1.4 – glycosidic bonds. Cellulose has a high degree of polymerization (<10,000) and high molecular weight of (<500,000), (as shown in Figure 2.3). Cellulose has a crystalline structure that provides strength to the cell wall of the biomass. The cellulose occupies about 40 – 60% of the cell wall and is represented by a generic formula $(C_6H_{10}O_5)_m$. It is very insoluble in solvents (Wang et al. 2017).

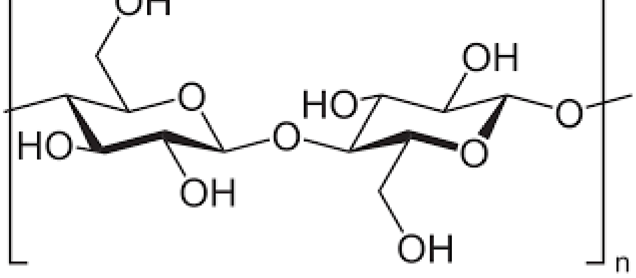


Figure 2.3. Molecular structure of cellulose (Shen et al. 2011).

(ii) Hemicellulose

Hemicellulose structure consists of a short chain of heteropolysaccharides and presents an amorphous and branched structure (Figure 2.4). This branched polymer has a lower degree of polymerization consisting of simple sugars (pentose and hexose) of 50 – 200 units (Basu et al. 2013). Hemicellulose has low strength when compared to cellulose. The degree of polymerization of hemicellulose is only approximately 200 on average and It is represented by generic formula $(C_5H_8O_4)_{n.}$ Hemicellulose is soluble in weak alkaline solutions and is easily hydrolysed by dilute acid or base. Its constituents of about 25 – 35% of dry weight of biomass (Munir et al. 2018).

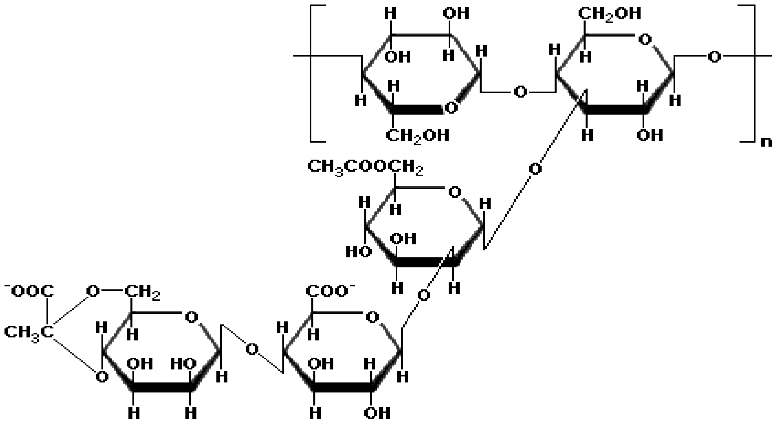


Figure 2.4. Molecular structure of hemicellulose (Zhou et al. 2017).

(iii) Lignin

Lignin has an amorphous polymer structure that is three-dimensional, which composed of propyl phenol units (Figure 2.5). Lignin component provides the support to the plant, allowing it to be impermeable and resistant towards the attack of microbial and oxidative stress. Lignin component account for 10 – 15% in the cell wall of biomass (Kumar et al. 2008). Lignin is highly resistant to degradation and biological digestion processes. Lignin is not soluble in strong acids such as sulphuric acids, which has a high molecular weight and soluble to acids, which has low molecular weight, and this biomass constituent is very resistant to conversion by many chemical agents (Vassilev et al. 2012).

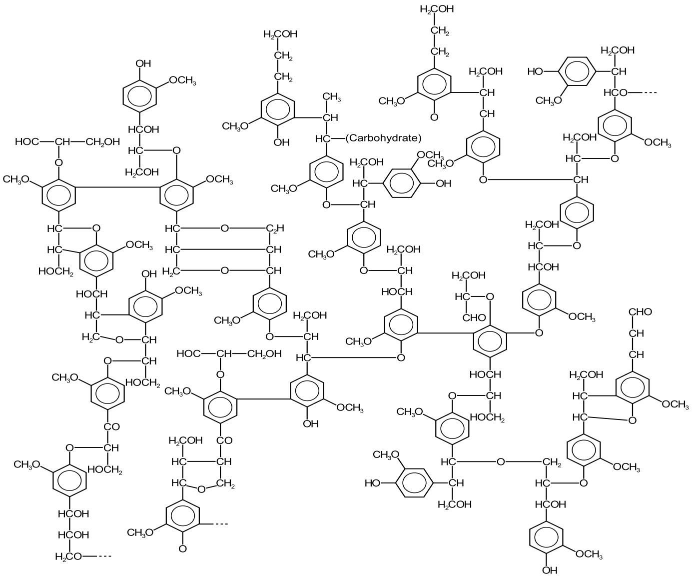


Figure 2.5. Molecular structure of lignin (Cesarino et al. 2012).

2.1.4. Biomass feedstock limitations

Biomass feedstock also has its own limitations such as high fixed carbon, that results in high unconverted char content, and a high oxygen content which results in the formation of oxygenates, that when mixed with other elements during the reactions may result in products such as NO_x, SO_x etc. These products are harmful to the environment as they emit gases that affects the atmosphere and results in global warming.

Biomass contains a high moisture content, which results in reduced efficiency of thermochemical conversion processes. Another limitation of biomass is that it consists of a low energy density, which makes biomass material difficult to handle, to store and transport. Thus, the transportation of the raw material may not economical under all circumstances. Therefore, based on the above-mentioned limitations, waste plastics material has been identified as a good supplement that has the potential of addressing the challenges that occur when biomass is individually gasified (Deparrois et al. 2019).

2.2. Waste Plastic feedstock

2.2.1. Introduction

Plastic is regarded as one of the most useful materials that can be employed for an extensive variety of purposes. It is used for everyday living activities and by different sectors such as construction, healthcare, electronic, automotive, packaging etc. The increased consumption of plastic over the years has resulted in a high accumulation of plastic in the environment. The global plastic production was estimated to be above 3 million tons in 2018 and is expected to increase to be 5 million tonnes by 2025 (Bai et al. 2019). Plastic is typically disposed in the landfills and the lack of management of landfills results in environmental issues.

Therefore, this section will elaborate as to how plastic waste can be converted into high value products. Factors such as properties of plastic, different types of plastic, various ways of treating plastic waste will be discussed as well as the factors that affect the thermochemical conversion of plastic waste.

2.2.2. Properties of plastic waste feedstock

Plastics polymers consists of long chains of molecules typically containing hydrogen, carbon, nitrogen, chlorine etc. Plastic waste has attractive properties such as low moisture content, high durability, high strength, unlike biomass feedstock, plastic has high energy density, which is influenced by its low moisture content. Plastic is highly viscous, especially at moderate temperatures and has low melting point, with low tensile strength and hardness.
Plastic has a high volatility, however, it is very sticky by nature, which is a challenge during feeding and during its thermal conversion process, since it end up causing agglomeration and clogging in the reactor, which increases the maintenance costs of the reactor (Lopez et al. 2017).

Above all, waste plastics has a potential of being converted into useable energy and therefore the volume of waste plastic ending up in landfills may be reduced (Al – Salem et al. 2017). Plastic waste has low to zero oxygen content. Therefore, co-feeding plastic and biomass reduces the high oxygen content associated with the biomass feed, that results in poor quality of the product. Plastic material has a high hydrogen content that can act as a hydrogen donor to the biomass fuel and has a high volatile matter, which has the potential of improving the quality of the product gas.

2.2.3. Types of plastic waste feedstock

There are different forms of plastic materials, that are used by different sectors such low density polyethylene (LDPE), high density polyethylene (HDPE), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) etc. These various types of plastic material are discussed as follows (Sharuddin et al. 2016):

- High density polyethylene (HDPE)

High density polyethylene (HDPE) accounts for about 34% of the global plastic market. The monomer used to make the HDPE (and LDPE) is ethylene which is represented by the generic chemical formula of $(C_2H_4)_n$. The HDPE has a high strength – to- density ratio which is due to its thermoplasticity. HDPE can be used in various applications such as for making detergent bottles, milk bottles, toys, oil containers etc. The HDPE has a high melting point when compared to other types of plastics.

- Low density polyethylene (LDPE)

Low density polyethylene (LDPE) consists of a long-chained branched polymer with weaker intermolecular bonds and low tensile strength and hardness. LDPE has better ductility than the HDPE since the side branching causes the structure to be less crystalline. LDPE can be easily moulded.

- Polystyrene (PS)

Polystyrene (PS) is made from the styrene monomers, its structure consists of long synthetic aromatic hydrocarbon chain with phenyl group, attached to every carbon atom. PS is represented by chemical formula of $(C_8H_8)_n$. Polystyrene is highly resistance to heat and very durable in terms of strength. While being very light in weight, its lightness makes it attractive to many industries. It is used in various industries such as packaging, electrical, construction, and medical.

- Polypropylene (PP)

Polypropylene (PP) is a saturated polymer with linear hydrocarbon chain and has a good chemical and heat resistance, as compared with other types of plastics. It is represented by formula of $(C_3H_6)_n$. This polymer type is produced via a chain – growth polymerization reactions, that includes propylene. When propylene is exposed to high temperatures, it gets soft very fast and can be easily moulded. Polypropylene consists of large thermal expansion and is highly resistant to organic solvents. Polypropylene is used to make flowerpots, office folders, car bumpers, furniture etc.

- Polyethylene terephthalate (PET)

Polyethylene terephthalate (PET) are polymers that are macromolecules, which are formed by monomers. These monomers react with each other to form a long polymeric chain. The chemical bonds of PET is formed by polycondensation of terephthalic acid and ethylene glycol. PET is used in the manufacturing of food products such as beverages, such as mineral water, soft drinks, and fruit juice containers. The PET plastics consists of intrinsic properties that are suitable for large capacity, light weight and pressure resistant containers. PET plastics are used for electrical insulation, printing of sheets, in magnetic tapes, X- ray and photographic film applications.

- Polyvinyl Chloride (PVC)

Polyvinyl Chloride (PVC) is made of a mixture of 57% chlorine and 43% carbon, this type of plastic is highly resistance to fire and typically used for electrical insulation. It is used for wire and cable insulation in making window frames, food oil, blood bags, automotive interior. However, when exposed to high temperature environments it releases hazardous substances such as dioxins.

2.2.4 Treatment methods of plastic waste feedstock

Plastic waste material can be managed using different methods, such as landfilling, incineration and recycling. The recycling method is categorized based on the mechanical and chemical recycling. Therefore, these treatment methods are discussed as follows:

- Landfill method

Landfill method is a traditional method that is used to dispose solid waste material in an open land space. The largest quantity of waste disposed is plastic waste material. Landfilling of plastic waste is inexpensive as compared to other form of waste treatment. However, the challenges associated with landfilling is t space limitation, due to the volume of waste that is increasing in an exponential rate. The high volume leads to lack of management of waste, which results in land pollution, and some of the waste end up being eroded during rainy seasons and carried away through streams and rivers and ends up in the oceans. Subsequently, the aquatic life also suffers due to the lack of treatment of plastic waste in the landfills.

The other factor that causes limited space in the landfills is that plastic waste, is non- biodegradable i.e., it degrades extremely slowly. When the plastic waste is mixed with other substances, a toxic leachate is generated, and toxic gases are emitted to the atmosphere (Miandad et al. 2017). However, a solution to the problem of limited space in the landfills can be addressed by concentrating on removing the anaerobic biodegradable organic compounds in the leachate (leachate treatment). This solution is still in the development stage, yet a few landfills have started implementing it (Bolyard et al. 2016).

- Incineration method

Incineration refers to a technique that comprises the combustion of feed materials to produce energy. Incineration is a useful method of reducing plastic waste, it can reduce 80 – 85% volume of solid waste (Hameed et al. 2021). A large amount of heat is produced from the incineration process and the heat is mostly used for vapour-based turbines for power generation and also in heat exchangers. The incinerators are operated at a temperature range of 800 – 1000°C. The main products produced from incineration is carbon dioxide and water. The disadvantage of this process is that it affects the atmospheric environment since a high amount of toxic gases such as CO_2, dioxins, NO_x, SO_x etc are emitted (Al- Salem et al. 2017).

- Recycling methods

The recycling method recovers and reprocesses plastic waste with the aim of producing new products. The recycling method is used as a form of waste plastic treatment and has a significant impact in waste reduction, since most of the disposed plastic waste materials, are recovered and re-used to manufacture high value products. There are two methods that are used in recycling, namely, mechanical and chemical recycling.

- Mechanical recycling

In the mechanical recycling method, plastic wastes are used as the feedstock material to manufacture secondary products without changing the chemical composition of the feedstock. Various internal processes are followed during the mechanical recycling of plastic waste, such as; waste collection, size reduction where they are either cut or shredded using shears and saws into smaller flakes which are easier to handle. (Miandad et al. 2017). Thereafter, contaminants such as paper bits, dust, smaller fragments etc are removed from the plastic waste using a cyclone separator.

After the removal of the contaminants, the plastic waste is separated as per their different densities, through the floatation process and lastly, they are milled and washed using water.

- Chemical recycling

During the chemical recycling of the plastic waste, chemical alteration in the polymer structure occurs. The difference between the chemical recycling and mechanical recycling is that, in the mechanical recycling, the plastic waste molecular structure does not change, while in the latter method it changes. Thermolysis methods are employed in the chemical recycling (Al – Salem et al. 2017). There are three techniques that are used in the thermolysis recycling method, namely the pyrolysis, gasification and hydrocracking. Other than the thermolysis technique, chemical recycling consists of processes such as hydrolysis, methanolysis, glycolysis (Miandad et al. 2017).

During the thermolysis, polymers undergo chain scission to produce low molecular weight compounds and monomers. In the pyrolysis process, the plastic wastes are converted in an inert atmosphere with or without catalysts in the absence of oxygen (Block et al. 2019). In the gasification process the conversion of plastic waste is conducted in the presence of sub-stoichiometric amounts of air relative to combustion, leading to the production of product gas such as CO, CO_2, CH_4 and H_2.

Then, lastly, during the hydrocracking process, hydrogenation of plastic waste is carried out in the presence of hydrogen gas. During the hydrocracking process, large molecules of the long – chains polymers are converted into small molecules substances and the products produced are oil, gas and char. This process occurs at a temperature range of 300 - 450°C and 2 – 15 MPa (Munir et al. 2018). The difference among these technologies are the operating conditions and the products produced. The main advantage of chemical recycling over mechanical recycling is the ability of treating the heterogeneous and contaminated polymers with limited use of pre-treatment.

2.3. Feedstock composition characterization

Determining the composition of the fuel is important since it provides the information about the characteristics and properties of the fuel. These characteristics serves as a good indicator of the quality of the feedstock material and the calorific value, which affects the overall quality of the product produced due to thermal treatment (Ren et al. 2020). There are two methods that are used to characterize the biomass fuel, namely the Proximate and Ultimate analysis.

The proximate analysis characterises the biomass in terms of fixed carbon, moisture content, ash and volatile matter, while the ultimate analysis gives an indication of the elemental constituents of the feed such as carbon, hydrogen, oxygen, nitrogen and sulphur (C, H, O, N and S). These elements play a major role during the thermochemical reactions. Ash content formed from the converted fuel is considered inert and is also an unwanted product of the fuel conversion.

(i) ***Volatile matter*** - refers to the condensable and non- condensable vapour that is emitted during pyrolysis in the absence of oxygen. Volatile matter is a function of temperature and heating rate. Plastic waste contains high volatile matter of approximately 90% as compared to the biomass which is around 46% (Rahman et al. 2021). This is because plastic waste is hydrophobic and has low moisture content, and low fixed carbon.

(ii) **Ash content** - is the inorganic solid residue that remains after the combustion process has taken place. The main components of ash are silica, aluminium, calcium, potassium etc. Biomass has higher ash content between the range of (0.1 – 36) %, as compared to the various types of plastics which ranges between (0 – 6.33) %, as shown in Table 2.2. (Wang et al. 2021).

(iii) **Moisture content** - refers to the amount of water that is within (intrinsic) and outside (extrinsic) of the fuel. The moisture content of the feedstock material has a great effect on the overall performance of the carbon conversion process. If the feedstock material has high moisture content, the temperature in the gasifier, decreases and automatically the chemical reaction rates also decrease, thus, resulting in a poor-quality syngas, with high char and tar content. Biomass typically has a higher moisture content as compared to plastic waste.

(iv) ***Fixed carbon*** - indicates the amount of solid carbon that remains after the volatile matter is removed. When the fixed carbon is high in the fuel, this results in a difficulty in the operation of the gasifier, which may cause slagging and agglomeration in the reactor, therefore, careful control of the operating parameters such as temperature, and gasifying agents such as air and steam is required. The formula of calculating the fixed carbon of the fuel is expressed in equation 2.2. Biomass has a high fixed carbon that is typically between (6.19 – 32.6) wt% whereas plastics has a fixed carbon that is between (0 – 19.48) wt%, as shown in Table 2.2 (Wang et al. 2021),

$$FC = 1 - M - VM - ASH \tag{2.2}$$

(v) ***Heating value (HV) of the feedstock material*** – the heating value is determined by calculation expressed using equation 2.3 and 2.4. This parameter is used to quantify the amount of energy content embedded in the feedstock, for the purpose of thermochemical conversion process. A feedstock material that has a high heating value, will yield a product gas of good quality (Zhang et al. 2019). There are two parameters used to determine the heating value of the feedstock material: the Higher Heating Value (HHV) and the Lower Heating Value (LHV). One of the equations used to determine the Higher Heating Value (HHV) is represented by equation 2.3 (Monir et al. 2020).

$$HHV_{feedstock} = 0.3491M_C + 1.1783\,M_H + 0.1005M_S - 0.1034M_O - 0.0151M_N - 0.0211\,M_A \quad (2.3)$$

Where, $HHV_{feedstock}$ is the higher heating value of the feed material (MJ/kg), M_C, M_H, M_S, M_O, M_N and M_{AC} are mass percentages of carbon, hydrogen, sulphur, oxygen, nitrogen and ash content for feedstock respectively. Lower Heating Value $(LHV)_{feedstock}$ of the feedstock material is determined through a calculation expressed by equation 2.4. The Lower Heating Value (LHV) is calculated by subtracting the heat of evaporation of water vapor from the higher heating value (HHV).

$$LHV_{feedstock} = HHV_{feedstock} - h_g\left(\frac{9H}{100} + \frac{Mc}{100}\right) \quad (2.4)$$

Where $LHV_{feedstock}$ is the Lower Heating Value (LHV) for feedstock (MJ/kg), H and M_c is the hydrogen and moisture content percentage of feedstock and h_g, is the latent heat of steam (2.260 MJ/kg) (Monir et al. 2020). The typical Lower Heating Values (LHV) for biomass are between (14.57 – 19.7) MJ/ kg and that of plastics are between (4.03 – 46.4) MJ/ kg. This shows that plastics consists of higher heating values that biomass, as shown in Table 2.2 (Wang et al. 2021).

Table 2.2 provides different values of the ultimate and proximate analysis of the biomass material. However, it should be noted that even, other types of feedstock materials such as coal, MSW, plastic waste etc. are also characterized using proximate and ultimate analysis method. The importance of characterizing the feedstock properties for biomass and plastic waste using the ultimate and proximate analysis prior to the commencement of the co-conversion process is discussed below:

Table 2. 2 Proximate, elemental analysis and LHV of typical kinds of plastics (Wang et al. 2021)

Plastics	**Elemental analysis (wt%)**					**Proximate analysis(wt%)**				
	C	H	N	O	S	VM	FC	Ash	Moisture	Lower Heating value (MJ/kg)
PET	62.51 – 66.2	3.7 – 4.9	0 – 0.05	28.9 – 34.2	0 – 0.55	83.92 – 90.57	9.43 – 13.9	0 – 4.4	0 – 0.46	21.25 – 4.034
HDPE	81.45 – 86.5	12.06 – 15.47	0 -0.34	0 -32.81	0-0.79	99.4 – 100	0 – 0.3	0 – 0.8	0	38.66 – 46.4
PVC	38.15 – 39.66	4.47 – 5.24	0 – 0.23	-	0 – 1.8	88.95 – 94.78	3.42 – 8.67	0 – 0.64	0.02 – 0.2	19.3 – 21.66
LDPE	82.18 – 8.35	13.38 – 16.37	0	0 – 1.45	0 – 0.2	99.08 – 100	0 – 0.3	0 – 0.3	0 – 0.2	43.1 – 46.15
PP	83.28 – 86.5	12.9 – 15.3	0 – 0.3	0 – 0.98	0 – 2.3	93.84 – 100	0 – 2.04	0-3.68	0 – 0.44	37.6 – 46.0
PS	86.06 -92.2	6.27 – 9.06	<0.1 – 5.73	0 – 1.4	0 – 1.22	94.33 – 100	0 – 4.55	0 – 0.98	0 – 0.86	37.45 – 43.58
PC	75.71	5.47	0	18.82	-	80.47	19.48	0.05	0	30.08
PU	62.69	6.32	6.37	24.01	0.63	83.20	10.60	6.20	-	26.03
ABS	75.44	8.19	4.74	3.44	8.19	100	0	0	0.05	38.09

Table 2.2 Continuing

Biomass	**Elemental analysis (wt%)**						**Proximate analysis(wt%)**				
		C	H	N	O	S	VM	FC	Ash (A)	Moisture (M)	Lower Heating value (MJ/kg)
Agricultural – residues	Corn stalk	47.5	6.1	0.8	45.6	-	73.8	15.0	5.8	5.4	15.7
	Rice straw	52.3	7.3	1.3	38.5	0.1	66.2	8.2	15.1	10.5	19.7
	Tobacco stalk	41.09	5.02	2.42	42.75	0.21	71.31	20.17	8.52	-	-
	Cottom stalk	47.95	5.50	3.24	43.31	-	64.92	22.10	5.52	7.46	16.3
	Sunflower residues	47.91	5.27	8.65	38.17	-	65.26	19.35	6.72	3.02	16.9
Forestry residues	Pinewood	48.72	6.52	0.23	44.41	0.12	85.6	14.2	0.2	-	17.65
	Bamboo	50.52	6.04	0.58	>42.80	0.09	83.95	16.05	1.95	6.14	17.87
	Beech wood	49.9	6.2	-	43.9	-	80.2	12.4	0.4	7.0	-
	Yellow poplar	47.8	6.3	0.2	45.8	-	86.2	13.3	0.1	0.5	-
	Olive residues	50.95	5.28	-	38.63	-	74.8	12.8	5.1	7.3	-
	Alder wood	47.50	6.37	0.29	40.85	0.15	87.55	-	1.3	4.5	19.62
	Paulownia wood	49.74	6.05	0.26	43.81	0.14	75.78	20.54	0.8	2.88	17.82
Food Production residues	Sugarcane Bagasse	42.07	5.60	0.26	52.01	0.06	71.79	11.33	5.97	10.91	17.24
	Walnut shell	47.50	6.39	0.46	45.65	-	76.38	15.21	0.33	8.06	16.69
	Peach stones	49.28	6.65	0.34	43.73	-	72.42	19.84	0.86	6.88	18.38
	Groundnut shell	41.0	6.3	1.0	41.2	0.2	68.7	21.1	10.3	-	-
	Bagasse	36.3	5.8	0.3	51.5	0	74.5	9.5	6.0	-	-
	Rice husk	36.0	4.8	1.2	22.3	0.2	51.4	12.1	36.5	-	-
Municipal organic wastes	Waste newspaper	39.78	5.50	0.10	54.62	-	78.2	9.5	11.2	6.5	14.57
	Year waste	52.50	6.83	1.28	39.3	-	72.1	17.7	10.2	5	-
	Food waste	51.68	6.21	1.14	40.97	-	70.7	18.5	10.8	4.4	-

	Potato	44.48	6.56	1.82	46.49	0.65	77.04	15.70	3.02	4.24	-
	Orange peel	47.32	5.75	1.39	42.45	0.18	76.49	20.60	2.91	-	18.47
	Rice	45.79	6.32	1.68	45.56	0.25	84.42	15.18	0.40	-	18.14
	Tissue paper	44.95	6.10	0.25	48.07	0.11	90.47	9.01	0.52	-	17.25
	Wool	59.33	4.19	2.62	31.00	1.53	84.76	14.00	1.24	-	20.92
Industry organic by-product	Rubber seed shell	44.31	4.38	0.51	50.67	0.13	80.98	6.62	3.81	8.59	-
	Black liquor lignin	63.42	5.83	0.81	29.94	-	69.01	25.77	1.58	3.65	-
	Macro-algae	32.71	5.38	4.85	51.85	2.01	53.45	8.40	25.24	12.91	15.47
	Switchgrass	46.55	5.75	0.48	42.02	-	-	-	2.63	2.6	-
Neat cellulose, hemicellulose, and lignin	Cellulose	42.23	6.36	0.03	51.34	0.03	93.75	6.19	0.06	-	-
		39.95	6.20	0	52.77	1.08	-	-	-	-	-
	Hemicellulose	39.18	6.32	0	54.50	0.01	74.54	18.34	2.00	5.12	-
		44.56	6.12	-	49.32	-	-	-	-	-	-
	Lignin	63.42	5.83	0.81	29.94	-	69.01	25.77	1.58	3.65	-
		62.45	5.68	0.56	30.61	0.70	62.90	32.60	2.70	1.80	-

*[Proximate analysis], **VM**: volatile matter, **A**: Ash, **FC**: Fixed Carbon, **M**: Moisture

*[Elemental analysis], **C**: Carbon, **H**: Hydrogen, **O**: Oxygen, **N**: Nitrogen, **S**: Sulfur

***PET** – Polyethylene terephthalate; ***HDPE** – High -density polyethylene, ***PVC** – Polyvinyl chloride, ***LDPE** – Low -density polyethylene, *** PS** – Polystyrene, ***PC** – Polycarbonate,

***PU** – Polyurethanes, ***ABS** – Acrylonitrile butadiene styrene

2.4 . Pre-treatment of the blended feedstock of biomass and plastics

Before the blended feedstock material can be converted into useful products it usually requires preparation first. Certain parameters such as moisture content, particle size and density require adjustment. It is of paramount importance to pre- treat the blended feedstocks, in order to avoid operational challenges that might result in low conversion efficiency and poor-quality product gas. Therefore, the following steps are involved in the pre- treatment of the blended feedstock material.

(i) Reduction of moisture content

The moisture content of the feedstock material is one parameter that requires pre – treatment, since thermochemical conversion processes are more efficient when the moisture content of the feedstock is within a specified limit. The moisture content is typically reduced by drying, which is endothermic, and requires substantial amounts of energy. Therefore, during drying of the feedstock material the feedstock is exposed to temperatures between 100 - 200°C (Baruah et al. 2014) and the intrinsic and extrinsic moisture content of the fuel is removed in a form of steam or water vapour.

As the fuel gets dried, the moisture content reduces. Depending on the type of feedstock material to be thermally converted, the typical suitable moisture content range for most gasifiers is between 5% to 35% (Sansaniwal et al. 2017).

(ii) Particle size of the fuel

It is vital that the particle size of the fuel be reduced and homogenous for effective performance of the thermochemical conversion process. The specification of the particle size assist in addressing issues such as difficulty in feeding, low carbon conversion efficiency etc.

The suitability of the particle size of the fuel depends on the type of reactor used. For instance, for the gasification process, a fluidized bed gasifier requires the particle of the feedstock to be sized, in accordance to the required specification. In order to allow for easy fluidization that maximizes the contact of the feedstock particle surface with the oxidant. An entrained – flow gasifier requires finer particles and a fixed bed gasifier permits larger particle sizes.

Therefore, to eliminate the above- mentioned challenges caused by the large size particles in the conversion process, different particle sizing techniques are used, such as crushing, milling, pelletization etc. to reduce the size of the particles to a suitable range.

(iii) Feedstock densification

The feedstock material, such as biomass, is typically characterized by low bulk density which make the fuel difficult to handle, store or transport. Therefore, a densification process is used to increase the density of the fuel and improve its characteristics. When the fuel is densified, it is easy to feed, and the carbon conversion efficiency is enhanced. The densification processes are divided into two sub- processes namely, torrefaction and pelletization.

- Torrefaction

Torrefaction is a pre-treatment method that is used to convert feedstock into a coal like material, with the aim of improving the characteristics of the fuel. The fuel is exposed to heat at temperatures between 200 – 300 °C in the absence of oxygen (Widyaya et al. 2018). During the heating of the fuel, some combustible gases are produced. However, the main product of torrefaction process is a densified solid feedstock material. During the torrefaction process the oxygen – to- carbon ratio of the fuel gets reduced.

- Pelletization

Pelletization is a mechanical process that compacts feedstock into pellets or briquettes with a uniform-size that is typically within of 6 – 25 mm (Clark et al. 2015). It is used to increase the density of the feedstock fuel, thus allowing easy handling, storage and transporting. During pelletization, the ash content of the fuel is reduced. The efficiency of the thermochemical conversion process is improved by pelletization of the feedstock (Ramos et al. 2018). Pelletization of the fuel provides the following benefits:

- Increases the calorific value of the feedstock
- Provides more homogeneous physical and chemical composition, thus lowers the pollutant emissions
- Reduces excess air requirements during the combustion
- Improves the carbon conversion efficiency.

2.5. Conversion Routes for blended feedstocks

There are two main routes that are used for conversion of biomass and other feedstock materials such as coal, plastic waste etc. These conversion routes are either biological or thermochemical. The mentioned routes are discussed in the following sections (Figure 2.6).

However, for this study the thermochemical route for the co- conversion of biomass and plastic waste is discussed in more detail.

2.5.1. Biological route

Biological processes use microorganisms, with the help of enzymes, to convert biomass into useful products (such as biofuels). Typically, two main processes are employed, anaerobic digestion or fermentation. Anaerobic digestion is a process that occurs in the absence of oxygen that converts organic material to biogas (a mixture of methane and carbon dioxide). Fermentation is a process that occurs in the absence of oxygen that converts sugars into alcohols (such as bioethanol) or hydrogen.

Biological route typically requires the feed material to be pre-treated. The pre-treatment is conducted in order to address the issue of the complex nature of lignocellulosic feedstock, to depolymerize the lignin component, which among the components of biomass, it is the most difficult to degrade. During the pre-treatment of biomass, its chemical structure changes (Shahbaz et al. 2020). The pre-treatment is also conducted to allow the enzymes, which acts as a catalyst to be able to access the biomass structure and facilitate its degradation.

The advantage of using biological processes when compared with other conversion processes such as thermochemical conversion is that, it may consume less energy, since the conversion occurs at ambient temperature and pressure. Also, the biological process, when compared to other processes, has minimum carbon dioxide emissions. However, the downside to this conversion route is that it is a very slow process, thus more time is required to produce the expected products (Zabed et al. 2019).

2.5.2. Thermochemical route

Thermochemical conversion route is the route that is used to convert feedstock fuels such as biomass, coal, plastic waste etc. into high-value fuels. In this route, high temperatures are employed to produce different products such as liquids, gases and solids. The thermochemical conversion route comprises of different technologies such as combustion, pyrolysis and gasification.

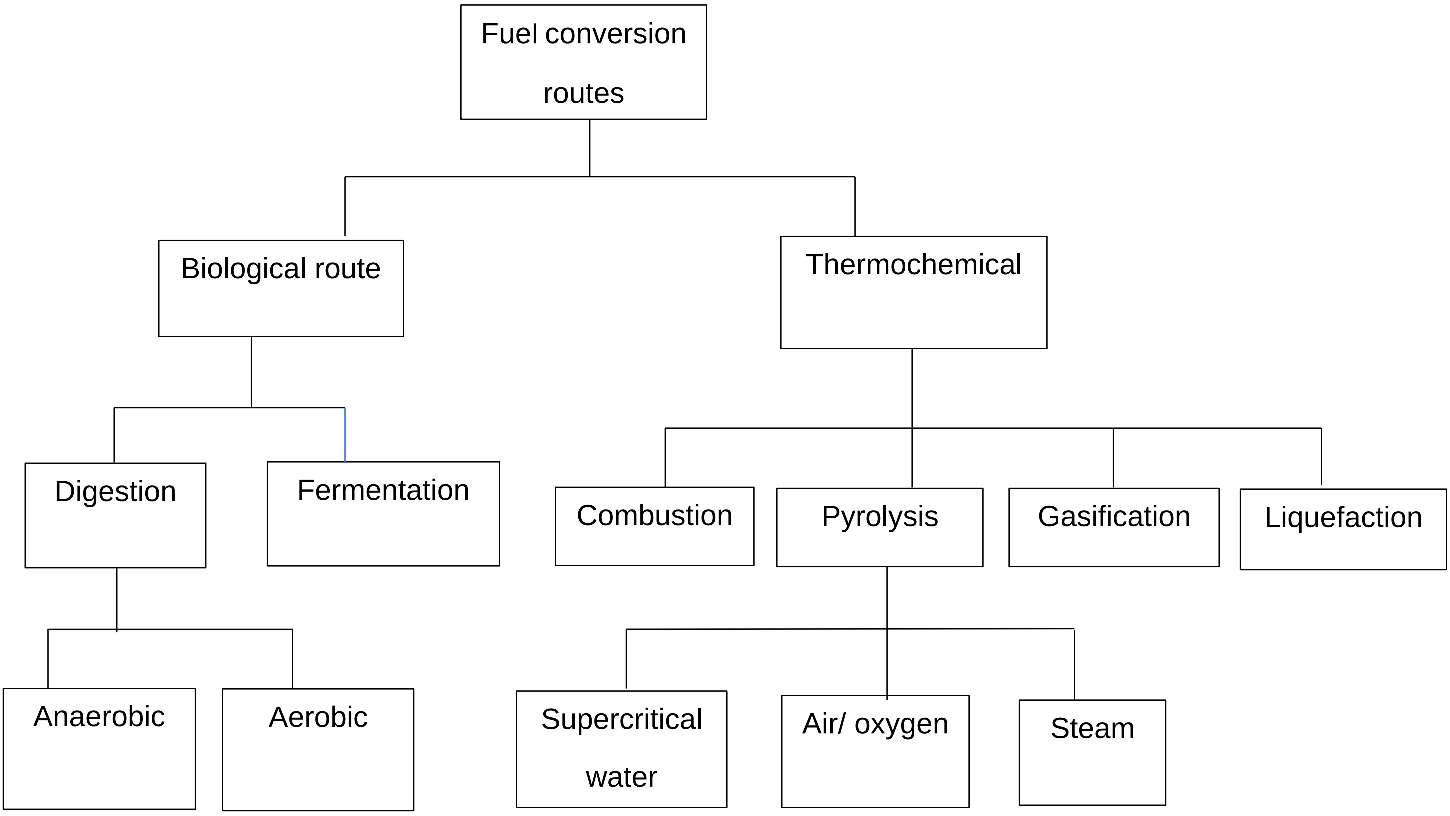


Figure 2.6. Different options of conversion of feedstock into fuel, gases or chemicals (Basu et al. 2013).

- Combustion

The combustion technology is the oldest form of thermochemical conversion routes that has predominately been for domestic purpose such as cooking and generating heat, for keeping homes warm, especially in the developing countries and in the rural areas. Wood material is the typical type of biomass that is used in the combustion process. Chemically, the combustion process is an exothermic reaction that occurs between the oxygen and feedstock fuel (Baskar et al. 2012). The main products produced is the hot gases that includes H_2O and CO_2 (Figure 2.7). These products are used in the steam boilers and heat exchangers to produce electricity.

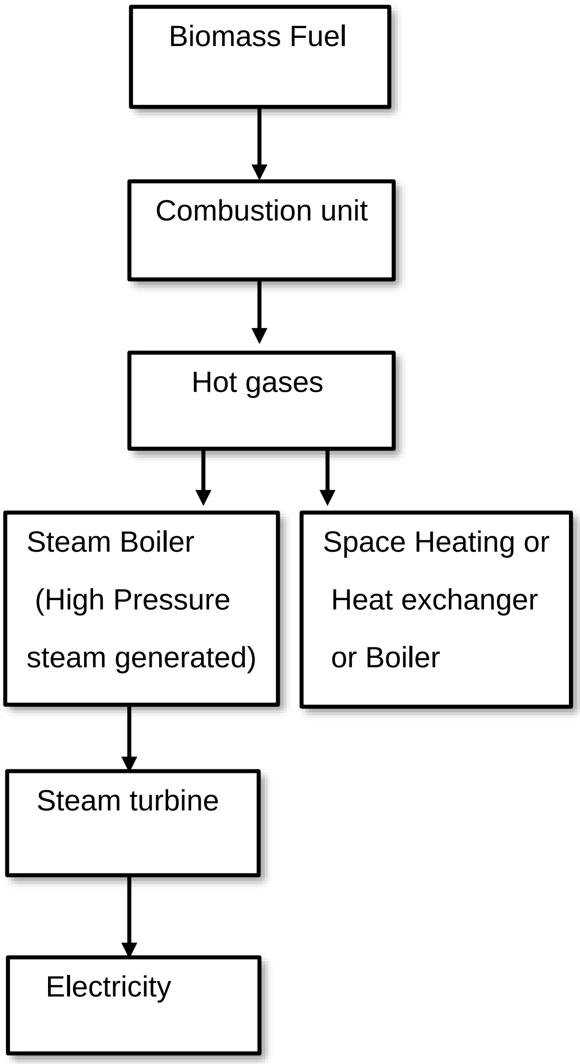


Figure 2.7. Combustion of biomass for heat and power generation (Baskar et al. 2012).

- Pyrolysis

Pyrolysis is a process that is used to decompose large molecules of the feedstock fuel into smaller ones. The feedstock material is thermally decomposed into gaseous (volatiles), liquid (tars) and solid (char) products, in the absence of oxygen, at a temperature range of 400 - 500°C (Brown et al. 2011).

The pyrolysis process is endothermic, and its reactions rely on the heat provided by exothermic reactions. The volatiles produced from pyrolysis includes water arising from the chemical decomposition of the feedstock fuel and gases such as CO_2, H_2 and CH_4. While tars comprise of anhydro-sugars and other highly oxygenated compounds from the decomposition of cellulose and hemicellulose in biomass fuel (Brown et al. 2011). Pyrolysis is employed into two pathways: fast and slow pyrolysis. In the fast pyrolysis, the heating rates are high and have short residence time. The main product produced from fast pyrolysis is bio- oil liquid, whereas in the slow pyrolysis, the residence time is long, and the heating rates are very low. Gas and solid char are the main products of slow pyrolysis.

- Gasification

Gasification process can be defined as the thermochemical conversion process, occurring at high temperatures (>700°C), that is used to convert carbon- based feedstock into combustible gases through a controlled supply of gasifying agent such as air, steam, carbon dioxide, oxygen or their combination (Ramos et al. 2018). The product produced from the gasification process is syngas, which comprises of CO, CO_2, H_2, CH_4 and H_2O.

2.6. Gasification /Co - gasification technology

2.6.1. Introduction

The work in the dissertation is based on co-gasification of biomass and plastic waste. However, co-gasification technology is considered as an extension of the gasification process, which involves the gasification of two or more types of feedstock materials simultaneously. These feedstocks are mixed at different blend ratios with the aim of enhancing the performance of the gasification process (improved gas yield, overall carbon conversion) and improving the quality of the syngas produced (Pio et al. 2020). This process is shown in Figure 2.8 (La Villetta et al. 2017).

Co - gasification process may assist in addressing the operational challenges experienced during the individual gasification of biomass and plastic waste, which results in poor quality of the produced syngas which has high tar content, lower calorific value of the syngas and low conversion efficiency due to the high moisture content in the feedstock (biomass). Correspondingly, the plastic acts as a hydrogen donor to biomass reducing the oxygenates in the product gas (Zhu et al. 2019).

Furthermore, the co- gasification of plastic and biomass may assist in reducing waste plastics in the landfills, since the plastics are converted into high value products. Co-gasification can also address the issue of intermittent supply of energy sources due to the seasonal availability of biomass. The co- gasification process may reduce the dependency on the fossil fuel, which due to their depletion, poses a risk of the lack of energy supply and sustainability (Wang et al. 2021).

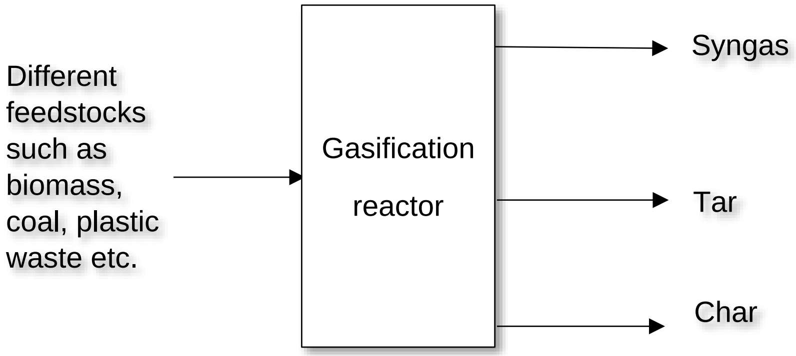


Figure 2.8. Schematic representation diagram of co- gasification to produce syngas and other by- product (La Villetta et al. 2017).

The blending of the different feedstock materials has resulted in many benefits, when compared to the individual gasification of feedstocks. Table 2.3 outlines the benefits of blending the feedstocks during gasification. The co-gasification of biomass and plastic waste can reduce greenhouse gases emissions such as NO_x, SO_x etc, as the percentage of plastic waste increases in the mixture, less toxic gases will be emitted since plastic waste contains a lower oxygen, nitrogen and sulphur content than biomass feedstock (Fazil et al. 2022)

Table 2.3. The advantages of using blended feedstocks in the co- gasification (Inayat et al. 2019).

Blends feedstocks	• The blending of different feedstocks contributes positively to the environment. For instance, the co-gasification of biomass and coal produces less CO_x, SO_x, NO_x, and H_2S emissions as compared to the emissions from coal gasification, due to the lower S, N, and Cl content in biomass • The blending of feedstock materials improves the chemical reactivity, due to the presence of alkali earth metals such as (K, Mg, Ca, and Na etc). Since these metals also acts as catalysts in the co- gasification process.

	• The blending of fuels improves the energy density of the mixed fuel and provide sustainability of availability of feedstock material. • Mixing of feedstocks, provides operational benefits, such as less pre- treatment processes, ease of feeding of the feedstock and provides better fluidization efficiency, for tar reduction. • The co - gasification of feedstock materials, reduce the operation challenges, such as stickiness in the plastics, lower formation of black powder etc. • The blending of feedstock fuels enhances the waste to energy production process. • The co - gasification of different fuels has offered an advantage of reducing the high volume of bio-solids and may reduce the volume of municipal waste. • Co – gasification of different feedstock reduces the ash and moisture content within the blended fuel, thus resulting in a syngas with improved quality and quantity. • Mixing of fuels improves the quality and the quantity of the product gas (syngas).

2.6.2. Gasification and Co - gasification chemical reactions

During the gasification and co- gasification process, different chemical reactions are taking place in the gasifier. These reactions are an interaction between the carbonaceous content of the fuel and the gasifying agents. Therefore, different products are produced, from the reactions taking place. The co – gasification chemical reactions are shown in Table 2.4.

Different stages occur in the gasification process due to the different reactions occurring (Zhu et al. 2019).

Table 2.4. The various complex chemical reactions that takes place during the gasification and co- gasification process – Main gasification reactions at 25˚C (Ruiz et al. 2013).

Char or gasification reactions		
Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$ + 172 kJ/mol	R1
Steam reaction	$C + H_2O \leftrightarrow CO + H_2$ +131 kJ/mol	R2
Hydrogasification reaction	$C + 2H_2 \leftrightarrow CH_4$ – 74.8 kJ/mol	R3
Partial oxidation reaction	$C + 0.5O_2 \rightarrow CO$ – 242 kJ/mol	R4
Oxidation reactions		
	$C + O_2 \rightarrow CO_2$ – 394 kJ/mol	R5
	$CO + 0.5\ O_2 \rightarrow CO_2$ – 284 kJ/mol	R6
	$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O$ – 803 kJ/mol	R7
	$H_2 + 0.5O_2 \rightarrow H_2O$ – 242 kJ/mol	R8
Shift reaction		
	$CO + H_2O \leftrightarrow CO_2 + H_2$ - 41.2 kJ/mol	R9
Methanation reactions		
	$2CO + 2H_2 \rightarrow CH_4 + CO_2$ – 247 kJ/mol	R10
	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ – 206 kJ/mol	R11
	$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$ – 165 kJ/mol	R14
Steam methane reforming reaction	$CH_4 + H_2O \leftrightarrow CO + 3H_2$ + 206 kJ/mol	R12
Partial methanation reaction	$CH_4 + 0.5\ O_2 \rightarrow CO + 2H_2$ -36 KJ/mol	R13

2.6.3. Final product of gasification/co- gasification (syngas)

The product for the co- gasification process of biomass and plastic waste is producer gas , which comprises of H_2, CH_4, CO_2, H_2O, N_2 and CO. However, syngas, which mainly consists of H_2 and CO, is the main product that is sought after since it is regarded as a high value product after being cleaned and unwanted by products such as char and tar are removed. The clean syngas can be further converted into different products. Electricity, heat, and power can be generated from the syngas, as well as fuels, chemicals such as methanol, di-methyl – ether

(DME) etc. The quality of syngas is usually indicated by using the H_2/CO ratio. For example, a H_2/CO ratio of 2, is preferred in the Fischer – Tropsch process, for the synthesis of liquid fuels. Another quality indicator is the calorific value (Chiodini et al. 2017). Therefore, the following section discusses the syngas cleaning process.

2.6.4. Gasification/Co - gasification stages

Gasification/Co- gasification takes place in four different stages namely: drying, pyrolysis, oxidation and reduction. The stages are based on the chemical reactions that are shown in Table 2.3 It is assumed that conceptually these stages occur sequentially and are described in detail as shown in Figure 2.11 (Brown et al. 2011).

(i) *Drying stage*

Drying is the first step of the gasification/ co - gasification process. It occurs when pre-treated feedstock is introduced into the reactor. Different feedstocks have different moisture content of 15 – 35% (Sansaniwal et al. 2017), depending on the type of feedstock material. The drying process is an endothermic process and energy in a form of heat is required, to reduce moisture content of the wet feedstock.

Therefore, this stage typically receives heat from the other stages of gasification such as exothermic reduction stage. During the drying process, the feedstock material intrinsic moisture is removed in a form of vapour or steam. The moisture content of the feedstock is reduced by heating the fuel to low temperatures between 100 - 200°C (Brown et al. 2011). The moisture content is typically required to be within a range of 10 – 15% (Widjaya et al. 2018), depending on the type of the fuel to be co- gasified. The drying process is represented by equation 2.5.

$$\text{Feedstock}_{\text{wet}} + \text{Heat} \longrightarrow \text{Feedstock}_{\text{dry}} + H_2O_{\text{vapour}} \tag{2.5}$$

(ii) *Pyrolysis stage*

The second stage of the gasification/co- gasification process is the pyrolysis stage, which involves the decomposition of the dried fuel at a temperature between 125 - 300°C (Brown et al. 2011), in the absence of oxygen. During the pyrolysis stage, the large molecules of feedstock fuel are decomposed into smaller one. Thus, during the pyrolysis stage of the gasification, the dried fuel particles of the fuel undergo primary decomposition, whereby volatile are released. The volatiles comprise of gases such as CO, CO_2, H_2, CH_4, ash (inorganic compounds), tar and unreacted char (Figure 2.9). Thereafter, the tar produced is further decomposed in the secondary pyrolysis step and more wood gas is produced (Kraft et al. 2016).

The pyrolysis stage is regarded as the most important stage of the co - gasification technology, since from this stage most of the feedstock material is converted into gases and vapours. Pyrolysis is endothermic, and thus, more heat is required. The pyrolysis stage is represented by equation 2.6 (Karl et al. 2016).

$$\text{Feedstock}_{\text{dry}} + \text{Heat} \rightarrow \text{Char} + \text{Volatiles (Gas + Tar)} \qquad (2.6)$$

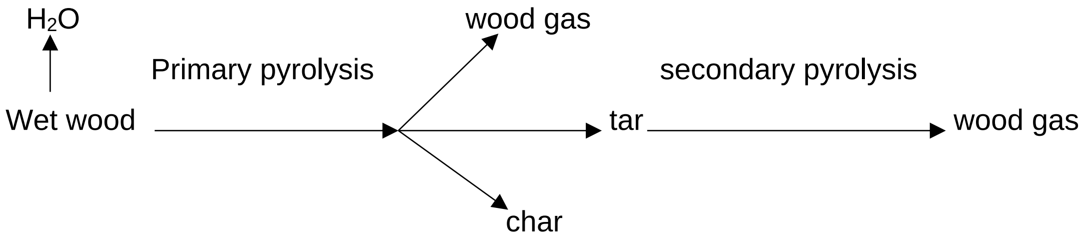


Figure 2.9. Reaction mechanism for wood particles during drying, (Karl et al. 2016).

(iii) *Oxidation stage*

The third stage that is involved in the gasification/co- gasification process is the oxidation stage. During the oxidation stage, gasifying agents such as air, steam, oxygen, carbon dioxide or a combination of these is injected into the gasifier, at a sub-stochiometric level, in order to avoid complete combustion. The oxygen from the gasifying agent reacts with the products produced from the pyrolysis stage and syngas.

The main products produced from the oxidation stage is the CO_2 and H_2O and by- product such as char and tar are produced. In the oxidation stage the exothermic reactions (Table 2.4) are highly active, therefore large amounts of energy is produced. The energy is released and utilised by the other stages of co - gasification process that are endothermic, such as drying and pyrolysis stages. Typically, the oxidation stage takes place within a temperature range of 500 - 700°C (Brown et al. 2011).

(iv) *Reduction stage*

The last stage of gasification/co- gasification, oxidized products such as H_2O and CO_2, are reduced by increasing the temperature in the gasifier to be above 700°C (Brown et al. 2011), see Figure 2.10. The remaining char from the pyrolysis stage is further converted into syngas, and tar is further cracked into hydrocarbons and into combustible gases. The reactions occurring in the reduction stage are homogeneous and the water gas shift (Table 2.4) is very active in this stage. Product gases which comprises of combustible gases such as carbon monoxide (CO), hydrogen (H_2), methane (CH_4), water vapour (H_2O), nitrogen (N_2) and carbon dioxide (CO_2) is produced from the reduction stage (Cao et al. 2018).

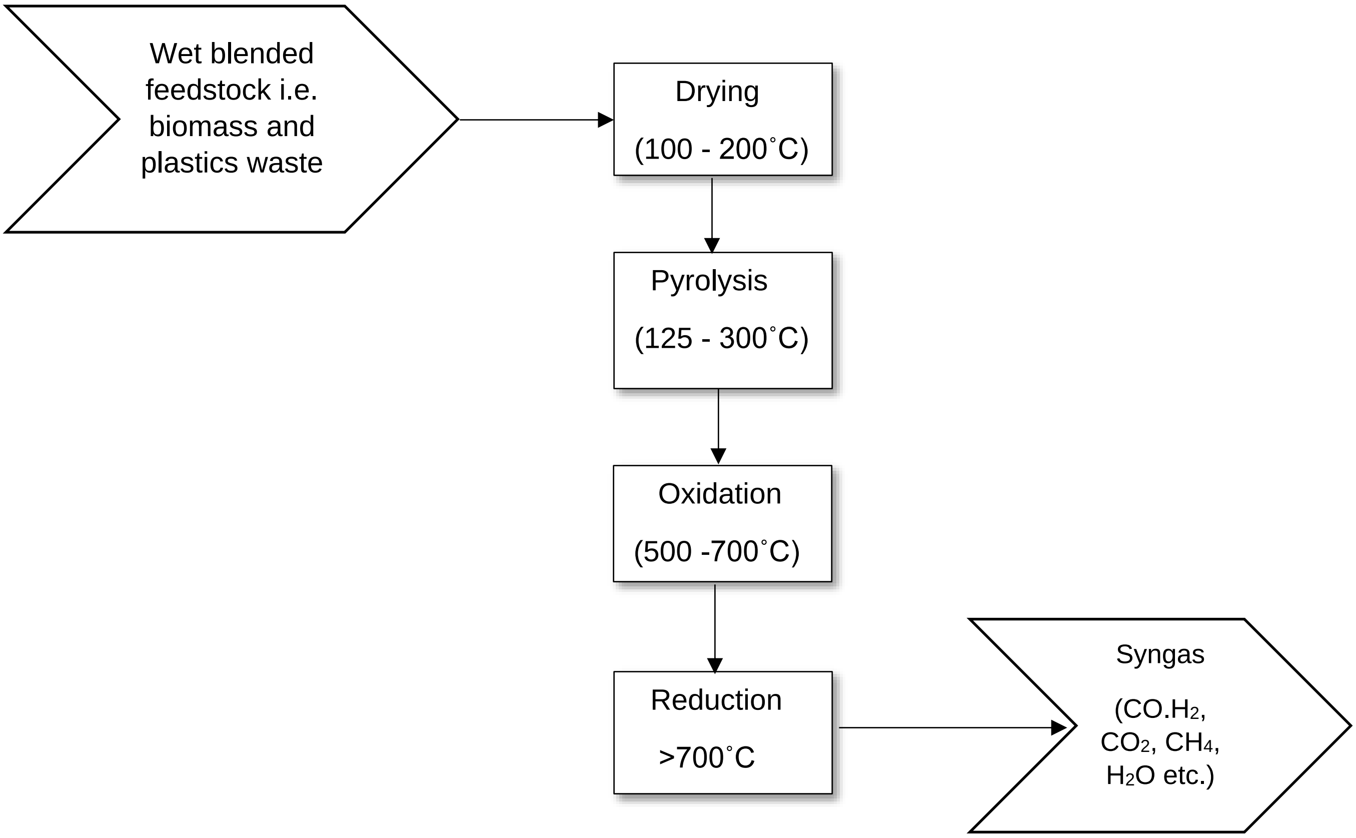


Figure 2.10. Schematic process diagram depicting the four stages of a gasification process (Brown et al. 2011).

2.6.5. Gasifiers used in gasification/co- gasification

The gasification/co- gasification of feedstocks takes place in an operating unit called a gasifier. The gasifier is regarded as the heart of the gasification process, since the conversion process occurs inside it. There are different classifications for gasifiers; it is classified based on the design, heat source, pressure operation and the gasifying agents used (Figure 2.11), (La Villetta et al. 2017). Therefore, in this section different classification of the gasifiers will be discussed.

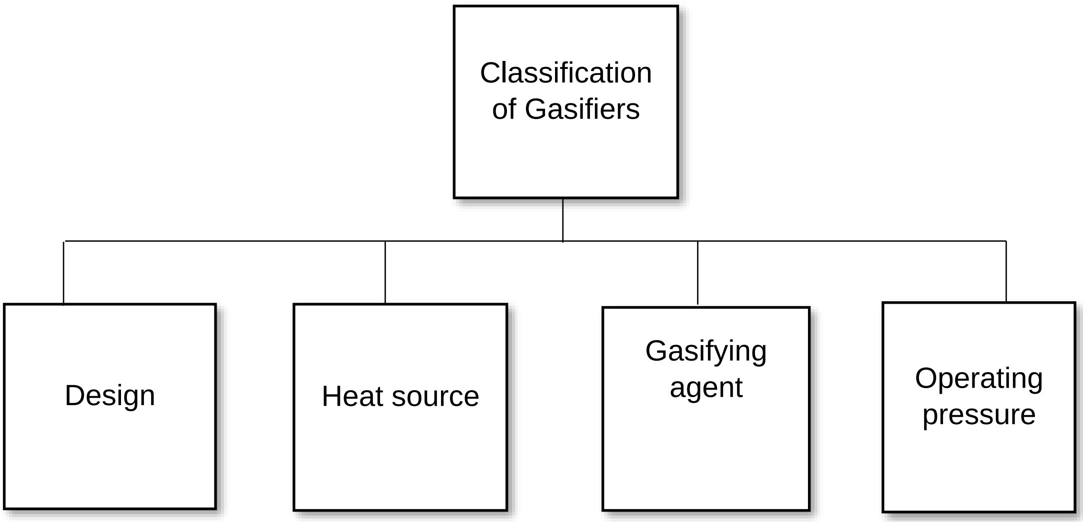


Figure 2.11. Classification of gasifiers.

2.6.5.1. Classification by - design

There are three designer types for the gasifiers, namely the fixed bed gasifiers, fluidized bed gasifiers and entrained flow gasifiers (Figure 2.12). These gasifiers are discussed as follows:

(i) Fixed bed gasifiers

The fixed bed gasifiers are the oldest type of gasifiers, and very easy to operate. They consist of a cylindrical vessel, with the feedstock introduced at the top of the vessel. The gasifier is separated into four zones (drying, pyrolysis, oxidation and gasification), where the gasification process takes place. The blended feedstock is introduced into the gasifier, either in counter or co- current to the flow of gasifying agent (steam, oxygen and air). The fixed bed gasifiers consist of two sub- categories; the downdraft and updraft gasifiers (Figure 2.12 (a) and (b)), (Mc-Kendry et al. 2002).

Fixed bed gasifiers operate at a pressure of 250 – 30 atm (Sansaniwal et al. 2017) and the fixed beds can be operated at a temperature of 1000˚C (Ramos et al. 2018). These gasifier types provide a long residence time, which allow an almost complete conversion of the carbon compounds.

- Updraft gasifier

The updraft fixed bed gasifier has four gasification stages (drying, pyrolysis, oxidation and gasification). The gasifying agent is introduced at the bottom of the gasifier while the feedstock is introduced at the top of the gasifier. The flow of the fuel and gasifying agent is counter current. The feedstock passes through the different stages within the gasifier. As the feed descends through the gasifier, it is exposed to higher temperatures in various stages of the gasifier. The heat produced from the oxidation and reduction stages i.e. steam reaction, shift reaction and methanation ascends to the drying and pyrolysis stages, the gases, volatiles and tar exit at the top of the gasifier. The syngas produced contains high tar content. Therefore, intensive cleaning for syngas is required, for the gas to be used in the downstream applications (Sansaniwal et al. 2017).

- Downdraft gasifier

The second design for the fixed bed is the downdraft fixed bed gasifier, which is constructed the same as the updraft fixed bed gasifier, except that the fuel and the gasifying agents flow in a co- current direction. The fuel is introduced into the gasifier from the top, while the gasifying agent is introduced from the sides. Therefore, the fuel descends and is mixed with the gasifying agent, and the produced product gas, leaves the reactor at the bottom. The syngas produced from the downdraft, contains a lower tar content, as compared to that produced from the updraft fixed bed gasifiers (Ruiz et al. 2013). These designs of gasifier are usually operated at a temperature range of between 900 - 1000˚C (McKendry et al. 2002).

(ii) Fluidized bed gasifiers

The second type of gasifier design is the fluidized bed gasifier, in which the feedstock particles are kept suspended by the oxidant flow. In the fluidized bed gasifiers, there are no restriction zones, as that of the fixed bed gasifiers. Therefore, the gasification occurs simultaneously during the mixing (Karl et al. 2018).

The fluidized bed gasifier consists of bed material, which is usually an inert material such as sand, silica, olivine etc. The main function of the bed material is to facilitate the heat transfer between the gasifying agents and feedstock fuel, to enable the gasifier to operate under isothermal conditions. These type of gasifiers designs are preferred due to their strong gas-to- solid contact, excellent mixing efficiency, improved temperature control and excellent degree of turbulence. Fluidized bed gasifiers can operate at pressures above atmospheric. The fluidized bed gasifiers can be operated at high temperatures between 800 - 1200˚C, to avoid the ash melting point which can cause agglomeration in the reactor, Figure 2.12 (c) (Allaudin et al. 2010). The fluidized bed gasifiers are classified into two designs based on the velocity of the fluidising medium, namely, bubbling fluidized bed gasifier (BFBG) and circulating fluidized bed gasifier (CFBG).

- Bubbling fluidized bed gasifiers (BFB)

In the bubbling fluidized bed gasifier design, the fuel feedstock enters the gasifier from the top, while the gasifying agent enters the gasifier from the bottom and passes through the reactor bed. During the fluidization process, the mixing of the gasifying agent and the fuel takes place. Heat is also transferred. However, the syngas produces, does contain tar content and intense syngas cleaning is required. The bubbling fluidized bed can be operated at low cost and requires less maintenance. Secondly, these gasifiers are typically operated at high temperatures between 800 - 1000˚C (Ruiz et al. 2013).

- Circulating Fluidized bed gasifiers (CFB)

The second design of the fluidized bed gasifier is the circulating fluidized bed gasifier (CFB), which operates in the same manner as the bubbling fluidized bed gasifier, except that it consists of a circulating loop. Which is used to retain the unreacted char, with the aim of increasing the yield. Therefore, the circulating loop, retains and return the solids back to the fluidizing section in the reactor, thus increasing the carbon conversion efficiency.

The other difference, is that the circulating fluidized bed gasifier, has a very high degree of turbulence and mixing. The gasifying agent flows at very high velocity, 3 – 10 m/s (Sansaniwal et al. 2017) as compared to the velocity used in the bubbling fluidized bed gasifier that has lower velocities between 1 - 3 m/s (Sansaniwal et al. 2017). This leads to an improved solid-gas contact and mixing. This gasifier design has a potential of accommodating very cohesive solids, that might be difficult to handle in the bubbling fluidized bed gasifier (Brown et al. 2011).

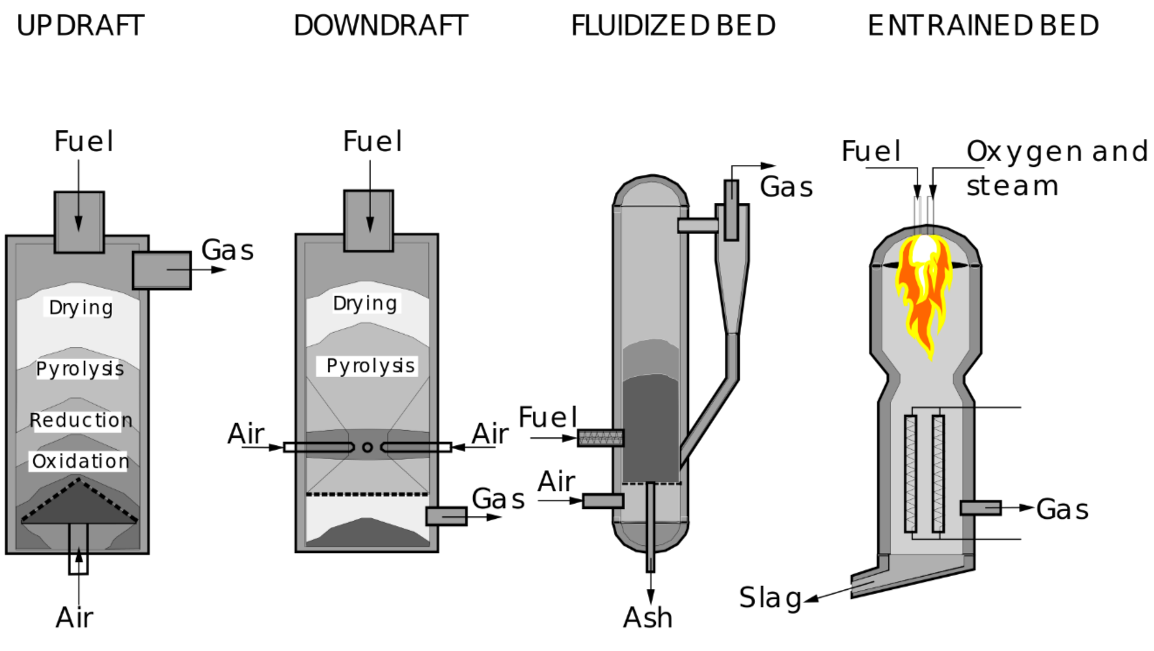
(iii) Entrained – Flow gasifier

The third gasifier design is the entrained flow gasifier. In the entrained flow gasifier, the powdered fuel and the gasifying agent such as oxygen both enter the gasifier from the top (Figure 2.12 (d)) and descend downward the gasifier. The gasifying agent that is mostly used for this gasifier design is oxygen, but other gasifying agents such as air and steam can still be used. The particle size of the fuel should be very small, between 75 – 100 µm (Situmorang et al. 2020). Therefore, this gasifier is typically used for coal gasification, since for biomass the constrain is the particle size which needs to be reduced, into the very small size, and that process is very expensive. The entrained flow gasifier is mostly preferred for coal conversion since coal particle size can be easily reduced as compared to that of biomass

The entrained flow gasifiers are operated at very high temperatures, as compared to both the fluidized and fixed bed gasifier designs. The temperature range is within 1400 - 1800°C (Situmorang et al. 2020) and the pressure used is high, within a range of 20 – 70 bar (Fazard et al. 2013), these operating conditions, assist in enhancing thermally destroy tar, oils, phenols and other heavy hydrocarbons to produce more H_2, CO and CH_4.

These gasifiers operate in a turbulent flow, high temperature and small particle size range and these operating specifications serves as an advantage for the overall performance of the entrained gasifiers. However, these operating parameters, especially the temperature, should be operated optimally as not to exceed the ash melting point in order to avoid slagging and agglomeration in the reactor, which results in unnecessary maintenance cost.

The carbon conversion efficiency of the entrained flow gasifiers is approximately between 98 – 99.5 % (La Villetta et al. 2017). The entrained flow gasifier has a very short residence time around 1 – 5 seconds (Situmorang et al. 2020), and high yield of the product gas.



(a) (b) (c) (d)

Figure 2.12. Main types of gasifiers (https:// en.wikipedia.org/wiki/Gasification).

2.6.5.2. Classification by – gasifying agent used

Gasifiers can also be classified based on the gasifying agents used. Therefore, gasifying agents such as air, steam and oxygen are used (Figure 2.13), and are discussed as follows:

- ***Air blown gasifiers*** – These gasifiers using air as a gasifying agent is termed air blown gasifiers. This type of gasifier is economical since air is abundant and inexpensive. The use of air activates the oxidation reactions, which are exothermic, and more heat is generated. The heat generated is supplied to the endothermic stages of the co-gasification such as drying and pyrolysis.

  However, the downside of using the air – blown gasifiers is that they produce a nitrogen rich syngas, which has a low calorific value around 4 – 6 MJ/m^3 Air-blown gasifiers are typically not effective for downstream applications such as chemical and fuels production.
- ***Steam / oxygen blown gasifiers*** - The other types of gasifiers are characterized as steam or oxygen gasifiers, since steam or the pure oxygen are used as the gasifying agent in the gasifier. Therefore, since steam is free of nitrogen, it tends to produce a syngas of high quality, which has a high calorific value as well. The only downside of

steam – blown gasifiers, is that, steam tends to decrease the gasifier temperature. Thus, automatically reducing the carbon conversion efficiency and may also result in operational issues such as agglomeration and fouling as the gasifier temperature becomes lower than the ash meting point.

- When pure oxygen is used in the gasifier, a high-quality product gas, is produced with a better calorific value (medium heating value = 10 – 16 MJ/Nm^3) and a hydrogen gas content around 30 – 60 vol.%, (Shen et al. 2008).

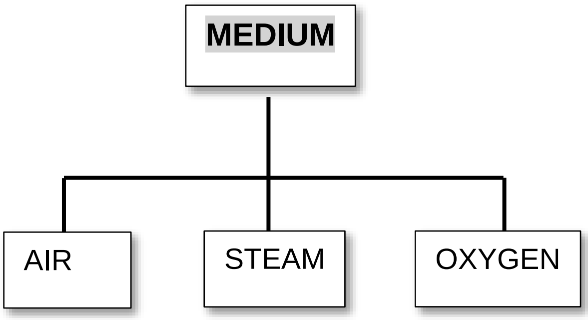


Figure 2.13. Gasification technology classification by medium and pressure (La Villetta et al. 2017).

2.6.5.3. Classification by – heat source

The gasifiers are also classified based on their heat source. There are two forms of classification by heat source for the gasifiers namely; the direct and indirect gasifiers. The direct gasifiers are also called autothermal gasifiers, since these gasifiers use the heat generated within the gasifier to facilitate the chemical reactions between the feedstock and the gasifying agents, and to enhance the carbon conversion efficiency.

Typically, in direct gasifiers, the gasifier is operated at high temperatures above 700 - 800°C (Karl et al. 2018), and gasifying such as air or oxygen are used, since they contain oxygen, and can facilitate oxidation reactions, which are highly exothermic. The only challenge with the indirect gasifiers is that if air is used as the gasifying agents, the product gas is highly contaminated with nitrogen.

The indirect gasifiers or allo-thermal gasifiers receive heat from other operating units such as heat exchangers. The gasifying agent that is typically used is steam, and the quality of the syngas produced it good, since syngas is nitrogen free. They can produce a product gas of good quality with high calorific value, which can be further used effectively in the various downstream applications.

Table 2.5 illustrates the operating parameter specifications for the various types of gasifiers. Each type of gasifier designs has their own specifications in terms of the operating parameters. It is also observed that each gasifier design, results in different output in terms of the tar content, product gas distribution and the lower heating values of the syngas. Therefore, it is important for the operator to carefully control the operating parameters and choose a suitable gasifier type that can produce high yields of syngas, that comprises of high calorific value (Ruiz et al. 2013).

Table 2.5. A comparison of various gasifiers (Ruiz et al. 2013).

Gasifier	**Downdraft**	**Updraft**	**Bubbling fluidized bed**	**Circulating fluidized bed**	**Entrained flow**	**Twin Fluidized bed**
Technology	Simple and proven. A simple reactor with low investment cost.		Plants with higher investment costs. Proven technology with coal.		Complex construction	
Fuel Particle size specification	<51 mm	<51 mm	<6 mm	<6mm	<0.15 mm	<6 mm
Maximum fuel moisture (%)	25	60	<55%	55%	<15%	11 -25%
Gas LHV, (MJ/Nm^3)	4.5 – 5.0	5 - 6	3.7 – 8.4	4.5 - 13	4 - 6	5.6 – 6.3
Tar, (g/Nm^3)	0.015 – 3.0	3.0 - 150	3.7 – 61.9	4. - 20	0.01 - 4	0.2 - 2
Ash and Particles in syngas	Low	High	High	High	Low	High
Reaction temperature, °C	1090°C	1090°C	800 - 1000°C	800 - 1000°C	1900°C	800 - 1000°C
Ash melting point	>1250°C	>1000°C	>1000°C	>1000°C	>1250°C	>1000°C

Syngas output temperature	700°C	200 - 400°C	800 - 1000°C	800 - 1000°C	>1260°C	800 - 1000°C
Admissible powers	Up to 1MWe	Up to 10MWe	1 – 20 MWe	2 – 100 MWe	5 – 100 MWe	2 – 50 MWe
Residence time	Particles remain in bed until discharged		Particles spend substantial time in the bed	Particles pass repeatedly through the circulating loop (few seconds)	Very short (few seconds)	Particles spend time in bed
Carbon conversion efficiency	High	High	High loss of carbon in ash	High	High	High
Process flexibility	Very limited. Any change in process variables needs a new design.		Flexible to loads less than design.		Very limited size and energy content of the fuel must be a narrow range.	Flexible to lead less than design.
Temperature profile	High gradients		Vertically almost constant, little radial variation.	Vertically almost constant.	Temperatures above the ash melting temperature.	Constant in the reactor.
Hot efficiency	85 – 90%	90 - 95%	89%	89%	80%	90 – 95%

***MWe – Mega Watt energy**

2.7. Gasification/Co – gasification process performance indicators

The successful performance of the gasification/co- gasification process for blended fuels greatly depends on the performance indicators, which indicates the effect of the operating parameters such as temperature, pressure, residence time, superficial velocity, gasifying agents etc. on the gasifier and on the product gas. Therefore, the following section defines the various performance indicators that are used to indicate the overall performance of the co-gasification process.

(i) Syngas yield (GY)

The specific gas yield – is defined as the ratio between gas produced and the feedstock fuel consumed. It is measured as a unit of mass or volume of producer gas per unit of mass of the fuel in a gasifier. This parameter is also known as the specific gas production (Silva et al. 2019). The specific gas production is represented by equation 2.7.

$$Y_{syngas} = \frac{V_{syngas}}{M_{feedstock\,fuel}} \left(\frac{Nm^3}{kg}\right) \tag{2.7}$$

Where V_{syngas} represents volume flowrate of the product gas, while the M, represents mass flow rate of the feedstock material that is consumed.

(ii) Heating value of product gas (HV)

Heating value or calorific value of a fuel or product gas (syngas) is defined as the amount of heat produced when the fuel was completely combusted. it is measured as the energy (kJ or MJ) per unit of mass or volume. The heating value can be expressed as a Higher Heating Value (HHV) or a Lower Heating Value (LHV). The HHV indicates the amount of heat produced when the feedstock material is combusted, and the products have cooled and returned to an ambient temperature of 25°C (Guo et al. 2014).

The Lower Heating Value (LHV) is calculated by subtracting the amount of heat that has vaporized from water vapour that generated during the combustion of the fuel. Among the two heating values, the lower heating value is the preferred indicator for the co- gasification as it considers the amount of energy that was lost through the water evaporation during the combustion reaction stage (Basu et al. 2013). The LHV of syngas can be determined through equation 2.8. using the molar fractions of the composition of the syngas.

$$LHV_{syngas} = 10.79\, x_{H2} + 12.63\, x_{CO} + 35.83\, x_{CH4} \tag{2.8}$$

where, *x* stands for molar fraction of each of the gaseous components (Tavares et al. 2018).

The Higher Heating Value (HHV) of each constituent is considered, according to equation 2.9 (Basu et al. 2013).

$$HV_{syngas} = \sum_{l} x_i HV_i \tag{2.9}$$

Where x_i represents the mole fraction of each chemical species contained on the syngas, *HV* represents the heating values of each chemical species i contained in the syngas that given in Table 2.6 (Silva et al. 2019).

Table 2.6. Heating values of gaseous compounds (Silva et al. 2019).

Chemical species	Formula	HHV (MJ/Nm^3)	LHV (MJ/Nm^3)
Hydrogen	H_2	12.74	10.78
Carbon monoxide	CO	12.63	12.63
Methane	CH_4	39.82	35.88
Hydrogen Sulphide	H_2S	25.10	23.14
Benzene	C_6H_6	142.89	141.41

(iii) Carbon conversion efficiency (CCE)

Carbon conversion efficiency (CCE) – is defined as the ratio of the amount of carbon in the product gas and amount of carbon in the feedstock fuel. The CCE is represented by equation 2.10

$$C_{conversion} = C_{syngas} / C_{fuel} \tag{2.10}$$

Where C_{gas} (mol_{carbon}) denotes carbonaceous content of the syngas and C_{fuel} , represent the carbon content of the feedstock fuel (mol_{carbon}) (Kihedu et al. 2016).

(iv) Cold gas efficiency (CGE)

The cold gas efficiency (CGE) is a very important performance indicator for the co- gasification process. The cold gas efficiency is defined by the ratio between the chemical energy of the produced gas and the chemical energy of the fuel. This performance indicator is expressed by equation 2.11 (Guo et al. 2014).

$$CGE = LHV_{syngas} \times Q_{syngas} / LHV_{feedstock} \qquad (2.11)$$

Where LHV_{syngas} implies the syngas lower heating value (MJ/Nm^3), Q_{syngas} represents the volumetric production of the syngas per mass of the feedstock material (kg/ N m^3), (Kihedu et al. 2016). The data in Table 2.7, illustrates, that different gasifier types, operates within a certain specification. Therefore, it is of paramount importance that the operator, uses the performance indicator that correlates to a specific type of the gasifier (La Villetta et al. 2017).

Table 2.7. Illustrates the performance indicators of the co- gasification process when different gasifier designs are used (La Villetta et al. 2017).

Performance indicators	Units	Updraft	Downdraft	BFB	CFB
CCE	%	-	91 – 98	76 – 91	86 – 97
LHV_{syngas}	$MJ/Nm^3{}_{gas}$	5.0 – 6.0	4.2 – 5.7	3.3 – 5.3	3.6 – 4.0
CGE	%	40 – 60	52.2 – 65	50 – 60	46 – 66
Tar	g/Nm^3_{gas}	20 – 100	0.1 – 1.2	1 – 15	1 – 15
Particulates	g/Nm^3_{gas}	0.1 – 10	0.1 – 0.2	2 – 20	10 – 35

2.8. Gasification/Co – gasification operating parameters

It is of paramount importance to identify and understand the key factors that affects the overall co- gasification performance. The various operating parameters are discussed in the sections that follow.:

2.8.1. Gasifier temperature

Temperature is a very important operating parameter for the co- gasification process. Most of the other operating parameters such as gasifying agents, catalyst etc. are interlinked with temperature. In a way that when the temperature is low, the carbon conversion efficiency in the gasifier drops, since when the temperature is low, the chemical reaction rates are low, thus less carbon material from the feed is converted.

For instance, in the case of a fluidized bed gasifier, it is difficult to reach a high degree of fluidization when the temperature is operated at low values. Similarly, the entrained flow gasifier requires very high temperature around 1990°C (see Table 2.4), (Ruiz et al. 2013). High temperature is required to enhance the chemical reaction rates, and high carbon conversion efficiency. Secondly when the temperature is set low, even if a catalyst employed in the gasifier, it will not be highly effective as when the temperature is high.

The temperature in the gasifier is related to the gasifying agents employed. When air is used as a gasifying agent, the temperature usually increases in the gasifier, and enhances the exothermic oxidation reactions, which leads to more heat being generated and the heat produced is supplied to the endothermic stages of co- gasification such as drying and pyrolysis. During high temperature operation, more tar and char are thermally cracked, and this enhances the yield of the syngas as well as more carbon in the feed is converted.

Temperature is also affected when steam is employed as a gasifying agent. When the steam is supplied to the gasifier, the temperature drops, and more heat is required to increase the temperature. Therefore, it is crucial that the temperature be controlled and selected at optimal values that will yield a high carbon conversion efficiency and syngas that is of good quality with high heating value. Therefore, for the co- gasification process the temperature is typically controlled between the range of 700 - 1900°C., depending on the type of a gasifier that is used, (see Table 2.4), (Ruiz et al. 2013).

2.8.2. Moisture content

Moisture content of the feedstock is one of the critical parameters that greatly affect the performance of the co- gasification process. This parameter has a huge impact on the carbon conversion efficiency. The moisture content of the wet feed material is typically between 30 - 60% (Ruiz et al. 2018) and has to be reduced to an acceptable range of moisture content for most gasifiers of 5 – 35% (Sansaniwal et al. 2017) using processes such a torrefaction and drying. When a wet feedstock is fed into the gasifier, it tends to be sticky and thus, very hard to pass through the gasifier.

Secondly, during the conversion process the feed with high moisture content that is not within the required specification, the moist feed tends to lower the temperature of the gasifier, which leads to the decrease in the chemical reactions rates. When the chemical reactions in the gasifier are no longer active, the carbon conversion efficiency decreases (Arena et al. 2013). This leads to the decrease of the performance for the gasifier. As a result, more char and tar are formed. The syngas produced, from the conversion of the untreated moisture content of the feed material, is that of poor quality, has low yield and is contaminated with tar and cannot be useful in the downstream applications. Therefore, it is of paramount importance that the moisture content of the feed be pre- treated prior to the commencement of the co- gasification process.

2.8.3. Particle size

The particle size of the fuel plays an important role in the co-gasification process, since in order to obtain a high carbon conversion efficiency, the particle size of the fuel is required to be within the required specification. When the particles of the feedstock are large it is difficult to be fed into the gasifier, the behaviour is similar to that of the feedstock material with high moisture content.

Different gasifier designs require different particle sizes. For instance, a fluidized bed gasifier, requires smaller particle sizes, in order to allow a high degree of fluidization. Smaller particle sizes, < 6mm (Ruiz et al. 2013), of the fuel also allows good mixing of the particles within the bed, high reactivity rates between the blended fuel and the gasifying agent and shorter residence time (see Table 2.4) This leads to a high carbon conversion efficiency.

The effect of the feedstock particle size is also observed in the entrained flow gasifiers, where the allowance of the particle size of the fuel is very narrow. Very small – like- powdered particle size less than 0.15 mm (Ruiz et al. 2013). This yields a high carbon conversion efficiency that is almost 98 – 99.5% (Watson et al. 2018) and the product produced from this gasifier, is of high quality, with very little tar and char.

2.8.4. Pressure

Pressure is an operating parameter that also plays a role in the overall performance of the gasifier and the entire co- gasification process. Therefore, this parameter is either under pressurized conditions or at atmospheric pressure. In most of the co- gasification technologies, the gasifier is operated at atmospheric pressure rather than under pressurized conditions, due to the fact that when the gasifier is operated under atmospheric pressure, it is easier to control the conversion process that is simultaneously operated under high temperature (Ruiz et al.

2013). Operating gasifiers at atmospheric pressures is also preferred due to its low-cost operation and is applicable for small-scale applications (Ruiz et al. 2013). The pressurized gasifier is very costly. However, it has less challenges such as high tar and low carbon conversion, and thus is very efficient in terms of producing a product gas that is of high quality, which consists of high heating value and high yield (Parthasarathy et al. 2020).

2.8.5. Residence time

Different gasifiers operate at different residence times. However, this parameter is influenced by the particle size of the fuel and other parameters such as the gasifier temperature. When the particle size of the fuel is small, like that required in the entrained flow, below 0.75µm, the residence time becomes very short, around 1 - 2 seconds (Ruiz et al. 2018). However, this is not the case for the fixed bed gasifier, which employs longer residence time around 5 seconds (Perez et al. 2008).

2.8.6. Superficial velocity

Superficial velocity (SV) is defined as the ratio of the syngas production mass flowrate at normal conditions and the narrowest cross- sectional area of the gasifier (La Villetta et al. 2017). This parameter is a function of temperature and highly influences the devolatilization of the feedstock in the pyrolysis stage. When the superficial velocity is low, the pyrolysis process will be slow, and more tar and char will be produced, inversely, when the superficial velocity is set at high value, fast pyrolysis will occur, thus reducing the tar and char formation.

High superficial velocity results in a high production of syngas, that has high energy content. The only disadvantage of operating at very high superficial velocity is that it significantly reduces the gas residence time, thus leading to lower efficiency in the tar cracking process. Therefore, it is paramount that the superficial velocity be set within a suitable operating range in order to avoid the high yield of tar and char. The suitable operating range for superficial velocity for the bubbling fluidized bed gasifiers is between 0.4 – 0.6 m/s (Sansaniwal et al. 2017).

2.8.7. Catalysts

Catalyst is one of the important parameters for the co- gasification process and has a great influence on the quality, yield, distribution and composition of the syngas. The addition of a catalyst in the gasifier enhances a high carbon conversion efficiency, since catalyst, increases the tar cracking efficiency and it improves the hydrogen yield in the product gas (Block et al. 2019).

There are various catalysts used in gasification processes. The commonly used ones are natural minerals catalyst such as dolomite, olivine and Ni- based catalysts. These catalysts are inexpensive and abundant (Kirubakaran et al. 2009). The downside of using catalysts is that in some processes as the tar decreases, the light hydrocarbon such as CH_4 increases. Catalysts can be used as primary or secondary catalyst for the co - gasification process. The primary catalysts are employed inside the bed of the gasifier and the secondary catalysts are typically utilized in the downstream catalytic processes. In other processes if two gasifiers are inter- connected the secondary catalyst is employed in the second gasifier.

For instance, olivine catalyst was used as a primary catalyst in the fluidized circulating bed gasifier, and an excellent tar cracking efficiency was observed, as well as the high H_2 content in the syngas and the overall gas yield. The syngas yield increased from 0.99 to 1.13 Nm^3/kg biomass, while tar content decreased from 18.9 to 11 g/Nm^3 (Koppatz et al. 2011).

2.8.8. Gasifying agents

The common gasifying agents used, as mentioned previously, are air, oxygen, steam, carbon dioxide or their combination. The molar flow rates of the gasifying agents affect the carbon conversion efficiency as well as the quality (in terms of composition and calorific value) and yield of the product gas (Arregi et al. 2018).

The flowrates of gasifying agents are typically denotes in terms of a ratio. The equivalence ratio (ER) is used to quantify the amount of air used as a gasifying agent. The flowrate of steam is expressed as a steam- to- fuel ratio (SFR), while the carbon dioxide is expressed as a carbon dioxide – to – carbon ratio (CO_2/C).

- **Equivalence ratio (ER)**

The equivalence ratio (ER) of air is defined as the ratio of an actual air provided to stoichiometric air needed for the process of the co- gasification. This operating parameter plays an important role in the co- gasification process as it has an influence in the quality of syngas, the yield of tar and the calorific content of the syngas produces and as well on the overall carbon conversion efficiency of the process (Sikarwar et al. 2016). ER is represented by equation 2.12 (Strezov et al. 2015).

$$ER = \frac{Actual\ air\ fuel\ ratio}{Stoichiometric\ air\ fuel\ ratio} \tag{2.12}$$

An ER value of 1 represents the stochiometric value of air required for complete combustion. An ER less than 1 represents a sub-stoichiometric value of air, which is typically the case in gasification processes. When the ER is operated at high values, the temperature in the gasifier increases and that leads to the activation of the oxidation reactions, which are exothermic (releases energy). The energy released is usually used in other endothermic stages of the co-gasification process such as drying and pyrolysis. Therefore, the high temperatures also enhance the tar cracking reactions, which results in low tar yield. High equivalence ratio (ER) enhances carbon conversion efficiency.

However, high values of ER, means higher nitrogen content (in the case of air-blown gasification), and therefore the product gas will be contaminated with nitrogen resulting in a product gas with a low-calorific value. The syngas product, produced from the high ER consists of low calorific value, typically within a range of 3 – 6 MJ/Nm^3 (Mishra et al. 2018).

Typically, the suitable operating of ER, for biomass feedstock is between 0.2 – 0.4 (Guan et al. 2016). At very low ER values, the temperature of the gasifier drops, thus leading to low reaction rates, high tar and char formation as well as very low carbon conversion efficiency. Operation of ER above the suitable point i.e. >0.4, results in very high production of the carbon dioxide (CO_2) concentration in the syngas and very low hydrogen (H_2) and carbon monoxide (CO) yields.

- **Steam – to - fuel – ratio (SFR)**

The steam – to- fuel ratio (SFR), which is defined as the ratio of the flow rate of steam to the dry fuel flowrate introduced into the gasifier as represented by equation 2.13 (Tavares et al. 2018).

$$SFR = \frac{Steam\ mass\ flow\ rate}{Feed\ fuel\ flow\ rate} \tag{2.13}$$

The steam -to-fuel-ratio (SFR) is an important operating parameter in the co- gasification process, since it directly influences the gas product yield, heating value of the syngas and the H_2 content of the syngas as well as the operating gasifier temperature. When SFR is increased, the partial pressure of H_2O inside the gasifier increases, and this favours the water-gas-shift reaction (WGS) and the steam reforming reaction (Table 2.3). Thus, facilitating a higher yield of gaseous product and higher CO_2 and H_2 concentration in the syngas, while the CO production decreases. The ratio of H_2/CO increases as the steam – to- fuel ratio is increased (Dang et al. 2021).

Operation at high steam – to – fuel values cause the temperature in the gasifier to decrease, and that lowers the carbon conversion efficiency, since the reaction rates becomes very low and less carbon gets converted into gases, and more tar content is generated.

For instance, a study to investigate the effect of varying steam to biomass ratio (SBR) on the product gas composition was conducted by Fremaux et al. (2015). Wood residues were used in the study as the biomass feedstock, and the reaction temperature was fixed at 900°C. The steam to biomass ratio (SBR) was varied between 0.5 to 1. It was deduced that as the SBR increased the production of H_2 increased from 38 (vol%) to 53 (vol%), CO_2 increased from 10 (vol%) to 18 (vol%) and CH_4 slightly increased from 10 (vol%) to 13(vol%), while the production of CO decreased significantly from 38 (vol%) to 21(vol%) respectively.

- **Oxygen**

Oxygen as a gasifying agent enhances the temperature in the gasifier, which in turn increases the chemical reaction rates and carbon conversion. When oxygen is utilized as a gasifying agent, the tar and char cracking reactions are also enhanced. The product gas produced from oxygen is of good quality with high calorific value, since unlike in the air content, pure oxygen is not mixed with nitrogen. However, the challenge is that pure oxygen is very expensive, when compared to air and steam, since an air separation is required.

Therefore, the efficient way of using oxygen in an inexpensive manner, is to mix oxygen with steam. The advantage of mixing these two gasifying agents with the biomass feedstock is that the gasifier temperature is maintained within the acceptable operating range and simultaneously, the quality of the product gas is not compromised due to the influence of the nitrogen, and the calorific value is between a range of 10.3 – 13.5 (MJ/Nm^3) as shown in Table 2.8 (Puig – Arnavat et al. 2010).

Table 2.8. The effect of different gasifying agent on the operating conditions and gas composition, for biomass feedstock (Puig – Arnavat et al. 2010).

	Air	**Steam (pure)**	**Steam– O_2 mixtures**
Operating conditions			
ER	0.18 -0.45	0	0.24 – 0.51
S/B (kg/ kg daf)	0.08 – 0.66	0.53 – 1.10	0.48 – 1.11
T (˚C)	780 – 830	750 – 780	785 – 830
Gas composition (% vol, dry basis)			
xH_2 (vol%, dry basis)	5.0 – 16.3	38 – 56	13.8 – 31.7
$x\,CO$ (vol%, dry basis)	9.9 – 22.4	17 – 32	42.5 – 52.0
xCO_2 (vol%, dry basis)	9.0 – 19.4	13 – 17	14.4 – 36.3
xCH_4 (vol%, dry basis)	2.2 – 6.2	7 – 12	6.0 – 7.5
xC_2H_4 (vol%, dry basis)	0.2 – 3.3	2.1 – 2.3	2.5 – 3.6
xN_2 (vol%, dry basis)	41.6 – 61.6	0	0
xH_2O *(g)* (vol%, wet basis)	11 – 34	52 – 60	38 – 61
Yields			
Tar (g/kg daf)	3.7 – 61.9	60 – 95	2.2 – 46
Char (g/kg daf)	Na	95 – 110	5 – 20
Gas (Nm^3/ kg daf)	1.25 – 2.45	1.3 – 1.6	0.86 – 1.14
LHV_{syngas} (MJ/Nm^3)	3.7 – 8.4	12.2 – 13.8	10.3 – 13.5

na: not available; daf: dry ash-free basis; ER: equivalence ratio; S/B: steam – to – biomass ratio (H_2O (kg/h) / biomass (kg daf / h).

2.8.9. Feedstock blend ratio

Blend ratio plays a vital role in the co- gasification process, since when two different feedstocks are mixed at different proportions, the composition of the feedstock material changes (i.e. the ultimate and proximate analysis are affected). The change in the composition of the raw feedstock material, directly affects the composition, yield and distribution of the product gas.

During the blending of feedstock materials, the elemental composition of the blended feedstock changes. For example, when the plastic waste material is mixed with biomass feedstock material, the composition of the fuel mixture changes. Plastic waste has high volatile matter and contains high hydrogen content, therefore, when mixed with the biomass it acts a hydrogen donor and provides some radicals that enhances the cracking of tar during the co-gasification process. Therefore, the high plastic waste ratio in the mixed feedstock results in the high yield of hydrogen in the syngas product (Kamble et al. 2019).

Similarly, biomass has a high volatile matter and contains high oxygen content, therefore, when these coal and biomass are blended, this results in an increase in CO_2 and CO in the product gas, due to its high reactivity and oxygen content.

It is important that the feedstock blend ratio be optimized in order to determine the synergistic effect in the product gas produced. Synergistic effects are observed when there is an interaction between the two different feedstock materials. Therefore, synergistic effects are observed during the co - conversion of two different feedstocks, that consists of different chemical and physical properties. Synergy is experienced when the quality of the products produced from the combined feedstocks is better than the product produced when gasified individually (Guo et al. 2016).

Ahmed et al. (2011) conducted a study to determine the effect of the co- gasification of polyethylene (PE) and wood chips (WC) on the syngas yield, and energy yield. The study was conducted using steam as a gasifying agent, which was fed to the gasifier at a constant rate of 7.72 g/min and the gasifier temperature was operated at 900°C. The feedstock blend ratios were varied from 0% PE to 100% PE respectively.

The results shows that as the polyethylene (PE) ratio was increased, the syngas yield increased from around 33 g at 0% PE, to 55 g at blend ratio of 80% PE, before decreasing to 33 g for 100% PE and the same trend was observed for hydrogen yield which also increased, from approximately 1.8 g for 0% PE and to a yield of 3.8 g at blend ratio of 80% PE, thereafter, the H_2 yield decreased to 3 g.

Furthermore, as the blend ratio increased from 0% PE, the energy yield increased from 500kJ to a maximum of 1400kJ at blend ratio of 80% PE before, decreasing to around 1000kJ at blend ratio of 100% PE. From the results, it was observed that among the feedstock mixtures, at a blend ratio of 80% PE, the superior results for syngas yield, hydrogen yield and energy yield were obtained. The increase did not follow a linear trend of the weighted average yield from the individual gasification of PE and WC. However, the blend of polyethylene (PE) and woodchips (WC) yielded the highest values of the syngas yield, hydrogen yield and energy yield.

This trend is expected based on the fact that the polyethylene is a plastic material, thus has a higher heating value. From the results it was seen that during the co- gasification of polyethylene and woodchips, adding a small amount of woodchips of 20% WC in the blend, resulted in higher energy yield than obtained from 100% PE sample.

Therefore, due to the high temperature steam gasification, the steam – hydrocarbons reforming reactions (Table 2.4) were promoted. Thus, resulting in high hydrogen content than expected by the weighted average yield. From the study it was concluded that the increase in the syngas yield, hydrogen yield and energy yield as the feedstock blend ratio of PE percentages increased, indicates the synergistic effect of the co - gasification of PE-WC.

Several studies were selected to show the effect of the operating parameters on the syngas product when the feedstock material is blended. A study conducted using Aspen Plus by Tevares et al. (2018), show the effect of equivalence ratio (ER) and temperature on the syngas composition and on cold gas efficiency (CGE) when air was used as a gasifying agent. The effect of ER on the syngas composition was tested using two feedstocks i.e. Polyethylene Terephthalate (PET) and biomass, being set at blend ratio of (50% PET + 50% Biomass) and (90% PET + 10% Biomass). The gasifier temperature was kept constant at 800°C.

The experiment was initially conducted using the feedstock mixture of (50% PET + 50% biomass), and the results showed that as the ER was increased from 0.1 to 1, the H_2 content in the syngas decreased from approximately 33% to 12%, CO concentration decreased from 53% to 30%, while the CO_2 content decreased slightly until an ER value of 0.7. The decrease of H_2 and CO as the ER increased, is attributed to the oxidation reactions (Table 2.4) which are promoted as the ER is increased. At values of ER greater than 0.7, the CO_2 content increased due to the combustion reactions. At an ER = 0.7, the CGE reached a maximum of 72% and decreased to 62%, as the ER increased above 0.7. The reason the CGE decreased is as CGE is a function of the lower heating value of syngas, and as the ER increases, the lower heating value of the product gas tends to decrease.

For the feedstock blend ratio of (90% PET + 10% biomass), as ER was increased from 0.1 to 1.0, the concentration of H_2 decreased from around 40% to 15%, CO decreased from 45% to 38%, while the CO_2 remained constant at 3%. The CGE slightly increased from 71% to 72% respectively.

From the results, it can be deduced that for both feedstock mixtures, an increase in ER reduces the formation of H_2 and CO in the syngas, thus resulting in poor syngas quality. However, at low ER values, the values of H_2 and CO were higher, and that is due to the promotion of gasification reactions. While for ER above 0.7, the formation of combustion products such as CO_2 increase.

It was noted that despite that the H_2 and CO composition in the syngas decreasing with an increasing ER value, the H_2 content from the feedstock with the blend ratio of (90% PET + 10% biomass) was higher than that obtained from the feedstock ratio of (50% PET +50% biomass). The results concluded that high ER are not suitable for the co- gasification of PET and biomass mixtures since it results in the H_2 and CO composition in the product gas to decrease.

In the same study Tevares et al. (2018) investigated the effect of steam as a gasifying agent on the syngas composition. Both feedstock mixtures namely; (50% PET + 50% biomass) and (90%PET + 10% biomass) were used. The steam to fuel ratio (SFR) was varied from 0.8 to 2.0. The results illustrated that when the feedstock was at a blend ratio of (50%PET + 50% biomass) and the SFR increased from 0.8 to 0.2, the composition of H_2 increased from 50% to 58%, CO content decreased from 38% to 19%, while CO_2 content increased from 13% to 25% respectively.

At a feedstock blend ratio of (90%PET + 10% biomass), a gasifier temperature of 800°C, and SFR varying from 0.8 to 2.0, the H_2 content in the product gas increased from 52 to 59%, CO decreased from 40% to 20%, while CO_2 increased from 8% to 19% respectively. The CGE was not calculated for the steam gasification of PET and biomass. Therefore, the results, shows that for both feedstock mixtures yielded more or less same amount of H_2 as the SFR was varied between 0.8 – 2.0. Lower CO_2 and higher CO compositions were attained for higher PET ratio.

Therefore, from both studies of using ER and SFR as the gasifying agents, it was observed, that increasing the SFR increases the H_2 content, regardless of the feedstock blend ratio. Based on this fact, it can be concluded that steam is a better gasifying agent as compared to ER for the co- gasification of PET and biomass at high temperature.

Similarly, in the same study of Tavares et al. (2018), investigated the effect of temperature on the syngas composition and on the cold gas efficiency (CGE) was investigated, in the presence of air, which was used as the gasifying agent. From the study, it was determined that when the temperature was varied between 400°C to 1200°C, and a blend ratio of (50% PET + 50% Biomass), and air is used as the gasifying agent, the H_2 and CO contents increased from 5% to 28% and from 0% to 54% respectively, while, CO_2 and N_2 concentrations decreased from 30% to 0% and 30% to 18% respectively. The cold gas efficiency (CGE) increased with an increasing temperature from 38% to 74%.

For a blend ratio of the feedstock was increased to (90% PET + 10% Biomass), and the temperature between 400 - 1200°C, in the presence of air which is used as the gasification agent. The results illustrated that the H_2 content in the syngas increased from 8% to 38%, the CO content increased from 0% to 44%, while CO_2 content decreased from 19% to 0%. H_2 and CO are promoted at the expense of CO_2, once the endothermic reactions are favoured, when the temperature is raised. CGE increased as the temperature increased from 600°C to 900°C and thereafter remained constant at 73% as the temperature was increased to 1200°C.

Therefore, from the study, it can be deduced that a high percentage of plastic waste (PET) in the blended feedstock material, increases the production of H_2 and CO content in the syngas. Increasing temperature for both feedstocks blend ratios i.e. (50%PET+50% biomass) and (90% PET + 10% biomass), increases the formation of H_2 and CO in the syngas. However, it was observed that at temperatures above 800°C, the composition of the syngas was no longer changing.

An experimental study was conducted by Lopez et al. (2015), in a spouted bed reactor at fixed gasifier to determine the effect of adding plastic waste (high density polyethylene) waste to the biomass (pine sawdust) feedstock, on the product gas composition and observe whether the addition of HDPE to the biomass feedstock results in a synergistic effect.

Biomass feedstock was initially gasified alone under the gasifier temperature set at 900°C and steam – to- fuel ratio set at 1. Olivine used as a catalyst to facilitate the tar cracking reactions. The H_2 concentration for the pure biomass feedstock was 40%. A 25% HDPE mixture with the biomass resulted in the concentration of H_2 in syngas slightly increasing from 40 to 42%. At a blend ratio of 50% HDPE, the production of H_2 in syngas increased tremendously from 42% to 57%. When the HDPE was gasified alone a maximum of 58% hydrogen was obtained.

From the results, the effect of co - feeding was observed on the H_2 production in syngas and it was clear that when the feedstock was at (50% biomass and 50% HDPE), the concentration of hydrogen in the syngas increased tremendously, almost similar to that obtained when pure

HDPE was gasified. The results appear to indicate that the blend ratio of 50% HDPE, yields a higher H_2 content, than a blend ratio of 25% HDPE.

The study also shows that the concentrations of CO and CO_2 in syngas, were not that affected by the co- feeding and the increasing of the blend ratio of the HDPE since the CO_2 at 100% biomass was 9%, when the feedstock blend ratio increased to 25% HDPE, the CO_2 was 8%, at blend ratio of 50% HDPE , the CO_2 content was around 7% and at 100% HDPE the CO_2 content, increased slightly to 7.5% respectively.

The same trend was observed in the formation of CO content, which when the feedstock was 0% HDPE the CO yield was round 28%, at blend ratio of 25% HDPE, the CO content became 29%, at blend ratio of 50% HDPE the CO content was approximately, 27% and at 100% HDPE the CO concentration was found to be around 27.5% respectively.

This can be explained in terms of the composition of HDPE which does not contain any oxygen, therefore, the CO and CO_2 were formed by the oxygen obtained from the steam supplied as well as the decarbonylation and decarboxylation reactions of the oxygenated compounds derived from the biomass decomposition.

The methane concentration was low due to the high gasification temperature of 900°C. The methane composition for the 25% HDPE blend was the same as that of pure biomass, being18% and when the ratio of HDPE was increased to 50% the concentration of methane decreased to 6%.

The effect of co - feeding of HDPE and biomass on tar content in syngas was also observed in the study. It was observed that when only biomass was gasified, the tar content was high at 58.2 gNm^{-3} in the syngas product. However, for a 25% HDPE blend, the tar content reduced to be around 50 gNm^{-3}. As the HDPE ratio was increased to 50%, and the tar content decreased significantly to 9.7 gNm^{-3}. When the feed was only HDPE, the tar content obtained was 5.1 gNm^{-3}, the drastic reduction of tar content from when biomass feedstock was gasified alone, clearly indicated the synergetic effect.

Furthermore, careful consideration should be taken when selecting a catalyst for the co-gasification process. This is shown through a study that was conducted when beech-wood and polyethylene feedstock were mixed and co - gasified in the fluidized bed gasifier. Silica sand was used as a bed material in the experiment with catalysts such as olivine, Na-Y zeolite and ZSM – 5 zeolites. The results showed that different catalyst have different catalyst activity in co- gasification of beech- wood and polyethylene. It is ranked as follows: Na-Y-Zeolite > ZSM -5 zeolite > Olivine (Zhu et al. 2019).

2.9. Syngas cleaning

As mentioned in the above sections that the syngas produced from the co - gasification process is required to be cleaned in order to alleviate the contaminants that might be present and that might affect its application downstream. Therefore, in the section below, the cleaning process is discussed.

The syngas is cleaned by removing the undesirable impurities such as sulphur, char, tar, ammonia, hydrochloric acid etc. The main reason why the syngas should be clean it is so that it can be suitable for the downstream applications such as in the Fischer- Tropsch process, synthesis of chemicals, methanol, ethanol, production of heat and electricity etc. Secondly, syngas should be cleaned to prevent problems such as corrosion, fouling, scaling etc. in the downstream equipment (Ruiz et al. 2013).

The syngas product is cleaned using different several methods such as physical cleaning or through using the thermal decomposition as well as catalytic conversion method (Sansaniwal et al. 2017). The equipment used to clean the product gas are cyclones, ceramic particles separators, rotating particle separators, wet electrostatic precipitator and water scrubber. Therefore, these cleaning methods are discussed below.

- **Physical gas cleaning process**

The physical gas cleaning process involve the filtration of the produced gas and wet scrubbing of contaminated product gas. The filtration method uses either high or low temperature filters. The high temperature resistant filters comprise of materials such as ceramics, composites and fibreglass. The low temperature filters use char coal, cotton fibres as the heat resistant material. The downside of using the filters is the fouling or tar or solid particulates, since when they have fouled, the filter pores get clogged, causing a pressure drop (Chiodini et al. 2017).

- **Thermal decomposition**

This method removes or reduces tar content in the syngas product. Heavy aromatic tar compounds are degraded into smaller or lighter species such as methane, H_2 and CO_2, at higher temperature of 1000˚C (Sansaniwal et al. 2017). During the thermal decomposition process, the equivalence ratio is also used to control the airflow into the reactor. This parameter is used to facilitate the oxidation reactions and increase the temperature in the reactor, thus cracking tars and reducing its content.

- **Catalytic tar conversion**

Tar is also reduced using the catalytic conversion. This method does not only reduce tar, but also eliminated other contaminants associated with tar such as ammonia. Unlike the physical and thermal gas cleaning processes, this method operates at the same temperature that the gas exits and therefore no cooling is required. Particulate matter and ammonia in the gas product are trapped and the product gas is cleaned and made suitable for the downstream applications.

2.10. Modelling of gasification/co - gasification systems

2.10.1. Introduction

The mathematical modelling of the co- gasification systems is developed mainly to conduct the preliminary design of the plant processes in industries. The mathematical models are utilized mainly to describe complex nature of the co - gasification process, since the co - gasification process is expressed by a complex set of chemical reactions. Models are effective methods of predicting the performance of the gasifier and optimizing the co - gasification process. Generally, the modelling provides qualitative and quantitative information about the gasifier (Safarian et al. 2019).

Models are used to determine and understand the effect on the nature and performance of the gasification process, when different input parameters such as blended feedstock and gasifying agents are introduced into the system (La Villetta et al. 2017). Models assist in determining the sensitivity of the gasifier performance when different operating parameters such as gasifying agents and different blend ratios of the feedstocks are varied.

There are different models that are used for modelling. These models are thermodynamic equilibrium models, kinetic models, phenomenological models and lastly, artificial neural network (ANN) models.

2.10.2. Kinetic models

Kinetic models are used to account for the reaction kinetics in the gasifier. These models consider the progression of the chemical reactions across the reactor. Therefore, kinetic models play an important role in designing, evaluating and improving the performance of the gasifier.

Kinetic models deliver very accurate and detailed results, since they take into account the geometry and kinetics of the reacting species at different positions along the reactor. The information of the chemical reactions across the different positions in the reactor allows the operator to determine the product composition at every position in the gasifier. They are particularly useful for gasification employing short residence times. Kinetic models are complex and very computationally intensive (Puig – Arnavat et al. 2010).

2.10.3. Thermodynamic equilibrium models

Thermodynamic equilibrium models are utilized to predict the composition and yield of the product gas, which is syngas. These models are applied based on the assumption that the input components react in a completely mixed condition, for an infinite time frame. The thermodynamic equilibrium models are efficient for providing insight and understanding of the relations between the feedstock fuel, process operating parameters, syngas yield and composition.

Therefore, these models function under the assumption that the system reaches the equilibrium state (Silva et al. 2019). It is very difficult to reach the thermodynamic equilibrium state, therefore, the outcomes of the model represent the maximum efficiency that can be obtained when a certain feedstock material is used in a system. Thermodynamic equilibrium models are much simpler and easier to implement when compared to kinetic models. These, models are independent of the gasifier design, and cannot predict the influence of the geometric or hydrodynamic parameters. General thermodynamic properties (such as enthalpy and Gibbs energy) are only required for equilibrium modelling (Bridgwater et al. 1995). Thermodynamic equilibrium models are operated using two sub-categories which are, the stoichiometric and non-stoichiometric method.

- **Stoichiometric approach**

In the stoichiometric approach, the equilibrium constants of an independent set of reactions are used. This method is based on the stoichiometry of the global reaction and chemical formula of the feedstock (Basu et al. 2013). In order to apply the stoichiometric approach, a set of reactions that will be used in the simulation should be selected, in order for the model to estimate the gas composition and distribution. The equilibrium constants are calculated for these reactions at the reaction temperature. The overall equilibrium composition of the preselected set of reaction is computed.

- **Non- Stoichiometric approach**

In the non- stoichiometric approach, no reactions are specified during the development of the co- gasification simulation process. Only a set of chemical species that are possible reactants and product such as CO, CO_2, H_2, H_2O etc are specified. Therefore, the model is developed only by using the input information of the elemental constituents of the feedstock materials, obtained from the ultimate analysis data. The non- stoichiometric approach uses the principle of the minimization of Gibbs energy, in order to achieve the thermodynamic equilibrium condition. When the Gibbs energy is minimum the system has achieved the equilibrium state (Puig – Arnavat et al. 2010).

2.10.4. Aspen Plus modelling

Within the Aspen Plus tool, there is an extensive input property data bank, that contains information for different chemical compounds. Aspen Plus also contain various block units (reactors, columns etc.) to model various chemical, physical or biological system. Thus, Aspen can be used for modelling and simulation of various systems and is not only limited to gasification. Another advantage of using Aspen Plus simulator is that the processing tool is flexible, as it can simulate different feedstock materials, such as biomass, coal, plastic waste etc. using the ultimate and proximate analysis of these compounds.

Therefore, the models created from Aspen Plus are capable of predicting the gasifier temperature, gas composition, gas heating value and overall carbon conversion efficiency, under various operating conditions such as equivalence ratio (ER), steam – to- fuel ratio (SFR) moisture content (MC), etc.

Tavares et al. (2020) conducted a study for the gasification of the Portuguese forest residues, using Aspen Plus process simulator. The model used the non- stoichiometric approach. From the study, the effect of varying temperature and steam to biomass ratio (SBR) on the product gas composition and its Lower Heating Value of the syngas (LHV) was investigated. It was deduced that when the temperature was varied from 600°C to 900°C, the H_2 and CO concentrations in the product gas increased, from 16% to 21% and 20% to 30% respectively. Whereas, CO_2 and CH_4 decreased from 16% to 8% and 4% to 0% respectively. The study also showed that as the temperature increased from 600°C to 900°C, the Lower Heating Value of the syngas product increased from 5.5 to 5.7 (MJ/m^3)

The effect of varying the steam to biomass ratio (SBR) from 0.1 – 2.0 on the product gas was also observed using Aspen Plus, in the same study, and the results indicated that when the SBR increased, the production of H_2 increased from 37% to 60%, CO_2 increased from 5% to 28% while, CO content decreased from 50% to 12% and CH_4 decreased from 8% to 0% respectively (Tavares et al. 2020).

Another study conducted using the Aspen Plus process simulator for the gasification of wood residues. The study used a RGibbs reactor which is based on the Gibbs minimization approach and applied the restricted equilibrium method (Pala et al. 2017). In this study the effect of varying the steam -to- biomass- ratio (SBR) from 0.2 to 1.0 on the product gas was investigated. The temperature in the gasifier was set at 900°C and it was observed that as the SBR was increased from 0.2 – 1., the production of H_2 and CO_2 increased from 56% to 62% and from 4% to 17%, while that of the CO and CH_4 decreased from 41% to 24% and from approximately 0.2% to 0% respectively (Pala et al. 2017).

2.10.5. Neural network models

The neural network models are the latest approach used to model the gasifiers. These models depend largely on the information from various experiments, which is programmed within the model and used to train the model. Therefore, the models are programmed in such a way that they interpret the process behaviour in a manner that is similar to the way a senior operator would interpret the process.

The neural network models have the ability to predict the behaviour of the gasifier, under different operating conditions. Therefore, proper function of neural network model relies on the known knowledge of the process (Basu et al. 2013). There are three categories of the neural network models that have been applied to gasification, namely; artificial neural network models (ANN), hybrid neural network (HNN) and multilayer feedforward neural network (MFNN) (Puig- Arnavat et al. 2010).

REFERENCES

Alauddin. Z, Lahijani. P, Mohammadi. M, Mohamed. A. R, (2010), Gasification of Lignocellulosic Biomass in Fluidized Beds for Renewable Energy Development: A Review, *Renewable and Sustainable Energy Reviews*,14, 2852 – 2862.

Al – Salem, S. M. M Antelava. A, Constantinou. A, Manos. G, Dutta. A, (2017), A Review on Thermal and Catalytic Pyrolysis of Plastic Solid Waste (PSW)*, Journal and Environmental Management*,197,177 – 198.

Arena. U, (2012), Process and Technological Aspects of Municipal Solid Waste Gasification: A Review, *Waste Management*, 32, 625 – 639.

Arregi. A, Amutio. M, Lopez. G. B, Olazar .M, (2018), Evaluation of Thermochemical Routes for Hydrogen Production from Biomass*, A Review*. *Energy Conversation and Management* ,165, 696 – 719.

Bai. B, Liu. Y, Wang. Q, Zou. J, Zhang. H, Jin. H, Li. X, (2019), Experimental Investigation on Gasification Characteristics of Plastic Waste in Supercritical Water, *Renewable Energy* ,135, 32 – 40.

Baruah. D, Baruah. D.C, (2014), Modeling of Biomass Gasification: A Review, *Renewable, Sustainable Energy Review*, 39, 806 – 815.

Basu. P, (2013), Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory, *Dalhouse University and Greenfield Research, Incorporated: Academic Press inprint, Elsevier Inc.*

Baskar .C, Baskar. S, Dhillion. R. S, (2012), Biomass Conversion*, The Interface of Biotechnology Chemistry and Materials Science, Springer Heidelberg, New York, Dordrecht. London.*

Block. C, Ephraim. A, Welss - Hortala. E, Minh. D, Nzhihou. A, Vandacasteele. C, (2019), Co-Pyrogasification of Plastics and Biomass, a Review, *Waste and Biomass Valorization* 10,483 – 509.

Bolyard. S.C, Reinhart. D.R, (2016), Application of Landfill Treatment Approaches for Stabilization of Municipal Solid Waste, *Waste Management*, 58, 22 – 30.

Bridgwater. A V, (1995), *T*he Technical and Economic Feasibility of Biomass Gasification for Power Generation*.* *Fuel*, 74, 631 – 653.

Brown. R.C, (2011), Thermochemical Processing of Biomass Conversion into Fuels. Conversion into Fuels, *Chemicals and Power*, First Edition, John Wily & Sons Ltd,6 – 48.

Cao. W, Li. J, Marti – Rossello. T, Zhang. X, (2018), Experimental Study on the Ignition Characteristics of Cellulose, Hemicellulose, Lignin and their Mixtures, *Journal of the Energy Institute* ,1 – 10.

Cao.Y, Fu. L, Mofrad. A, (2019), Combined – gasification of Biomass and Municipal Solid Waste in a Fluidized Bed Gasifier, *Journal of the Energy Institute* ,92, 1683 – 1688.

Cao. C, Bian .C, Wang. G, Bai. B, Xie. Y, Jin. H, (2020), Co- gasification of Plastic Waste and Soda Lignin in Supercritical Water, *Chemical Engineering Journal* ,388, 124277.

Cesarino.I, Araujo.P, Domingues. A. P, Mazzafera. P, (2012), An Overview of Lignin Metabolism and its Effect on Biomass Recalcitrance, Brazilian Journal of Botany,35,303 – 311.

Chiodini. A, Bua. L, Carnelli. L, Zwart. R, Vreugodenhill. B, Vocciante. M, (2017), Enhancements in Biomass – to – Liquid Process: Gasification Aiming at High hydrogen/ Carbon Monoxide Ratios for Direct Fischer Tropsch Synthesis Applications, *Biomass and Bioenergy*, 106, 104 – 114.

Chum. H. L, Oveed. R. P, (2001), Biomass and Renewable Fuels. *Fuel Processing Technology*, 71, 187 – 195.

Clark. J, Deswarte. F, (2015), Introduction to Chemicals from Biomass, *John Wiley & Sons, Second edition*.

Deparrois. N, Singh. P. I, Burra. K. G, Gupta. A. K, (2019), Syngas Production from Co-Pyrolysis and Co- gasification of Polystyrene and Paper with CO_2, *Applied Energy*, 246, 1 – 10.

Dang. Q, Zhang. X, Zhou. Y, Jia. X, (2021), Prediction and Optimization of Syngas Production from a Kinetic – Based Biomass Gasification Process Model, *Fuel Processing Technology*, 212,106604.

Fan. H, Gu. H, Hu. S, Yuan. H, Chen. Y, (2019), Co-pyrolysis and Co-gasification of Biomass and Polyethylene: Thermal Behaviours, Volatile Products and Characteristics of their Residues, Journal of the Energy, Institute, 92,1926 – 1935.

Guo. F, Dong. Y, Dong. L, Guo. C, (2014), Effect of Design and Operating Parameters on the Gasification Process of Biomass in a Downdraft Fixed Bed: An Experimental Study, *International Journal Hydrogen Energy*, 39, 5625 – 33.

Guan. R, Kaaewpanha. M, Hau. X, Abudula. A, (2016), A Catalytic Steam Reforming of Biomass Tar: Prospects and Challenges, *Renewable Sustainability Energy Review*, 58, 450 – 461.

Fazard. S, Mandegari. M. A, Gorgens. F. J, (2016), A Critical Review on Biomass Gasification, Co - Gasification, and their Environmental Assessments, *Biofuel Research Journal* ,12, 483 – 495.

Fremaux. S, Beheshti. S, Ghassami .H, Markadeh. R. S, (2015), An experimental Study on Hydrogen- Rich Gas Production via Steam Gasification of Biomass in a Research - Scale Fluidized Bed, *Energy Conversion Management*, 91, 427 – 432.

Hameed. Z, Aslam. M, Khan. Z, Maqsood. K, Ataba. A. E, Ghauri. M, Khurran. M. S, Rehan. M, Nizam. A, (2021), Gasification of Municipal Solid Waste Blends with Biomass for Energy Production and Resources Recovery: Current Status, Hybrid Technology and Innovative Prospects. *Renewable and Sustainable Energy Reviews*, 136,110375.

Inayat .M, Sulaiman. S.A, Kurnia. J.C, Shahbaz. M, (2019), Effect of Various Blended Fuels on Syngas Quality and Performance in Catalytic Co- gasification: A Review, *Renewable and Sustainable Energy Reviews*, 105, 252 – 267.

Kamble. A.D, Saxena. V.K, Chavan. P. D, Mendhe. V. A, (2019), Co- gasification of Coal and Biomass an Emerging Clean Energy Technology: Status and Prospects of Development in Indian Context, *International Journal of Mining Science and Technology* ,29 ,171 – 186.

Kannapan. P. G, Nagarajan.V.M, Krishnan.A, Malolan. R, (2020), A Critical Review on the Influence of Energy Environmental and Economical Factors on Various Processes used to Handle and Recycle Plastic Wates: Development of a Comprehensive Index. *Journal of Cleaner Production*, 274 – 123031.

Karl. J, Proll. T, (2018), Steam Gasification of Biomass in Dual Fluidized Bed Gasifiers: A Review, *Renewable and Sustainable Energy Reviews,* 98, 64 – 78.

Kartal. F, Ozveren. U, (2021), A comparative Study for Biomass Gasification in Bubbling Bed Gasifier using Aspen HYSYS, Bioresource Technology Reports,13,100615.

Kihedu. J, H, Yoshiie.R, Naruse.I, (2016), Performance Indicators for Air and Air-Steam Auto – thermal Updraft Gasification of Biomass in Packed Bed Reactor. *Fuel Processing Technology*,141, 93 – 98.

Kirubakaran. V, Siva Ramakrishnan. N. R, Sekar. T, Premalatha. M, Subramanian. P, (2009), A Review on Gasification of Biomass, *Renewable and Sustainable Energy Reviews*, 13, 179 – 186.

Koppatz. S, Pfeifer. C, Hofbauer. H, (2011), Steam Gasification of Various Feedstocks at a Dual Fluidised Bed Gasifier: Impacts of Operation Conditions and Bed Materials, *Biomass Conversion Biorefinery*,1,39 – 53.

Kraft. S, Kuba. M, Kirnbauer. F, Bosch. K, Hofbauer. H, (2016), Optimization of a 50MW Bubbling Fluidized Bed Biomass Combustion Chamber by means of Computational Particle Fluid Dynamics. *Biomass and Bioenergy*, 89, 31 – 39.

Kumar. R, Singh. S, Singh. O, (2008), Bioconversion of Lignocellulosic Biomass: Biochemical and Molecular Perspectives, *Industrial Microbial Biotechnology*, 35 ,377 – 391.

Kumar. A, Jones. D. D, Hanna. M. A, (2009), Thermochemical Biomass Gasification a Review of the Current Status of the Technology*,* Energies. 2, 556 – 581.

Kumar. G, Dharmaraja. J, Arvindnarayan. S, Shoba. S, Bakonyi. P, Saratale. G. D, Nemestothy. N, Belafi. B. K, Yoon. J, Kim. S, (2019), A Comprehensive Review on Thermochemical, Biological, Biochemical and Hybrid Conversion Methods of Bio- derived Lignocellulosic Molecules into Renewable Fuels, *Fuel*, 25, 352 – 367.

La Villetta. M, Costa. M, Massarotti. N, (2017), Modelling Approaches to Biomass Gasification: A Review with Emphasis on the Stoichiometric Method, *Renewable and Sustainable Energy Reviews,* 74, 71 – 88.

Lopez. G, Erkiaga. A, Amutio. M, Bilbao. J, Olazar. M, (2015), Effect of Polyethylene Co-feeding in the Steam Gasification of Biomass in a Conical Spouted Bed Reactor, *Fuel*, 153, 393 – 401.

Lopez. G, Artetxe. M, Amutio. M, Alvarez. J, Bilbao. J, Olazar. M, (2018), Recent Advance in Gasification of Waste Plastics. A Critical Review, *Renewable and Sustainable Energy Reviews*, 82, 576 – 596.

Lopez. G, Artexte. M, Amutio. M, Bilbao. J, Olazar. M, (2017), Thermochemical Routes for the Valorization of Waste Polyolefinic Plastics to Produce Fuels and Chemicals: A Review, *Renewable and Sustainable Energy Reviews* ,73 (2017) 346 – 368.

Miandad. R, Barakat. M.A, Aburiazaiza. A. S, Rehan. M, Ismail. I.M.I, Nizami. A. S, (2017), Effect of Plastic Waste Types on Pyrolysis Liquid Oil, *International Biodeterioration and Biodegradation*,119, 239 – 252.

Mishra. A, Gautam. S, Sharma. T, (2018), Effect of Operating Parameters on Coal Gasification, *International Journal Scientific Technology*,5,113 – 125.

Monir. M.U, Aziz. A. A, Kristantl. R. A, Yousuf. A, (2020), Syngas Production from Co-gasification of Forest Residue and Charcoal in a Pilot Scale Downdraft Reactor, *Waste and Biomass Valorization*, 11, 635 – 651.

McKendry. P, (2002*), Energy Production of Biomass (Part 3): Gasification Technologies, Bioresource Technology* ,83 ,55 – 63.

Munir. D, Irfan. M. F, Usman. M. R, (2018), Hydrocracking of Virgin and Waste Plastics A Detailed Review, *Renewable and Sustainable Energy Review*, 90, 490 – 515.

Munir. U, Aziz. A. A, Kristanti. R. A. Yousuf. A, (2018), Gasification of Lignocellulosic Biomass to Produce Syngas in a 50KW Downdraft Reactor, *Biomass and Bioenergy*, 119, 335 – 345.

Pala. L.P. R, Wang. Q, Kolb. G, Hessel. V, (2017), Steam gasification of Biomass with Subsequent Syngas Adjustment using Shift Reaction for syngas Production: An Aspen Plus Model, *Renewable Energy*, 101, 484 – 492.

Palma. C. F, (2013), Modelling of Tar Formation and Evolution of Biomass Gasification: A Review, Applied Energy,111,129 – 141.

Parthasaathy. P, Narayanan. K. S, (2014), Hydrogen Production from Steam Gasification of Biomass: Influence of Process Parameters on Hydrogen Yield: A Review*, Energy*, 66,570 – 579.

Pio. D.T, Tarelho. L. A. C, Tavares. A. M. A, Matos. M. A. A, Silva. V, (2020), Co- gasification of Refused Derived Fuel and Biomass in a Pilot - Scale Bubbling Fluidized Bed Reactor, *Energy Conversion and Management*, 206, 112476.

Puig – Arnavat. M, Bruno. J. C, Coronas. A, (2010), Review and Analysis of Biomass Gasification Models, *Renewable and Sustainable Energy Reviews* ,14, 2841 – 2851.

Rahman. M.H, Bhoi. P.R, (2021), An Overview of Non-Biodegradable Plastics, Journal of Cleaner Production, 294,126218.

Ramos. A, Monteiro. E, Silva. V, Rouboa. A, (2018), Co – gasification And Recent Developments on Waste – To – Energy Conversion: A Review, *Renewable and Sustainable Energy Reviews*, 81,380 – 398.

Ramzan. N, Ashraf. A, Naveed. S, Malik. A, (2011), Simulation of Hybrid Biomass Gasification Using Aspen Plus: A Comparative Performance Analysis for Food, Municipal Solid and Poultry Waste, *Biomass and Bioenergy* ,35, 3962 – 3969.

Ren. J, Liu. Y, Zhao. X, Cao. J, (2020), Methanation of syngas from biomass gasification; An overview, *International Journal of Hydrogen Energy*, 45, 4223 – 4243.

Ruiz. J. A, Juarez. M. C, Morales. M. P, Munoz. P, Mendivil. M. A, (2013), Biomass Gasification for Electricity Generation: Review of Current Technology Barriers, *Renewable and Sustainable - Energy Reviews*,18,174 -183.

Safarian. S, Unnporsson. R, Richter. C, (2019), A Review of Biomass Gasification Modelling, *Renewable and Sustainable Energy Reviews*, 110, 378 – 391.

Sansaniwal. S. K, Pal. K, Rosen. M. A, Tyagi. S.K, (2017), Recent Advances in the Development of Biomass Gasification Technology: A Comprehensive Review. *Renewable and Sustainable Energy Reviews* ,72, 363 – 384.

Silva. I.P, Lima. R.M.A, Silva. G.F, Ruzene. D.S, Silva. D. P, (2019), Thermodynamic Equilibrium Model Based on Stoichiometric Method for Biomass Gasification: A Review of Model Modifications, *Renewable and Sustainable Energy Review*, 114,109305.

Sikarwar. V. S, Zhao. M, Clough. P, Yao. J, Zhong. X, Memon. M.Z, Shah. N, Anthony. E. J, Fennell. P. S, (2016), An Overview of Advances in Biomass Gasification, Energy, *Environmental Science* ,9, (10), 2927 – 3304.

Situmorang. Y.A, Zhao. Z, Yoshida. A, Abudula. A Guan. G, (2020), Small – Scale Biomass Gasification System for Power Generation (<200 kW class): A Review, *Renewable and Sustainable Energy Reviews*, 117, 109486.

Shahbaz. A, Al – Ansan. T, Aslam. M, Khan. Z, Inayat. A, Athar. M, Naqvi. S.R, Ahmed. M. A, McKay. F, (2020), A state-of-the-Art Review on Biomass Processing and Conversion Technologies to Produce Hydrogen and its Recovery via Membrane Separation, *International Journal of Hydrogen Energy*, 45, 15166 – 15195.

Sharuddin. S.D. A, Abnisa. F, Daud. W.M.A. W, (2016), A Review on Pyrolysis of Plastic of Plastic Waste*, Energy Conversion and Management*, 115, 308 – 326.

Shen. D, Xiao. R, Gu. S, Luo. K, (2011), The Pyrolytic Behaviour of Cellulose in Lignocellulosic Biomass: A Review, RSC Advances, 1, 1641 – 1660.

Shen. L, Xiao. Y, (2008), Simulation of Hydrogen Production from Biomass Gasification in Interconnected Fluidized Beds. *Biomass and Bioenergy*,32, 120 – 127.

Tavares. R, Ramos. A, Rouboa. A, (2018), Microplastics Thermal Treatment by Polyethylene Terephthalate – Biomass Gasification, *Energy Conversion and Management* ,162, 118 – 131.

Tavares. R, Monteiro. E, Tabet. F, Rouboa. A, (2020), Numerical Investigation of Optimum Operation Conditions for Syngas and Hydrogen Production from Biomass Gasification using Aspen Plus, *Renewable Energy*, 146, 1309 – 1314.

Vassilev. S. V, Baxter. D, Andersen. L. K, Vassillev. C. S, Morgan. T. T, (2012), An Overview of the Organic and Inorganic Phase Composition of Biomass, *Fuel*, 94,1 – 33.

Wang. S, Dai. G, Yang. H, Luo. Z, (2017), Lignocellulosic Biomass Pyrolysis Mechanism: A State – of – the - Art Review, *Progress in Energy and Combustion Science*, 62, 33 – 86.

Watson. J, Zhang. Y, Si. B, Chen. W, De- Souza. R, (2018), Gasification of Biowaste: A Critical Review and Outlooks, *Renewable and Sustainable Energy Review*, 83, 1 – 17.

Wei. J, Wang. M, Wang. F, Song. X, Yu. G, Liu. Y, Vuthaluru. H, Xu. J, Xu. Y, Zhang. H, Zhang. S, (2021), A Review on Reactivity Characteristics and Synergy Behavior of Biomass and Coal Co-gasification. International Journal of Hydrogen Energy, 46, 17116 – 17132.

Widyaya. E.R, Chen. G, Bowtell. L, Hills .C, (2018), Gasification of non- woody Biomass: A Literature Review, *Renewable and Sustainable Energy Review*, 89, 184 – 193.

Zabed. H.M, Akter. S, Yun. J, Zhang. G, Awad. F.M, Qi. X, Sahu. J. N, (2019), Recent Advances in Biological Pre-treatment of Microalgae and Lignocellulosic Biomass for Biofuel Production, *Renewable and Sustainable Energy Reviews*,105,105 – 128.

Zhang. Y. Xu. P, Liang. S, Liu. B, Shuai, Li. B, (2019), Exergy analysis of Hydrogen Production from Steam Gasification of Biomass: A Review, *International Journal of Hydrogen Energy*, 44, 14290 – 14302.

Zhou. X, Li. W, Mabon. R, Broadbelt. L. J, (2017), A Critical Review on Hemicellulose Pyrolysis, Energy Technology, 5, 52 – 79.

Zhu. H. L, Zhang. Y.S, Materazzi. M, Aranda. G, Brett. D. J. L, Shearing. P. G, (2019), Co - gasification of Beech-wood and Polyethylene in a Fluidization – Bed Reactor, *Fuel Processing Technology* ,190, 29 – 37.

Chapter 3: Methodology

3.1. Introduction

This chapter provides the description of how the non- stoichiometric thermodynamic equilibrium model for the co-gasification of biomass and polyethylene (waste plastic) is developed using the Aspen Plus process simulation software. The specification of the components and their properties, the selection of the thermodynamic model, the specification of the input streams, the selection and specification of the various block units in the process blocks will be described. Finally, the validation of the model using experimental data is discussed.

3.2. Modelling in Aspen Plus

Aspen Plus, a steady state process simulation software, is a powerful tool that is used to create a model of a chemical process and to describe the behavior and the performance of a system. Aspen Plus (version 10), was used for the modelling of the co- gasification process and to conduct a parametric study.

This process simulation tool is chosen based on its numerous advantages in modelling systems such as it is an easy software to develop different models, it is flexible, can accommodate different types of components, both conventional and non- conventional, which are in different phases i.e. liquid, solid and or gases. Also, different parameters can be varied and their effect on the output can be observed. Aspen Plus software is used to develop the thermochemical equilibrium model, based on a non- stoichiometric approach (based on Gibbs energy minimization)**.**

The model in Aspen Plus is developed by specifying the stream class, the system components using the built-in data- base and identifying the conventional and non- conventional components. The process flowsheet is defined by using the unit operation blocks and material and energy streams are connected in the flowsheet. The composition, flowrates and operating conditions in the feed streams are specified and, in the unit operation blocks the operating conditions are specified.

- Component selection

The first step in the development of the simulation was to specify all the components that were to be used in the process simulation (see Appendix A for detailed list of components). The biomass, polyethylene and ash components were defined as non- conventional solid components, as the exact chemical formula for these components are not available in Aspen Plus.

Table 3.1. Ultimate and Proximate analysis for pine sawdust (determined using an elemental analyzer) and polyethylene (Al Amoodi et al. 2013).

	Biomass (pine sawdust)	**Plastic waste (polyethylene)**
Source	*Ultimate analysis (wt.% dry basis)*	
C	45.5	85.8
H	5.0	13.9
O	47.1	0
N	0.05	0.12
S	0	0.03
Ash	2.35	0.15
Source	*Proximate analysis (wt.% dry basis)*	
FC	18.45	0.00
VM	79.20	99.85
ASH	2.35	0.15

The enthalpy and density of the feedstock materials such as biomass, polyethylene and their relative blend ratios, which are considered as non- conventional components, were calculated by selecting the algorithm of HCOALGEN (enthalpy) and DCOALIGT (density). These parameters are calculated based on the component attributes of the biomass (pine sawdust) and plastic waste (low density polyethylene) feedstocks, which used information from their respective ultimate and proximate analysis (Table 3.1). The particle size distribution for non-conventional components was not considered in the simulation. The stream class was chosen to be “MIXCINC”, since the simulation comprised of both conventional and non- conventional solids.

- Property Method selection

In Aspen Plus, it is necessary to select an appropriate thermodynamic model, to calculate the various thermodynamics properties of input and output streams. The physical property method of Peng-Robinson equation of state with Boston – Mathias alpha is selected and is used to estimate all the thermodynamic properties of the conventional components in the co-gasification process. This property method was selected based on its ability to correlate the low operating pressure with the higher operating temperatures >700°C that are typically used in the co- gasification process (Ramzan et al. 2011).

- Block Specification

The co- gasification simulation model is developed through the selection of three -unit operation blocks, namely; RYield, RGibbs and a cyclone (Figure 3.1). The main functions of these selected operation blocks are described in Table 3.2.

The unit block that are embedded in the software are used to represent the different stages of the co – gasification process are used to represent the different stages of the co- gasification process. The initial stages, which is drying, is not included in the developed co- gasification process flowsheet shown in Figure 3.1 since the feedstock to be converted is already dried.

Therefore, from Aspen Plus software the RYield reactor is chosen as the block operation unit that will represent the pyrolysis (decomposition) stage and the reactor RGibbs (gasification) is chosen to represent the co - gasification stage and the cyclone is used as the solid separator. The block units' names and IDs as per the developed flow sheet are shown in Table 3.2. Each unit is briefly described as per their specific function. The calculator is used, to create the FORTRAN statement, which calculates the Yield distribution of the products from the pyrolysis stage (Shown in Appendix A). The calculator block formulates the FORTRAN statement using the information from the ultimate and proximate analysis of biomass (pine sawdust) and plastic waste (low density polyethylene).

Table 3.2. Description of the model block units for co- gasification process.

Name of Block unit	**Block ID**	**Block description**
RYield	Decomp	The RYield" DECOMP" is used to as a pyrolyser to decompose the large molecules of the feedstock material into smaller molecules. The non-conventional components are converted into conventional components. This reactor uses an inbuilt calculator block which uses the information of the non- conventional components from ultimate and proximate analysis to create a FORTRAN statement, that is used to calculate the yield distribution. C, H, O, N, S etc. (Ramzan et al. 2011).
RGibbs	Gasifier	RGibbs reactor is used to model the co-gasification process at equilibrium conditions using Gibbs energy minimization to model single – phase or simultaneous phase chemical equilibrium reactions. It also predicts the syngas composition (Gagliano et al. 2017).
Cyclone	Separate	The Cyclone "SEPARATE" is used to separate solids from gases.

3.3. Aspen Plus simulation assumptions

The developed flowsheet of the co- gasification of biomass and polyethylene was based on the assumptions stated below, which are used to simplify the model. The assumption made, are applied to the thermodynamic equilibrium model, that uses the non- stoichiometric approach (Donolo et al. 2006).

- The process is at steady state
- The products of the devolatilization are H_2, CO, CO_2, CH_4, H_2O and char
- The syngas produced comprises mainly of H_2, CO, CO_2, CH_4, N_2 and H_2O
- The gasifier is operated at atmospheric pressure.

- There is no pressure drop in the gasifier.
- Tar formation is not produced and no carbon present in product stream.
- Heat lost by the gasifier is neglected.

3.4. Process description

The blended feedstock of biomass and polyethylene at their respective blend ratios, biomass and polyethylene which is non- conventional solids enters the pyrolyzer (‘DECOMP”) through either stream “BIOMASS, PE and FEED MIX”, depending on the specific feed that is simulated. The feed enters the “DECOMP”, represented by the RYield, (shown in Figure 3.1) at the temperature of 25°C and pressure of 1 atm and at feed rate of 2000 kg/hr. The ultimate and proximate analysis data (Table 3.1) is used to specify the component attributes of the feedstocks, which is required in order to use the simulation calculator and form the FORTRAN statement, that simulates the non- conventional components, into conventional one and calculate the yield.

The products from the “DECOMP”, which are in its elemental constituents such as C, H, O, N and S goes to the RGibbs reactor, represented by “GASIFIER” (shown in Figure 3.1). These products leave the decomposer through the exit stream “CONVE”. Heat is transferred from the “DECOMP” to the “GASIFIER” via stream “Q- DECOMP” to provide the GASIFIER the required heat to maintain adiabatic operation. The “Q- DECOMP” stream is a virtual stream which is used to indicates that there is heat associated with the decomposition of non-conventional feedstock such as biomass into its elemental constituents since Aspen does not recognize biomass as a component.

The “DECOMP” unit is operated at the pyrolyzer temperature of 500°C, and pressure of 1 atm (Monir et al. 2020). In the pyrolyzer the large molecules of the non- conventional feedstock material, is broken down into smaller molecules, that is conventional. The feed is broken down into elemental constituents such as C, H, O, S and N, in the absence of oxygen. The products produced from “DECOMP” (RYield) is volatiles such as CO, CO_2, H_2O, H_2, CH_4 and N_2 respectively.

RGibbs reactor “GASIFIER”, is used in the simulation model to simulate the co- gasified feed materials (plastic waste and biomass) and to represent the gasification process that includes the partial oxidation and reduction stages. This unit is set at pressure of 1 atmosphere, and the temperature is influenced by the gasifying agents and the heat produced from the

“DECOMP”. RGibbs is a thermodynamic equilibrium model, based on the non- stoichiometric approach, that uses the minimization of Gibbs energy to calculate the composition of the product stream from a given feed stream composition (Corella et al. 2006).

The products from “DECOMP” enters the “GASIFIER” and is simulated by reacting with the gasifying agents such as air, steam, carbon dioxide or their combination that are added to the “GASIFIER” partially. The operating parameters of these gasifying agents used to react with the components in the in the reactor, are namely the equivalence ratio (ER), steam – to- fuel ratio (SFR) and carbon dioxide (CO_2/C).

During the partial oxidation, different oxidation reactions are occurring, and more volatiles are produced. Simultaneously, in the reduction stage, homogeneous and heterogeneous reactions are taking place. When steam is added as a gasifying agent, the steam and reforming reactions also occurs, and more volatiles are produced as more char content reacts with the gasifying agents. The main product produced from the “GASIFIER” is the synthesis gas or syngas, which comprises mainly of H_2, H_2O, CO, CO_2, CH_4 and N_2.

The syngas product leaves the “GASIFIER” through exit stream called “PRODUCT”. This stream feeds into the cyclone unit, which is the separator, and is called “SEPARATE” (Figure 3.1) that is used to remove solids from the gas. This block unit uses a split fraction, which is set at 1, (Basu et al. 2013) to separate the solids from the syngas. It has two separate outlet streams namely, the syngas stream is called “GASES” and solids stream called “SOLIDS”

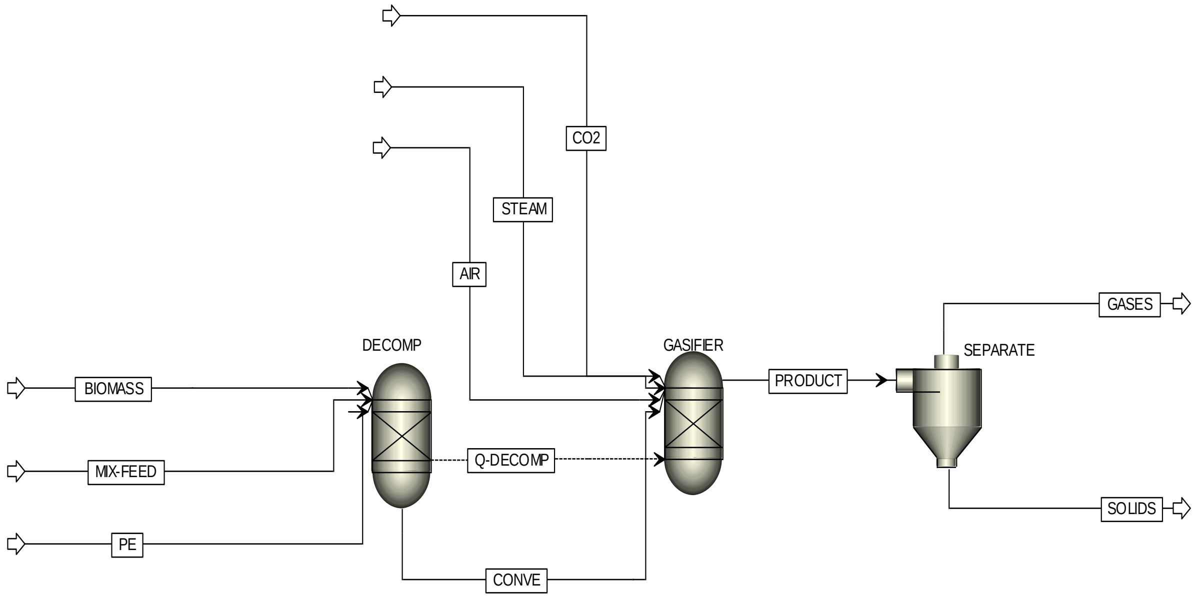


Figure 3.1. Flow- sheet for the process simulation for the co - gasification of biomass and polyethylene.

3.5. Model Validation

3.5.1. Model validation for single feedstock (biomass)

The model was validated by comparing the outputs of the simulation with previous experimental work for the gasification of rice husks (Loha et al. 2013). The values of proximate and ultimate analysis were required as inputs to the simulation, are shown in Table 3.3. These values are required in order to conduct the validation of the simulation model.

Table 3.3. Ultimate and proximate analysis for rice husk feedstock (Loha et al. 2013).

Source	*Ultimate analysis (wt.%)*	*Source*	*Proximate analysis (wt.%)*
C H N Cl S O Ash	38.43 2.97 0.49 0 0.07 36.36 21.68	Moisture, % Fixed carbon Volatile matter Ash	9.95 14.99 55.54 19.52

The operating conditions shown below that were used to validate the process model (Figure 3.1), are the same as that were used during the gasification of rice husk feedstock in the laboratory (Loha et al.2013).

- Equivalence ratio (ER): 0.35
- Temperature: 750°C
- Steam –to - biomass ratio (SBR): 0.5
- Rice husk feed rate: 55 kg/hr

The composition expressed as a percentage (%) in Figure 3.2 is used instead of the concentration. The composition in the product gas is calculated as the moles of a specific component/ total number of moles. Whereas, the concentration is typically used for solutions. Furthermore, concentration is defined as the number of moles per unit volume.

The results for the comparison between the experimental values (Loha et al. 2013) and Aspen Plus model values are compared in Figure 3.2. The experimental data is for the rice husk feedstock which was gasified using the fluidized bed gasifier. Figure 3.2 indicates that the results for the molar fractions of H_2, CO, CO_2 from the Aspen Plus model are in agreement with the values from the experimental data for the gasification of rice husk. The exception being the molar fraction of methane (CH_4), which demonstrated an appreciable difference between the model (almost negligible) and experimental data (2.1%).

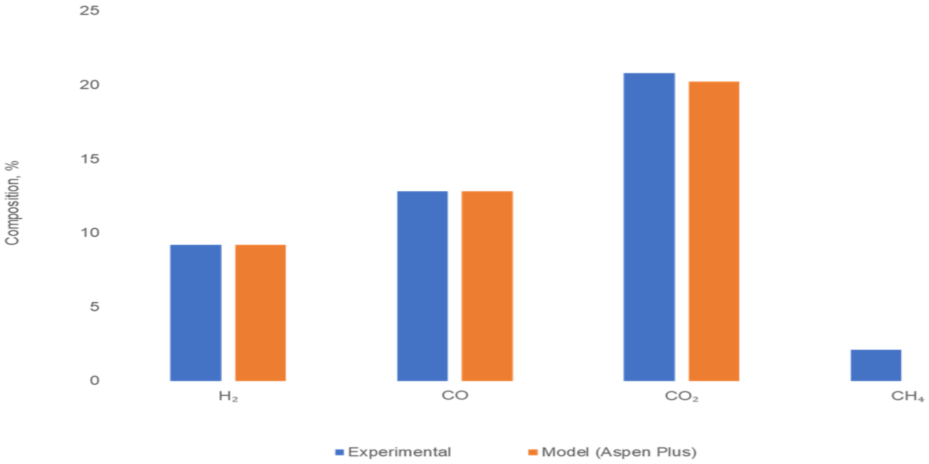


Figure 3.2. Comparison of Aspen Plus values with the experimental values.

The validation method of this work was based on the relative error (ε_r), which is the ratio between the absolute error (i.e., the difference between the modeled (Aspen Plus), X_m and experimental, X_e, values) and the experimental value (equation 3.1). Relative errors are better method for model validation, since they are able to determine the model over or underestimations based on whether the relative error is positive or negative, respectively (De Andres et al. 2019).

$$Relative\ error\ (\%) = \frac{Aspen\ Plus\ value - Literature\ value}{Literature\ value} \times 100\% \quad \text{.........................(3.1)}$$

Therefore, the relative error between the model and experimental literature results was calculated (Table 3.4). The relative error results show that the model (Aspen Plus) and experimental values for syngas composition, are in good agreement and are considered acceptable i.e. (the relative error for each of the variables were within +/- 15%). According to De Andres et al. (2019) when the species in the syngas, indicates a percentage error that is below +/- 15% between the process model values and laboratory experiment values indicates a good agreement. The Lower Heating Value (LHV) of the syngas (calculated using equation 3.2) and H_2/CO ratio are also displayed in Table 3.4.

Table 3.4. Model validation: Comparison of the experimental and model composition results for biomass gasification.

Parameter	Experimental (X_e)	Model (Aspen Plus), (X_m)	Error (%)
H_2	9.2	9.202	0.02
CO	12.8	12.8	0.000
CO_2	20.8	20.24	- 2.69
CH_4	2.1	$1.7*10^{\wedge-10}$	-99.9
LHV syngas (MJ/Nm^3)	3.38	2.61	- 22.8
H_2/CO ratio	0.718	0.719	0.139

The higher relative error observed for the methane component are considered acceptable and the model is considered reliable since this work is based on an equilibrium model, which neglects significant gasification issues such as system kinetics and fluid dynamics. Moreover, the high methane composition in the syngas from the experimental gasification may be attributed to the partial cracking of volatiles during pyrolysis and the methane reforming reaction which could also have an influence on the over – prediction of the H_2 and under – prediction of methane (Tavares et al. 2020).

Furthermore, similar observations were also found in the study conducted by Rosha et al. (2021). A high deviation between the methane composition predicted by the model and experimental data was found (97.4%). Pellerine et al. (2007) stated that at ER values above 0.3, equilibrium models predict very little to no CH_4 formation due to the high temperature in the gasifier. However, equilibrium conditions are not reached, and methane is present in the syngas.

3.5.2. Model validation for the co-gasification of biomass (straw) and plastic waste (polyethylene).

The model was further validated by comparing the outputs of the simulation with experimental work for the co- gasification of straw and polyethylene (PE) feedstocks (Yu et al. 2014). The values of proximate and ultimate analysis were used as an inputs to the simulation, are shown in Table 3.5.

Table 3.5 Ultimate and Proximate analysis of Straw and polyethylene (as-received basis) (Yu et al. 2014).

Ultimate analysis (wt.%)					
	C	H	N	S	O
Straw	30.26	5.53	0.62	0.22	36.85
PE	83.96	11.02	-	0.38	3.99
Proximate analysis (wt.%)					
	Moisture	Ash	Volatile	Fixed carbon	LHV (KJ/kg)
Straw	12.42	14.10	61.05	12.43	14395
PE	0.65	-	99.35	-	46753

The model for the co-gasification is similar to that displayed in Figure 3.1, except that the feedstock is not only biomass but, contains the percentage of polyethylene. The blend ratio that was used for the validation of the model was (20%PE + 80% biomass). From the study conducted by Yu et al. (2014) the equivalence ratio (ER) was fixed at a value of 0.25, and the gasifier temperature was kept constant at 1000°C. Air was utilized as a gasifying agent. In order to attain similar results in this study, the equivalence ratio (ER) was adjusted until the temperature in the gasifier reached 1000ºC.

The validity was measured using the relative error (ε_r) method, which has been explain previously. The output values of the product gas obtained from the experimental work (Yu et al. 2014), agree with the values obtained from Aspen Plus for the co-gasification of biomass and plastic waste (Figure 3.3). Furthermore, based on the relative error, the model and experimental values for the syngas composition are in good agreement and are considered acceptable i.e. (the relative errors for each of the variable were within +/- 15%). The relative error for the composition are shown below in Table 3.6.

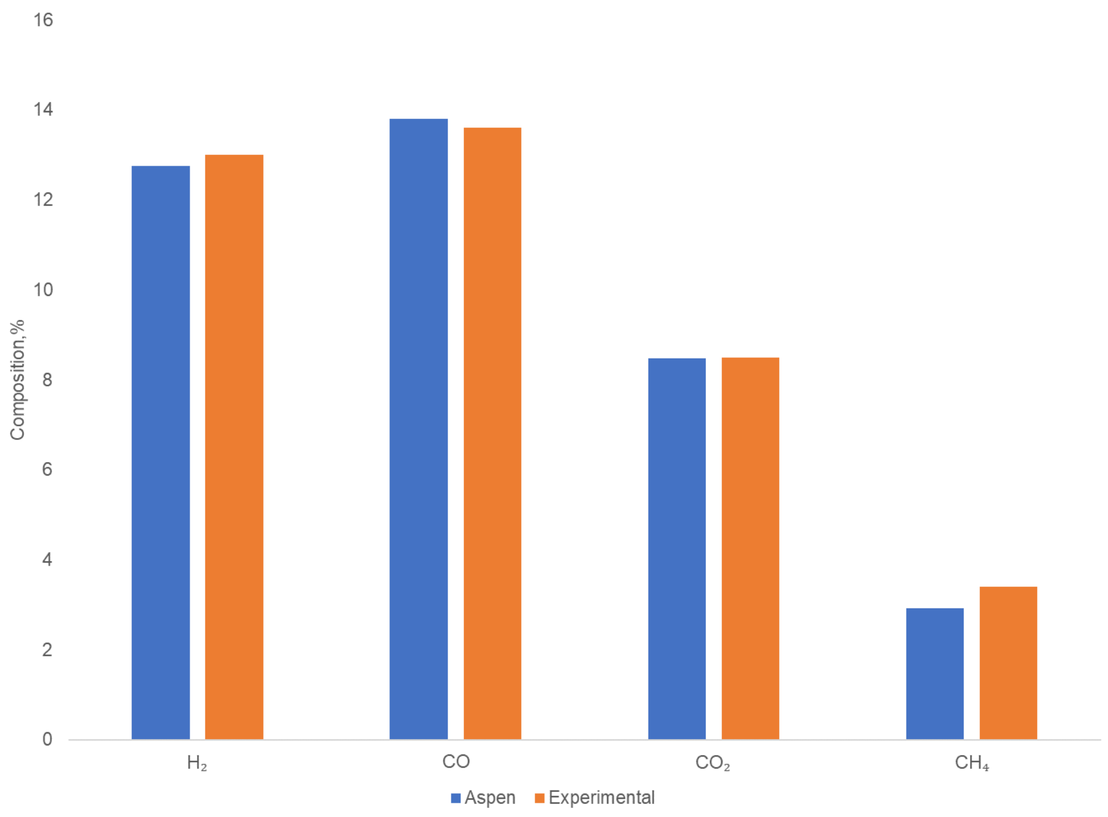


Figure 3.3. Comparison of Aspen Plus values with the experimental values using biomass and plastic waste data.

Table 3.6. Model validation: Comparison of the model and experimental composition results for the co-gasification of biomass and plastic waste.

Parameter	Experimental (Xe)	Model (Aspen Plus), (X_m)	Error (%)
H_2	13	12.76	-1.846
CO	13.6	13.81	1.471
CO_2	8.5	8.47	-0.353
CH_4	3.4	2.93	-13.82

The Aspen predictions indicates that during the co-gasification of biomass and plastic waste, there is a percentage of methane present as compared to a very small amount of methane (almost) negligible obtained in biomass gasification. This is due to the presence of plastic waste in the feedstock mixture, which contains hydrocarbons, therefore as the equivalence ratio is increased, the thermal cracking of longer chains hydrocarbons to smaller chain hydrocarbons occurs and thus causing an increase in the methane composition in the product gas (Fazil et al. 2022).

3.6. Application of the developed Aspen Plus model

The model developed in Aspen Plus is used to conduct a parametric study and sensitivity analysis. The effect of using different feedstock, blended and unblended on the product gas quality and distribution is examined. Furthermore, the effect of ER, SFR and CO_2/C or their combination on the product gas composition, H_2/CO ratio and Lower Heating Value, Gas Yield (GY) and Cold Gas Efficiency (CGE) are determined using various equations. For instance, the Gas Yield (GY) was determined by using equation (2.7), the Cold Gas Efficiency (CGE), was found by using equation (2.11) and the Lower Heating Value (LHV) was determined by using equation (2.8) respectively. The performance indices are defined as follows:

- Synergistic effect analysis

Initially, a qualitative approach was used to assess the synergistic effect between the biomass and plastic waste (polyethylene) feedstock. For every component in the gas mixture, at various operating conditions, the composition of hydrogen, syngas yield, or carbon monoxide (CO) composition, or Lower Heating Value (LHV) of the individual feedstock was compared with the amount obtained from the blended feedstock. Secondly, a quantitative method to determine the extent of the synergistic effect for biomass and plastic waste was determined using the equation 3.3:

$$Y_{calculated} = a \text{ x } Y_{polyethylene} + (1- a)\, Y_{biomass} \tag{3.2}$$

$$\Delta Y = \frac{Y_{model} - Y_{calculated}}{Y_{calculated}} \; x \; 100\% \tag{3.3}$$

$Y_{calculated}$ represents weighted – average value of a specific output parameter such as gas flow rate, gas yield as well as energy output. $Y_{polyethylene}$ and $Y_{biomass}$, represent the model results of the gas flow rate, gas yield and energy output from the gasification of pure feedstock. (a) in the equation represents mass fraction of polyethylene in the mixture sample. Lastly, ΔY, represent the extent of the synergistic effect, with higher values signifying a greater synergistic effect.

REFERENCES

Al Amoodi. N, Kannan. P, Al Shoaibi. A, Shrinivasakannan. C, (2013), Aspen Plus Simulation of Polyethylene Gasification under Equilibrium Conditions, *Chemical Engineering Communication*, 200, 7 – 9.

Basu. P, (2013), Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory, *Dalhouse University and Greenfield Research, Incorporated: Academic Press inprint, Elsevier Inc.*

Corella. J, Toledo. J.M, Molina. G, (2006), Calculation of the Conditions to get less than 2g tar/mn^2 in a Fluidized Bed Biomass Gasifier, *Fuel, Processing Technology*, 87, 841 – 846.

De Andres. J.M, Vedrenne. M, Brambilla. M, Rodriguez. E, (2019), Modelling and Model Performance Evaluation of Sewage Sludge Gasification in Fluidized Bed Gasifiers using Aspen Plus, *Journal of the Air & Waste Management Association*, 69:1, 23 – 33.

Doherty. W, Reynolds. A, Kennedy. D, (2009), The Effect of Air Preheating in a Biomass CFB Gasifier using Aspen Plus Simulation, *Biomass and Bioenergy*,33:9,1158 – 1167.

Donolo. G, Simon. G. D, Fermeglia.M*,* (2006), Steady State Simulation of Energy Production from Biomass by Molten Carbonate Fuel Cells. *Journal of Power Sources*, 158, 1282 – 1289.

Fazil. A, Kumar. S, Mahanjani. S.M, (2022), Downdraft Co-gasification of High Ash Biomass and Plastics, Energy,243,123055.

Gagliano. A, Nocera, Bruno. M, Cardillo. G, (2017), Development of an Equilibrium – Based Model of Gasification of Biomass by Aspen Plus, *Energy Procedia*, 111, 1010 – 1019.

Kaushal. P, Tyagi. R, (2017), Advanced Simulation of Biomass Gasification in a Fluidized Bed Reactor, *Renewable Energy*,101, 629 – 636.

Loha. C, Chattopadhyay.H, Chatterjee. P. K, (2013), Energy Generation from Fluidized Bed Gasification of Rice Husk, *Journal of Renewable and Sustainable Energy*,5, 04311.

Monir. M. U, Aziz. A. A, Kristanti. R. A, Yousuf. A, (2020), Syngas Production from Co-gasification of Forest Residue and Charcoal in a Pilot Scale Downdraft Reactor, *Waste and Biomass Valorization*, 11, 635 – 651.

Nikoo. M.B, Mahinpey. N, (2008), Simulation of Biomass Gasification in Fluidized Bed Reactor using Aspen Plus, *Biomass and Bioenergy*, 32, 1245 – 1254.

Pellegrini. L.F, De Oliveira Jr. S, (2007), Exergy analysis of Sugarcane Bagasse gasification, *Energy*, 32, 314 – 327.

Ramzan. N, Ashraf. A, Navad.S, Malik. A, (2011), Simulation of Hybrid Biomass Gasification using Aspen Plus: A Comparison Performance Analysis is for Food, Municipal Solid and Poultry Waste, *Biomass and Bioenergy*, 35, 3962 – 3969.

Rosha. P, Kumar. S, Vikram. S, Ibrahim, Al-Muhtaseb. A.H, (2021), H_2- enriched Gaseous Fuel Production via Co-gasification of an Algae-Plastic Waste Mixture using Aspen Plus, *International Journal of Hydrogen Energy*, http://doi.org/10.1016/j.ijhydene.202111.092.

Rupesh. S, Muraleedharan .C, Arun. P, (2016), Aspen Plus Modelling of Air-Steam Gasification of Biomass with Sorbent Enabled CO_2 Capture, *Resource – Efficient Technologies*, 2,94 – 103.

Tavares. R, Monteiro. E, Tabet. F, Rouboa. A, (2020), Numerical Investigation of Optimum Operation Conditions of Syngas and Hydrogen Production from Biomass Gasification using Aspen Plus. *Renewable Energy* ,146, 1309 – 1314.

Yu. H, Yang. X, Jiang. L, Chen. D, (2014), Experimental Study on Co-gasification Characteristics of Biomass and Plastic Wastes, Bioresources, 9, 5615 – 5626.

Chapter 4: Results and Discussion

4.1. Introduction

The Aspen Plus simulation tool was used to develop a non-stoichiometric equilibrium gasification model, based on the minimization of Gibbs energy. The model was employed to investigate the influence of the feed composition, by using different feedstock materials such as biomass and polyethylene (individual gasification), and their respective blend ratios, on the product gas composition and to observe if there are synergistic effects due to co- gasification. As mentioned in section 3.5, the compositions are expressed as percentages (%) in all the figures. The composition in the product gas is calculated as the moles of specific component /total number of moles.

This chapter is divided into three sections, the first section will discuss the effect of using different gasifying agents such as air, steam, and carbon dioxide and the combinations of these gasifying agents on the product gas composition, syngas calorific value, and H_2/CO ratio when the feedstock is biomass only. The second section will discuss the effect of using different gasifying agents and their relative mixtures on the product gas composition, heating value as well as its H_2/CO ratio when the feedstock is plastic waste (polyethylene). The last section has the same objectives, except that the feedstock material is a mixture of biomass (pine sawdust) and plastic waste (polyethylene) and will be co- gasified at different blend ratios such as (25%PE + 75% biomass), (50% PE + 50% biomass) and (75% PE + 25% biomass). In this section, the effect of the blend ratio on the product gas composition, heating value, gas yield (GY), cold gas efficiency (CGE) and quality will be observed. The synergistic effect between these two co- gasified materials will be investigated.

The operating parameters that will be used to determine the effect of the gasifying agents are the equivalence ratio (ER) which represents the air and oxygen as a gasifying agents, steam – to- fuel ratio (SFR), which is for steam addition to the gasifier and carbon dioxide – to- carbon (CO_2/C) ratio which represents carbon dioxide as a gasifying agent.

Section one: Biomass Gasification

4.1.1. Effect of equivalence ratio on the product gas composition when air and oxygen are used as gasifying agents

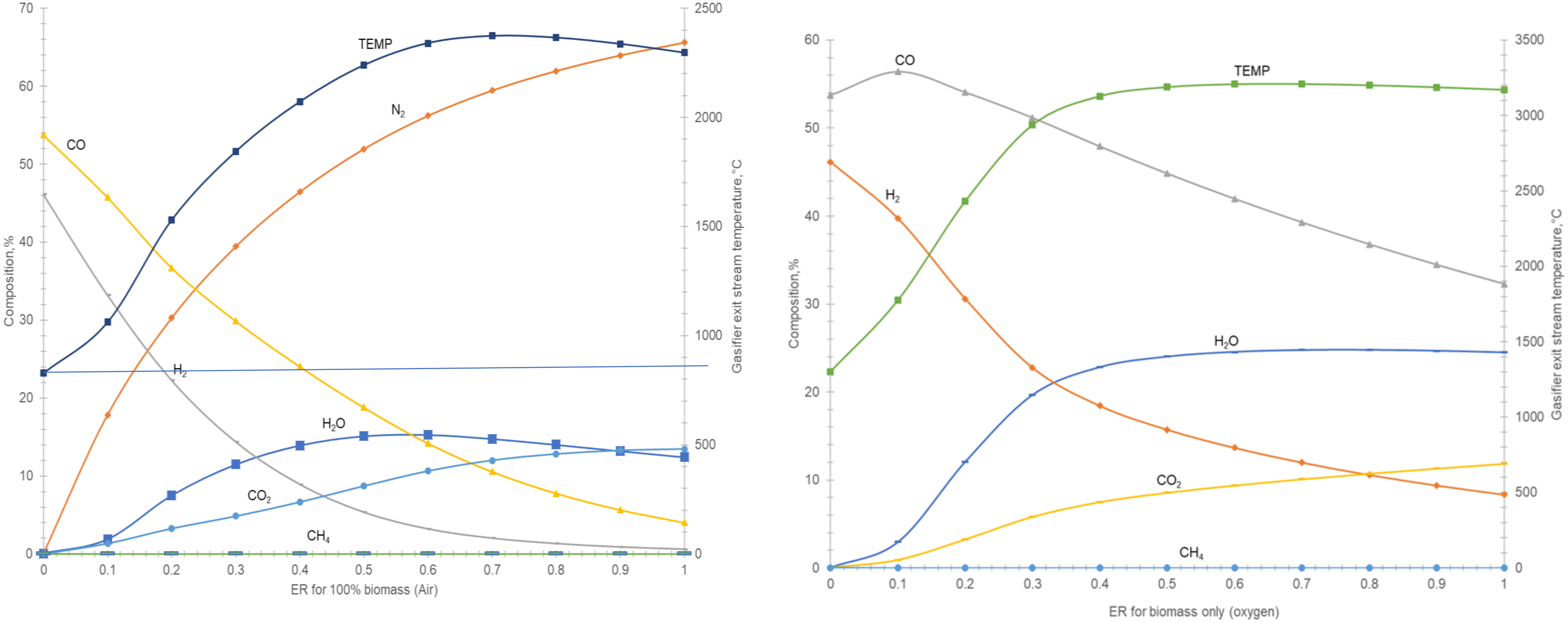
Figure 4.1.1 shows the effect of equivalence ratio (ER) on the product gas composition when (a) air and (b) oxygen are used as gasifying agents. The equivalence ratio is varied from 0 to 1. Figure 4.1.1 (a) shows that when air is used as a gasifying agent, an increase in ER, increases the temperature of the gasifier from about 850°C to 2296°C, whereas when oxygen is used as a gasifying agent, the temperature increased from 1302°C to 3170°C. However, practically in real gasifiers, these high temperatures might not be achieved due to the gasifier, not being fully insulated. The use of oxygen results in a higher temperature increases than air. This is because air consists of 79% nitrogen and 21% oxygen. The high percentage of nitrogen in the air, (nitrogen is regarded as an inert), as the heat of reaction of C/O_2 (oxidation) reaction is required to heat an additional 3.76 moles of nitrogen, thus resulting in lower gasifier temperatures than that attained from the use of oxygen.

Figure 4.11 (a) and (b) shows that the increase of ER from 0.1 – 1, the composition of H_2 and CO in the product gas decreases. High H_2 and CO are favoured at low ER values below 0.3. due to chemical reactions such as the partial oxidation reaction (R4) and partial methanation reaction (R13), which are promoted at this ER range. Above ER of 0.3, the temperature increases significantly with the increasing ER.

In Figure 4.1.1 (a) N_2 increases with the increasing amount of air and CH_4 remained constant, almost negligible. The decrease in the composition of H_2 and CO as ER increases is attributed to the oxidation reactions such as (R5) to (R8) since the incoming oxygen oxidizes the H_2 and CO to produce H_2O and CO_2. The same trend is observed in Figure 4.1.1 (a) is observed in Figure 4.1.1 (b), except that the CO curve in Figure 4.1.1 (b) does not immediately decrease as ER increases, however, it steadily increases and then reaches a maximum point of 56.4% at ER equals to 0.1 before decreasing.

From Figure 4.1.1 (a) and (b) it is observed that the highest H_2 and CO composition are obtained when oxygen is used as a gasifying agent, since air is diluted with nitrogen. The highest H_2 content obtained from oxygen as a gasifying agent is 46.1% at ER equal to 0.02 and the highest H_2 composition from the air is 44.1% at ER equal to 0.01. For CO content, when oxygen is used as gasifying agent a highest of 56.1% at ER equals to 0.1 was attained.

In comparison, when air was used the highest CO content of 46.1% at ER equals to 0.1 was attained.



(a)

(b)

Figure 4.1.1. Effect of equivalence ratio on the product gas composition, when (a) air and (b) oxygen are used as gasifying agents.

The findings of this study with regards to the effect of air and oxygen on composition when the equivalence ratio is varied agree with the findings from a study conducted by Zheng et al. (2016). Zheng et al. (2016) conducted a laboratory scale experimental study using an entrained flow gasifier for the gasification of biomass (rice husks), to investigate the effect of the equivalence ratio on the product gas when air and oxygen are used as gasifying agents. The equivalence ratio was varied from 0.1 to 0.5, and it was observed that when air gasifying agent was used the H_2 decreased from 35 vol% to 15 vol%, CO decreased from around 30 vol% to 21 vol%, CO_2 increased from 2 vol% to 10 vol%, and N_2 increased from 20 vol % to 58 vol%.

When oxygen was used in the study conducted by Zheng et al. (2016), a similar trend as that in this study was observed at which as ER increased the H_2 decreased from 42 vol% to 27 vol%, CO decreased from 40% to 25%, CO_2 increased from 5 % to 55%.The difference between these two studies is that the CO_2 from this study slightly increased with ER, while that from the study conducted by Zheng et al. (2016) the increase of the CO_2 composition is significant. Another difference between these two studies is that the CO composition in this study is higher than that obtained by Zheng et al. (2016).

This is because the biomass feedstocks used between the two studies are different, as pine sawdust was used in this study and, rice husk used in the study conducted by Zheng et al. (2016). Therefore, the elemental carbon content which influence the CO composition is different. Secondly, the type of reactor used in these studies are different. Zheng et al. (2016) used an entrained flow reactor, while in this study, a RGibb (equilibrium) reactor is used, which also has an influence on the product gas composition. The observation that oxygen as a gasifying agent provides high values of the product gas composition as compared to when air is used were noted in both this study and the study by Zheng et al. (2016).

4.1.2. Effect of steam gasifying agent on the product gas composition.

This section discusses the effect of steam content on the product gas. The steam-to-biomass (SBR) is varied from 0 to 5. The aim is to determine the influence of adding steam on the product gas composition. Figure 4.1.2 shows that as the steam content increased from 0 to 5, the temperature in the gasifier decreased from 1302°C to 520°C, due to the endothermic reactions in the gasifier which are promoted with an increase in steam flowrate.

Figure 4.1.2 shows that as the SBR increases, H_2 composition decreases.H_2 content is high at low SBR values between 0 – 1.5. In this SBR range steam is added at a low flowrate and the low amount of steam enhances the steam related reactions such as steam reaction (R4), water gas shift reaction (R9), reverse methanation reforming reactions (R11), (R14) and, steam reforming reaction (R12). During the occurrence of these reactions, steam consumes the available char and CH_4 to produce H_2 and CO in the product gas. However, as more steam is added through high SBR values above 1.5, these reactions are limited and the additional steam reduces the gasifier temperature, and these reactions are no longer enhanced. Instead, excess steam ends-up in the product gas. As displayed in Figure 4.1.2. CH_4 is negligible throughout the range of SBR.

As SBR increases the CO_2 composition increases and reaches a highest value of 16.2% at SBR equal to 2.2. The CO composition decreases with an increase in SBR. The reason for the CO decreasing is because the addition of steam to the gasifier promotes the water gas shift reaction (R9), in which steam consumes CO to produce H_2 and CO_2. As a results Figure 4.1.2 shows that the highest CO composition of 54.0%. was achieved at SBR equals to 0.05 and the highest H_2 composition was found to be 46.0% at SBR equals to 0.01.

Figure 4.1.1 (a) and (b) and 4.1.2 shows that when comparing various gasifying agents used in the study, it was found that amongst the gasifying agents used (air, steam, and oxygen), oxygen provides the highest H_2 composition of 46.1% at ER of 0.02, as compared to when steam and air are used as a gasifying agent for biomass gasification. A maximum H_2 composition of 46.0% is obtained at ER equals to 0.01 when steam is used and lastly a maximum H_2 composition of 39.8% at ER equals to 0.05 when air is used. Air produces a low product gas composition (H_2 and CO) as compared to the other types of gasifying agents because of nitrogen dilution.

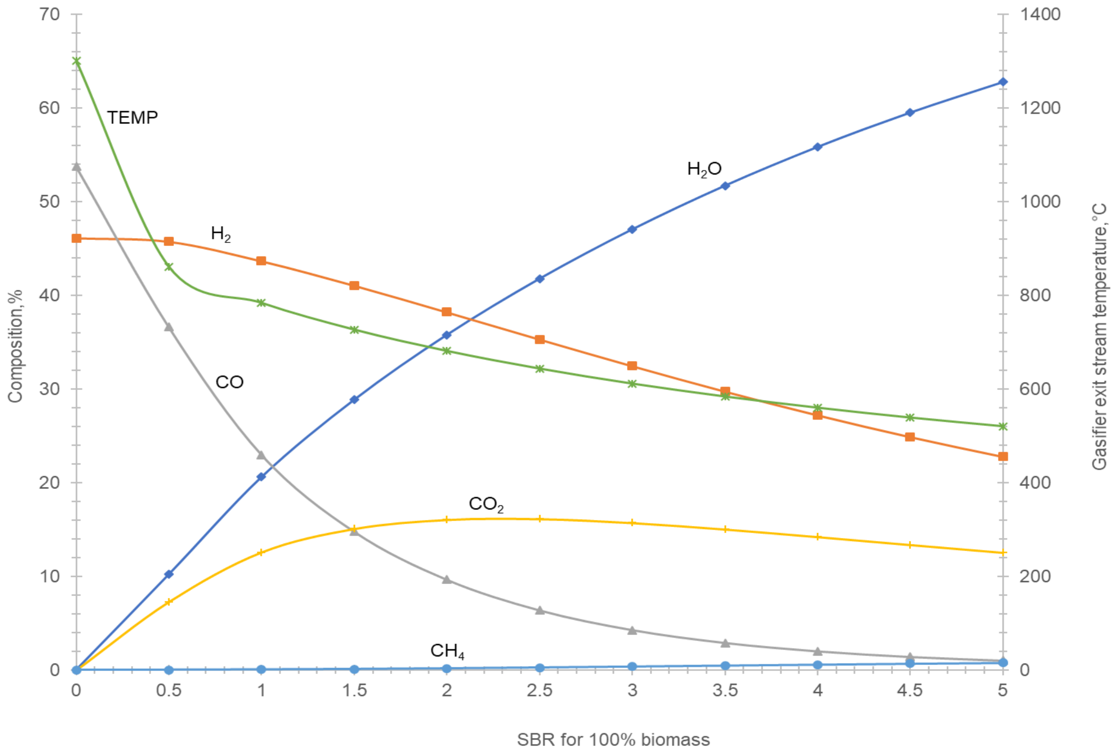


Figure 4.1.2. Effect of the steam -to- biomass ratio (SBR) on the product gas for biomass gasification.

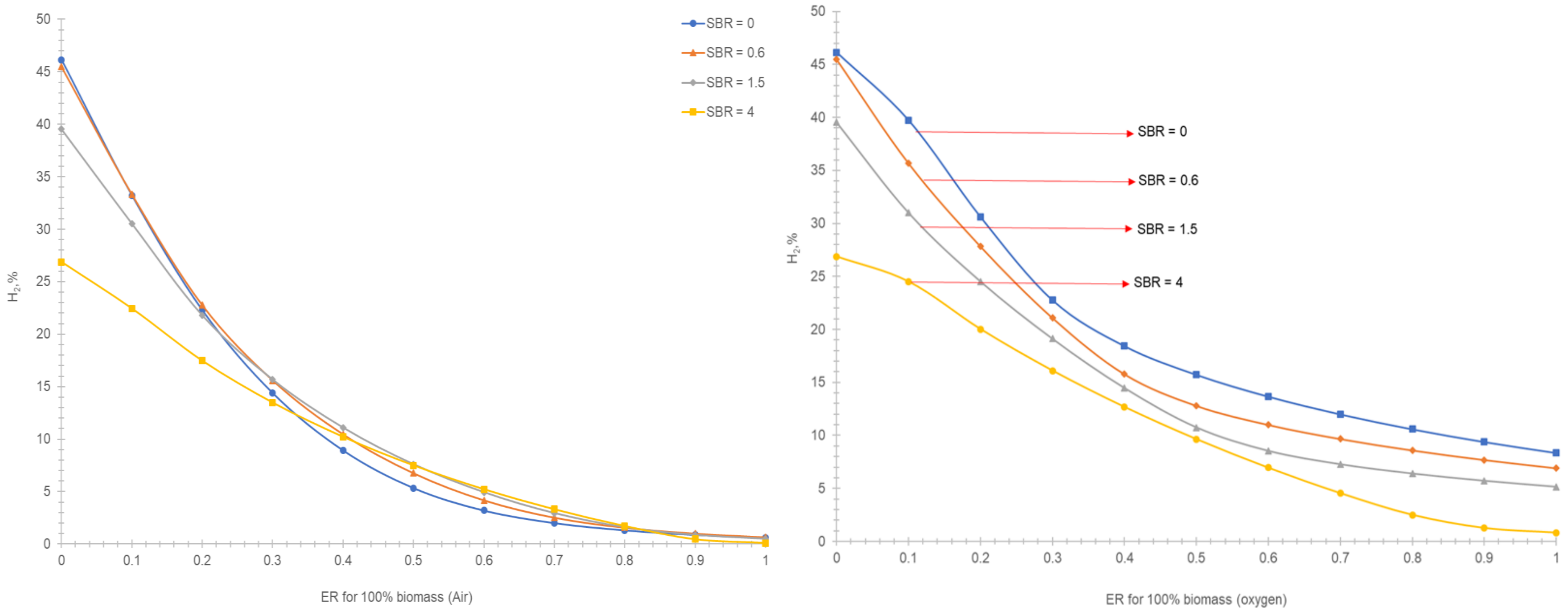
Franco et al. (2003) conducted an experimental study for the gasification of pine sawdust, using a fluidised bed gasifier. The gasifier temperature was fixed at 800°C and the SBR values were varied from 0.4 to 0.9 and the high H_2 content of 31% was achieved at SBR equal to 0.6, and as SBR increased further the amount of the H_2 content decreased. Similar observation obtained in this study, since at low SBR value of 0.6, the high H_2 of about 46.0% is attained and as SBR increases the amount of H_2 content decreases.

In terms of the CO content in the product gas, Franco et al. (2003) reported that a high CO content of about 47% was attained at SBR equal to 0.5 and as SBR increased to 0.8, the amount of CO decreased as well to be about 39%. Similarly, in this study, an SBR range between 0.5 – 0.8 the amount of CO in the product gas, decreased from 37.9% to 28% respectively. The difference in the amount of H_2 and CO produced from the two studies, might be explained that, it is due to the different types of the gasifiers used, since they consist of different configurations. Franco et al. (2003) used fluidized bed gasifier to gasify the pine sawdust feedstock, and in this study, gasifying the same type of feedstock, the equilibrium gasifier is used. The other contributing factor to the difference in the CO content from these two studies can be attributed to way in which heat is added to the system. For instance, Franco et al. (2003), provided heat for reactions, by utilising an electrical furnace at a constant temperature of 800°C, for all ER values. Whereas, in this study heat inside the gasifier (equilibrium), depends soley on the gasifying agent (steam) used, and that has an influence on the CO composition.

4.1.3. Effect of using air - steam and oxygen – steam mixtures as gasifying agents on the H_2 composition of the product gas.

Figure 4.1.3 (a) and (b) shows the effect of the equivalence ratio (ER) on the H_2 composition of the product gas, when air and oxygen are used as gasifying agents. The equivalence ratio is varied from 0 to 1 and the steam is added to the gasifier at different flow rates through SBR equals to 0.6 (low steam flowrate), SBR equals to 1.5 (medium steam flowrate) and SBR equals to 4 (high steam flowrate). This section aims to determine the operating parameters and type of gasifying agent that provides a high H_2 composition in the product gas.

Figure 4.1.3 (a) and (b) shows that a high H_2 content is favoured at low ER values below 0.3, and as the equivalence ratio increases from 0 – 1, the of H_2 decreases significantly. This trend is observed for all the different SBR values, and irrespective of the type of gasifying agent (air or oxygen) used. The decrease in H_2 in the product gas as the equivalence ratio increases is expected since an increase in ER allows more oxygen to the gasifier, and that results in the promotion of the oxidation reactions such as (R5) to (R8), and these reactions oxidizes the H_2 into H_2O. Figure 4.1.3 (a) and (b) shows that the high H_2 content is limited to an SBR range between 0 – 1.5. At SBR values above 1.5, the H_2 content is low. Therefore, this means that H_2 content is favoured at low ER values, and at low steam flowrates.



(a) (b)

Figure 4.1.3. Effect of equivalence ratio (ER) and different steam – to- biomass ratio (SBR) on the H_2 composition, when (a) air and (b) oxygen are used as gasifying agents.

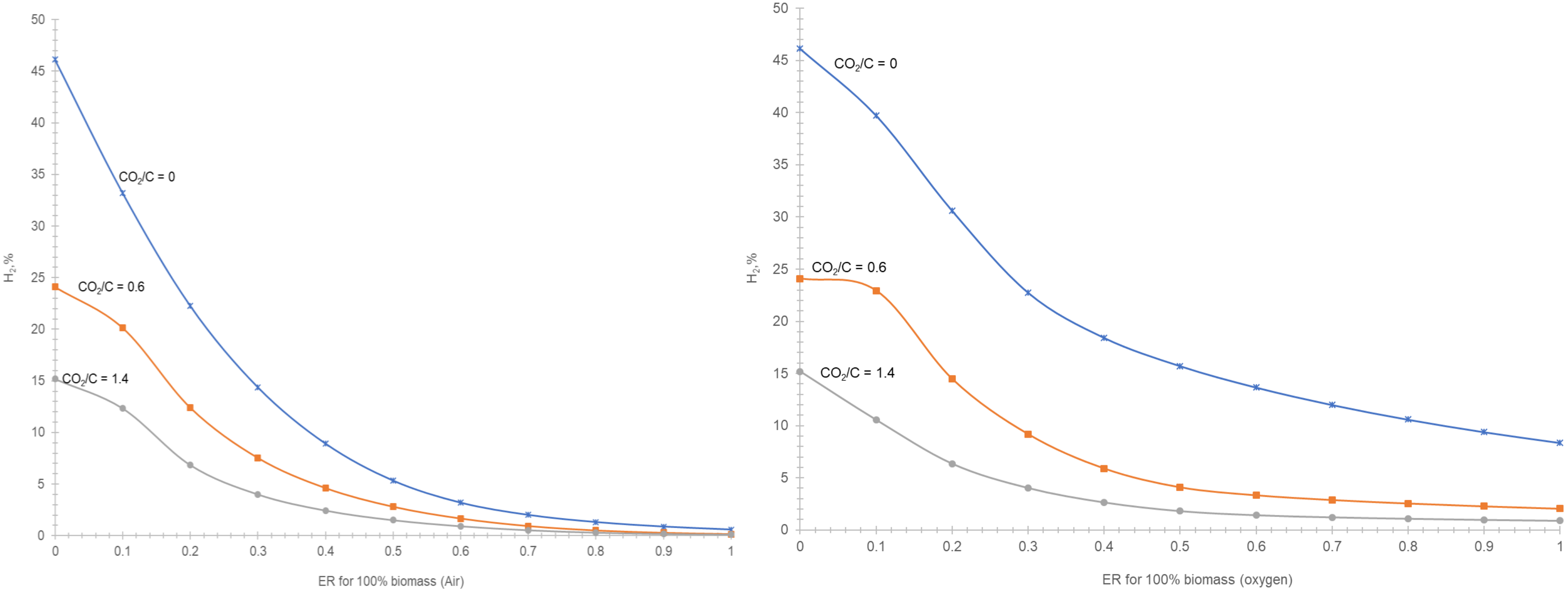
Figure 4.1.3 (a) and (b) shows that when air- steam mixture was used as a gasifying agent, the highest H_2 content of 39.0 % was achieved at ER equals to 0.05 and SBR equals to 0.6. In the case of oxygen – steam mixture as gasifying agent the highest H_2 composition of 44.0% at ER equals to 0.05 and SBR equals to 0.6 was achieved. Figure 4.1.3 (a) and (b) show that oxygen – steam mixtures provides a higher H_2 composition than air – steam mixtures. When the H_2 composition obtained from air (Figure 4.1.1 (a)) is compared with that obtained from the air – steam mixtures as a gasifying agent, it is observed that the addition of steam increase the H_2 content at ER values equal to 0.3 – 1. Figure 4.1.2 (b) oxygen is compared with oxygen – steam mixtures it is deduced that the addition of steam decreases the H_2 content in the product gas, for all the different ER values.

The literature exploring the influence of air- steam or oxygen – steam mixtures as gasifying agents on the H_2 composition of the product gas when the equivalence ratio was varied is very limited. In the literature, it is either one parameter i.e. SBR value is fixed, while the other i.e. ER is varied or vice versa.

4.1.4. Effect of using air-carbon dioxide and oxygen-carbon dioxide mixtures as gasifying agents on the H_2 composition in the product gas.

Figure 4.1.4 (a) and (b) shows the effect of the equivalence ratio on the H_2 content of the product gas, when air and oxygen are used as gasifying agents and equivalence ratio is varied from 0 to 1. Carbon dioxide is added to the gasifier at different flow rates, with the CO_2/C ratio equals to 0.2 (low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (high carbon dioxide flowrate). Figure 4.1.4 (a) and (b) show that as ER increases, the H_2 composition decreases and as the carbon dioxide flow rate increases the H_2 composition decreases. The decrease in the H_2 composition in the product gas as ER increases is attributed to the oxidation reaction (R8), which oxidizes H_2 into H_2O.

As more carbon dioxide is added, the H_2 composition decreases, due to chemical reactions such as reverse water – gas shift reaction (R9), in which H_2 is consumed by the incoming carbon dioxide to form CO and H_2O. Furthermore, this can be explained by the Le Chatelier's principle, which states that when the amount of carbon dioxide (as reactant) increases the equilibrium of the reaction will shift towards the direction of the products, that is the reason, the H_2 decreases as ER and CO_2 increases. High H_2 co are favoured at low ER below 0.3 and low carbon dioxide flowrates such as CO_2/C ratio equals to 0.2. At low ER range and low CO_2/C ratios, the chemical reactions which promote the increase of H_2 composition include the steam reforming reaction (R10) and methanation reaction (R13).



(a) (b)

Figure 4.1.4. Effect of equivalence ratio (ER) and different carbon dioxide – to- carbon ratios (CO_2/C) on the H_2 composition of the product gas when (a) air and (b) oxygen are used as gasifying agents.

Figure 4.1.4 (a) shows that when air- carbon dioxide mixtures are used as a gasifying agent a H_2 composition of 23.0% is achieved at ER equal to 0.05 and CO_2/C ratio equal to 0.6, while when oxygen – carbon dioxide mixtures are used a high H_2 composition of 24.0% can be achieved at ER equal to 0.05 and CO_2/C ratio equal to 0.6. This implies that oxygen – carbon dioxide mixture is a better gasifying agent mixture as compared to air- carbon dioxide mixture. (Although, the difference in composition is 1%, because of the low ER value.).

However, from Figure 4.1.1 to 4.1.4, it is deduced that mixtures of gasifying agents decreases the H_2 in the product gas for biomass (pine sawdust) gasification, as higher amounts of H_2 are achieved when individual gasifying agents are used. Table 4.1.1 shows the recommended operating conditions and gasifying agent at which high H_2 compositions can be achieved.

Figure 4.1.1. to 4.1.4 shows that the highest H_2 content can be achieved at the pyrolysis stage, which occurs during the decomposition of biomass, before a gasifying agent is added (for all types of gasifying agents). The highest H_2 content attained during the biomass decomposition is 46.0% at ER equals to zero, SBR equal to zero and CO_2/C ratio equal to zero.

Figure 4.1.1 to 4.1.4 indicates that amongst the different types of gasifying agents used in this study (during the gasification stage of biomass), steam provides the highest H_2 composition in the product gas, followed by oxygen > oxygen – steam mixture > oxygen-carbon dioxide mixture. In the case of air and air – related gasifying agents compared to steam, in descending order, steam provides higher H_2 composition > air – steam mixture > air > air – carbon dioxide mixture. (This observation is based on the highest H_2 composition attained at different conditions such as ER, SBR and CO_2/C ratio).

Islam et al. (2020) conducted a study using the Aspen simulation for a fluidized bed gasifier for biomass (pine wood) gasification in order to determine the effect of different gasifying agents such as steam, oxygen, hydrogen peroxide and air on the product gas composition. The results from the study conducted by Islam et al. (2020) corroborates with the results found in this study that the gasifying agent that provides a higher H_2 composition in the product gas, as the equivalence ratio is varied, is steam is used as a gasifying agent, followed by oxygen, thereafter the oxygen – steam mixture, air, air – steam mixture, oxygen – carbon dioxide and lastly air – carbon dioxide.

Table 4.1.1 shows the highest values of H_2 composition of the product gas achieved from the different gasifying agents at different operating conditions. Table 4.1.1 shows that the highest

H_2 composition is attained when steam is used as a gasifying agent, at low ER range between 0 – 0.4, and SBR equal to 0.6 and CO_2/C ratio equal to 0.6.

Table 4.1.1. The recommended gasifying agents and operation conditions, for achieving high H_2 compositions.

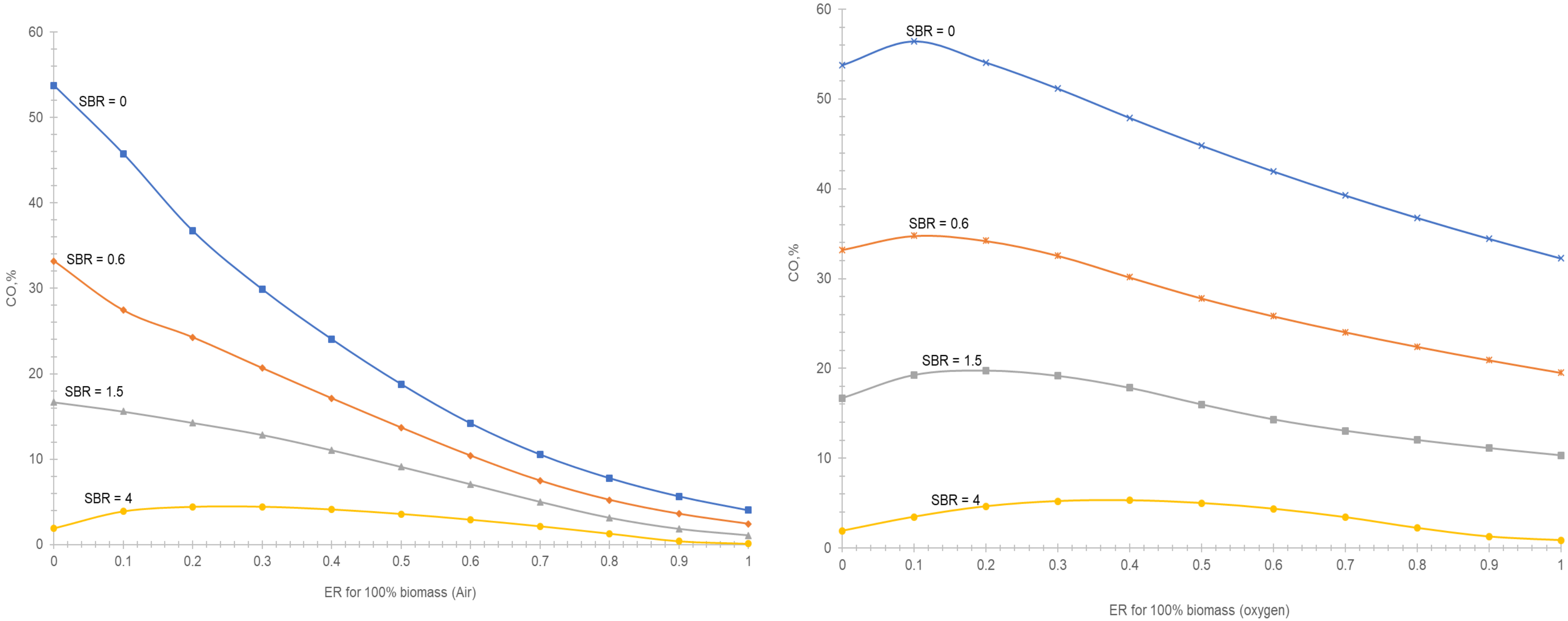
Gasifying agent	**H_2 Composition (%)**			
	High values achieved	**ER**	**SBR**	**CO_2/C Ratio**
Air	46.0 39.8	0 0.05	-	-
Steam	46.0	-	0.1	-
Oxygen	46.0 44.0	0 0.05	-	-
Air – steam mixture	46.0 39.0	0 0.05	0 0.6	-
Oxygen – steam mixture	46.0 44.0	0 0.05	0 0.6	
Air- carbon dioxide mixture	46.0 23.0	0 0.05	-	0 0.6
Oxygen – carbon dioxide mixture	46.0 24.0	0 0.05	-	0 0.6

4.1.5. Effect of using air – steam and oxygen – steam mixtures as gasifying agents on the CO composition of the product gas.

Figure 4.1.5 (a) and (b) shows the effect of equivalence ratio (ER) on the CO composition of the product gas, when Figure 4.1.5 (a) air and Figure 4.1.5 (b) oxygen are used as gasifying agents, and steam is added at different flowrates through SBR equals to 0.6,1.5 and 4.

Figure 4.1.5 (a) shows that as the ER increases the CO decreases for all the different SBR values, except for SBR equals to 4, which begins by increasing with the increasing ER and then reach a highest value before decreasing as ER increases further. Figure 4.1.5 (b) shows that as the ER increases the CO composition increases and reaches a maximum value, then decreases as ER increases further. Furthermore, as the steam content increases the CO composition decreases. Figure 4.1.5 (a) and (b) illustrates that high CO composition is favoured at low ER below 0.4 and low SBR values between 0 – 0.6. The high CO composition is attributed to chemical reactions such as steam reaction (R2), steam reforming of methanation (R12) and partial methanation reaction (R13). The reduction of the CO composition as SBR increases is mainly attributed to the water-gas shift reaction (R9). Furthermore, according to Le Chatelier’s principle, the decrease in the CO composition is due to the increase of steam (as a reactant) in the water gas shift reaction (R9), that results in the equilibrium shifting in the direction of the forward reaction, thus favouring H_2 and CO_2, which leads to a decrease in CO.

Figure 4.1.5 (a) and (b) shows that when oxygen – steam mixture as a gasifying agent was used, a highest CO composition of 35.0% was achieved at SBR equals to 0.6 and ER equals to 0.1 and when air- steam mixture was used a high CO composition of 28.0% was achieved at ER equals to 0.05 and SBR equals to 0.6. Figure 4.1.5 (a) and (b) show that oxygen – steam mixtures as a gasifying agent provides a higher CO composition than air- steam mixtures as a gasifying agent. This is due to the nitrogen dilution in the air- steam mixtures. It is noticed that the CO composition produced from air only is higher than that produced when air is mixed with steam. The same is true for the oxygen case i.e. the CO composition is lower when oxygen is mixed with steam as compared to that produced from oxygen only.



(a)

(b)

Figure 4.1.5. Effect of equivalence ratio (ER) and different steam – to- biomass ratios (SBR) on the CO composition, when (a) air and (b) oxygen are used as gasifying agents.

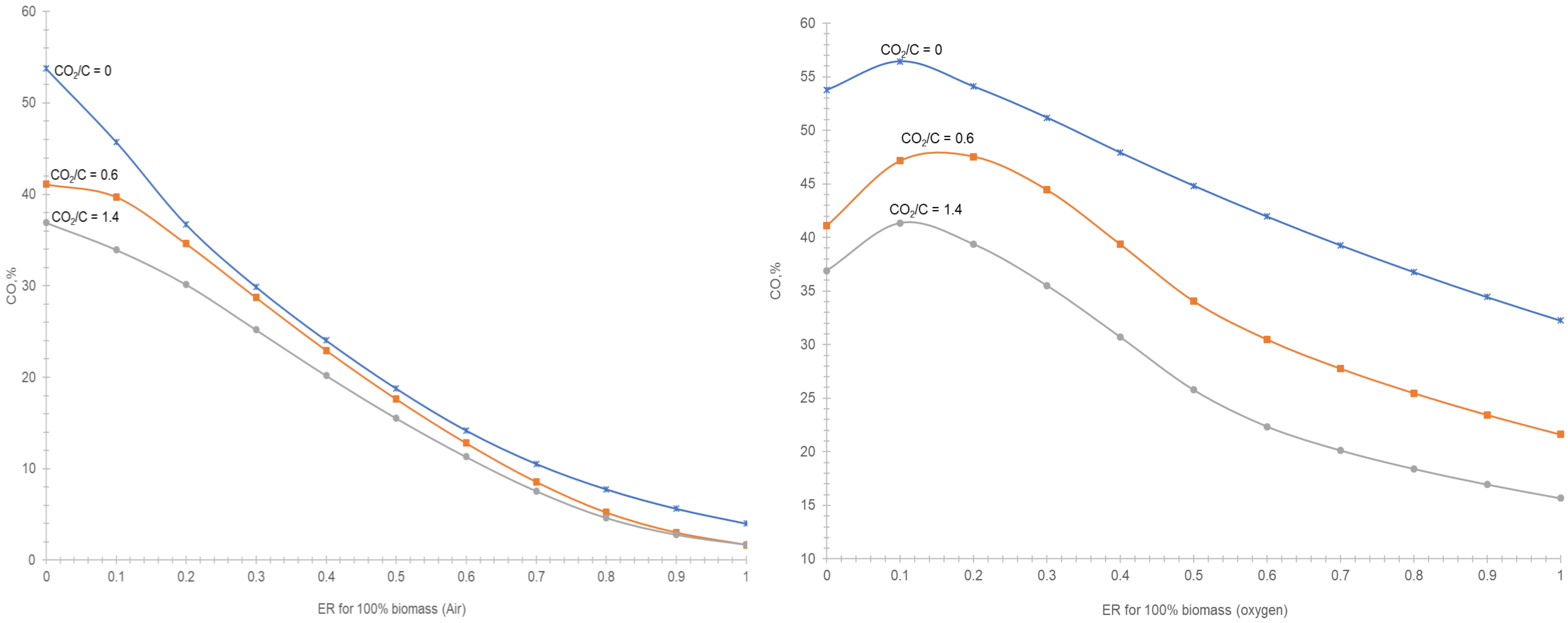
4.1.6. The Effect of using air – carbon dioxide and oxygen - carbon dioxide mixture gasifying agents on the CO composition.

Figure 4.1.6 (a) and (b) shows the effect of the equivalence ratio (ER), varied from 0 to 1, on the CO composition in the product gas when biomass is gasified. Air and oxygen are used as gasifying agents and carbon dioxide is added to the gasifier at different flow rates i.e. CO_2/C ratio equals to 0.6 (low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (high carbon dioxide flowrate).

Figure 4.1.6 (a) and (b) shows that as ER increases the CO composition decreases and as the carbon dioxide increases, the CO decreases. Figure 4.1.6 (a) and (b) shows that high CO composition is favoured at low ER below 0.2 and low CO_2/C ratio equals to 0.6. The high CO composition is attributed to chemical reactions such as the Boudouard reaction (R1), reverse methane CO_2 reforming reaction (R10), and methanation reaction (R13). Conversely, the low CO composition is ascribed to the reverse water- gas shift reaction (R9) and oxidation reaction (R6). At high ER values, the CO is oxidized by the oxidation reaction (R6).

Figure 4.1.6 (a) and (b) shows that when the oxygen – carbon dioxide mixture is used as a gasifying agent a high CO content of 48.0% is achieved at ER equal to 0.14 and CO_2/C ratio equal to 0.6 while when air - carbon dioxide mixture as gasifying agent is used, a high CO composition of 41.0% is achieved at ER equal to 0.05 and CO_2/C ratio equal to 0.6. These results indicate that oxygen – carbon dioxide mixture as a gasifying agent is a better gasifying agent than air- carbon dioxide mixture, since air- carbon dioxide mixture is diluted with the nitrogen content.

It is deduced that a high CO in the product gas is achieved from the use of the individual gasifying agents, than when gasifying agent mixtures are used during the biomass (pine sawdust) gasification. Therefore, from Figure 4.1.1 to 4.1.6 it is deduced that a high amount of CO can be produced if oxygen is used as a gasifying agent and at low ER, low SBR and low CO_2/C ratio values. The values of CO composition are shown in Table 4.1.2 for different gasifying agents and operating conditions are used.



(a) (b)

Figure 4.1.6. Effect of equivalence ratio and different carbon dioxide–to–carbon ratios on the CO composition, when (a) air – and (b) oxygen are used as gasifying agents.

Table 4.1.2 shows the highest values of CO content achieved from the different gasifying agents at different operating conditions during the gasification of the biomass. However, it should be noted that the CO attained during the gasification stage is lower than that attained during from the pyrolysis stage, for all the gasifying agents, except when oxygen is used as a gasifying agent. Oxygen increases the CO content during the gasification stage of the biomass; thus, a high CO is attained.

Table 4.1.2 shows that the highest CO composition is attained when oxygen is used as a gasifying agent, followed by steam, then oxygen – carbon dioxide and air (in a descending order).The highest values of CO can be achieved at ER values below 0.15 and SBR of 0.6 and CO_2/C ratio equal to 0.6.Table 4.1.2 shows that high CO content can be achieved only when the different gasifying agents are introduced to the gasifier at low flowrates, during the biomass (pine sawdust) gasification.

Table 4.1.2. The recommended gasifying agents and operation conditions, for achieving high CO composition.

Gasifying agent	**CO Composition (%)**			
	High values achieved	**ER**	**SBR**	**CO_2/C Ratio**
Air	54.0 48.0	0 0.05	- -	- -
Steam	52.0	-	0.1	-
Oxygen	54.0 56.1	0 0.1	- -	- -
Air–steam mixture	54.0 28.0	0 0.05	0 0.6	- -
Oxygen – steam mixture	54.0 35.0	0 0.11	0 0.6	- -
Air–carbon dioxide mixture	54.0 41.0	0 0.05	- -	0 0.6

4.1.7. Effect of equivalence ratio and SBR on the H_2/CO ratio of the syngas.

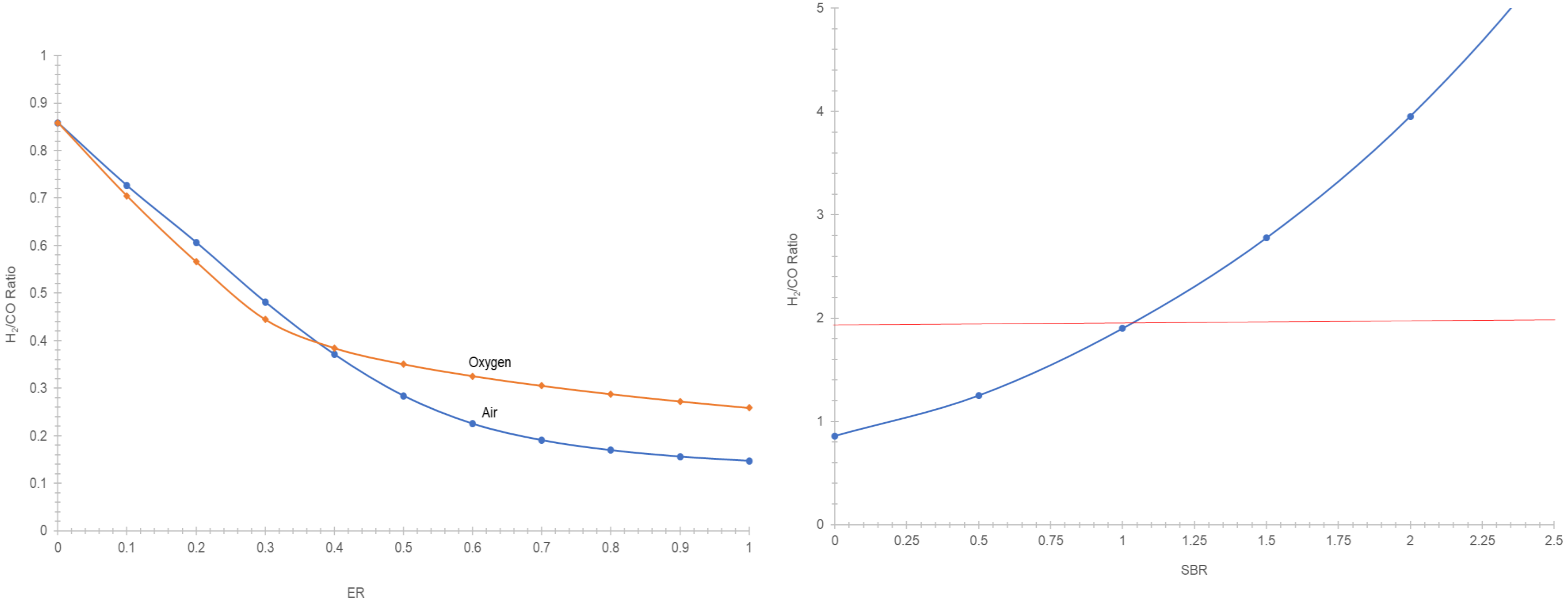
Figure 4.1.7 (a) show the effect of equivalence ratio (ER) on the H_2/CO ratio of the syngas, when the equivalence ratio is varied from 0 to 1. Air and oxygen are used as gasifying agents. The ratio of H_2/CO for the syngas is a very important operating parameter since it provides an indication if the syngas produced is suitable for use as a raw material to produce high value products in the downstream applications such as the Fischer – Tropsch process for the liquid synthesis process, for the methanol production, di-methyl ether production etc. The recommended H_2/CO ratio that is used to indicate a good quality syngas is 2. Therefore, in this section it will be determined which operating conditions, and what type of gasifying agent can provide a H_2/CO ratio of 2, when the equivalence ratio is varied.

Figure 4.1.7 (a) shows that as ER increases the H_2/CO ratio decreases. This shows that the high H_2/CO ratio is favoured at low ER values below 0.3. This is because at low ER values, the gasifier temperature is gradually increasing, which has a positive influence on the H_2 and CO production, which is attributed to activation of partial methanation reaction (R13) and partial oxidation reaction (R4). However, the H_2 composition is higher than the CO composition, leading to a higher H_2/CO ratio. As ER increases further, the H_2 and CO are oxidized by the favoured oxidation reactions such (R5) to (R8) into H_2O and CO_2, which subsequently reduces the H_2/CO ratio of the syngas.

Figure 4.1.7 (a) shows that the recommended H_2/CO ratio of 2 was not achieved, when air and oxygen were used as a gasifying agents, as the H_2/CO ratio was below the value of 2 for all ER values. This is because the CO composition produced is higher than the H_2 composition in the product and this is caused by the high fixed carbon in the biomass (pine sawdust).Figure 4.1.7 (a) shows that even though the recommended H_2/CO ratio of 2 was not achieved, the H_2/CO ratio of the syngas produced from the use of oxygen as a gasifying agent is higher than the H_2/CO ratio of the syngas produced from air. This is because air contains a high nitrogen content, which lowers both H_2 and CO compositions in the product gas.

Figure 4.1.7 (b) shows the effect of the steam – to - biomass ratio (SBR) on the H_2/CO ratio of the syngas when steam is used as a gasifying agent. The SBR is varied from 0 to 2.5. Figure 4.1.7 (b) shows that as SBR increases the H_2/CO ratio of the syngas increases. As a result, the recommended H_2/CO ratio of 2 is achieved at SBR equal to 1.1. In Figure 4.1.7 (b) it is observed that as SBR increases the H_2/CO ratio of the syngas increased and this is due to the promotion of chemical reactions such as steam reaction (R2), water- gas shift reaction (R9), steam reforming reaction (R12) and reverse methanation reforming reactions (R11) and

(R14). Furthermore, the reason for the increase in the H_2/CO ratio as SBR increases is because as SBR increases, H_2 increases while CO composition decreases significantly (Figure 4.1.2).



(a)

(b)

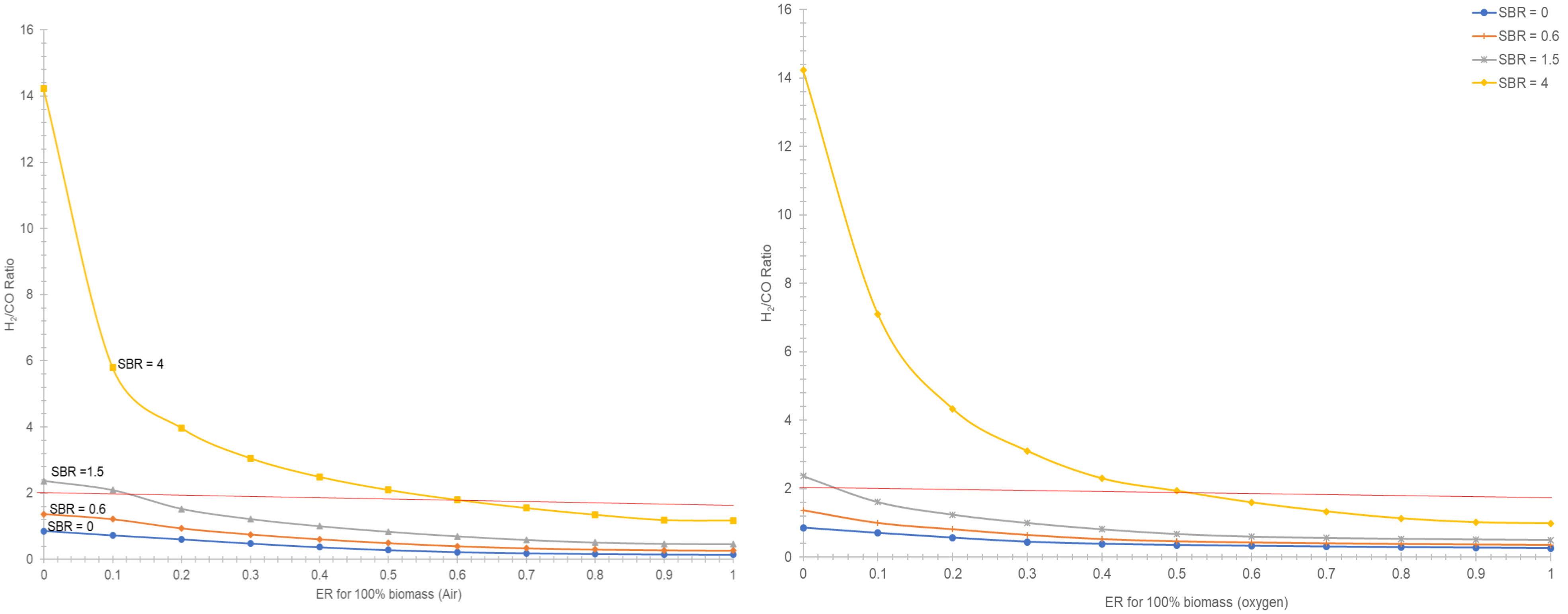
Figure 4.1.7. Effect of equivalence ratio (ER) on the H_2/CO ratio of the syngas when (a) air and oxygen, (b) steam are used as gasifying agents.

4.1.8. Effect of equivalence ratio on the H_2/CO ratio of the syngas when air- steam and oxygen – steam mixtures as gasifying agents are used.

Figure 4.1.8 (a) and (b) shows the effect of equivalence ratio on the H_2/CO ratio of the syngas when ER is varied from 0 to 1, when air and oxygen are used as gasifying agents. Steam is added at different flow rates (SBR equals to 0.6 (low steam flowrate), SBR equals to 1.5 (medium steam flowrate) and SBR equals to 4 (high steam flowrate)).

Figure 4.1.8 (a) and (b) show that as ER increases the H_2/CO ratio of the syngas decreases and as the steam flowrate increases the H_2/CO ratio increases. The decrease in the H_2/CO ratio as ER increases is due to the oxidation reactions such as (R5) to (R8), which are promoted at high ER values and tends to oxidize the H_2 and CO into CO_2 and H_2O. It is observed that high H_2/CO ratio of the syngas is favoured at low ER values below 0.4. The addition of steam increases the H_2/CO ratio of the syngas, which is attributed to chemical reactions such as water gas reaction (R9), steam reaction (R2), reverse methanation reforming reactions (R11) and (R14) and steam reforming reaction (R12).

Figure 4.1.8 (a) and (b) shows that when air – steam mixtures are used as a gasifying agent, the recommended H_2/CO ratio of 2 was achieved at ER equals to 0.11 and SBR equals to 1.5 and also at SBR equals to 4 and ER equals to 0.6. When oxygen – steam mixtures were used, the recommended H_2/CO ratio of 2 was achieved at SBR equals to 1.5 and ER equals to 0.2 and at SBR equals to 4 and ER equals to 0.5.



(a)

(b)

Figure 4.1.8. Effect of equivalence ratio (ER) on the H_2/CO ratio of the syngas, when steam is added at different flow rates when (a) air and (b) oxygen are used as gasifying agents.

4.1.9. Effect of equivalence ratio on the H_2/CO ratio of the syngas when air- carbon dioxide and oxygen-carbon dioxide mixtures are used as gasifying agents.

Figure 4.1.9 (a) and (b) shows the effect of equivalence ratio (ER) on the H_2/CO ratio of the syngas, when air and oxygen are used as gasifying agents. The equivalence ratio is varied from 0 to 1 and the carbon dioxide is added to the gasifier at different flow rates (CO_2/C ratio equals to 0.6 (low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (high carbon dioxide flowrate).

Figure 4.1.9 (a) and (b) illustrates that the H_2/CO ratio is high at low ER values, due to chemical reactions such as the methanation reaction (R13) which is promoted at low ER. However, as the ER increases the H_2/CO ratio of the syngas decreases. Similarly, when the CO_2/C ratio increases the H_2/CO ratio decreases. The decrease in the H_2/CO ratio of the syngas as carbon dioxide is added to the gasifier, is attributed to the Boudouard reaction (R2) and partial oxidation reaction (R4) which promotes the production of CO as the carbon dioxide in the gasifier increases, which lowers the H_2/CO ratio of the syngas. The reverse water gas shift reaction (R9) and the reverse methanation reactions (R10) also contribute to the reduction in the H_2/CO ratio of the syngas. The reduction in the H_2/CO ratio of the syngas as ER increases is attributed to the oxidation reactions such as (R5) to (R8), which are promoted at high ER values due to the high oxygen content. Figure 4.1.9 (a) and (b) show that the recommended H_2/CO ratio of 2, was not achievable when carbon dioxide was combined with air and oxygen.

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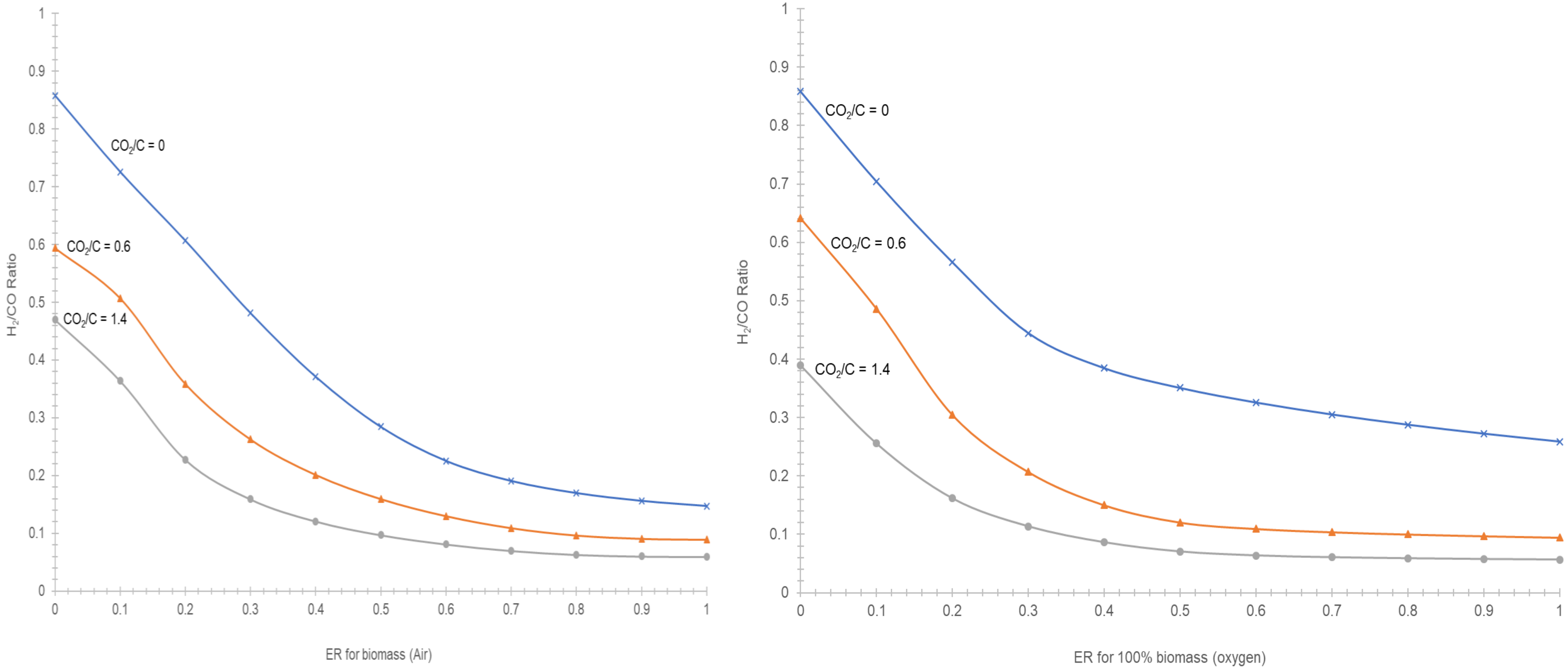

(a)

(b)

Figure 4.1.9. Effect of equivalence ratio (ER) on the H_2/CO ratio of the syngas, when carbon dioxide is added to the gasifier at different flow rates when (a) air and (b) oxygen are used as gasifying agents.

Table 4.1.3 shows the operating conditions and different types of gasifying agents, at which the recommended H_2/CO ratio of 2 can be obtained. Table 4.1.3 shows that when the different gasifying agents are used, the recommended ratio of 2 is achieved from steam, air- steam and oxygen – steam mixtures from the operating at low ER and low SBR values. The addition of carbon dioxide to the gasifier, does not produce syngas with the recommended H_2/CO ratio of 2.

Table 4.1.3. The recommended gasifying and operating parameters that can be used to produce the H_2/CO ratio equal to 2, for biomass gasification.

Gasifying agent	**H_2/CO ratio of the syngas**			
	H_2/CO value achieved	**ER**	**SBR**	**CO_2/C Ratio**
Air	<2	-	-	-
Steam	2	-	1.1	-
Oxygen	<2	-	-	-
Air- Steam mixture	2 2	0.04 0.6	1.5 4	-
Oxygen – steam mixture	2	0.12 0.5	1.5 4	-
Air – carbon dioxide mixture	<2	-	-	-
Oxygen – carbon dioxide mixture	<2	-	-	-

4.1.10. Effect of equivalence ratio on the Lower Heating Value (LHV) of the syngas.

Figure 4.1.10 (a) shows the effect of the equivalence ratio (ER) on the Lower Heating Value (LHV) of the syngas. The equivalence ratio is varied from 0 to 1, with air and oxygen used as gasifying agents. The Lower Heating Value (LHV) of the syngas is an important parameter that indicates the energy content of the syngas produced. Therefore, it is important to determine which gasifying agent(s) can provide a high calorific value of the syngas and which operating conditions can be employed to provide a high calorific value of the syngas.

Figure 4.1.10 (a) shows that as the equivalence ratio increases, the Lower Heating Value (LHV) of the syngas decreases. It is observed that the Lower Heating Value (LHV) is higher at low ER values below 0.3. This is due to chemical reactions such as partial oxidation reaction (R4) and methanation reaction (R13). The decrease of the Lower Heating Value (LHV) as the ER increases is attributed to the oxidation reactions such as (R5) to (R8) which are promoted by the increase in oxygen to the gasifier. The available H_2 and CO are oxidized to form H_2O and CO_2 in the product gas, which do not contribute to the LHV.

Figure 4.1.10 (a) shows that the Lower Heating Value (LHV) when oxygen is used as a gasifying agent is higher than that when air is used. This is because air contains a high nitrogen content, which lowers the composition of the combustible gases such as CO, H_2 and CH_4 in the product gas. Figure 4.1.10 (a) shows that the Lower Heating Value (LHV) from oxygen as gasifying agent is 11.8 MJ/Nm^3 at ER equals to 0.04 and the Lower Heating Value (LHV) when air is used is found to be 11.0 MJ/Nm^3 at ER equals to 0.04.

Figure 4.1.10 (b) shows the effect of steam – to - biomass ratio (SBR) on the Lower Heating Value (LHV) of the syngas when steam is used as a gasifying agent. The same trend as that observed in Figure 4.1.10 (a) is observed in Figure 4.1.10 (b), whereby as the SBR increases the lower heating value decreases. This is due to chemical reactions such as the reverse water - gas shift reaction (R9), reverse methanation reforming reactions such as (R11), (R14) and steam reforming reaction (12). More steam results in excess H_2O in the product gas, which does not contribute to the LHV.

Figure 4.1.10 (b) shows that the highest Lower Heating Value (LHV) can be achieved at low SBR values below 0.3. For example, the Lower Heating Value (LHV) of 11.2 MJ/Nm^3 was achieved at SBR equals to 0.1. Figure 4.1.10 (a) and (b) shows that the highest lower heating value is achieved when steam is used as a gasifying agent, followed by oxygen and lastly air.

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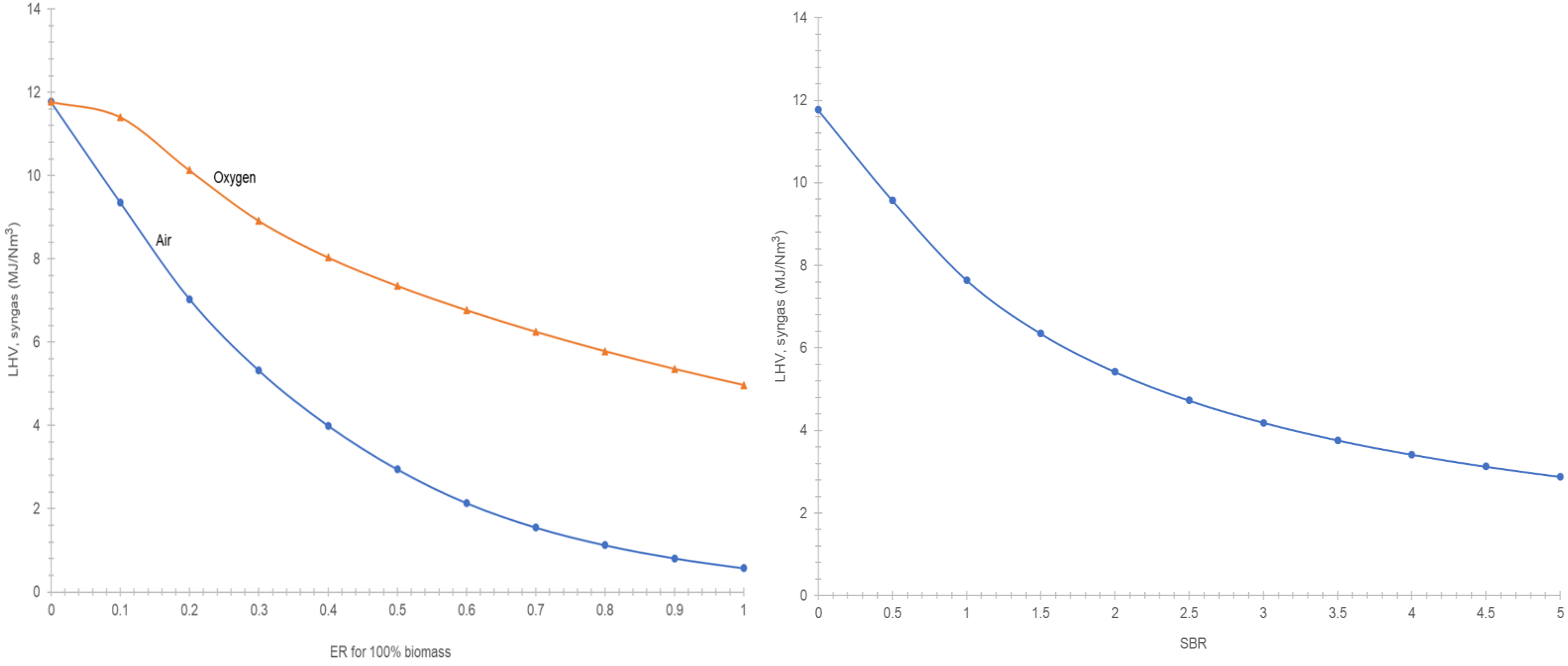


(a) (b)

Figure 4.1.10. Effect of equivalence ratio (ER) and steam – to- biomass ratio (SBR) on the Lower Heating Value (LHV) of the syngas when (a) air and oxygen gasifying agent and (b) steam gasifying agent are used.

Zheng et al. (2016) conducted a study on a laboratory - scale using an entrained flow gasifier for the gasification of the biomass (rice husks) The study was conducted to investigate the influence of air and oxygen as gasifying agents on the Lower Heating Value (LHV) of the syngas. The equivalence ratio was varied from 0.1 to 0.5. Zheng et al. (2016) obtained similar trend as in this study, as the ER increased from 0.1 to 0.5 the Lower Heating Value (LHV) of the syngas decreased, for both air and oxygen as gasifying agents.

Zheng et al. (2016) illustrate that as ER increased the Lower Heating Value (LHV) from oxygen decreased from 17 MJ/Nm^3 to 7 MJ/Nm^3 and that from air decreased from 13.8 MJ/Nm^3 to 4 MJ/Nm^3. Another observation from the study conducted by Zheng et al. (2016) is observed in this study is that the Lower Heating Value (LHV) produced from the use of oxygen as a gasifying agent is higher than that produced from the air as a gasifying agent. The trend is similar as well, since the increase of the ER reduces the Lower Heating Value (LHV) of the syngas. However, it is noticed that the values obtained from the study conducted by Zheng et al. (2016) are somewhat higher than that obtained from this study. The difference in values is attributed to the gasifier temperature. Zheng et al. (2016) kept the gasifier temperature constant at 1000°C, while in this study the gasifier temperature is dependent on the flowrate at which the gasifying agent (air) is added to the gasifier. Secondly, different types of biomass types are used such as that Zheng et al. (2016) used the rice husk whereas this study employed pine sawdust, also contributes towards the different values of lower heating values attained.

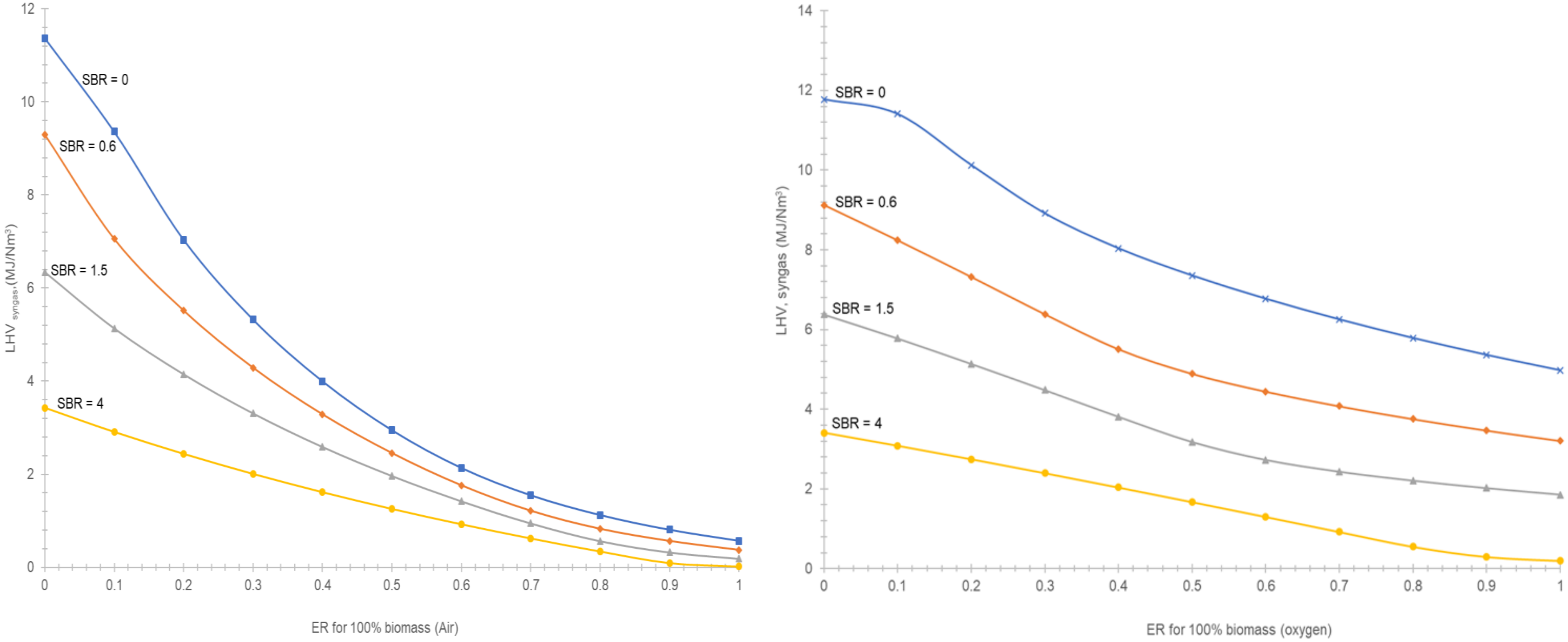
Tavares et al. (2020) conducted a study using the Aspen Plus simulator for biomass (Portuguese forest residues) gasification. The study aimed to investigate the effect of the SBR on the lower heating value of the syngas. The SBR was varied from 0 to 0.2 and similar observations as in this study were found. The increase in SBR from 0 to 0.2 decreased the LHV from 12.5 MJ/m^3 to 8 MJ/m^3. Tavares et al. (2020), obtained the same finding as in this study that the lower heating value is higher at low SBR, since at low SBR values, a high composition of CH_4, CO, and H_2 is achieved.

4.1.11. Effect of equivalence ratio on the lower heating value (LHV) of the syngas when air – steam and oxygen – steam mixtures as a gasifying agent are used.

Figure 4.1.11 (a) and (b) show the effect of equivalence ratio (ER) on the Lower Heating Value (LHV) of the syngas when air and oxygen are used as gasifying agents. The equivalence ratio is varied from 0 to 1. Steam is added to the gasifier at different flow rates (SBR equals to 0.6 (low steam flowrate), SBR equals to 1.5 (medium steam flowrate) and SBR equals to (high steam flowrate)). The effect of adding steam at different flowrate is evaluated and the operating conditions that allow for a high lower heating value is determined.

Figure 4.1.11 (a) and (b) show that when ER increases the lower heating value of the syngas decreases and when the steam flowrate increases, the lower heating value of the syngas decreases. The decrease in the Lower Heating Value (LHV) as steam content increases is attributed to the reverse water – gas shift reaction (R9), steam reforming reaction (R12), reverse methanation reforming reactions (R11), and (R14) which are promoted as steam is used as gasifying agents.

Figure 4.1.11 (a) and (b) shows that at low ER values below 0.3 and low SBR values, a high Lower Heating Value (LHV) of the syngas can be achieved. Figure 4.1.11 (a) and (b) show that the lower heating value (LHV) of the syngas produced when an oxygen – steam mixture is used is higher than from an air – steam mixture. As a result, a value of 8.8 MJ/Nm^3 at SBR equals to 0.6 and ER equals to 0.05 was obtained from oxygen – steam mixture as a gasifying agent, and a value of 8.0 MJ/Nm^3 was achieved at SBR equals to 0.6 and ER equals 0.05, when air - steam mixture was used as a gasifying agent.



(a) (b)

Figure 4.1.11. Effect of equivalence ratio (ER) on the Lower Heating Value (LHV) of the syngas at different steam flow rates when (a) air and (b) oxygen are used as gasifying agents.

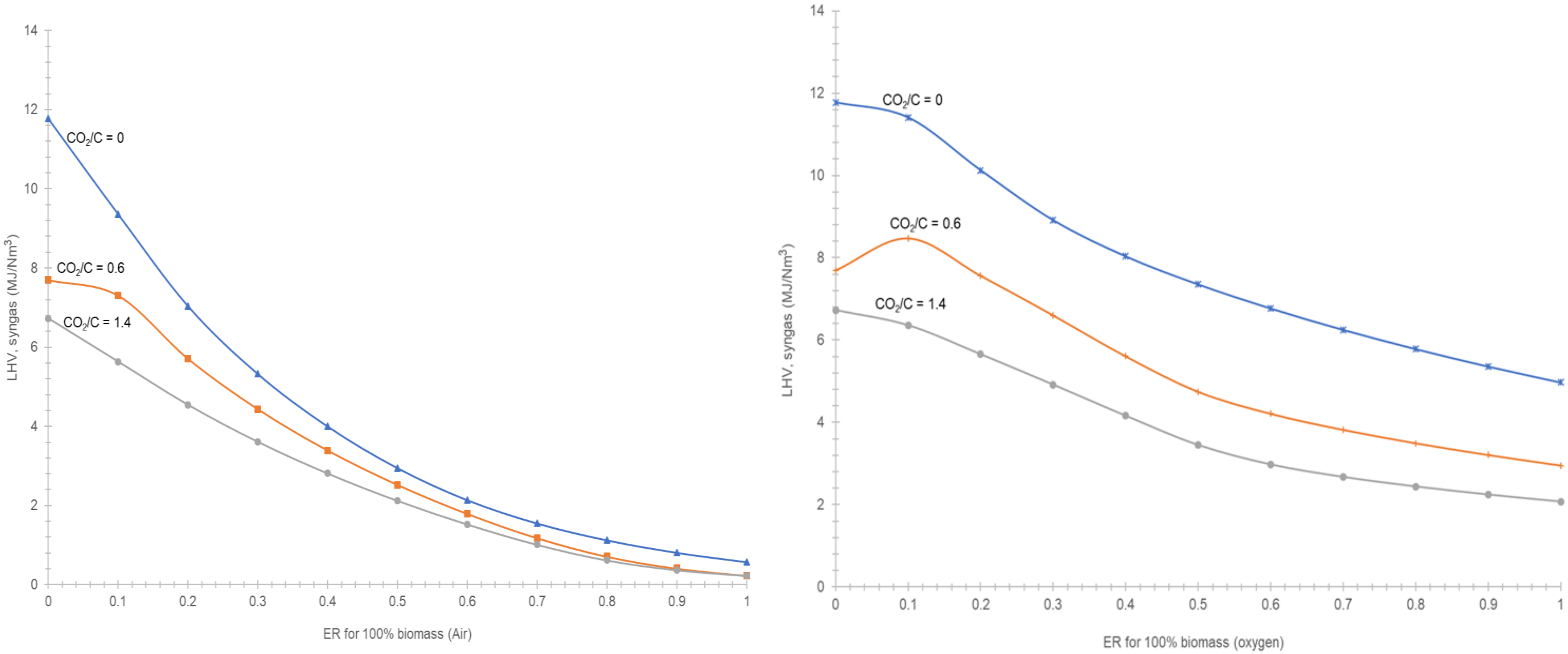
4.1.12. Effect of equivalence ratio on the Lower Heating Value (LHV) of the syngas when air – carbon dioxide and oxygen-carbon dioxide mixtures as a gasifying agent are used.

Figure 4.1.12 (a) and (b) show the effect of equivalence ratio (ER) on the Lower Heat Value (LHV) of the syngas. The equivalence ratio is varied from 0 to 1 and air and oxygen are used as gasifying agents. The carbon dioxide is added to the gasifier at different flow rates (CO_2/C ratio equals to 0.6 (low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (high carbon dioxide flowrate)). The influence of the CO_2/C ratio and ER on the lower heating value of the syngas is evaluated.

Figure 4.1.12 (a) and (b) shows that when the equivalence ratio (ER) increases the lower heating value of the syngas decreases. Also, when the carbon dioxide flow rate increases the lower heating value decreases. The decrease in the Lower Heating Value (LHV) of the syngas as ER and CO_2/C ratio increases is attributed to the oxidation reactions such as (R5) to (R8), reverse water gas shift reaction (R9), methanation reforming reaction (R14) and reverse methane CO_2 reforming reaction (R10). During the occurrence of these chemical reactions the combustible gases such as H_2, CO and CH_4 are consumed by oxygen and carbon dioxide to mainly produce H_2O and CO_2. Figure 4.1.12 (a) and (b) shows that the highest Lower Heating Values can be achieved at lower ER below 0.3 and CO_2/C ratio equals to 0.6.

Figure 4.1.12 (a) and (b) illustrates that the high Lower Heating Value (LHV) of 7.9 MJ/Nm^3 was achieved at ER equals to 0.04 and CO_2/C ratio equals to 0.6 when air- carbon dioxide mixture is used as a gasifying agent and a Lower Heating Value (LHV) of 8.4 MJ/Nm^3 was achieved at CO_2/C ratio equals to 0.6 and ER equals to 0.1 when oxygen – carbon dioxide was used as a gasifying agent. Figure 4.1.12 (a) and (b) show that the oxygen - carbon dioxide mixtures as a gasifying agent provides a high Lower Heating Value (LHV) of the syngas than that produced from the air - carbon dioxide mixtures as a gasifying agent.

From Figure 4.1.10 to 4.1.12 it is deduced that when air is compared with its relative mixtures such as air- steam and air – carbon dioxide, the highest Lower Heating Value (LHV) is achieved when it is only air is used as a gasifying agent. Whereas, in the case of oxygen and its relative mixtures, it is observed that the highest Lower Heating Value (LHV) is achieved when only oxygen is used as a gasifying agent, followed by oxygen - steam and lastly oxygen – carbon dioxide mixture as gasifying agents are used. The highest values and the recommended operating values for different gasifying agents are shown in Table 4.1.3.



(a) (b)

Figure 4.1.12. Effect of equivalence ratio on the Lower Heating Value (LHV) of the syngas when carbon dioxide is added into the gasifier at different flowrates and (a) air and (b) oxygen are used as gasifying agents.

Table 4.1.4 shows that the highest Lower Heating Value (LHV) of the syngas is found when oxygen is used, followed by steam, at operating conditions such as at lower ER values below 0.15 and SBR below 0.6 and CO_2/C ratio equal to 0.6.

Table 4.1.4. Recommended operating conditions for the different gasifying agents for the recommended H_2/CO ratio of 2 and Lower Heating Value (LHV) of the syngas when the equivalence ratio is varied.

Gasifying agent	**Lower heating value (LHV) of the syngas (MJ/Nm^3)**			
	High values achieved	**ER**	**SBR**	**CO_2/C Ratio**
Air	11.0	0.04	-	-
Steam	11.2	-	0.1	-
Oxygen	11.8	0.04	-	-
Air- Steam mixture	8.0	0.05	0.6	-
Oxygen – steam mixture	8.8	0.05	0.6	-
Air – carbon dioxide mixture	7.6	0.02	-	0.6
Oxygen – carbon dioxide mixture	8.4	0.1	-	0.6

Section two: Polyethylene gasification

4.2. Introduction

The following section discusses the effect of using the different gasifying agents such as air and/ or oxygen, steam, carbon dioxide and their mixtures on the product gas composition, in particular, the hydrogen (H_2), and carbon monoxide (CO) compositions, as well as the H_2/CO ratio of the syngas and Lower Heating Value (LHV) of the syngas for polyethylene gasification. The flowrate of the different gasifying agents are varied in order to compare the output and determine the operating parameters that enable high H_2 and CO composition, a H_2/CO ratio equal to 2 and a high Lower Heating Value (LHV) of the syngas.

4.2.1. Effect of the equivalence ratio (ER) on the composition when air and oxygen are used as a gasifying agents.

Figure 4.2.1 (a) and (b) shows the effect of the equivalence ratio (ER) on the outlet temperature and product gas composition when (Figure 4.2.1 (a)) air and (Figure 4.2.1(b)) oxygen are used as a gasifying agents for polyethylene gasification. The equivalence ratio (ER) is varied from 0.1 to 1. It should be noted that the ER for polyethylene begins at 0.1, as at ER equal to zero, there is insufficient heat input to maintain the thermochemical reactions in the gasifier.

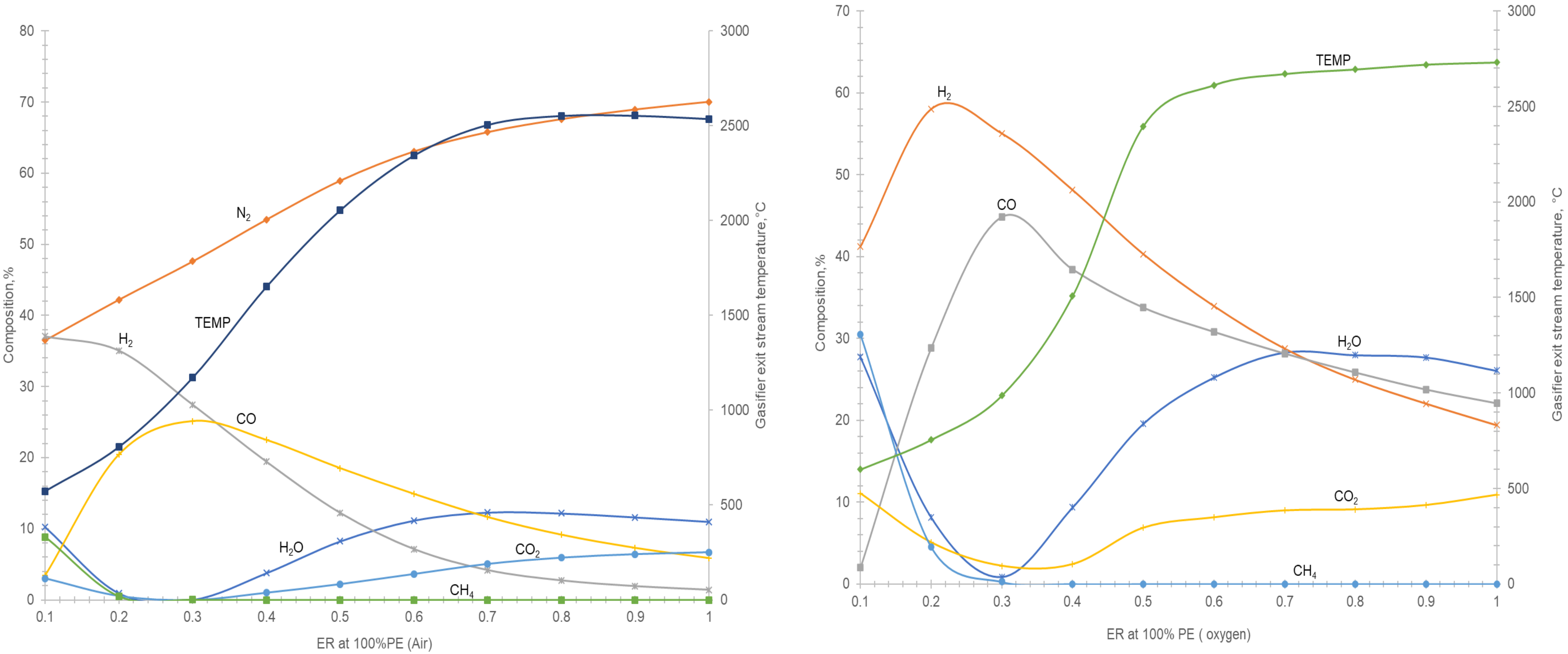
Figure 4.2.1 (a) and (b) shows that when ER increases from 0.1 to 1 the temperature in the gasifier also increased. It is noticed that between the range of ER from 0.1 to 0.3, the temperature rises steadily. However, from ER equal to 0.3 to 0.7, the temperature increased sharply, due to the enhancement of the oxidation reactions such as (R5) to (R8) which are exothermic. This trend is observed from both air and oxygen. Between ER values of 0.7 to 1, the curve appears to be flat meaning that the temperature is approximately constant, the oxidation reactions i.e. (R5) to (R8) have taken place at this ER range.

Similar findings were observed in a study conducted by Xiao et al. (2007) that shows that as the equivalence ratio increases, the temperature in the gasifier increased. Xiao et al. (2007) conducted laboratory scale experiments for the gasification of mixed plastics in a fluidized bed gasifier using air as a gasifying agent.The equivalence ratio was increased from 0.20 to 0.45, which resulted in an increase in the temperature in the gasifier from around 720°C to 950°C.

While in this study when the equivalence ratio is varied from 0.20 – 0.45 , the temperature in the gasifier increased from 800°C - 1800°C.The increase of the temperature,as the equivalence ratio increases is due to the exothermic reactions such as (R5) to (R8) which increases the heat in the gasifier, resulting in an increased temperature. Therefore, the difference between the two studies is the temperature rise, which can be caused by the difference in reactor type used in each study. In this study, equilibrium modelling is applied, while in the study conducted by Xiao et al. (2007) a fluidised bed reactor is used, which may limit the temperature increase.In both studies, the temperature of the gasifier is a function of the equivalence ratio, and it can be observed that ER has a strong influence on the temperature when air was used as a gasifying agent for mixed plastics.

Figure 4.2.1 (a) shows that when air is used as a gasifying agent, an increase in ER from 0.1 to 1, results in a decrease in the H_2.The H_2 composition is higher at low ER values below 0.3. The highest H_2 composition of 37.07% is achieved at ER equals to 0.1. It is observed that when the ER increased the CO composition increased gradually and then reached a peak value of 25.14% at ER equals to 0.3 before decreasing with increasing ER.

Figure 4.2.1 (b) shows that as ER increases the H_2 composition increases and reached a maximum value of 58.02% at ER equals to 0.24, and thereafter decreases with an increasing ER. The CO composition increases with an increasing ER values and reached a peak value of 45.0% at ER equals to 0.31, and as the ER increases, the CO decreased. Figure 4.2.1 (b) depicts that when oxygen is used as a gasifying agent, higher H_2 and CO compositions are obtained as compared to air. This is because air is diluted with nitrogen, which tends to lower the H_2 and CO composition in the product gas. However, the diasadvantage of using oxygen is that it would require a costly air separation unit. It is also, deduced that high H_2 and CO composition are favoured at low ER and temperatures regardless of the type of the gasifying agent used.



(a)

(b)

Figure 4.2.1. Effect of equivalence ratio (ER) on the product gas composition when (a) air and (b) oxygen are used as gasifying agents during the polyethylene gasification.

The high H_2 and CO composition from both Figure 4.2.1 (a) where air is used as a gasifying agent and Figure 4.2.1 (b) where oxygen is used as a gasifying agent are ascribed to the partial oxidation reaction (R4) and methanation reaction (R13). However, as ER and temperature increases in the gasifier the oxidation reactions such as (R5) to (R8) are favoured and as a result, the available H_2 and CO composition are oxidized to form H_2O and CO_2. The H_2O and CO_2 composition increases with the increasing ER values.

Figure 4.2.1 (a) and (b) illustrates that at an ER equal to 0.1, the product components from depolymerization such H_2O and CO_2 are high. As the ER increases, these composition decreases at low ER between a range of 0.1 to 0.3 . The decrease of these components is attributed to chemical reactions such as the Boudouard reaction (R1), reverse methane CO_2 reforming reaction (R10) and reverse methanation reforming reaction (R11) and steam – reforming reaction (R12).

Arena et al. (2009) conducted an experimental study for polyethylene gasification, using a fluidized bed gasifier, and air as a gasifying agent. The effect of ER on the product gas composition was investigated. ER was varied from 0.15 to 0.36. The H_2 composition decreased from 33% to 31%. A similar trend is observed in this study as ER increased from 0.15 – 0.36, the H_2 content decreased from 36.0% to 22% respectively. The difference in the H_2 values between these two studies is the way in which the temperature in the gasifier is maintained. Arena et al. (2009) used an electrical furnace to heat up the gasifier and maintain the gasifier temperature at 900°C. However, in this study the temperature in the gasifier is controlled by the incoming air, at different flowrates through the variation of ER values.

From the study of Arena et al. (2009) it is observed that the CO composition, increased and reached a highest value of 23% at ER equals to 0.25 and thereafter decreased with increasing ER. Similarly,in this study, it was observed that the CO composition, increased with increasing ER, and reached a highest value of 25.14% at ER equal to 0.3, before decreasing as ER increased. Lastly, Arena et al. (2009) determined that as ER increased, the CH_4 composition decreased, thus the highest value was found to be 11% at ER equal to 0.2. In this study , the CH_4 composition decreased as ER increased, thus the highest composition was found to be 8.84% at ER equals to 0.1.

4.2.2. Effect of steam – to – polyethylene ratio (SPR) on the production gas.

Figure 4.2.2 shows the effect of the steam content as a gasifying agent on the product gas composition for polyethylene gasification. The SPR is varied from 0.5 to 5 and ER is fixed at 0.2 and oxygen is used as a gasifying agent.The value of ER equal to 0.2 is chosen based of the high H_2 content attained as shown in Figure 4.2.1 (b). Futhermore, when ER is set at 0.2, heat is provided to the gasifier to enhance the endothermic reactions as the addition of steam only decreases the gasifier temperature, which limits the the endothermic reactions.The aim of this section is to observed at which operating parameters a high H_2 and CO composition can be attained.

It is observed from Figure 4.2.2 that as SPR increases, the temperature in the gasifier decreases. Figure 4.2.2. depicts that as SPR increases, the H_2 and CO_2 composition increases while CO and CH_4 composition decreases. The CH_4 composition drops because of the steam – reforming reaction (R12) which is favoured at low SPR values. The CO composition decreases as steam is added to the gasifier due to the influence of the water gas shift reaction (R9). The high H_2 and CO_2 composition is also attributed to the water gas shift reaction (R9) and water gas reaction (steam reaction) R2, which are favoured when steam is used as gasifying agent. The addition of steam caused the H_2 composition to increase and reach a maximum value of 40.6% at SPR equals to 3.5. The CO_2 composition reached a maximum of 16% at SPR equals to 1.6.

When the effect of steam as a gasifying agent (Figure 4.2.1) is compared with air and oxygen as a gasifying agent (Figure 4.2.2), it is observed that oxygen provides a higher H_2 and CO composition in the product stream than that produced from either steam or air. Steam provides a higher H_2 composition as compared to air but a lower CO composition than that produced from air.

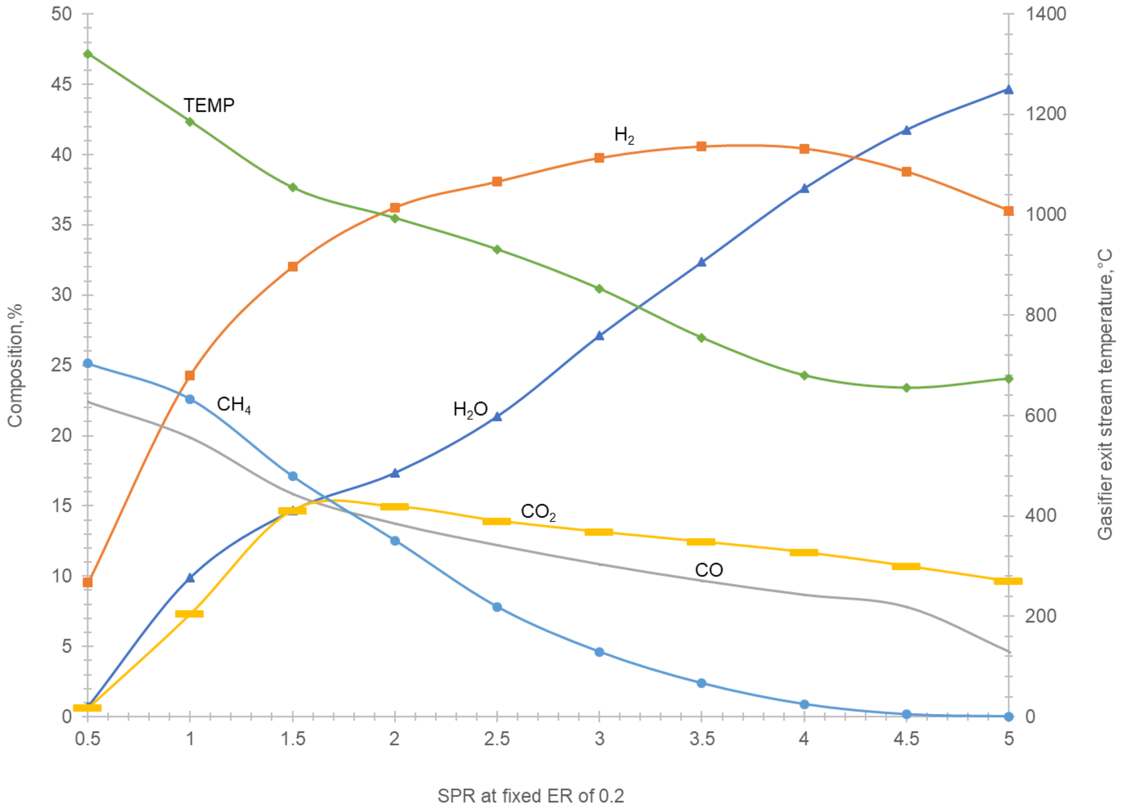


Figure 4.2.2. Effect of SPR on the product gas composition from polyethylene gasification at a fixed ER of 0.2 (oxygen as gasifying agent).

A similar trend of the product gas composition is reported in a study conducted by Erkiaga et al. (2013). An experimental study of the gasification of the high density polyethylene using the conical spouted bed reactor was conducted. The SPR was varied from 0 to 2, and ER values was not set, instead air was introduced to the gasifier at constant flowrate of 20L/min and the gasifier was operated at constant temperature of 900°C.

It was observed that the H_2 composition increased from 29 vol% to 62 vol%, and CO_2 increased slightly from approximately 2% to 5%. The CO and CH_4 compositions decreased from approximately from 29 vol% to 27 vol% and from 29 vol% to 17 vol% respectively as SPR increased. The values attained from Erkiaga et al. (2013) are higher than that attained in this study. This difference can be attributed to the way in which the gasifier temperature is maintained. For instance, in the study conducted by Erkiaga et al. (2013) the gasifier was placed within a radiant oven to ensure that constant heat was supplied to it and the gasifier temperature was maintained at a constant value of 900°C. Whereas, in this study the gasifier temperature is dependent on the flowrate of the gasiying agent that is being introduced to the reactor. The ER is fixed at 0.2 to maintain heat in the gasifier while varying steam.

4.2.3. Effect of equivalence ratio (ER) and (SPR) using air- steam and oxygen steam mixture as gasifying agents.

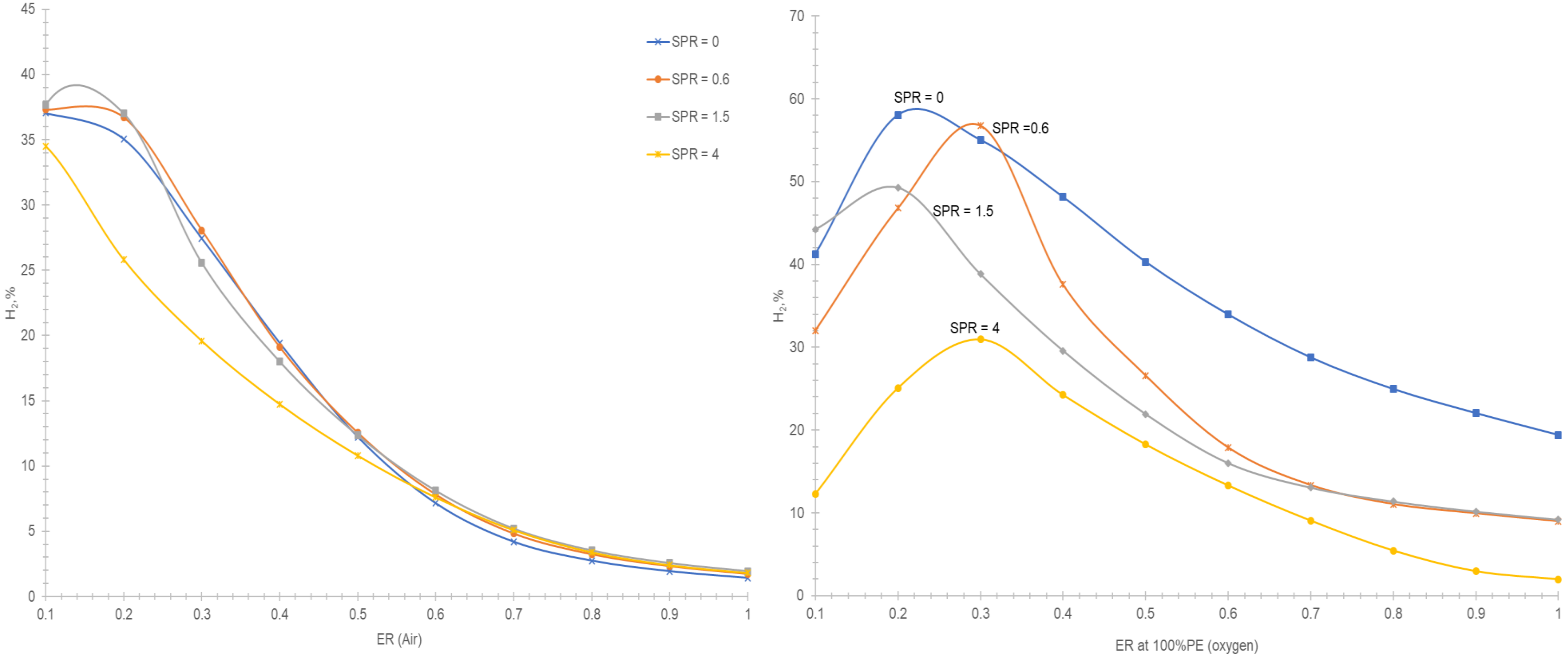
Figure 4.2.3 (a) representing an air- steam mixture as a gasifying agent and (b) representing an oxygen – steam mixture as a gasifying agent, shows the effect of using the equivalence ratio (ER) on the H_2 composition of the product gas when steam is added at different flow rates (SPR equal to 0.6 which represents low steam flow rate, SPR equal to 1.5 which represents medium steam flowrate and SPR equal to 4 which represents high steam flowrate). The equivalence ratio is varied from 0.1 to 1. The aim of this section is to determine the effect of mixing air and steam and oxygen and steam as gasifying agents on the product composition.

Figure 4.2.3 (a) shows that as the equivalence ratio (ER) increases, the H_2 composition decreases for all SPR values except for SPR equals to 1.5, which increases with an increasing ER and then reach a maximum value, and thereafter decreases as ER increases further. A similar trend is observed in Figure 4.2.3 (b) as the H_2 content for all SPR values, increase with increasing ER and reach a maximum value, and thereafter decreases as ER increases further. The decrease in H_2 as ER increases is because of the oxidation reactions such as (R5) to (R8) which are promoted at high ER values, and these reactions oxidize the H_2 into H_2O, resulting in a reduced H_2 content in the gasifier.

Figure 4.2.3 (a) and (b) shows that at low ER values below 0.4, the addition of steam at SPR range between 0 – 1.5 increases the H_2 content. This is because the steam reactions such as water gas shift reaction (R2), water gas shift reaction (R9) and steam – reforming reaction (R12) are promoted. Furthermore, the addition of the steam, causes the equilibrium of the steam reactions to shift in the forward direction resulting in an increased H_2 content, at the expense of char, CO and CH_4. (This observation corroborates with Figure 4.2.2).

Figure 4.2.3 (a) and (b) shows that at high ER values above 0.4 - 1, oxidation reactions such as (R5) to (R8) are promoted and the temperature increases which in turn influences the equilibrium to move towards the forward direction which leads to the oxidation of the H_2 to H_2O. that is the reason the high H_2 is observed only at SPR equal to 0.6. Figure 4.2.3 (a) and (b) indicates that at fixed SPR values the variation of ER influences the gasifier temperature and influences the direction at which the equilibrium would shift towards to and that determines the level of H_2 content in the product gas.

Figure 4.2.3 (a) and (b) shows that at SPR equals to 4, the H_2 is low due to the high steam flowrate i.e., limits the enhancement of the steam reactions which increases the H_2 content in the product gas.



(a)

(b)

Figure 4.2.3. Effect of equivalence ratio (ER) and different steam – to- polyethylene ratio (SPR) on the H_2 composition, when (a) air and (b) oxygen are used as gasifying agents.

Figure 4.2.3 (a) shows that when air - steam mixture is used a gasifying agent, a maximum H_2 composition of 39.0% was achieved at ER equals 0.14 and SPR equals to 1.5. Whereas in Figure 4.2.3 (b) the highest H_2 composition of 57.8% is achieved at SPR equals to 0.6 (low steam flowrate) and ER equals to 0.3. At higher SPR values such as SPR equal to 4, the H_2 composition in the product gas composition is low, which indicates that at SPR equal to 4 there is excess steam in the gasifier, which is observed in both cases i.e. Figure 4.2.3 (a) and (b).

Figure 4.2.3 (a) and (b) shows that the oxygen – steam mixture attains a higher H_2 composition than air- steam mixtures. It is also deduced from Figure 4.2.3 (b) and Figure 4.2.1 (b) that the use of oxygen only provides the highest H_2 composition when compared to oxygen - steam mixtures as a gasifying agent. The difference in the composition between the oxygen only and oxygen – steam mixture gasifying agent is only 0.22%. It is observed that the addition of steam when air is used as a gasifying agent (Figure 4.2.3 (a)) increased the H_2 composition of the product gas, since the H_2 composition has increased by 2% from the H_2 composition obtained when only air was used as a gasifying agent (Figure 4.2.1 (a)).

Al Amoodi et al. (2007) conducted a study using Aspen Plus simulation of polyethylene gasification to determine the effect of varying the equivalence ratio at different steam flowrates on the product gas composition, in particular, the H_2 composition in the product gas. The steam flowrates used were SPR corresponding to 0.6 (low steam flowrate) and 4 (high steam flowrate). Air was used as a gasifying agent.

The findings from the study conducted by Al Amoodi et al. (2007) and are similar to this study. The study of Al Amoodi et al. (2007), shows that when the equivalence ratio was varied from 0.1 to 0.3, using air as a gasifying agent and SPR equals to 0.6, a H_2 composition of around 36% at ER equals to 0.2 was achieved. However, when SPR was increased to 4, the H_2 composition decreased to be around 32% at ER equals to 0.17.

Similar observations as in this study, when the ER is varied from 0.1 to 0.3, air used as a gasifying agent and SPR equal to 0.6 the H_2 composition of 37.7% at ER equals to 0.2 and when the SPR is equal to 4, the H_2 composition has decreased to be at 29.0% at ER equals to 0.17. The values of the composition attained in both studies are similar due to the same operating conditions applied and feedstocks (polyethylene) used for the gasification of polyethylene.

4.2.4. Effect of the equivalence ratio (ER) and (CO_2/C) ratio on H_2 composition using air- carbon dioxide and oxygen – carbon dioxide mixture as gasifying agents.

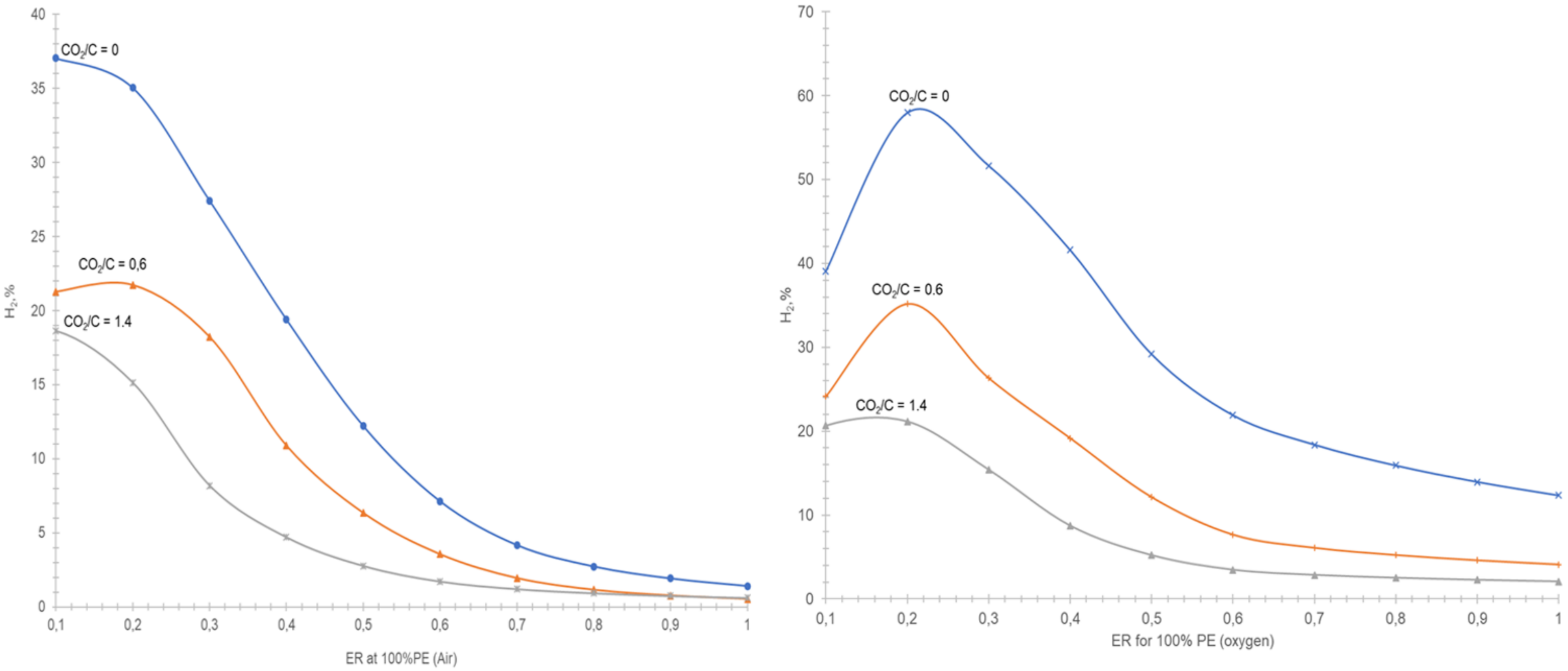
This section discusses the effect of equivalence ratio on the H_2 composition when air- carbon dioxide and oxygen – carbon dioxide mixtures are used as gasifying agents for polyethylene gasification. The main objective of this section is to determine if these mixtures provide a high H_2 composition as compared to the other types of the gasifying agents that have been previously discussed such as air, steam, oxygen and their relative mixtures. Secondly, the operating conditions that enables a high H_2 composition when air- carbon dioxide and oxygen – carbon dioxide mixtures are used, are determined. The equivalence ratio is varied from 0.1 to 1 and the carbon dioxide flowrates are varied between CO_2/C ratio equals to zero (no carbon dioxide flowrate), CO_2/C ratio equals to (low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (high carbon dioxide flowrate).

Figure 4.2.4 (a) shows that as the ER increases from 0.1 to 1, the H_2 compositions decreased, when air is used as a gasifying agent. However, in Figure 4.2.4 (b), which considers oxygen as a gasifying agent, as the ER increased, the H_2 increased and reached a peak value, before decreasing as ER further increased. The difference in the trend between the different gasifying agents used, may be attributed to the increase in nitrogen composition, which results in the H_2 composition to steeply decrease as ER increases for the air case.

Figure 4.2.4 (a) and (b) shows that as the flowrate of carbon dioxide increases, the H_2 composition decreases. As a result, it is observed that the highest H_2 composition of 22.0% is achieved at CO_2/C ratio equal to 0.6 at ER equal to 0.1 when air – carbon dioxide mixtures are used and a maximum H_2 composition of 35.0% is achieved at CO_2/C ratio equal to 0.6 and ER equal to 0.2 for oxygen-carbon dioxide mixtures. When Figure 4.2.4 (a) is compared with Figure 4.2.4 (b), it is noticed that the oxygen – carbon dioxide mixture provides a higher H_2 composition than air – carbon dioxide mixture. This is because air- carbon dioxide mixture is diluted with nitrogen.

Figure 4.2.4 (a) and Figure 4.2.4 (b) shows that the highest H_2 composition is favoured at low ER range below 0.3. The high H_2 composition in the product gas, is attributed to the reverse methanation reaction (R10) and methanation reaction (R13). While, the reduction of the H_2 composition at higher ER values and higher carbon dioxide flowrate such as CO_2/C ratio equal to 1.4, are ascribed to the oxidation reaction (R8), reverse water gas shift reaction (R9).

It is noticed from Figure 4.2.1 (b) and Figure 4.2.4 (b) that amongst the different types of gasifying agent the use of oxygen only as gasifying agent provides the highest H_2 composition as compared to when oxygen combined with carbon dioxide. However, the oxygen – carbon dioxide mixtures provides a higher H_2 composition when compared to other gasifying agents such as air, air – steam, and steam. The values and the operating conditions for the maximum H_2 composition for different gasifying agents are shown in Table 4.2.1.



(a)

(b)

Figure 4.2.4. Effect of equivalence ratio (ER) and carbon dioxide (CO_2/C ratio) on the H_2 composition when (a) air and (b) oxygen are used as gasifying agents.

Table 4.2.1 shows the maximum values of the H_2 composition achieved when different gasifying agents such as oxygen, air, steam and their relative mixtures are used. It is observed that oxygen as a gasifying agent produce high H_2 composition, followed by oxygen – steam mixture, oxygen – carbon dioxide, then, air – steam mixture and air and lastly, air- carbon dioxide mixture.

Table 4.2.1. Recommended gasifying agents and operating conditions for the H_2 composition of the product gas.

Gasifying agent	**H_2 composition (%)**			
	Maximum value	**ER**	**SPR**	**CO_2/C Ratio**
Oxygen	58.02	0.24	-	-
Air	37.07	0.1	-	-
Steam	40.6	0.2	1.6	-
Air – steam mixture	39.0	0.14	1.5	-
Oxygen – steam mixture	57.8	0.3	0.6	-
Oxygen – carbon dioxide mixture	35.0	0.2	-	0.6
Air - carbon dioxide mixture	22.0	0.1	-	0.6

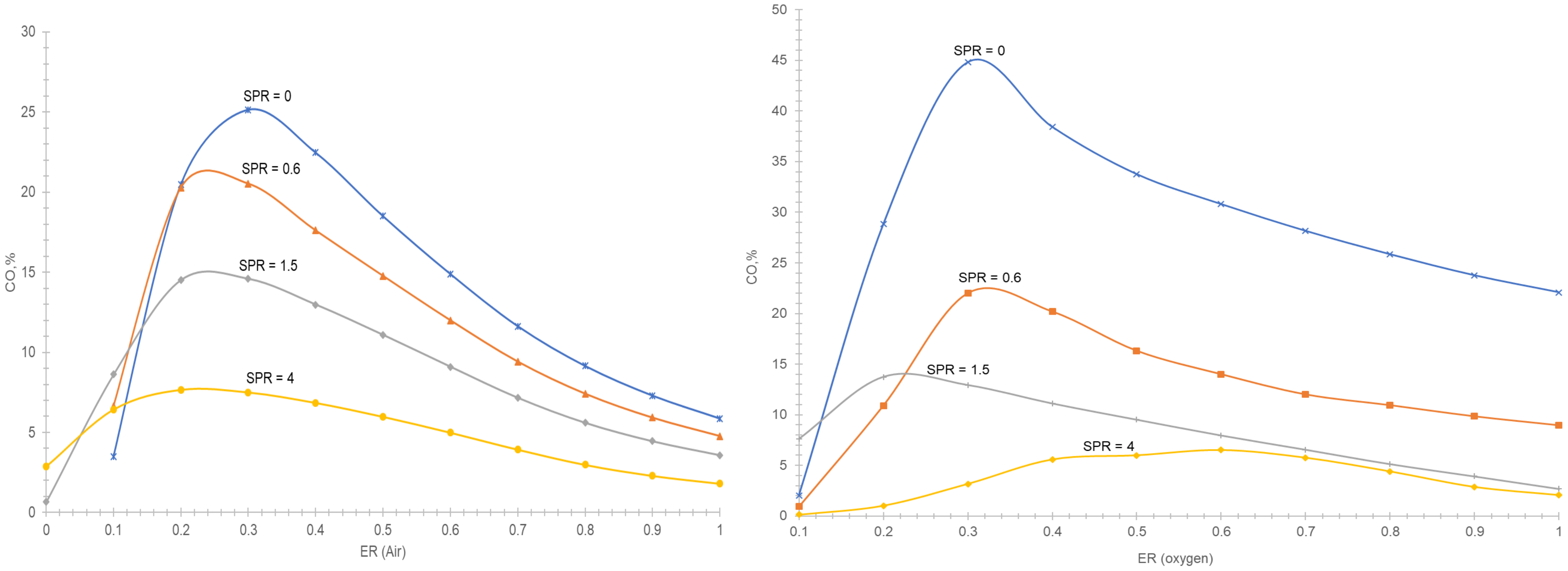
4.2.5. Effect of the equivalence ratio (ER) and SPR on the CO composition when air-steam and oxygen steam gasifying agents are used.

This section discusses the effect of equivalence ratio on the CO composition in the product gas composition, when different gasifying agents such as air- steam mixture, oxygen – steam mixture, air- carbon dioxide mixture and oxygen carbon dioxide mixture are used. The equivalence ratio is varied from 0 to 1. The SPR is varied from 0 to 4. The CO_2/C ratio is varied from 0 to 1.4. The aim of this section is to determine the operating parameters that provides a high CO composition in the syngas. Determining the CO composition is important as CO is one of the main components of syngas.

Figure 4.2.5 (a) and (b) shows the effect of equivalence ratio on the CO composition of the product gas when air – steam and oxygen – steam mixtures are used for polyethylene gasification respectively. The curves of the CO composition depict a similar behaviour for both air- steam and oxygen – steam mixtures, in that as ER increases, the CO composition increases, and reaches a maximum value, thereafter, decreases as ER continues to increase. Both Figure 4.2.5 (a) and (b) shows that the highest CO compositions are achieved at ER below 0.5. It is observed that the increase in SPR, decreases the CO composition of the product gas. This applies to both cases i.e. Figure 4.2.5 (a) and Figure 4.2.5 (b).

At low ER and SPR values, the high CO composition is attributed to chemical reactions such as the steam reaction (R2), Boudouard reaction (R1), reverse water – gas shift reaction (R9) and methanation reaction (R12) and (R13). At higher ER values, the chemical reactions such as the exothermic oxidation reactions such as (R5) to (R7) are promoted and oxidize the CO into CO_2 in the product gas.

Figure 4.2.5 (a) and (b) shows that oxygen – steam mixtures provides a higher CO composition as compared to that achieved when air- steam mixtures are used. Therefore, Figure 4.2.5 (a) shows that a maximum CO value of 21% at an ER equal to 0.22 at SPR equal to 0.6 is achieved when air- steam is used. Figure 4.2.5 (b) shows that a maximum CO of 22.5% at ER equals to 0.32 at SPR equal to 0.6 was obtained when oxygen – steam mixture was used. It can also be concluded that the higher the steam flowrate, the greater the reduction in the CO composition. The literature on the use of air - steam and oxygen – steam mixtures for polyethylene gasification is very scarce. As a result, no comparison with the literature was possible.



(a)

(b)

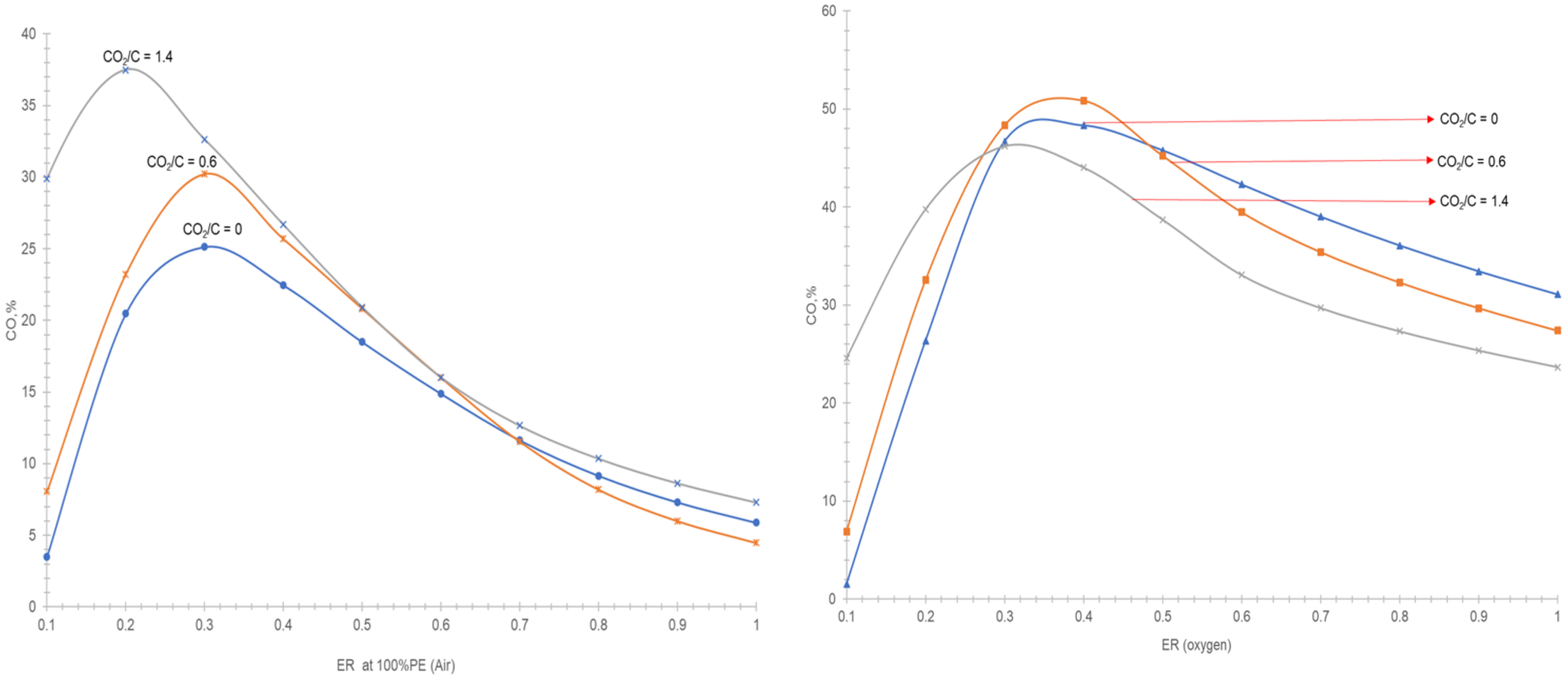
Figure 4.2.5. Effect of equivalence ratio (ER) and steam flowrate (SPR) on the CO composition, when (a) air and (b) oxygen are used as gasifying agent.

4.2.6. Effect of the equivalence ratio (ER) and CO_2/C on the CO composition when air-carbon dioxide mixture and oxygen-carbon dioxide mixtures are used.

This section discusses the effect of the equivalence ratio (ER), varied from 0 to 1, on the CO composition of the product gas when air (Figure 4.2.6 (a)) and oxygen (Figure 4.2.6 (b)), are used as gasifying agents. Carbon dioxide is added to the gasifier at different flowrates (CO_2/C ratio between 0, 0.2 and 1.4).

From Figure 4.2.6 (a) and (b), it is observed that the CO composition at different CO_2/C ratio follows a similar trend, in that, at low ER values below 0.5 the curves increase with increasing ER values and attain a maximum value, thereafter, decreases as ER increases. The decrease in CO at high ER is due to the exothermic oxidation reactions such as (R5) to (R7). Figure 4.2.6 (a) and (b) shows that the high CO compositions are favoured at low ER below 0.4.

Figure 4.2.6 (a) shows that the maximum CO composition of 37.5% is achieved at CO_2/C ratio equals to 1.4 and ER equals to 0.2, when air – carbon dioxide mixture is used as a gasifying agent. For an oxygen – carbon dioxide mixture, a maximum CO composition of 51% is obtained at ER equals to 0.36 and CO_2/C ratio equals to 0.6. Figure 4.2.6 (a) and (b) shows that a higher CO composition is produced when oxygen – carbon dioxide mixtures are used as the gasifying agent. The reason for the high CO composition can be due to the char- carbon dioxide conversion, through the reverse water gas reactions (R9), Boudouard reaction (R2) and reverse methanation reaction (R10).



(a)

(b)

Figure 4.2.6. Effect of equivalence ratio (ER) and different carbon dioxide – to- carbon ratio (CO_2/C) on H_2 composition, when (a) air – carbon dioxide and (b) oxygen – carbon dioxide mixtures are used as gasifying agents.

Table 4.2.2 shows the recommended operating conditions that can provide a high CO composition for the polyethylene gasification, when different types of the gasifying agents are used. Table 4.2.2 shows that the highest CO composition in the product gas can be achieved when oxygen – carbon dioxide mixture is used as a gasifying agent, followed by the oxygen, air – carbon dioxide mixture, oxygen – steam mixture, air and air – steam mixture. The high CO composition in the product gas can be achieved at ER values below 0.4, SPR values of 0.6 and CO_2/C ratios of 0.6.

Table 4.2.2 shows that the mixing of the gasifying agents, increases the amount of CO produced in the product gas, as compared to when single gasifying agents are used. It is observed from the Table 4.2.2 that in order to obtain a high CO content, SBR, ER and CO_2/ C ratio can be maintained at low values. Except for the case in which air is mixed with carbon dioxide, an increased amount of carbon dioxide is recommended in order to increases the production of the CO in the product gas.

Table 4.2.2. The recommended operating parameters to achieve a high composition of CO in the product syngas.

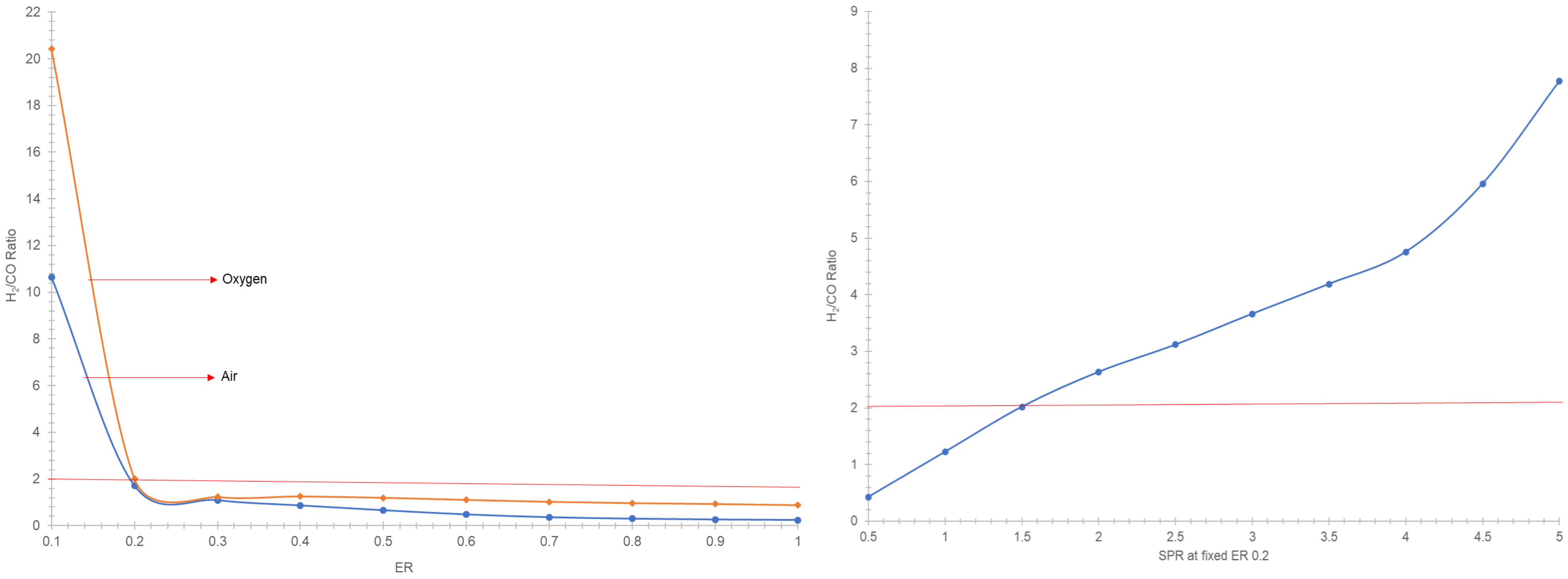
Gasifying agent	**CO composition (%)**			
	Maximum value	**ER**	**SPR**	**CO_2/C Ratio**
Oxygen	45.0	0.31	-	-
Air	25.1	0.3	-	-
Air – *s*team mixture	21.0	0.22	0.6	-
Oxygen – steam mixture	22.5	0.32	0.6	-
Oxygen – carbon dioxide mixture	51.0	0.36	-	0.6
Air - carbon dioxide mixture	37.5	0.2	-	1.4

4.2.7. Effect of the equivalence ratio (ER) and SPR on H_2/CO ratio of the syngas.

This section discusses the effect of the equivalence ratio (ER) and steam –to - polyethylene ratio (SPR) on the H_2/CO ratio of the syngas. The equivalence ratio (ER) is varied from 0 to 1. Various gasifying agents such as air, steam, oxygen, air- steam mixture, oxygen – steam mixture, air- carbon dioxide mixture and oxygen – carbon dioxide mixture are used during the polyethylene gasification. The aim of this section is to determine the operating conditions at which a H_2/CO ratio of 2 is obtained.

Figure 4.2.7 (a) shows the effect of equivalence ratio on the H_2/CO ratio of the syngas, when air and oxygen gasifying agents are used. Figure 4.2.7 (a) shows that as the ER increased from 0.1 to 1 the H_2/CO ratio of the syngas decreased. At low ER values below 0.3, the H_2/CO ratio of the syngas is high , since the H_2 composition is high and that of CO is low (Figure 4.2.1). The chemical reaction that are favoured at low ER values when air and oxygen are used is the methanation reaction (R13). At ER values greater than 0.3, the oxidation reactions i.e. (R5) to (R8) takes place and the available H_2 and CO are oxidized to form H_2O and CO_2, reducing the H_2/CO ratio. Figure 4.2.7 (a) depicts that the recommended H_2 /CO ratio of 2, can be achieved when air and oxygen are used as a gasifying agents, at an ER value equal to 0.2.

Figure 4.2.7 (b) shows the effect of using steam as a gasifying agent on the H_2/CO ratio of the syngas. The steam – to- polyethylene ratio (SPR) is varied from 0.5 to 5. ER is fixed at 0.2 so as to maintain the auto thermal conditions of the gasifier, since the addition of steam promotes endothermic reactions in the gasifer. Figure 4.2.7 (b) depicts that when the steam flow increases, the H_2/CO ratio of the syngas increased (Figure 4.2.2). This is due to the increase in the H_2 composition, which is attributed to the steam reactions such as the water gas shift reaction (R9) and other steam related reactions such as the reverse methanation reforming reactions (R11),(R14), and steam reforming of methane reaction (R12). From Figure 4.2.7(b) it is observed that the recommended H_2/CO ratio of the syngas of 2 is achieved at SPR equal to 1.5 and ER equal to 0.2.



(a)

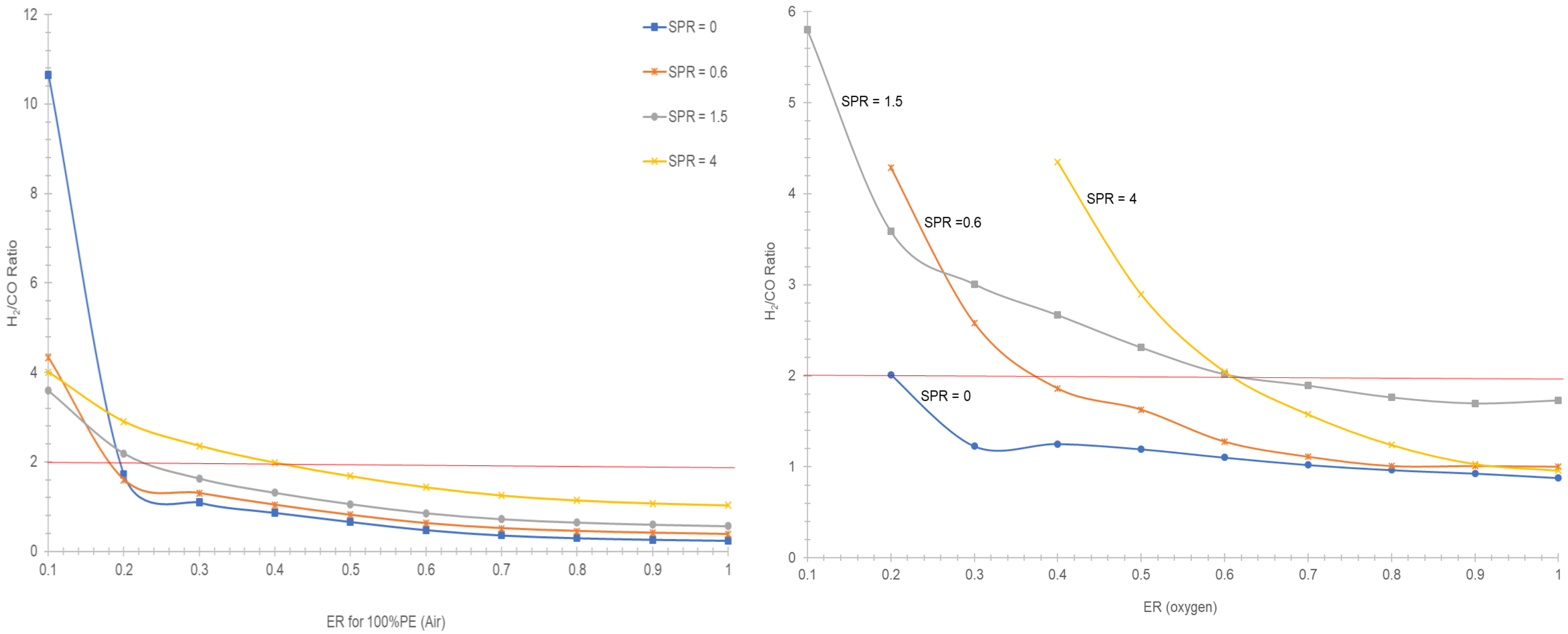
(b)

Figure 4.2.7. Effect of the equivalence ratio on the H_2/CO ratio of the syngas.when (a) air, oxygen and (b) steam are used as gasifying agents.

4.2.8. Effect of the equivalence ratio (ER) and SPR on the H_2/CO ratio of the syngas when air – steam mixtures and oxygen – steam mixtures are used as gasifying agents.

Figure 4.2.8 (a) and (b) shows the effect of varying the equivalence ratio from 0.1 to 1 on the H_2/CO ratio of the syngas, when the air- steam and oxygen – steam mixtures are used as gasifying agents respectively. The aim of this section is to determine the operating parameter at which the recommended H_2/CO ratio of 2 is achieved when air- steam mixture and oxygen – steam mixtures are used as gasifying agents.

Figure 4.2.8 (a) and (b) shows that as ER increases, the H_2/CO ratio of the syngas decreases, due to the exothermic oxidation reactions such as (R5) to (R8) which are favoured at high ER. As SPR increases, the H_2/CO ratio increases. Figure 4.2.8 (a) and (b) show that the recommended H_2/CO ratios of 2 are achieved at ER values below 0.5 when air- steam mixture is used as a gasifying agent, while the recommended H_2/CO ratios of 2 are achieved at ER below 0.7 when oxygen – steam mixture is used. The responsible chemical reactions for high H_2/CO ratios when steam is added to the gasifier, and air and oxygen are used as gasifying agents, are the water gas shift reaction (R9), methanation reaction (R13), steam reaction (R2), reverse methanation reforming reactions (R11), (R14) and steam reforming of methanation reaction (R12). These reactions promotes an increase in the H_2 composition in the product gas, which increases the H_2/CO ratio of the syngas.



(a)

(b)

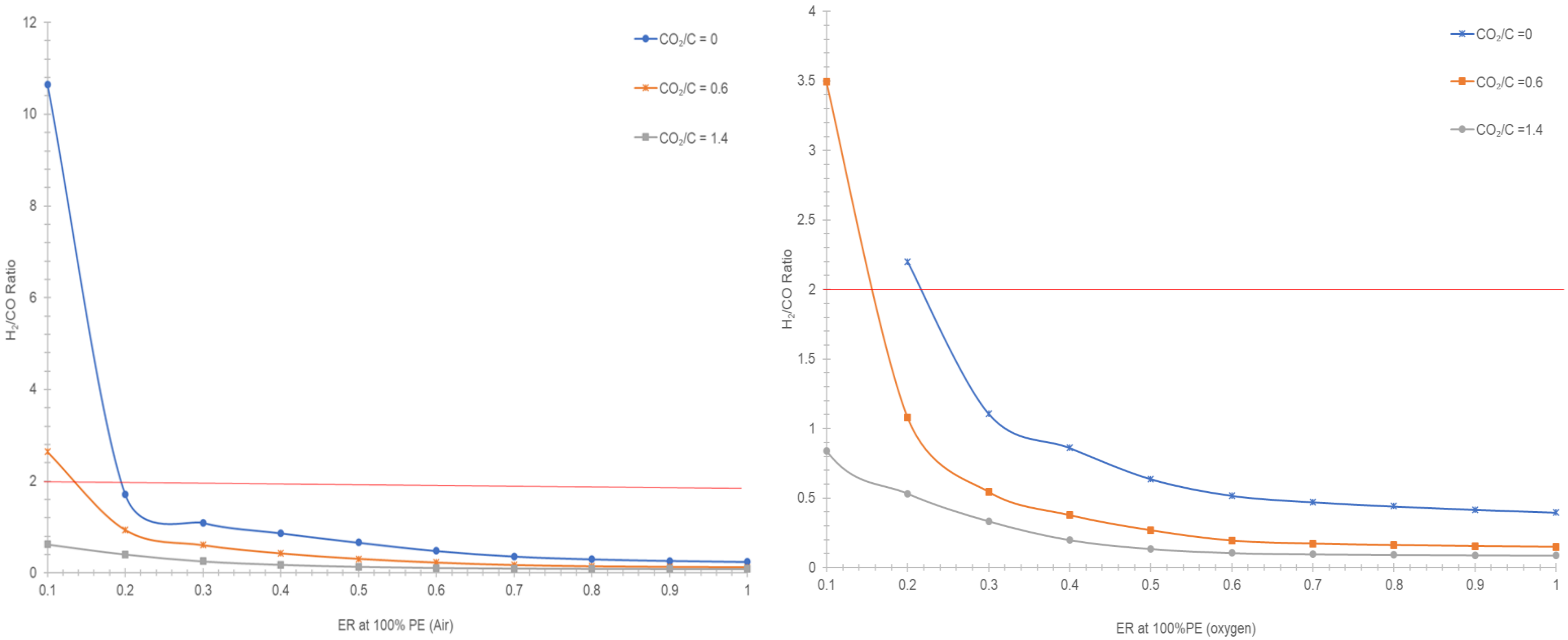
Figure 4.2.8. Effect of using equivalence ratio on the H_2/CO ratio of the syngas when (a) air – steam mixture and (b) oxygen – steam mixture gasifying agent are used .

4.2.9. Effect of equivalence ratio (ER) and CO_2/C ratio on the H_2/CO ratio of the syngas when air- carbon dioxide mixtures and oxygen – carbon dioxide mixtures are used as gasifying agents.

Figure 4.2.9 show the effect of equivalence ratio on the H_2/CO ratio when air- carbon dioxide mixtures and oxygen – carbon dioxide mixtures are used as gasifying agents for the gasifcation of the polyethylene. The equivalence ratio is varied from 0 to 1. The CO_2/C ratio is varied from 0 to 1.4. Figure 4.2.9 (a) and (b) shows that when the ER increases from 0 to 1, the H_2/CO ratio of the syngas decreases. Thus, this ratio is only high at low ER values since at low ER values the production of H_2 and CO is high. However, as ER increases the oxidation reactions such as (R5) to (R8) oxidizes the H_2 and CO in the product gas to form H_2O and CO_2.

It is observed from Figure 4.2.9 (a) and (b) that for both air – carbon dioxide and oxygen – carbon dioxide mixtures used as gasifying agents, the addition of the carbon dioxide reduces the H_2/CO ratio of the syngas. This is attributed to the Boudoard reaction (R1) and the reverse water gas shift reaction (R9),which increases the CO composition, and when the CO is higher than the H_2 composition the H_2/CO ratio tends to decrease.

Figure 4.2.9 (a) indicates that the recommended H_2/CO ratio equal to 2, is achieved at ER range between 0.14 – 0.21 and at CO_2/C ratio equal to 0 – 0.6 when air – carbon dioxide mixture and in Figure 4.2.9 (b) when oxygen – carbon dioxide mixture as gasifying agents mixtures are used it shows that the recommended H_2/CO ratio of 2 can be achieved from ER range of 0.18 – 0.24 and CO_2/C ratios of 0 – 0.6. This indicates that gasifying agents improves the quality of syngas when mixed. However, it is noted that when air - carbon dioxide and oxygen – carbon dioxide mixtures are used as gasifying agent, the recommended H_2/CO ratio is not achieved at high carbon dioxide flowrate such as CO_2/C ratio equal to 1.4. Unlike in Figure 4.2.8 (a) and (b) of air- steam and oxygen - steam mixtures as gasifying agent where from all the different steam flowrates the recommended H_2/CO ratio of 2 was attained. The results in Figure 4.2.9 indicates that high flow rate of carbon dioxide contributes negatively towards the quality of the syngas



(a)

(b)

Figure 4.2.9. Effect of equivalence ratio on H_2/CO ratio of the syngas when (a) air- carbon dioxide mixtures and (b) oxygen – carbon dioxide mixtures are used as as gasifying agents.

Table 4.2.3 shows the different gasifying agents and operating conditions, at which the recommended H_2/CO ratio can be attained. Table 4.2.3 shows that the recommended H_2/CO ratio can be obtained at low ER values below 0.7, for all types of gasifying agents, and in the case of SPR, the H_2/CO can be attained from low to high flowrate, depending on the type of the gasifying agent used. It is observed that in the case of carbon dioxide content, the ratio of H_2/CO can be achieved at flowrate. Table 4.2.3 shows that for the polyethylene gasification all the gasifying agents (single and mixed) can be used to produce a good quality syngas.

Table 4.2.3. Recommended gasifying agents and operating conditions for a H_2/CO ratio of 2.

Gasifying agent	**H_2/CO Ratio of 2 for the syngas**		
	ER	SPR	CO_2/C Ratio
Air	0.2	-	-
Oxygen	0.2	-	-
Steam	0.2	1.5	-
Air – steam mixture	0.18 0.24 0.4	0.6 1.5 4	- - -
Oxygen – steam mixture	0.38 0.62 0.62	0.6 1.5 4	- - -
Air - carbon dioxide mixture	0.14	-	0.6
Oxygen – carbon dioxide mixture	0.16	-	0.6

4.2.10. Effect of the equivalence ratio (ER) and SPR when air, oxygen and steam are used as a gasifying agents on the lower heating value (LHV) of the syngas.

This section discusses the effect of the equivalence ratio, varied from 0.1 to 1, on the Lower Heating Value (LHV) of the syngas for different types of the gasifying agents such as air, oxygen, steam and their relative mixtures. The aim of this section is to determine which gasifying agent and the operating conditions provides the highest heating value of the syngas produced.

Figure 4.2.10 (a) shows the effect of equivalence ratio on the Lower Heating Value (LHV) of the syngas, when air and oxygen are used as gasifying agents. It is observed that both curves of the lower heating value of the syngas follow a similar trend. As the ER increased from 0.1 to 1, the curves of the Lower Heating Value (LHV) decreased. The decrease in the lower heating value of the syngas can be attributed to the increase in the equivalence ratio, which the favours the oxidation reactions (R5) to (R8). As the equivalence ratio is increased the available H_2, CO and CH_4 compositions are oxidized to form CO_2 and H_2O.

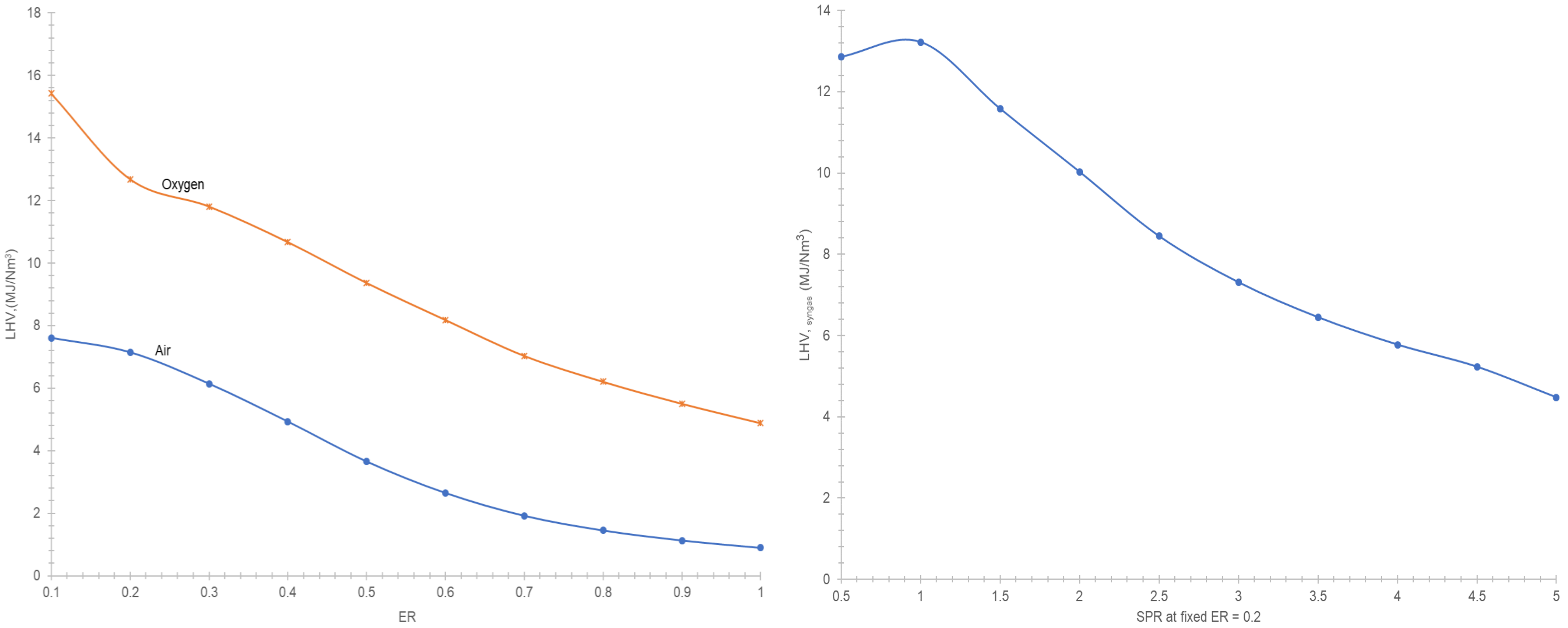
Figure 4.2.10 (a) depicts that oxygen provides a higher lower heating value of the syngas as compared to air. This is because air is diluted by the nitrogen content. The highest Lower Heating Value (LHV) of the oxygen is found to be 15.2 MJ/Nm^3 at ER equals to 0.1 and that of air is found to be 7.60 MJ/Nm^3 at ER equals to 0.1. It is apparent from the 7.82 MJ/Nm^3 difference between the lower heating values, that oxygen is the more suitable gasifying agent.

Du et al. (2014) conducted a study for the simulation of polyethylene gasification in a conical spouted gasifier. Aspen Plus software was used for the simulation of the polyethylene gasification. The gasifier temperature was kept constant at 700°C and air was used as a gasifying agent. The effect of varying the equivalence ratio from 0.2 – 0.6 on the Lower Heating Value (LHV) of the syngas was investigated.

Du et al. (2014) determined that an increase in the equivalence ratio from 0.2 – 0.6, lowered the lower heating value of the syngas from 13 MJ/Nm^3 to 3.3 MJ/Nm^3. A similar trend is observed in this study as an increase in ER from 0.2 – 0.6, decreases the lower heating value from 7.2 MJ/Nm^3 – 3 MJ/Nm^3. The difference in the values of the Lower Heating Values (LHV) attained can be attributed to the difference in the gasifier temperatures, which has a significant effect on the product gas composition. Du et al. (2014) has kept the gasifier at a constant

temperature of 700°C, whereas in this study the temperature in the gasifier is maintained by the flowrate of the incoming air.
Figure 4.2.10 (b) shows the effect of steam -to- polyethylene ratio (SPR) on the Lower Heating Value (LHV) of the syngas. The SPR is varied from 0.5 to 5. Figure 4.2.10 (b) illustrates that as the SPR increased, the lower heating value of the syngas decreased. The decrease in the lower heating value as SPR increases, is due to the excess steam increases the H_2O content in the syngas.

It is observed that at SPR equals to 1, the Lower Heating Value (LHV) of the syngas reached a maximum value of 13.2 MJ/Nm^3. This lower heating value of the syngas is attributed to the reactions such as the steam reaction (R2), water gas shift reaction (R9), reverse methanation reaction (R11) and, methanation reaction (R12). Figure 4.2.10 (a) and (b) depicts that amongst the three gasifying agents, oxygen provides the highest lower heating value, followed by steam and lastly air. It is also noted that the high calorific value of the syngas is favoured at low ER and SPR values.



(a)

(b)

Figure 4.2.10. Effect of the equivalence ratio on Lower Heating Value (LHV) of the syngas when (a) air, oxygen and (b) steam are used as gasifying agents.

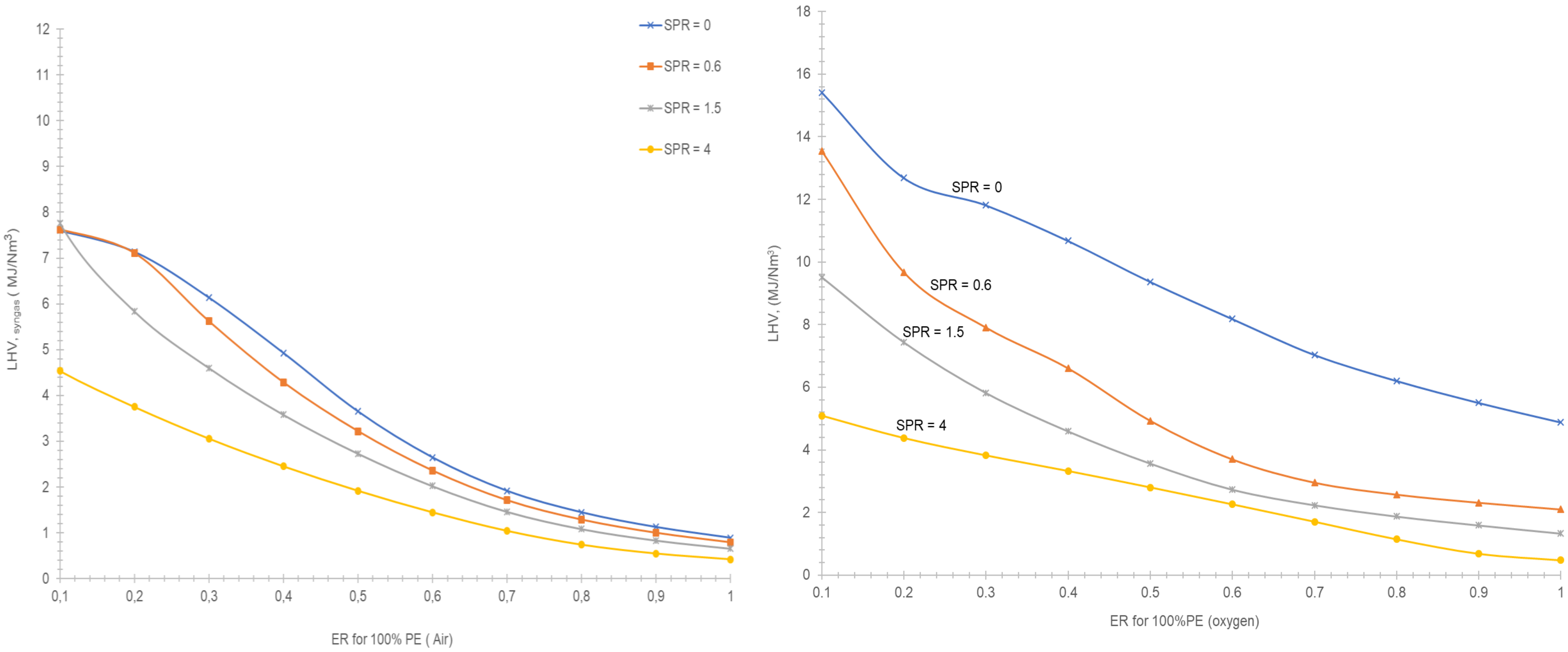
4.2.11. Effect of air- steam mixtures and oxygen – steam mixtures on the lower heating value (LHV) of the syngas.

Figure 4.2.11 (a) and (b) shows the effect of equivalence ratio (ER) on the Lower Heating Value (LHV) of the syngas, when air – steam and oxygen – steam mixtures are used as gasifying agents respectively. The equivalence ratio is varied from 0 to 1, and the SPR from 0 to 4. The aim of this section is to determine the most appropriate gasifying agent and operating parameters at which a high Lower Heating Value (LHV) of the syngas can be achieved**.**

Figure 4.2.11 (a) and (b) shows that as the ER increases, the lower heating value of the syngas decreases. At low ER values, the lower heating value is significantly high and as the equivalence ratio increases, the lower heating value decreases. The reason for this behaviour at low ER values, is due to the influence of the chemical reactions such as the steam reactions (R2), reverse methanation reaction (R11), steam methane reforming reactions (R12) and partial methanation reaction (R13) which are favoured at low ER values. From these reactions more of the combustible gases such as CO, H_2 and CH_4 are formed, thus leading to a higher heating value of the syngas. Figure 4.2.11 (a) and (b) indicates that when the equivalence ratio is varied a high lower heating value can be achieved at low ER values irrespective of the type of the gasifying agent used.

It is also observed from Figure 4.2.11 (a) and (b) that the addition of steam (SPR equals to 1.5 and 4) in the gasifier lowers the Lower Heating Value (LHV) of the syngas, due to the excess H_2O. Thus, the highest Lower Heating Value (LHV) is obtained at low steam flowrate (SPR equals to 0.6). Figure 4.2.11 (a) illustrates that when air- steam mixtures are used, the highest lower heating value of 7.62 MJ/Nm^3 is achieved at SPR equal to 0.6 and ER equal to 0.1. Figure 4.2.11(a) and (b) shows that the addition of the steam reduces the lower heating value of the syngas. In Figure 4.2.11(b), it is observed that a lower heating value of the syngas of 13.5 MJ/Nm^3 is achieved at ER equals to 0.1 and SPR equals to 0.6.

Figure 4.2.11 (a) and (b) depicts that an oxygen – steam mixture provides a higher lower heating value of the syngas as compared to air- steam mixtures. This is due to the nitrogen content that dilutes the syngas. Figure 4.2.11(b) illustrates that, even though the oxygen – steam mixtures provides higher lower heating values when compared to the air and air- steam mixtures, oxygen is the most appropriate gasifying agent for the polyethylene gasification as it provides the highest lower heating value of the syngas amongst the gasifying agents.



(a)

(b)

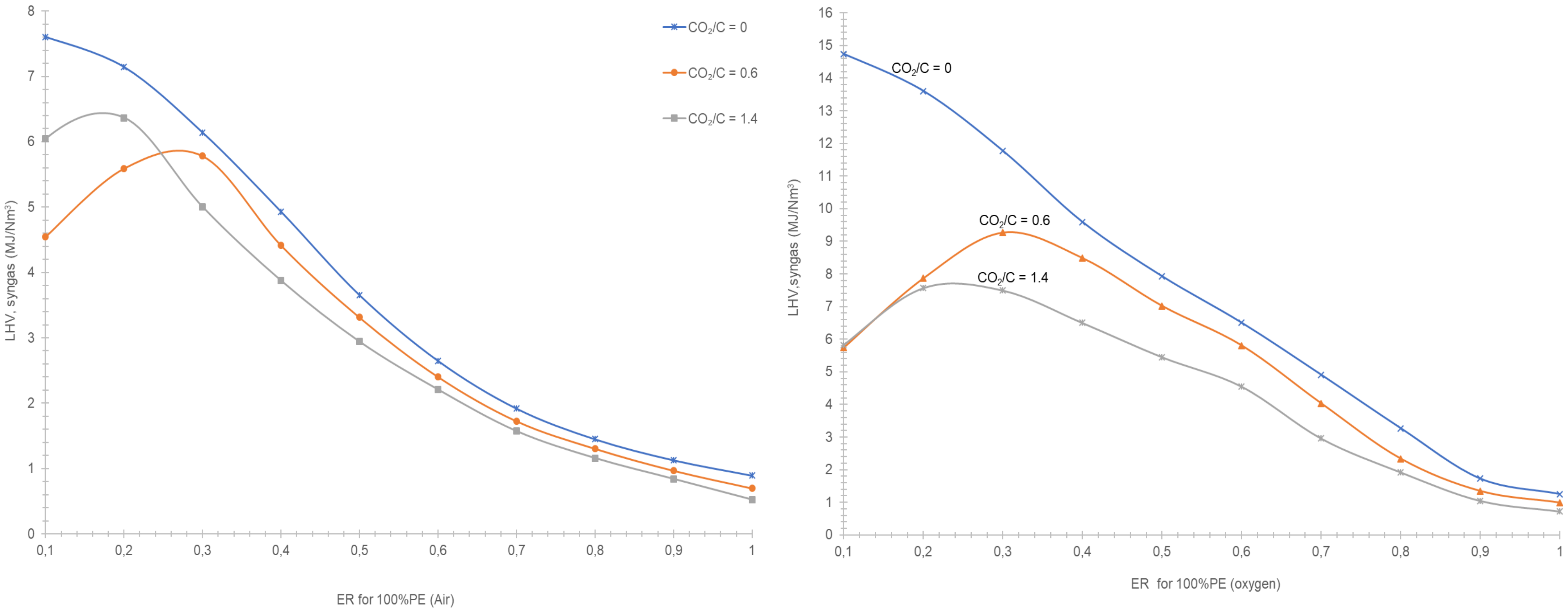
Figure 4.2.11. Effect of the equivalence ratio on Lower Heating Value (LHV) of the syngas when (a) air – steam mixtures and (b) oxygen – steam mixtures are used as gasifying agents.

4.2.12. Effect of using air- carbon dioxide mixtures and oxygen – carbon dioxide mixtures as gasifying agents on the lower heating value (LHV) of the syngas.

This section discusses the effect of equivalence ratio on the Lower Heating Value (LHV) of the syngas when air- carbon dioxide and oxygen – carbon dioxide mixtures are used as gasifying agents for polyethylene gasification. The carbon dioxide is added into the gasifier at low flowrate (CO_2/C ratio equals to 0.6) and high flowrate (CO_2/C ratio equals to 1.4). The aim of this section is to determine the influence of adding carbon dioxide on the Lower Heating Value (LHV) of the product gas.

Figure 4.2.12 (a) and (b) shows that for CO_2/C ratio equal to 0.6 and 1.4, as ER increases the lower heating value of the syngas increases and reach a maximum value, and thereafter, decreases with the increasing ER. The curves of CO_2/C ratio equal to 0, the Lower Heating Value (LHV) decreases as ER increases. Figure 4.2.12 (a) illustrates that the high Lower Heating Value (LHV) is favoured at low ER values between a range of 0.1 – 0.4. This is because at low ER values the concentrations of CO, H_2 and CH_4 are high, and the responsible chemical reactions for these components when carbon dioxide is added into the gasifier are the Boudouard reaction (R1), partial oxidation reaction (R4), reverse water gas shift reaction (R9), reverse methanation reaction (R10) and methanation reaction (R14). At higher ER values, the exothermic oxidation reactions such as (R5) to (R8) are promoted and as a result the present combustible gases such as CO, H_2 and CH_4 are oxidized to form CO_2 and H_2O.

Figure 4.2.12 (a) shows that the highest LHV of the syngas of 6.5 MJ/Nm^3 is achieved at ER equal to 0.16 and CO_2/C ratio equal to 1.4 when air – carbon dioxide mixture is used as a gasifying agent and Figure 4.2.12 (b) shows that the highest LHV of the syngas of 9.2 MJ/Nm^3 is achieved at ER equal to 0.32 and CO_2/C ratio equal 0.6, when oxygen – carbon dioxide mixture is used as a gasifying agent. The mixture of oxygen and carbon dioxide produces a higher lower heating value as compared to air – carbon dioxide mixtures. From Figure 4.2.12 (a) and (b) it is deduced that the higher Lower Heating Value (LHV) can be obtained at low ER below 0.4 and at low carbon dioxide flowrates through CO_2/C ratio equals to 0.2.



(a)

(b)

Figure 4.2.12. Effect of the equivalence ratio on Lower Heating Value (LHV) of the syngas, when (a) air- carbon dioxide mixtures and (b) oxygen – carbon dioxide mixtures are used as gasifying agents for polyethylene gasification.

Table 4.2.4 shows the different gasifying agents and operating conditions, at which the high lower heating value of the syngas can be achieved .Table 4.2.4 shows that the highest Lower Heating Value (LHV) is obtained when oxygen is used as agsifying agent, followed by the oxygen – steam mixture as gasifying agent. Table 4.2.4 depicts that the highest Lower Heating Values (LHV) of the syngas, when different gasifying agents are used, are achieved at ER values between 0.1 – 0.32 , SPR value of 0.6 equal to 1 and CO_2/C ratio equal to 0.6.

Table 4.2.4. The recommended operating conditions for determination of the high Lower Heating Values (LHV) of the syngas during the polyethylene gasification.

Gasifying agent	**Lower heating value (LHV) of the syngas.**			
	Highest values obtained (MJ/Nm^3)	ER	SPR	CO_2/C Ratio
Air	7.6	0.1	-	-
Oxygen	15.4	0.1	-	-
Steam	13.2	0.2	0.9	-
Air – steam mixture	7.62	0.1	0.6	-
Oxygen – steam mixture	13.5	0.1	0.6	-
Air - carbon dioxide mixture	6.5	0.16	-	1.4
Oxygen – carbon dioxide mixture	9.2	0.32	-	0.6

4.3. Introduction

This section discusses the effect of the co- gasification of biomass and polyethylene on the product gas composition, in particular, the H_2 and CO composition, H_2/CO ratio of the syngas and Lower Heating Value (LHV) of the syngas. The co- gasification of biomass and polyethylene at various blend ratios such as (0% PE + 100% biomass), (25% PE + 75% biomass), (50%PE + 50% biomass), (75% PE + 25% biomass) and (100% PE + 0% biomass) are considered. The effect of using different gasifying agents such as oxygen, and oxygen-steam and oxygen – carbon dioxide on the product gas composition, H_2/CO ratio and LHV of the syngas, are also discussed in this section.

The effect of varying the different operating parameters such as the equivalence ratio (ER), steam – to – fuel ratio (SFR) and carbon dioxide – to – carbon ratio (CO_2/C) is evaluated in this section. The aim of this section is to determine the effect of the co- gasification of biomass and polyethylene, in terms of enhancing the synergistic effect between biomass and polyethylene on various blends with the objective of improving the yield of the product gas, the energy content of the product gas and the quality of the syngas. The operating parameters used are the equivalence ratio (ER), SFR equals to 0.6 (indicates low steam flowrates), SFR equals to 1.5 (indicates high steam flow rate), CO_2/C ratio equals to 0.6 (represents low flowrate of the carbon dioxide) and CO_2/C ratio equals to 1.4 (represents a higher carbon dioxide flowrate).

This section discusses oxygen and its mixtures as gasifying agents only, since it has been observed from the biomass and polyethylene gasification sections that oxygen provides a better syngas output as compared to air.

Section three: Co- gasification of biomass and polyethylene

4.3.1. Effect of using oxygen only as a gasifying agent on the H_2 composition of the product gas.

Figure 4.3.1 shows the effect of the equivalence ratio on the H_2 composition of the product gas, when oxygen is used as a gasifying agent and the equivalence ratio is varied from 0.1 to 1. The effect of the different feedstock compositions such as (0% PE + 100% biomass), (25% PE + 75% biomass), (50% PE + 50% biomass), (75%PE + 25% biomass) and (100% PE + 0% biomass) is evaluated, with the aim to determine which feedstock provides a higher H_2 composition for the co- gasification of biomass and polyethylene and to determine if there is a synergy between biomass and polyethylene feedstock.

Figure 4.3.1 shows that as the ER increases, the H_2 composition decreases, except for the 100% PE+ 0% biomass feedstock, which begins by increasing with an increasing ER and reach a maximum value, and thereafter decreases as ER increases further. The highest H_2 composition for all the different feedstock materials, are favoured at ER below 0.3. The high H_2 composition at low ER values, when oxygen is used as a gasifying agent, is attributed to the chemical reactions such as the methanation reaction (R13). The decrease in the H_2 composition as ER increased is ascribed to the chemical reactions such as the oxidation reaction (R8). This shows that irrespective of the type of feedstock used for the gasification and co- gasification process, an increase in ER, reduces the H_2 composition.

Figure 4.3.1 shows that for the co- gasification of biomass and polyethylene and ER between 0.1 – 0.18, a high H_2 composition is produced from the blended feedstocks, for instance for a blend ratio of (25% PE + 75% biomass) a high H_2 value of 51.5% is attained at ER equal to 0.1, whereas for blend ratio of (50% PE + 50% biomass) a maximum H_2 of 54% is achieved at ER equals to 0.1 and for a blend ratio of (75% PE + 25% biomass) a high H_2 composition of 56.0% is attained at ER equal to 0.1 is attained. The high H_2 content attained from the mixed feedstocks at low ER values indicates that a synergistic effect between biomass and polyethylene is evident.

Amongst the feedstock blends, a blend ratio of (75% PE + 25% biomass), provides a highest H_2 composition. This might be attributed to the high volatile matter in the polyethylene feedstock which result in a rich H_2 content during the co- gasification process.

The co- gasification of biomass and polyethylene feedstocks provides a lower H_2 composition than from the 100% PE at ER values above 0.2. This indicates that when only oxygen is used, regardless of the feedstock composition used, the addition of oxygen as a gasifying agent at high flowrates promotes the oxidation reactions such as (R5) to (R8) and that leads to the decrease of H_2 in the product gas.

It is acknowledged that below ER equal to 0.1 (pyrolysis stage), there is a possibility that H_2 is higher than that achieved at ER equals to 0.1. However, the co- gasification of biomass and polyethylene is limited to ER equal to 0.1. Below ER equal to 0.1, the temperature in the gasifier is very low and gasification reactions are inhibited. This is because below ER equal to 0.1, the temperature in the gasifier is between 200 - 500°C. Furthermore, at this range, the pyrolysis process is dominant, due to the deficiency in oxygen and low temperatures (Rosha et al. 2021).

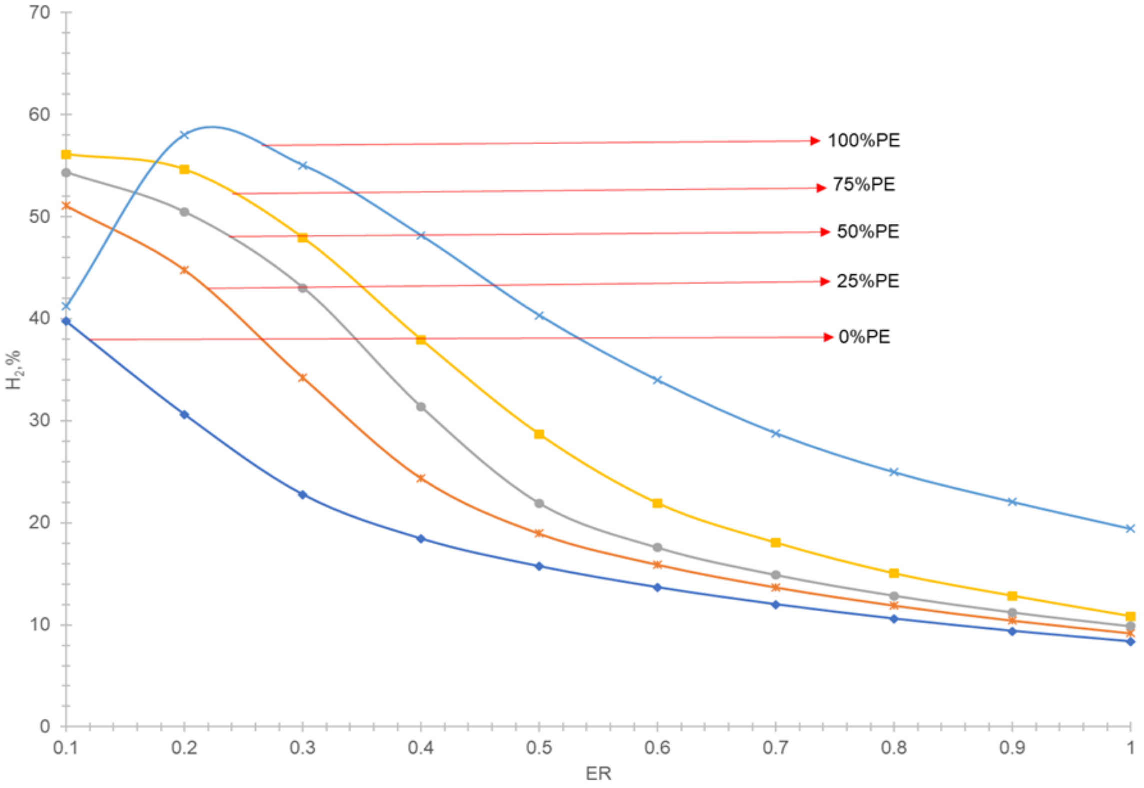


Figure 4.3.1. Effect of the equivalence ratio on the H_2 composition of the product gas, when oxygen is used as a gasifying agent.

The effect of using oxygen as a gasifying agent on the product composition is also observed in a study conducted by Tavares et al. (2018). The study was conducted in a fixed bed gasifier at a constant temperature of 800°C, using Aspen Plus simulation for the co- gasification of biomass and terephthalate (PET). Tevares et al. (2018) reported that when the equivalence ratio was increased from 0.1 – 1, for the blend ratio of (50% PET + 50% biomass) in the presence of the oxygen as a gasifying agent, the H_2 content in the product gas decreases from 30% (ER equals to 0.1) to 0% (ER equals to 1).

Similarly, as in this study for the blend ratio of (50% PE + 50% biomass) an increase in ER from 0.1 to 1, caused the H_2 to decrease from 54% (ER equals to 0.1) to 12% (ER equals to 1). The basis of the comparison is to provide supporting evidence from literature with the aim of illustrating the effect of increasing ER on the H_2 composition in the product gas. For instance, in Figure 4.3.2 indicates that irrespective of the different feedstock types used, gasifier settings etc. an increase in the equivalence ratio, decreases the H_2 composition in the product gas. The set of data displayed in Table 4.3.1 shows the different feedstock composition that was used in the study of Tavares et al. (2018).

The reason for this trend can be attributed to the oxidation reactions (R5) to (R8) which oxidizes the H_2 into H_2O as ER increases. There is a difference in the values of the H_2 content attained from both studies (Figure 4.3.1.1). This difference is attributed to the different feedstock composition of the polyethylene terephthalate (PET) and polyethylene (PE) and that of the biomass feedstocks since in this study pine sawdust was gasified whereas in the study conducted by Tavares et al. (2018) vine prunings were used as biomass (Table 4.3.1).

The ultimate analysis of the feedstocks used from both studies is displayed in Table 4.3.1, indicating the difference in the feedstock composition in particular the hydrogen content. It is indicated that polyethylene and pine sawdust contains a higher hydrogen content as compared to PET and vine prunings, which contributes to a higher H_2 content from this study as compared to the study conducted by Tavares et al. (2018) at the same ER range (Figure 4.3.2.

Table 4.3.1. Ultimate analysis for PET vs PE and vine prunings vs pine sawdust.

Elements	Plastic materials ultimate analysis		Biomass ultimate analysis	
	PET	PE	Vine prunings	Pine sawdust
Carbon (C)	63.01%	85.8%	41.2%	45.5%
Hydrogen (H)	4.27%	13.9%	2.2%	5.0%
Nitrogen (N)	0.04%	0.12%	5.5%	0.05%
Oxygen (O)	32.69%	0%	50.6%	47.1%

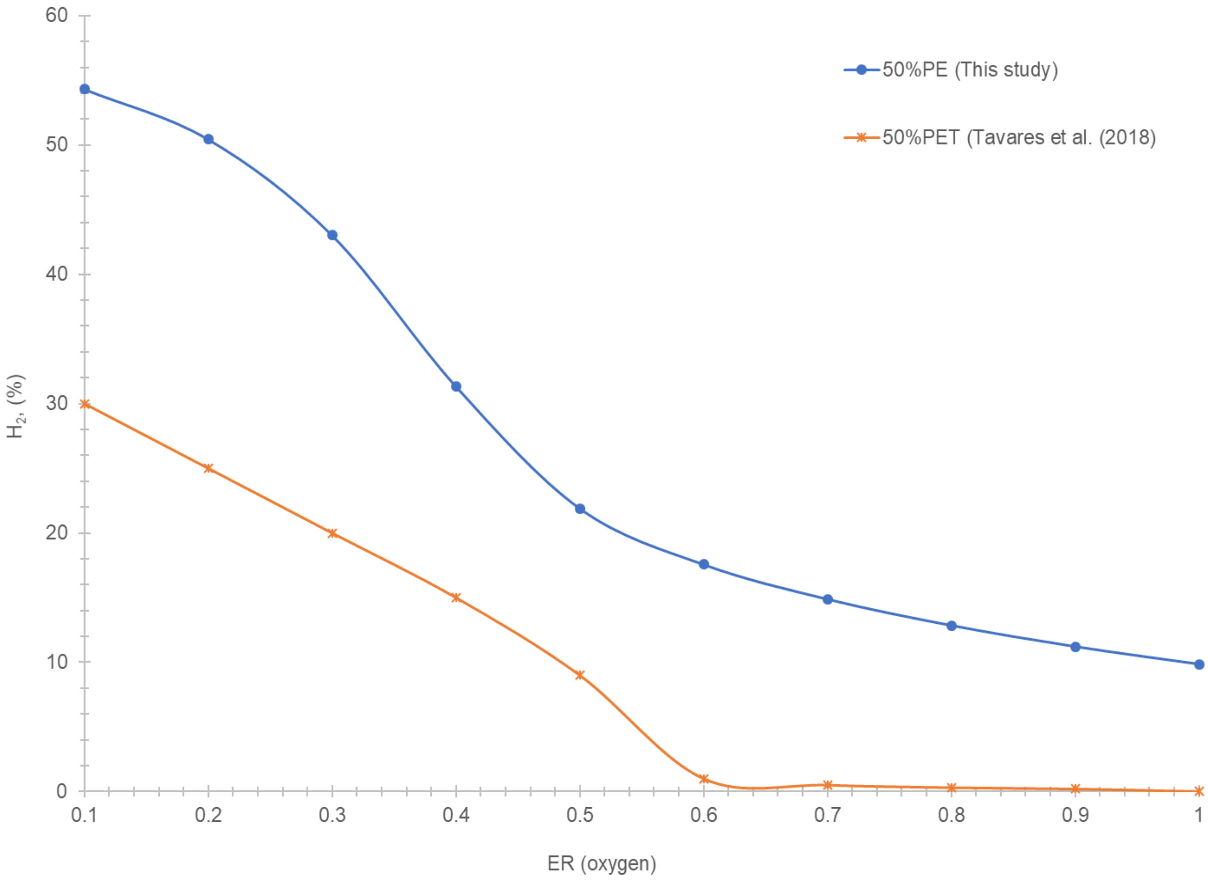


Figure 4.3.2. Effect of the equivalence ratio on the H_2 composition of the product gas composition, when oxygen is used as a gasifying agent (comparison of H_2 content attained between Tavares et al. (2018) and in this study).

4.3.2. Effect of oxygen as a gasifying agent on the CO composition of the product gas.

Figure 4.3.3 shows the effect of the co- gasification of biomass and polyethylene on the CO composition of the product gas when oxygen is used as a gasifying agent. The equivalence ratio is varied from 0.1 to 1. Figure 4.3.4 shows that as the ER increases, the CO composition initially increases as ER increases, reaches a peak value, and thereafter decreases at higher ER values for all the feedstocks except for the biomass feedstock.

Figure 4.3.3 shows that a higher CO composition is favoured at ER value below 0.4. The high CO composition at low ER values is attributed to chemical reactions such as the partial oxidation reaction (R4) and methanation reaction (R13), which consumes the available CH_4 to produce H_2 and CO in the product gas. At higher ER values the chemical reactions such as the oxidation reactions (R5) to (R7) are promoted and these reactions oxidize the CO into CO_2.

Figure 4.3.3 shows that as the percentage of the polyethylene is increased in the feedstock mixtures, the CO composition decreases. This is because polyethylene has no oxygen content. Thus, the highest CO composition of 56.4% is achieved at ER equals to 0.1 from the biomass feedstock. Amongst the blend ratios, (25% PE + 75% biomass) provides a maximum CO composition of 54.2% at ER equals to 0.22 and a high CO composition of 51.8% is attained at ER equal to 0.32 for both blend ratios of (50% PE + 50% biomass) and (75% PE + 25% biomass). Figure 4.3.4 shows that the co- gasification of biomass and polyethylene favours the production of the CO content between ER values of 0.2 – 0.6.

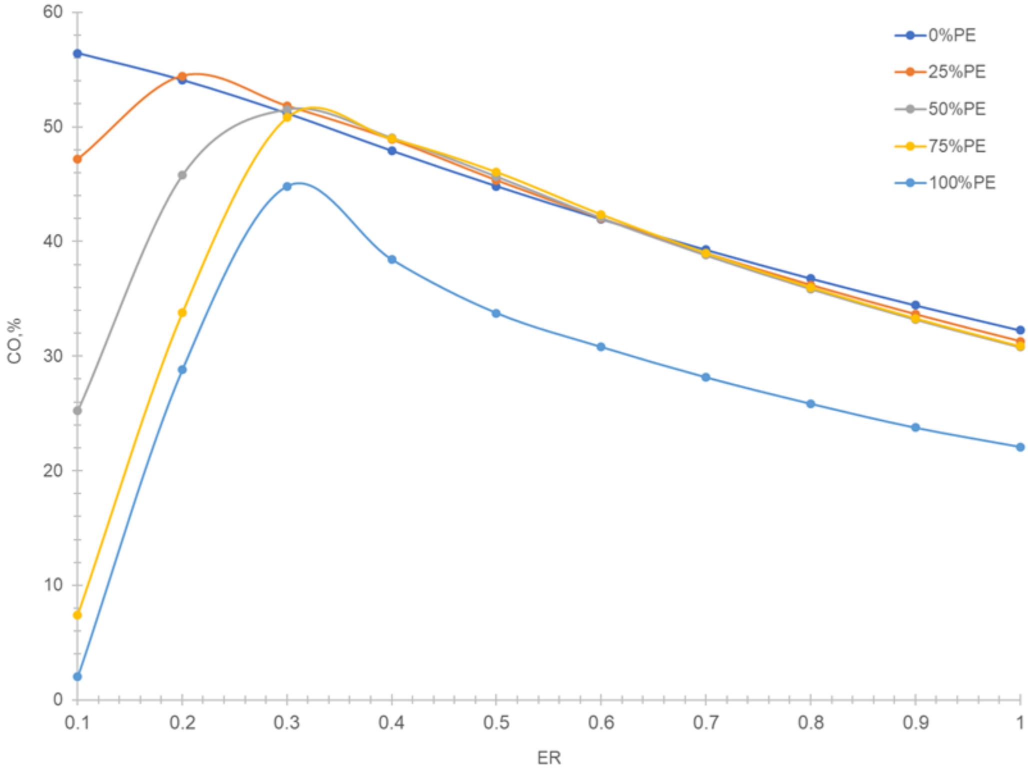


Figure 4.3.3. Effect of the equivalence ratio on the CO composition of the product gas composition, when oxygen is used as a gasifying agent.

Park et al. (2016) conducted study for the co- gasification of biomass (wood pellets) and high-density polyethylene (HDPE), in a two- stage gasification system. The thermal plasma gasifier temperature was kept constant at 800 K, and ER was varied from 0.38 – 0.85. The aim of the study was to determine the influence of varying the equivalence ratio on the CO composition of the product gas composition and the effect of increasing the percentage of the polyethylene in the feedstock mixture on the CO composition.

The blended feedstock of (70% HDPE + 30% biomass) was chosen from the study conducted by Park et al. (2016) to compare with the blend ratio of (75% PE + 25% biomass) used in this study, since their blend ratios are close to each other. Oxygen was used as a gasifying agent in both studies. Similar findings were observed from the study conducted by Park et al. (2016) and in this study. Park et al. (2016) reported that as ER increased from 0.38 to 0.85, the CO composition increased, then reached a peak with the maximum CO composition of around 42% at ER equals to 0.47, thereafter, decreased with an increasing ER.

A similar trend is observed in this study from a blend ratio of (75% PE + 25% biomass) when the ER increases from 0.35 to 0.85, the CO increases as well and reached a maximum value of 52% at ER equals to 0.34, and thereafter decreases as ER increases further.

The difference in the CO composition attained from both studies can be attributed to the different feedstocks that were co- gasified, the different feedstock compositions have a significant effect on the yield of the CO content in the product gas, since the feedstocks consists of differing carbon content. Furthermore, the way in which the gasifier temperature is maintained is different in both studies. For instance, Park et al. (2016) maintained the gasifier temperature constant at 800K, while in this study the gasifier temperature depends on the variation of the ER values. The manner in which temperature is controlled in the gasifier has an effect on the CO composition attained in the product gas from both studies.

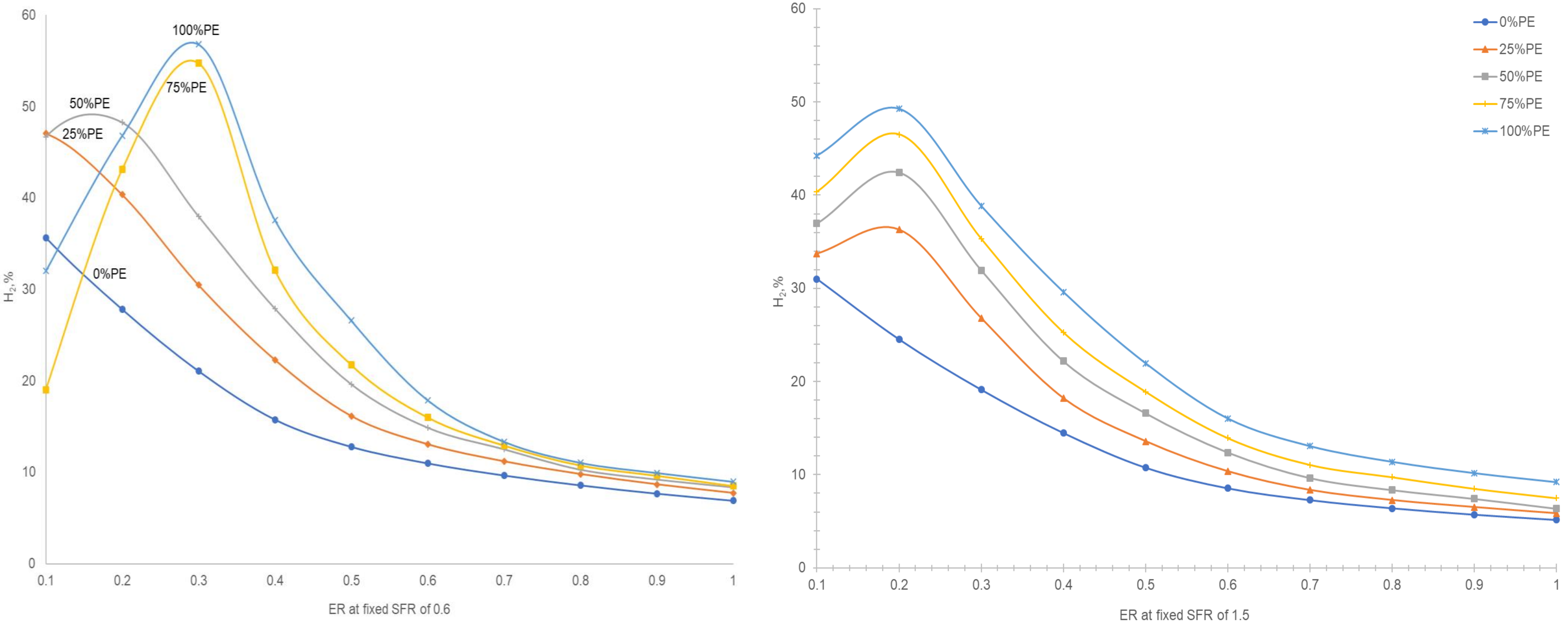
4.3.3. Effect of oxygen – steam mixture as a gasifying agent on the H_2 composition of the product gas.

Figure 4.3.4 (a) and (b) shows the effect of the equivalence ratio (ER) on the H_2 composition of the product gas, when a mixture of oxygen and steam are used as a gasifying agent. Two cases are considered. Figure 4.3.4 (a) represents a case when steam is added at low flowrate

(SFR equals to 0.6) and Figure 4.3.4 (b) represents the case with higher steam flowrate (SFR equals to 1.5).

Figure 4.3.4 (a) and (b) shows that the H_2 composition for the feedstock that contains a low percentage of PE in their blends such as the biomass feedstock and a blend ratio of (25% PE + 75% biomass), decreases as ER increases. While the H_2 composition of the feedstocks which contains a high percentage of polyethylene material in their blends such as (50% PE + 50% biomass), (75% PE + 25% biomass) and (100% PE + 0% biomass) follow a different trend, as the H_2 composition increases with increasing ER values, and then reach a maximum value and thereafter, decreases as ER increases further.

Figure 4.3.4 (a) shows that at SFR equals to 0.6 and low ER values below 0.2, the co-gasification of biomass and polyethylene produces a high the H_2 composition. As a result, high H_2 composition is attained from the blended fuels when compared to the individual feedstocks such as 100% biomass and 100% polyethylene. Figure 4.3.5 (a) shows that from a blend ratio of (50% PE + 50% biomass) a maximum H_2 of 49% is attained at ER equals to 0.16 and SPR equals to 0.6, whilst a blend ratio of (25% PE + 75% biomass) a H_2 composition of 46% is achieved at ER equals to 0.1 and SPR equals to 0.6.



(a)

(b)

Figure 4.3.4. Effect of the equivalence ratio (oxygen is used as a gasifying agent) on the H_2 composition when different flowrates of steam are used (a) SFR equals to 0.6 and (b) SFR equals to 1.5.

The high H_2 values attained from the mixed feedstocks shows that the co- gasification of biomass and polyethylene has resulted in a synergistic interaction between the biomass and polyethylene when oxygen – steam mixture is used as a gasifying agent at low ER values and low steam flow rate.

Figure 4.3.4 (b) is an additional case, at which the aim is to determine the effect of adding steam at high flowrate through SFR equals to 1.5, while varying the ER from 0.1 – 1 on the H_2 content of the product gas. It is observed that when the steam is added to the gasifier at high flowrate, high H_2 content is obtained from the individual feedstock such as polyethylene. This indicates that the co- gasification of biomass and polyethylene does not favour the addition of steam at high flow rate. This indicates that at high steam flowrate, there is no synergistic interaction between biomass and polyethylene.

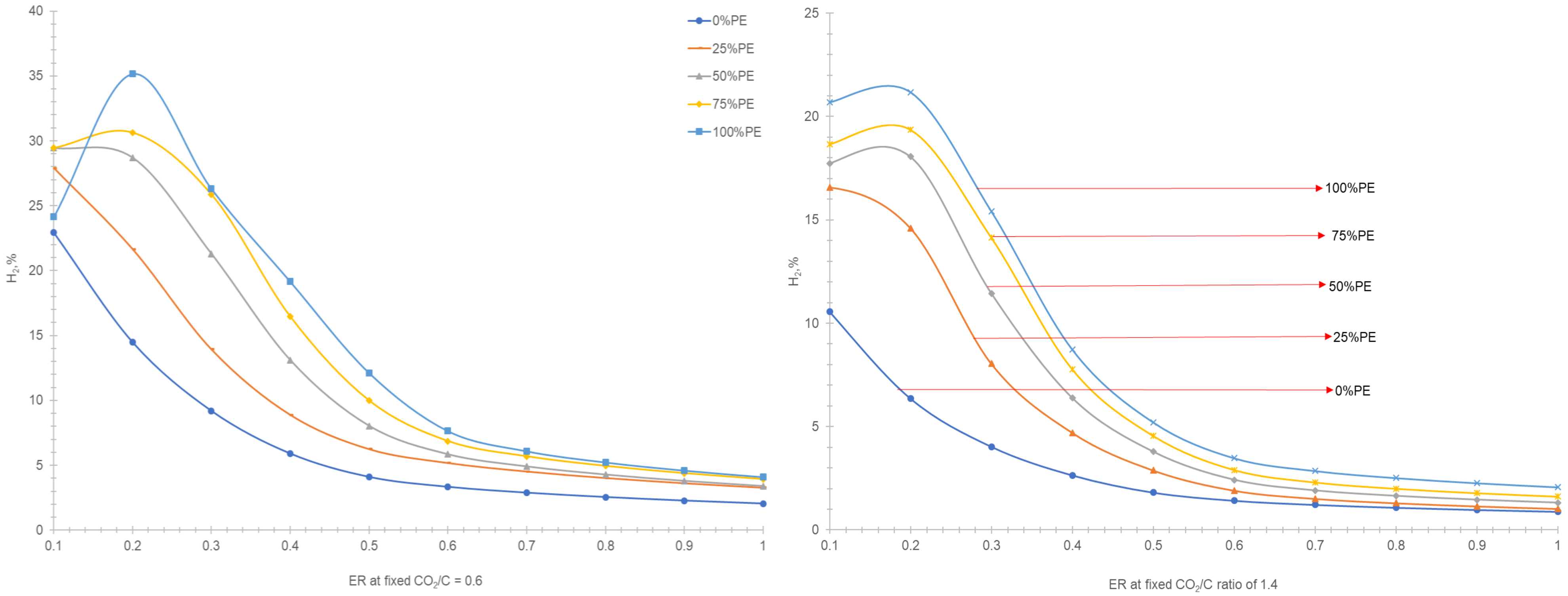
From Figure 4.3.4 (a) and (b) it was noted that the highest H_2 compositions are obtained when the steam is added at low SFR values (SFR= 0.6), then when the steam is introduced to the gasifier at high flowrate (SFR =1.5), at all ER values. This might be attributed to the fact that high steam flowrate tends to lower the gasifier temperature, thus limiting the steam reactions from taking place.

4.3.4. Effect of oxygen – carbon dioxide mixtures on the H_2 composition of the product gas.

Figure 4.3.5 shows the effect of the equivalence ratio (ER) on the H_2 composition in the product gas, when oxygen and carbon dioxide are used as a gasifying agents for the co-gasification of biomass and polyethylene. Carbon dioxide is added to the gasifier at different flowrates i.e. (CO_2/C ratio equals to 0.6 (representing a low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (representing a higher carbon dioxide flowrate)). The equivalence ratio is varied from 0.1 to 1.

The aim of this section is to determine the effect of varying the flowrate of carbon dioxide and determine if there is a synergistic interaction between biomass and polyethylene when oxygen – carbon dioxide mixture is used as a gasifying agent.

Figure 4.3.5 (a) and (b) shows that the H_2 composition of the feedstocks which contains low percentage of the polyethylene in their blends such as biomass and a blend ratio of (25%PE + 75% biomass) decreases as ER increases. While the H_2 composition of the feedstocks which contains high percentage of polyethylene in their blends such as the (50% PE + 50% biomass), (75% PE + 25% biomass) and (100% PE + 0% biomass) initially increase with the increasing ER, then reach a maximum value before decreasing as ER further increases.



(a)

(b)

Figure 4.3.5. Effect of the equivalence ratio (ER) (oxygen is used as a gasifying agent) on the H_2 composition of the product gas, when carbon dioxide is added (a) at low flowrate through CO_2/C ratio equals to 0.6 and (b) increased flowrate through CO_2/C equals to 1.5.

Figure 4.3.5 (a) and (b) shows that a high H_2 composition is favoured at low ER values between 0.1 – 0.3. The increase in the H_2 content in the blend ratios in Figure 4.3.5 (a) might be attributed to the interaction between the polyethylene feedstock and biomass. The long chains in the polyethylene structure are broken down into smaller fragments. Thus, resulting in the promotion of the chemical reactions such as the methanation reaction (R13) which results in producing more H_2 in the product gas.

Figure 4.3.5 (a) shows that the co – gasification of biomass and polyethylene favours high H_2 content at low ER values between the range of 0.1 – 0.14. For instance, from a blend ratio of (25% PE + 75% biomass) a high H_2 content of 28.0% is attained at ER equal to 0.1 and CO_2/C ratio equals to 0.6. From a blend ratio of (50% PE + 50% biomass) a high H_2 composition of 29.0% is attained at ER equals to 0.14 and CO_2/C ratio equals to 0.6 and also for a blend ratio of (75% PE + 25% biomass) a maximum H_2 content of 30.0% is attained at ER equals to 0.14 and CO_2/C ratio equal to 0.6. The high H_2 composition attained from blend ratios indicates that between biomass and polyethylene there is a synergistic effect, when oxygen – carbon dioxide is used as a gasifying agent.

Figure 4.3.5 (b) shows that when the flowrate of carbon dioxide increases from CO_2/C ratio equals to 0.6 to 1.4, and ER is varied from 0.1 – 1. The highest H_2 is attained from the individual feedstock (polyethylene), instead of the mixed feedstocks. The H_2 composition attained from the CO_2/C ratio equals to 1.4 is lower than that achieved when CO_2/C ratio equals to 0.6 was used. This can be attributed to that; the addition of carbon dioxide at high flowrate limits the chemical reaction such as reverse methane CO_2 reforming reaction (R10) which is responsible for the increase of the H_2 content in the product gas, while promoting the reverse water- gas shift reaction (R9) which enhances the reduction of the H_2 in the product gas. Furthermore, Figure 4.3.5 (a) shows that at low carbon dioxide flow rate high H_2 composition are attained at different ER values, as compared to that attained at high carbon dioxide flowrate (Figure 4.3.5 (b)).

Table 4.3.2 shows the maximum of H_2 composition produced from different blend ratios during the co- gasification of biomass and polyethylene. The data displayed in Table 4.3.2 shows that at various blended feedstocks, the highest H_2 composition is attained, at low ER below 0.4, low SFR equals to 0.6 and low CO_2/C ratio equals to 0.6. This indicates that for the co-gasification of biomass and polyethylene produces positive results since the high H_2 content is achieved from the bended feedstocks, thus indicating that there is synergistic interaction between biomass and polyethylene from the blended feedstocks at various blend ratios.

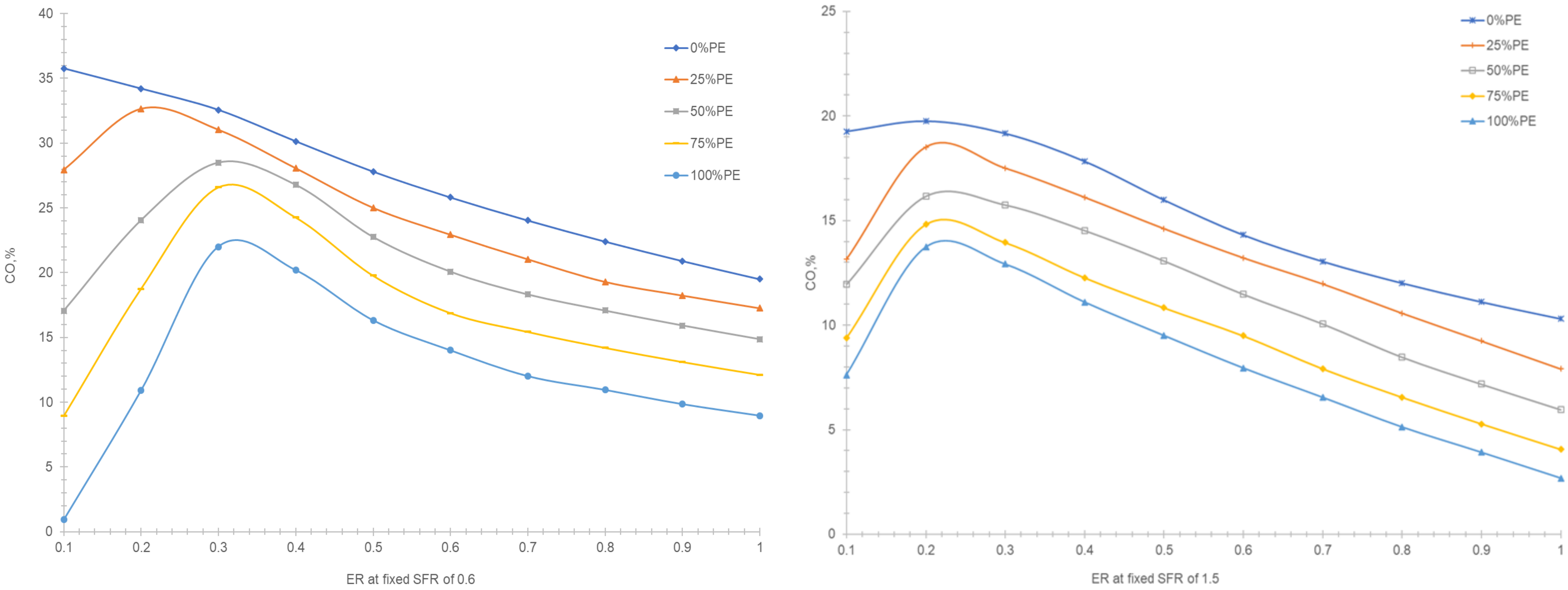
Table 4.3.2. Recommended operating conditions and gasifying agents for the different blend ratios on the H_2 composition of the product gas.

Component: H_2 (%)				
Gasifying agent:	**oxygen**			
Blend ratio (BR)	**Amount**	**ER**	**SBR**	**CO_2/C ratio**
25% PE + 75% BM	51.5.0	0.1	-	-
50% PE + 50% BM	54.0	0.1	-	-
75% PE + 25%BM	56.0	0.1	-	-
Gasifying agent:	**oxygen – steam mixture**			
25% PE + 75% BM	46.0	0.1	0.6	-
50% PE + 50% BM	49.0	0.16	0.6	-
75% PE + 25%BM	54.5 44.0	0.34 0.12	0.6 1.5	- -
Gasifying agent:	**oxygen – carbon dioxide mixture**			
25% PE + 75% BM	28.0	0.1	-	0.6
50% PE + 50% BM	29.0	0.14	-	0.6
75% PE + 25%BM	30.2	0.14	-	0.6

*** BM – stand for biomass**
*** PE – stand for polyethylene**

4.3.5. Effect of using oxygen – steam as a gasifying agent on the CO composition of the product gas composition.

Figure 4.3.6 (a) and (b) shows the effect of the equivalence ratio on the CO composition when different flow rates of steam are used, such as SFR equals to 0.6 (represents low steam flowrate) and SFR equals to 1.5 (represents a higher steam flowrate). The equivalence ratio (ER) is varied from 0.1 to 1. Figure 4.3.6 (a) and (b) shows that as ER increases, the CO composition increases, then reached a peak value, before decreasing with an increasing ER. This trend is the same for all the feedstocks except for biomass in Figure 4.3.6 (a). Figure 4.3.6 (a) and (b) shows that the highest CO composition in the product gas composition are favoured at ER below 0.4.



(a)

(b)

Figure 4.3.6. Effect of the equivalence ratio (oxygen is used as a gasifying agent) on the CO composition of the product gas, when (a) SFR is equals to 0.6 (b) when SFR is equals to 1.5.

It is deduced from Figure 4.3.6 (a) and (b) that for all the different feedstocks at different ER values the addition of the PE to biomass reduces the CO composition in the product gas. This is due to the low fixed carbon in the polyethylene feedstock, lack of oxygen content and strengthened water gas shift reaction (R9) which causes the CO to be consumed by steam to produce H_2 and CO_2 in the product gas. Figure 4.3.6 (a) shows that during the co- gasification of biomass and polyethylene the highest CO composition of 36.0% is achieved at ER equals to 0.1 and SFR equals to 0.6 from biomass feedstock. This indicates that the co- gasification of biomass and polyethylene does not favour the production of the CO composition of the product gas and there is no synergy between biomass and polyethylene.

The high CO composition at low ER values can be attributed to the chemical reactions such as the water gas reaction (R2) (steam reaction), partial oxidation reaction (R4), steam - reforming reaction (R12) and methanation reaction (R13). At ER values above 0.4, the CO composition obtained from all the feedstocks decrease, due to the oxidation reactions (R5) to (R8), which oxidizes the CO into CO_2.

Figure 4.3.6 (b) shows the effect of increasing the steam flowrate from SFR of 0.6 to 1.5 on the CO composition of the product gas during the co- gasification of biomass and polyethylene. It is observed that the addition of more steam causes the reduction in the CO composition of the product gas. As a result, a higher CO is attained from low SFR equals to 0.6 instead of CO from SFR equals to 1.5 for all ER values and for all feedstocks. Figure 4.3.6 (a) and (b) shows that the addition of more steam during the co- gasification does not enhance the synergistic interaction between biomass and polyethylene, this is because a high CO content is achieved from the individual feedstocks instead of the blended mixtures.

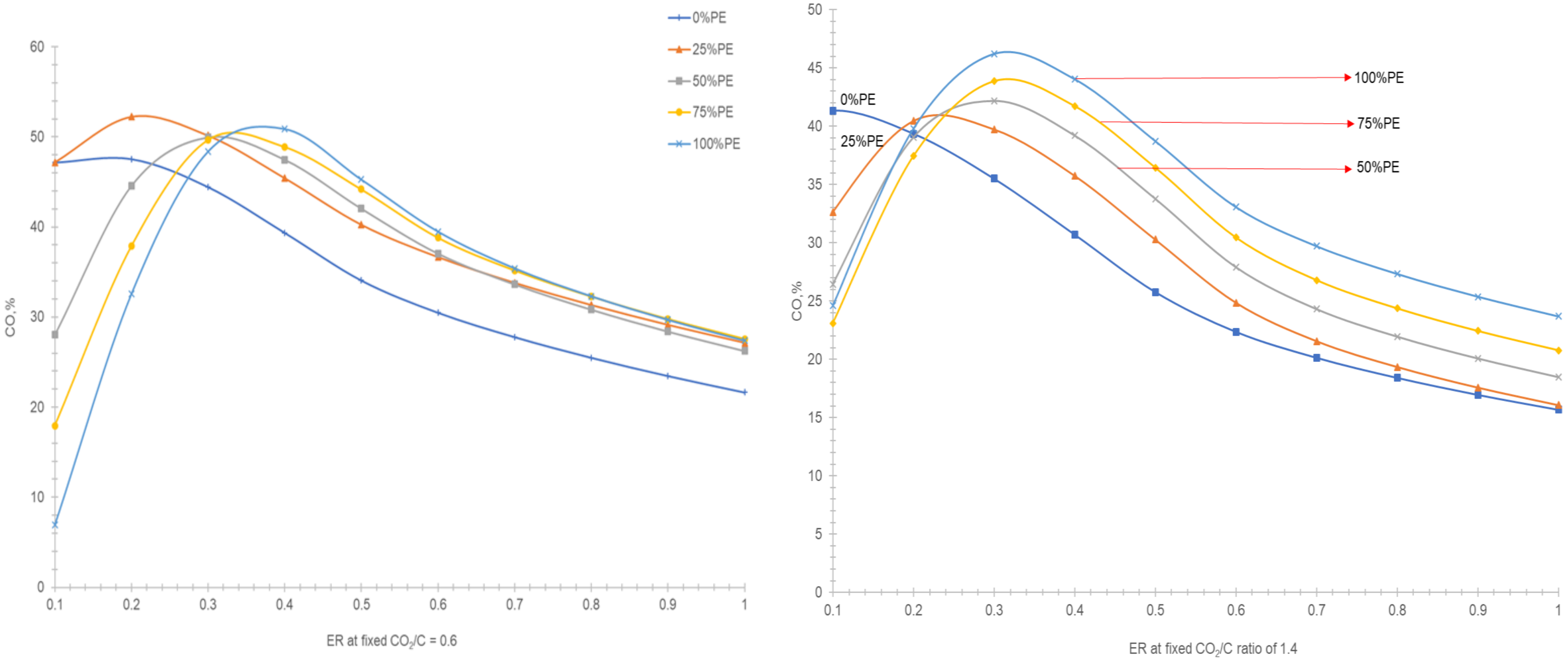
4.3.6. Effect of using oxygen – carbon dioxide mixtures as a gasifying agent on the CO composition of the product gas.

Figure 4.3.7 (a) and (b) shows the effect of the equivalence ratio, varied from 0 to 1, on the CO composition of the product gas composition, when oxygen is used as a gasifying agent and carbon dioxide is added into the gasifier at different flowrates (CO_2/C ratio equals to 0.6 (indicating low carbon dioxide flowrates) and CO_2/C ratio equals to 1.4 (indicating a higher carbon dioxide is added)).Figure 4.3.7 (a) shows that the CO composition of biomass decreases as ER increases. The CO composition of the blended feedstocks and polyethylene increase with an increase in ER, reaches a maximum value and thereafter decreases as ER increases further.

Figure 4.3.7 (a) and (b) shows that the high CO composition is favoured at low ER values below 0.4. The high CO composition is attributed to the chemical reactions such as the Boudouard reaction (R1), reverse water gas shift reaction (R9), reverse methane CO_2 reforming reaction (R10), partial oxidation reaction (R4) and methanation reaction (R13). Figure 4.3.7 (a) and (b) Furthermore, shows that the addition of polyethylene to the blended fuels in the presence of oxygen – carbon dioxide mixture as a gasifying agent, increases the CO composition in the product gas. This can be attributed to the interaction between the oxygenated volatiles from biomass pyrolysis and free radicals and volatiles from polyethylene decomposition and due to the strengthened reverse CO_2 reforming reaction (R10) (Li et al. (2021).

Figure 4.3.7 (a) shows that the co – gasification of biomass and polyethylene favours a high CO content in the product gas when carbon dioxide is introduced to the gasifier at low flowrate (CO_2/C ratio equals to 0.6). This is observed when from a blend ratio of (25% PE +75% biomass) a maximum CO content of 52% is attained at ER equal to 0.22 and CO_2/C ratio equals to 0.6, from the blend ratio of (50% PE + 50% biomass) a high CO of 50% is attained at ER equals to 0.28 and from a blend ratio of (75% PE + 25% biomass) a maximum CO content of 50% is attained from at ER equals to 0.28 and CO_2/C ratio equals to 0.6. At low ER values below 0.4, the high CO composition attained from the blend ratios in comparison to the individual feedstocks indicates that there is synergistic effect between biomass and polyethylene.

However, in the case where more carbon dioxide is introduced to the gasifier i.e. CO_2/C ratio equals to 1.4 (Figure 4.3.7 (b)), it is observed that the co- gasification of biomass and polyethylene does not promote a high CO composition in the product gas, since a high CO is not attained from the blended feedstocks but it is attained from the individual feedstock which is the polyethylene. This can be attributed to the volatiles from when carbon dioxide was introduced at low carbon dioxide, reacted with the available char via the Boudouard reaction (R1) to form CO in the product gas (Deparrois et al. (2019). As a result, when the carbon dioxide is introduced at high flowrate, there is no char left to react. As a result, the incoming carbon dioxide remains unreacted. Figure 4.3.7 (b) shows that there is no synergy between biomass and polyethylene feedstock. Therefore, Figure 4.3.7 (a) and (b) shows that the highest CO composition produced at high carbon dioxide flowrate through CO_2/C ratio equals to 1.4 is lower than the high CO produced from when the carbon dioxide is introduced to the gasifier at low flow rate through CO_2/C ratio equals to 1.4 for all the ER values.



(a) (b)

Figure 4.3.7. Effect of the equivalence ratio (oxygen is used as a gasifying agent) on the CO composition, when carbon dioxide is added to the gasifier at different flowrates (a) CO_2/C ratio equals to 0.6 (b) CO_2/C ratio equals to 1.4.

Table 4.3.3 shows the highest CO composition produced from different blend ratios during the co- gasification of biomass and polyethylene is achieved at ER below 0.5 and at low flowrates of steam and carbon dioxide through SFR equal to 0.6 and CO_2/C ratio equals to 0.6. Table 4.3.3 indicates that the synergistic effect between biomass and polyethylene is enhanced when the operating conditions such as ER and CO_2/C ratio are used.

Table 4.3.3. Recommended operating conditions and gasifying agents for the achievement of the maximum CO content in the product gas when different blend ratios for the co – gasification of biomass and polyethylene.

Component: CO (%)				
Gasifying agent:	**oxygen**			
Blend ratio (BR)	**Amount**	**ER**	**SFR**	**CO_2/C ratio**
25% PE + 75% BM	54.2	0.22	-	-
50% PE + 50% BM	51.8	0.32	-	-
75% PE + 25%BM	51.8	0.32	-	-
Gasifying agent:	**oxygen – steam mixture**			
25% PE + 75% BM	-	-	-	-
50% PE + 50% BM	-	-	-	-
75% PE + 25%BM	-	-	-	-
Gasifying agent:	**oxygen – carbon dioxide mixture**			
25% PE + 75% BM	52.0	0.22	-	0.6
50% PE + 50% BM	50.0	0.28	-	0.6
75% PE + 25%BM	50.0	0.28	-	0.6

*** BM – stand for biomass**

*** PE – stand for polyethylene**

4.3.7. Effect of using oxygen as a gasifying agent on the H_2/CO ratio of the syngas.

Figure 4.3.8 (a) and (b) shows the effect of the equivalence ratio on the H_2/CO ratio of the syngas, when oxygen is used as a gasifying agent for the co- gasification of the different feedstocks. The equivalence ratio is varied from 0.1 to 1. Figure 4.3.8 (a) and (b) shows that an increase of ER from 0.1 – 1, decreases the H_2/CO ratio of the syngas. This trend is observed in all the feedstocks.

The H_2/CO ratios of the syngas for the feedstocks are favoured at low ER values below 0.3, since an increase in ER results in a decrease in the H_2/CO ratio. The high H_2/CO ratio of the syngas is attributed to chemical reactions such as the partial oxidation reaction (R4) and the methanation reaction (R13). At higher ER values, the oxidation reactions (R5) to (R8) are favoured and oxidize the H_2 and CO into H_2O and CO_2 in the product gas.

Figure 4.3.8 (a) depicts that the recommended H_2/CO ratio of 2 is not achieved when the biomass and feedstocks with lower percentage of polyethylene such as a blend ratio of (25% PE + 75% biomass) were gasified. However, from the feed mixtures which contains higher percentage of polyethylene in their mixtures such as the blend ratio of (50% PE + 50% biomass) and (75% PE + 25% biomass) the recommended H_2/CO ratio of 2 is achieved.

From a blend ratio of (50% PE + 50% biomass) the recommended H_2/CO ratio of 2 is attained at ER equals to 0.1, for a blend ratio of (75% PE + 25% biomass) the recommended H_2/CO ratio of 2 is achieved at ER equals to 0.2 and for a feedstock of (100% PE + 0% biomass) the recommended H_2/CO ratio of 2 is achieved at ER equals to 0.2. This is expected because polyethylene has high volatile matter and more H_2 can be produced during the co- gasification process, that leads to a high H_2/CO ratio of the syngas. Figure 4.3.8 (a) shows that a recommended H_2/CO ratio of 2, is achieved at low ER values, below 0.3. The attainment of the recommended H_2/CO ratios of 2 of the syngas from the blended feedstocks when oxygen is used as a gasifying agent indicates that the co – gasification of biomass and polyethylene contributes positively towards improving the syngas quality.

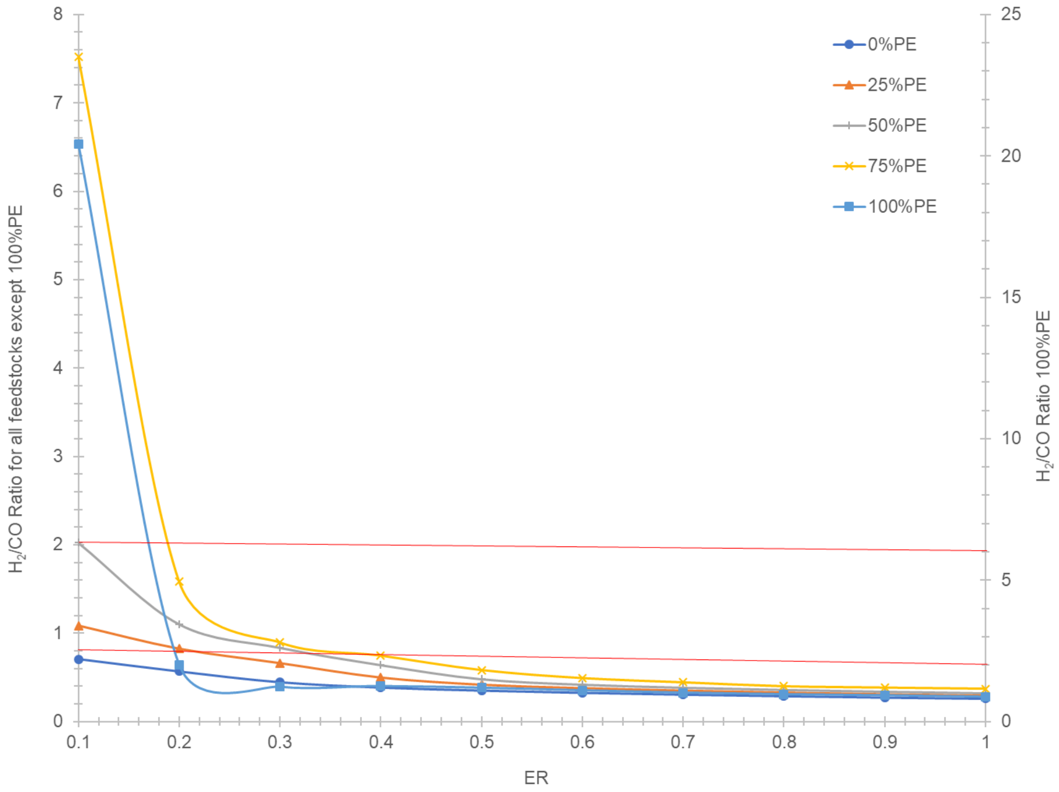


Figure 4.3.8. Effect of the equivalence ratio on the H_2/CO ratio of the syngas when oxygen is used as a gasifying agent for the gasification of the different blend ratios.

4.3.8. Effect of oxygen – steam mixtures as a gasifying agent on the H_2/CO ratio of the syngas.

Figure 4.3.9 (a) and (b) shows the effect of the equivalence ratio on the H_2/CO ratio of the syngas, when oxygen and different steam flowrates (SFR equals to 0.6 (low steam flowrate) and SFR equals to 1.5 (higher steam flowrate)) are used as gasifying agents, for the co-gasification of the different feedstocks. Figure 4.3.9 (a) and (b) shows that as ER increases, the H_2/CO ratio of the syngas decreases. The reason for the decrease in the H_2/CO ratio is due to the exothermic oxidation reactions such as (R5) to (R8) which are promoted at high ER values, at which the available H_2 and CO in the gasifier are oxidized to H_2O and CO_2 in the product gas.

Figure 4.3.9 (a) and (b) shows that the highest H_2/CO ratio of the syngas is favoured ER values below 0.8. The chemical reactions that are favoured at low ER when an oxygen – steam mixture is used as a gasifying agent are the steam reaction (R2), partial oxidation reaction (R4), water – gas shift reaction (R9), reverse methanation reforming reactions (R11) and (R14) and steam reforming reaction (R12) and methanation reaction (R13).

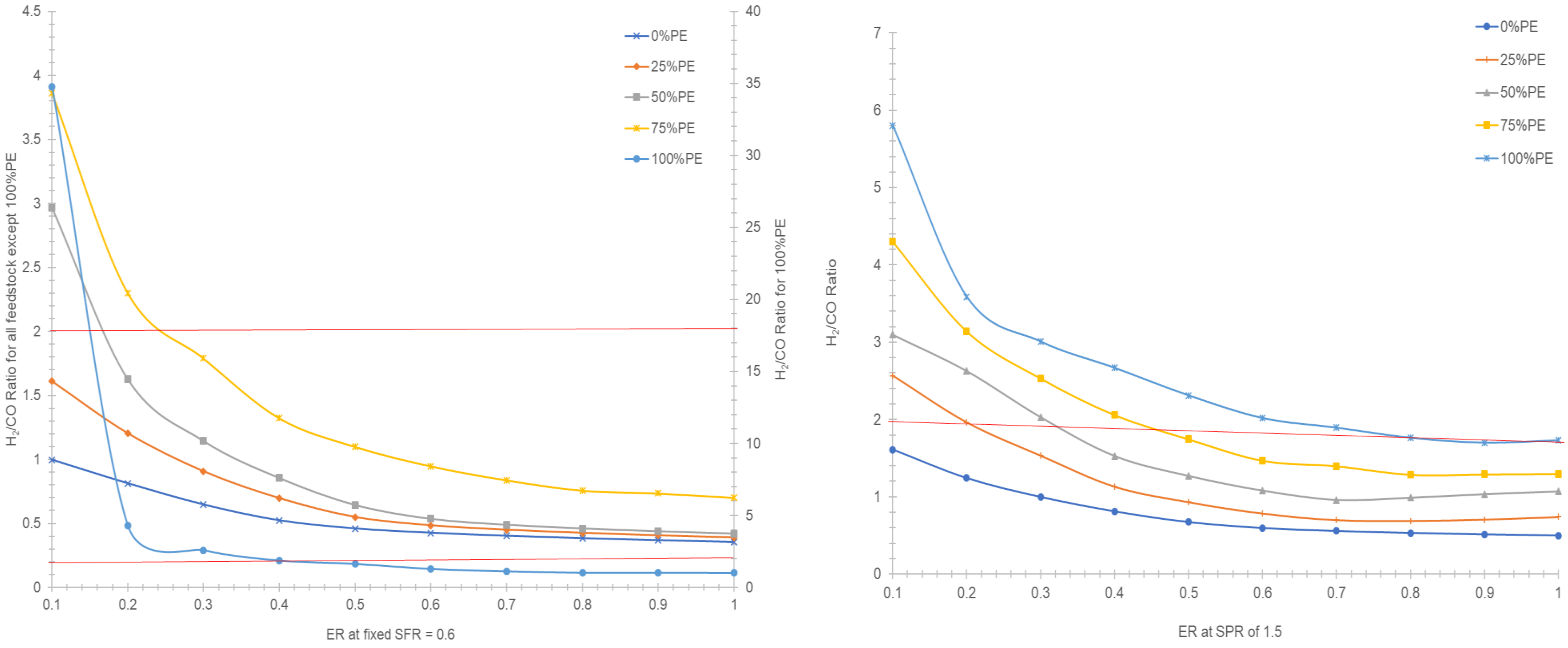
Figure 4.3.9 (a) and (b) shows that an increase in the percentage of polyethylene in the feed mixture increases the H_2/CO ratio of the syngas. This is because polyethylene contains a high percentage of volatile matter, which releases a higher H_2 content during the co- gasification process leading to an increase in the H_2 composition and that increases the H_2/CO ratio of the syngas in the feedstock blends. As a result, Figure 4.3.9 (a) shows that the feedstocks that contains a high percentage of polyethylene have achieved the recommended H_2/CO ratio of 2. For instance, from a blend ratios of (50% PE + 50% biomass) a H_2/CO ratio of 2 is attained at ER equals to 0.18 and SFR equals to 0.6, from a blend ratio of (75% PE + 25% biomass) the H_2/CO ratio of 2 is achieved at ER equals to 0.24 and SFR equals to 0.6 and for feedstock of (100% PE + 0% biomass) the recommended H_2/CO ratio of 2 is attained at ER equals to 0.4 and SFR equals to 0.6. The achievement of the H_2/CO ratio of the syngas, from the blended feedstocks shows that when oxygen – steam mixture is used as a gasifying agent mixture, the co- gasification of biomass and polyethylene enhances the quality of syngas.

However, from feedstocks with low percentage of polyethylene such as the blend ratio of (25% PE + 75% biomass) and biomass, the recommended H_2/CO ratio of 2 was not achieved. This is due to the high oxygen content of the biomass feedstock which leads to a high CO content in the product gas, resulting in a decreased H_2/CO ratio of the syngas.

Figure 4.3.9 (b) shows that when SFR equals to 1.5, all the feedstocks that contains a percentage of the polyethylene achieved the recommended H_2/CO ratio of 2, except for biomass feedstock. This is because biomass contains a high oxygen content, thus lowers the production of the H_2 and increases the CO composition in the product gas composition.

Figure 4.3.9 (b) shows that from a blend ratio of (25% PE + 75% biomass) a recommended ratio of 2 is achieved at ER equals to 0.2 and SFR equals to 1.5, from a blend ratio of (50%PE + 50% biomass) a H_2/CO ratio of 2 is attained at ER equals to 0.32 and SFR equals to 1.5 and from a blend ratio of (75% PE + 25% biomass) a recommended H_2/CO ratio of 2 is attained at ER equals to 0.45 and SFR equals to 1.5.

Figure 4.3.9 (a) and (b) shows that since the recommended H_2/CO ratio of 2 can be attained, this implies that the co- gasification of biomass and polyethylene during the use of oxygen – steam mixture as a gasifying agent improves the quality of the syngas, irrespective of the steam flowrate.



(a)

(b)

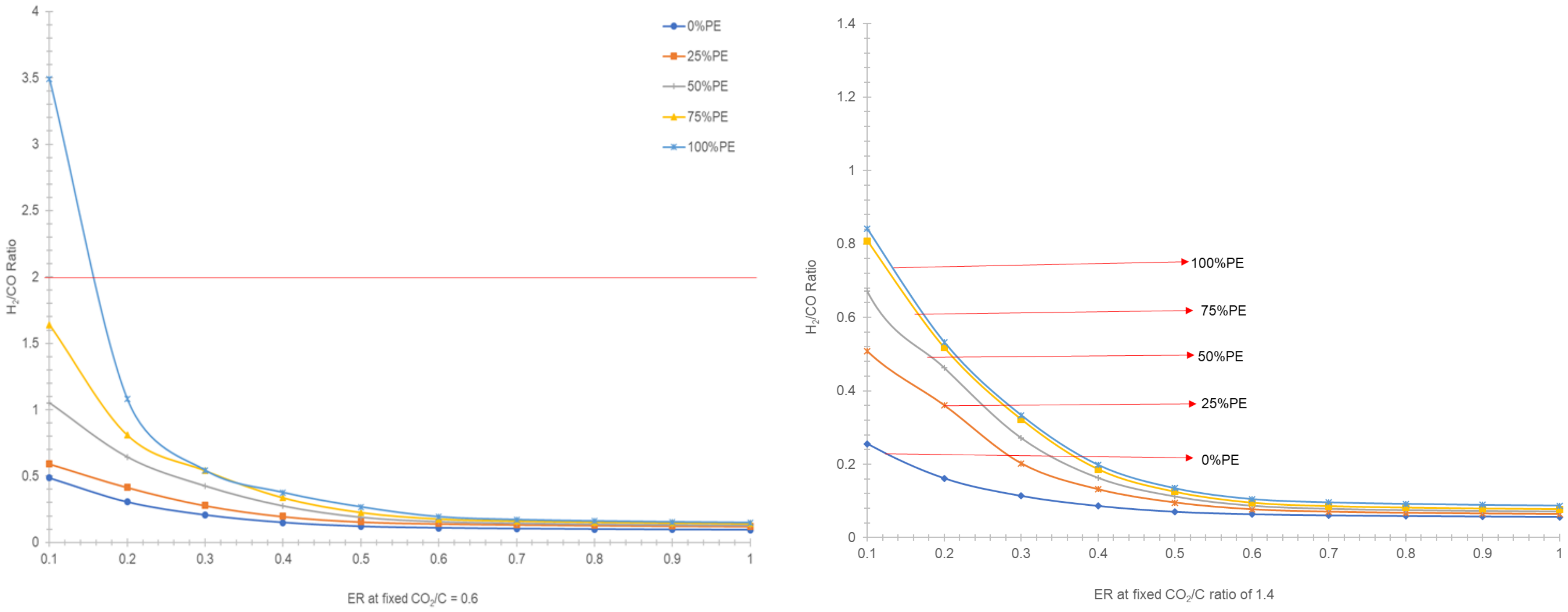
Figure 4.3.9. Effect of the equivalence ratio (oxygen is used as a gasifying agent) on the H_2/CO ratio of the syngas, when the steam is added to the gasifier at different flowrates (a) SFR equals to 0.6 and (b) SFR equals to 1.5.

4.3.9. Effect of oxygen – carbon dioxide mixtures as a gasifying agent on the H_2/CO ratio of the syngas.

Figure 4.3.10 (a) and (b) illustrates the effect of the equivalence ratio on the H_2/CO ratio of the syngas, when oxygen and different carbon dioxide flowrates (CO_2/C ratio equals to 0.6 (represents low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (represents an increased carbon dioxide flowrate from that of CO_2/C ratio equals to 0.2) are used as gasifying agents, for the co- gasification of the different feedstock., when oxygen is used as a gasifying agent and the equivalence ratio is varied from 0.1 to 1.

Figure 4.3.10 (a) and (b) shows that as ER increases, the H_2/CO ratio of the syngas decreases. High H_2/CO ratios of the syngas are favoured at low ER values below 0.4. The chemical reactions which promotes the high H_2/CO ratio of the syngas when oxygen – carbon dioxide mixture is used as a gasifying agent are the Boudouard reaction (R1), partial oxidation reaction (R4), water- gas shift reaction (R9), reverse methane CO_2 reforming reaction (R10) and methanation reaction (R13). At ER values above 0.4, the decrease in the H_2/CO ratio is attributed to the chemical reactions such as the exothermic oxidation reactions (R5) to (R8), which oxidizes the H_2 and CO into H_2O and CO_2. It is noticed from Figure 4.3.10 (a) and (b) that as the percentage of the polyethylene in the feedstock mixtures increases, the H_2/CO ratios also, increased. This is because polyethylene has a high hydrogen content as compared to biomass.

Figure 4.3.10 (a) shows that the recommended H_2/CO ratio of 2 is not achieved from the blended feedstocks, instead it is achieved from the polyethylene material. In Figure 4.3.10 (b) the recommended H_2/CO ratio of 2 is not achieved from both individual and blended feedstocks when the flowrate of carbon dioxide is increased from CO_2/C ratio equals to 0.6 to 1.4. This implies that for the co – gasification of biomass and polyethylene, the use of oxygen – carbon dioxide mixture as a gasifying agent does not promote a good quality syngas. This indicates that oxygen – carbon dioxide gasifying agent mixture is not suitable for the co-gasification of biomass and polyethylene.



(a) (b)

Figure 4.3.10. Effect of the equivalence ratio (oxygen is used as a gasifying agent) on the H_2/CO ratio of the syngas when carbon dioxide is added (a) CO_2/C ratio equals to 0.2 and (b) CO_2/C ratio is increased to 1.4.

Table 4.3.4 indicates that the good quality syngas is achievable from the blend ratios of biomass and polyethylene, at low ER values below 0.4, for all blend ratios. However, in terms of the steam content, Table 4.3.4 shows that there is a freedom of varying the steam at low (through SFR equals to 0.6) and high flowrates (through SFR equals to 1.5), any of the operating conditions will allow the determination of the recommended H_2/CO ratio of the syngas can be achieved.

Table 4.3.4 exhibits that the addition of carbon dioxide to the gasifier, is not good to produce syngas with high quality since the recommended H_2/CO ratio of 2, was not achieved from all the blended fuels. Therefore, it is not necessary to add carbon dioxide to the oxygen, as a gasifying agent mixture during the co- gasification of biomass and polyethylene. The addition of carbon dioxide to the gasifier does not enhance the quality of the syngas between biomass and polyethylene materials, with regard to the quality of syngas.

Table 4.3.4. Recommended operating conditions and gasifying agents for the co- gasification of biomass and polyethylene on the H_2/CO ratio of the syngas.

H_2/CO ratio of the syngas				
Gasifying agent:	**oxygen**			
Blend ratio (BR)	**Recommended Value**	**ER**	**SBR**	**CO_2/C ratio**
25% PE + 75% BM	-	-	-	-
50% PE + 50% BM	2	0.1	-	-
75% PE + 25%BM	2	0.2	-	-
Gasifying agent:	**oxygen – steam mixture**			
25% PE + 75% BM	2	0.2	-	1.5
50% PE + 50% BM	2	0.18 0.32	0.6 1.5	-
75% PE + 25%BM	2	0.24 0.45	0.6 1.5	- -
Gasifying agent:	**oxygen – carbon dioxide mixture**			
25% PE + 75% BM	2	-	-	-
50% PE + 50% BM	2	-	-	-
75% PE + 25%BM	2	-	-	-

*** BM – stand for biomass**

*** PE – stand for polyethylene**

4.3.10. Effect of oxygen on the Lower Heating Value (LHV) of the syngas.

Figure 4.3.11 shows the effect of the equivalence ratio on the Lower Heating Value (LHV) of the syngas, when oxygen is used as gasifying agents, for the co- gasification of the different feedstocks, the equivalence ratio is varied from 0.1 to 1.

It is observed from Figure 4.3.11 that the Lower Heating Value (LHV) of the syngas for the individual feedstocks such as biomass and polyethylene feedstocks decreases as ER increases. While the LHV of the syngas of the blended feedstocks such as (25% PE + 75% biomass), (50% PE + 50% biomass) and (75% PE + 25% biomass) initially increase with increasing ER, and reach a maximum value, and thereafter decreases as ER increases further.

Figure 4.3.11 shows that the Lower Heating Value (LHV) of the syngas is higher at low ER values below 0.4 for all the feedstocks. This can be ascribed to the chemical reactions such as the partial oxidation reaction (R4) and methanation reaction (R13) which are promoted at low ER values. At higher ER above 0.4 the oxidation reactions such as (R5) to (R8) are favoured and oxidize the combustible gases such as CO, H_2 and CH_4 into CO_2 and H_2O.

Figure 4.3.11 shows that the co- gasification of biomass and polyethylene does not favour high LHV of the syngas, since the highest LHV of the syngas is attained from the individual feedstock (polyethylene) not from the blended feedstock. This shows that when oxygen is used as a gasifying agent, there is no synergy between biomass and polyethylene feedstocks.

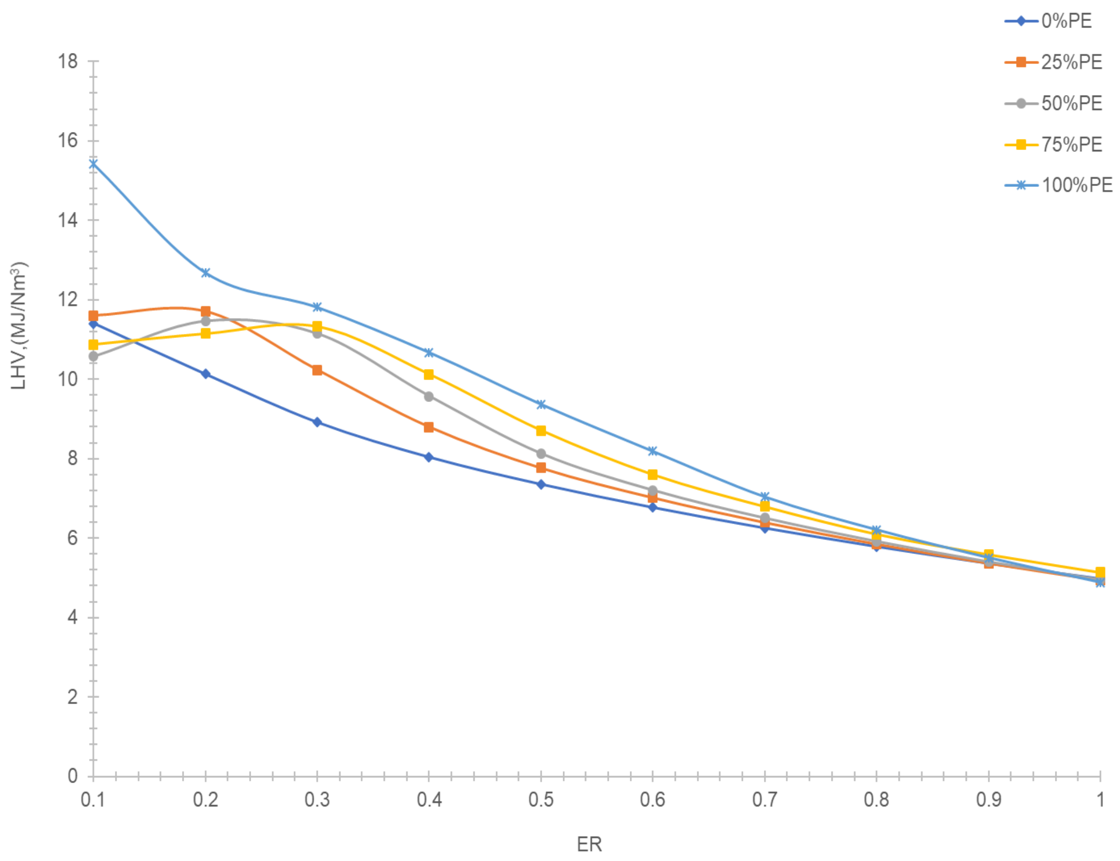


Figure 4.3.11. Effect of the equivalence ratio on the Lower Heating Value (LHV) of the syngas when oxygen is used as a gasifying agent.

4.3.11. Effect of oxygen – steam mixture as a gasifying agent on the Lower Heating Value (LHV) of the syngas.

Figure 4.3.12 (a) and (b) shows the effect of equivalence ratio on the Lower Heating Value (LHV) of the syngas, when oxygen and steam are used as gasifying agents for the co – gasification of biomass and polyethylene. Steam is introduced to the gasifier at different steam flowrates i.e. (SFR equals to 0.6 (indicates a low steam flowrate) and (b) SFR equals to 1.5 (higher steam flowrate)).

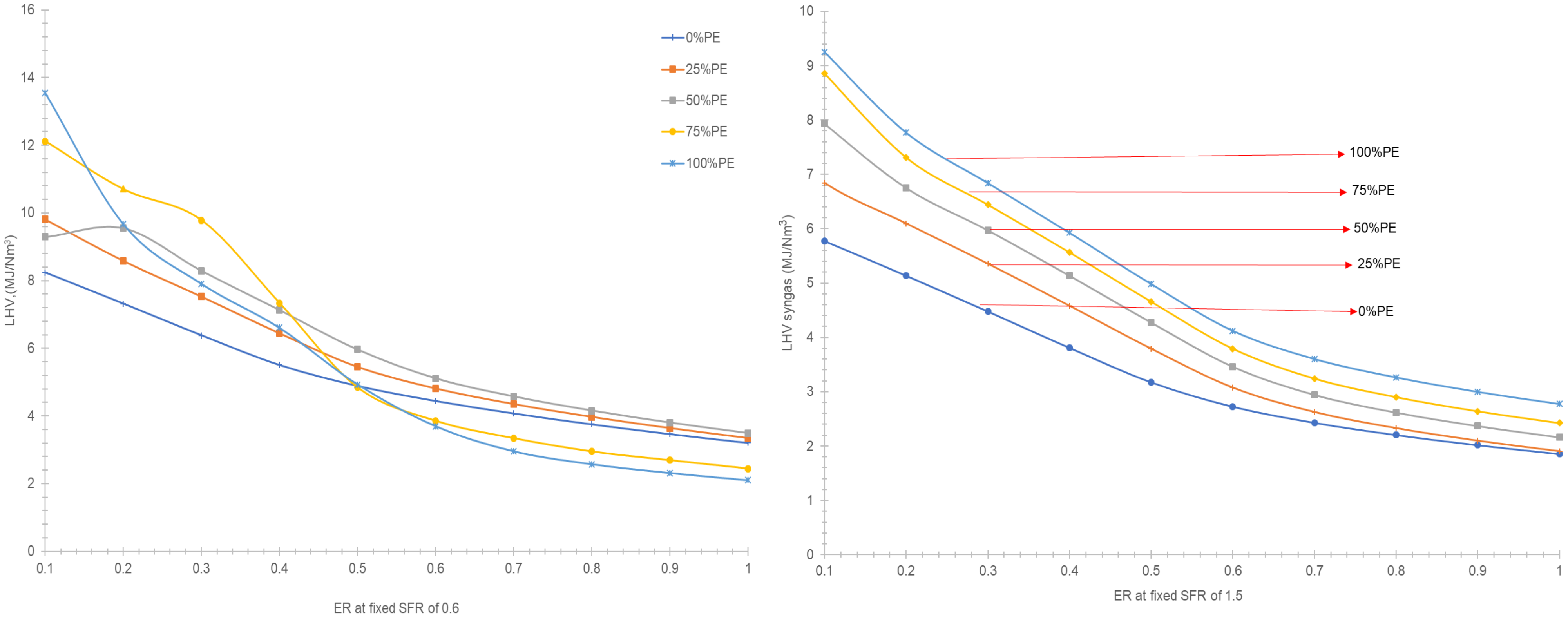
Figure 4.3.12 (a) shows that an increase of ER causes the Lower Heating Values (LHV) of the individual feedstocks such as polyethylene and biomass, as well as the feedstock that contains lower percentage of polyethylene such as the blend ratio of (25% PE + 75% biomass) to decrease. While, the lower heating values of the feedstocks with blend ratio of (50% PE + 50% biomass) and (75% PE + 25% biomass) increases with an increasing ER and reach a maximum value and thereafter decreases as ER increases further.

Figure 4.3.12 (a) and (b) shows that an increase in the percentage of polyethylene in the blended feedstock increases the LHV of the syngas. This is expected that the polyethylene produces a high LHV of the syngas as compared to that of the biomass and the mixtures. However, in this case Figure 4.3.12 (a) shows that a high LHV is attained from the blended feedstock instead of the individual feedstocks at ER range between 0.2 - 1. This is expected since during the interaction between biomass and polyethylene, the polyethylene acts as a hydrogen donor to the biomass contents generated from the pyrolysis stage. Thus, resulting in a high lower heating values in the blended feedstocks than that in the individual feedstocks.

Furthermore, from Figure 4.3.12 (a) it is observed that from the blend ratio of (50% PE + 50% biomass) a high LHV of 9.6 MJ/Nm^3 is attained at ER equals to 0.22 and SFR equals to 0.6 and from the blend ratio of (75% PE + 25% biomass) a high LHV of 10.7 MJ/Nm^3 is obtained from ER equals to 0.2 and SFR equals to 0.6. The interaction between biomass and polyethylene enhances the calorific value of the syngas in the blended feedstocks, resulting in a high LHV of the syngas. This indicates that between biomass and polyethylene there is a synergistic effect.

The high LHV of the syngas in all the feedstocks is attributed to the chemical reactions such as the steam reaction (R4), water – gas shift reaction (R9), steam – reforming reaction (R12) and methanation reaction (R13) which are promoted at low ER values below 0.4.

Figure 4.3.12 (b) shows that the addition of steam at higher flowrate through SFR equal to 1.5 decreases the LHV of the syngas. Since the high steam flowrate inhibits the promotion of the steam reactions which enhances the production of the combustible gases such as H_2, CO and CH_4 and that leads to a decrease in the LHV of the syngas. As observed in Figure 4.3.12 (b) unlike in the case of SFR equals to 0.6 (Figure 4.3.12 (a), the LHV of the blended feedstocks is lower than that attained from an individual feedstock (polyethylene). This indicates that the addition of steam at high flowrate in the presence of oxygen as a gasifying agent does not promote a synergistic interaction between biomass and polyethylene during the co-gasification process.



(a)

(b)

Figure 4.3.12. Effect of the equivalence ratio (oxygen is used as a gasifying agent) on the Lower Heating Value (LHV) of the syngas when steam flowrate is varied (a) SFR equals to 0.6 (b) SFR equals to 1.5.

Baloch et al. (2016) conducted study using a bench scale experimental rig for the co-gasification of rice straw and polyethylene. Steam was used as a gasifying agent and introduced to the gasifier at 2 ml/ min, and the temperature of the gasifier was fixed at 900°C. The polyethylene percentage was increased from 0% PE to 75% PE in the biomass blends. Similar observations as in this study were observed, for the influence of the increasing of the polyethylene percentage in the blends on the lower heating value of the syngas.

It was observed that when the percentage of polyethylene increased from 0% to 75%PE, the lower heating value of the syngas increased, from 11.9 MJ/Nm^3 to 15.4MJ/Nm^3. This observation is the same as in this study whereby as the percentage of PE increased from 0% PE to 75% PE the lower heating value increased from around 6.4 MJ/Nm^3 to 10.0 MJ/Nm^3 (75% PE + 25% biomass) at fixed ER equals to 0.3 (point where LHV of the syngas from the blended feedstock, is at maximum) from Figure 4.3.13 (a).

The difference between the values of the LHV obtained in this study and the study conducted by Baloch et al. (2016) is influenced by factor such as the different biomass feedstocks, such as that Baloch et al. (2016) used rice straw as biomass, whereas this study pine sawdust is used as a biomass feedstock. Furthermore, the different operating conditions of the gasifier temperatures employed in both studies influences the amount of the LHV attained in the syngas. For instance, in the study conducted by Baloch et al. (2016) the gasifier temperature was set constant at 900°C at which the reactor was placed in an electrically heated oven to maintain the constant temperature, while in this study the temperature in the gasifier is influenced by the gasifying agents used (flowrates of steam and oxygen).

4.3.12. Effect of oxygen – carbon dioxide mixture as a gasifying agent on the lower heating value (LHV) of the syngas.

Figure 4.3.13 (a) and (b) shows the effect of equivalence ratio (ER) on the Lower Heating Value (LHV) of the syngas when oxygen and carbon dioxide are used as gasifying agents. Carbon dioxide is added to the gasifier at different carbon dioxide flowrates (CO_2/C ratio equals to 0.6 (indicates low carbon dioxide flowrate) and CO_2/C ratio equals to 1.4 (higher carbon dioxide flowrate for the co- gasification of the different feedstocks.

Figure 4.3.13 (a) shows that as ER increases, the Lower Heating Value (LHV) of the syngas for the feedstocks that contains a low percentage of polyethylene such as (25% PE + 75%

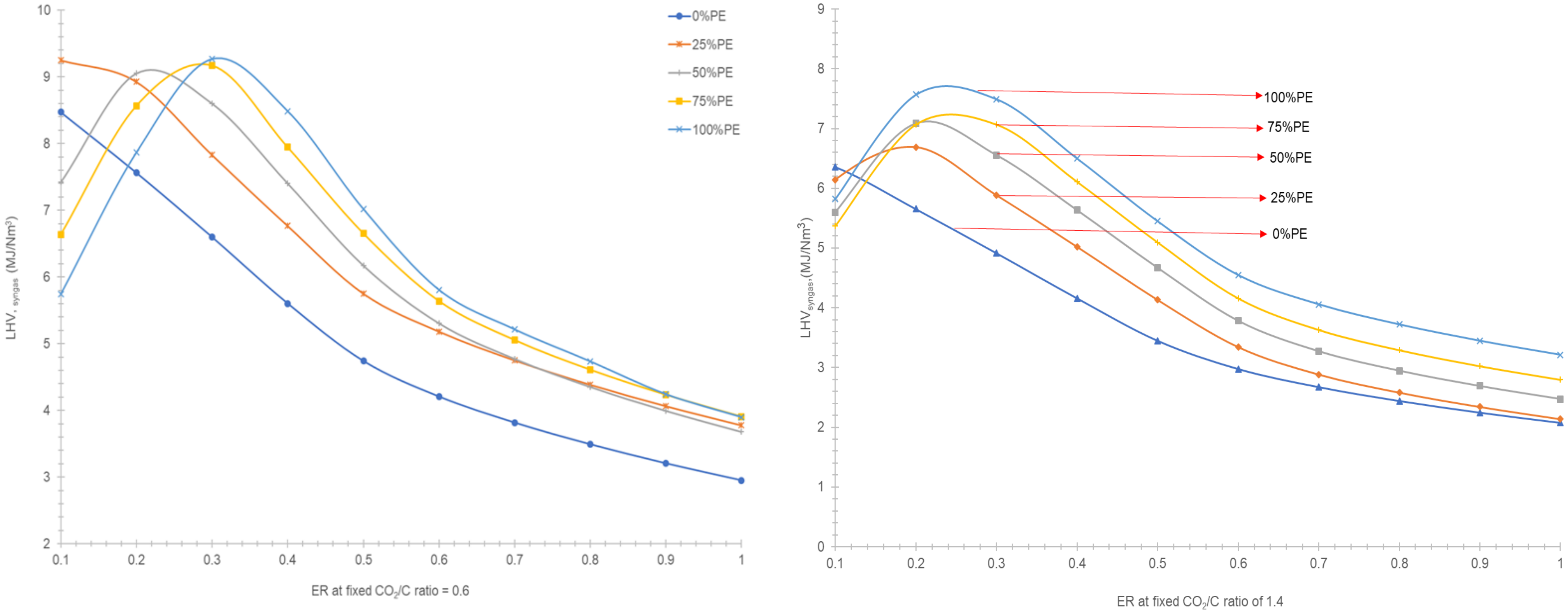
biomass) and biomass the Lower Heating Values (LHV) of the syngas decreases as ER increases. However, the lower heating values for the feedstocks which contains high percentage of polyethylene initially increases and reaches a peak point, thereafter, decreases as ER increases further.

In Figure 4.3.13 (b) the same trend is observed for all the different feedstocks except for LHV of the biomass feedstock, which decreases as ER increases. From Figure 4.3.13 (a) and (b) it is observed that the increase in the percentage of polyethylene in the feedstock mixtures increase the lower heating value of the syngas. This is due to the H_2 and CH_4 produced from the decomposition of the polyethylene material, which results in an increase in combustion gas, which lead to an increased LHV (Baloch et al. (2016).

Figure 4.3.13 (a) and (b) shows that the high values of the LHV of the syngas are favoured at low ER below 0.4. At higher ER values above 0.4, the lower heating value of the syngas decreases. The high lower heating value of the syngas at low ER for all the feedstocks, when an oxygen – carbon dioxide mixture is used as a gasifying agent, is attributed to the chemical reactions such Boudouard reaction (R2), partial oxidation reaction (R4), reverse water gas reaction (R9), reverse methanation CO_2 reforming reaction (R10) and methanation reaction (R13). Then, the chemical reactions responsible for the decrease of the lower heating value of the syngas at higher ER values are, the oxidation reactions such as (R5) to (R8), which oxidizes the CO and H_2 into H_2O and CO_2.

Figure 4.3.13 (a) and (b) shows that the highest lower heating value is produced from the blended feedstocks and polyethylene. As a result, from a blend ratio of (25% PE + 75% biomass) a high LHV of the syngas of 9.2 MJ/Nm^3 is attained at ER equals to 0.1 and CO_2/C ratio equal to 0.6. From a blend ratio of (50% PE + 50% biomass) a maximum LHV of 9.18 MJ/Nm^3 is attained from ER equals to 0.22 and CO_2/C ratio equals to 0.6 and from a blend ratio of (75% PE + 25% biomass) a maximum LHV of 9.19 MJ/Nm^3 is achieved at ER equals to 0.28 and CO_2/C ratio equals to 0.6.

The high LHV of the syngas attained from the blended feedstocks for the co- gasification of biomass and polyethylene, shows that there is synergistic effect between biomass and polyethylene feedstocks, when oxygen – carbon dioxide mixture as a gasifying agent is used and when carbon dioxide is added at low flowrate through CO_2/C ratio equals to 0.6.



(a) (b)

Figure 4.3.13. Effect of the equivalence ratio (ER) (oxygen is used as a gasifying agent) on the Lower Heating Value (LHV) of the syngas when carbon dioxide flowrate is varied (a) CO_2/C ratio equals to 0.6 and (b) CO_2/C ratio equals to 1.4.

Figure 4.3.13 (b) shows the that the addition of carbon dioxide at high flowrate decreases the LHV of the syngas, for all the feedstocks, when compared with the LHV attained at low carbon dioxide flowrate (CO_2/C ratio equal to 0.6) from Figure 4.3.13 (a) at all ER values. Figure 4.3.13 (b) shows that the highest LHV of the syngas is attained from the individual feedstock (polyethylene) instead of the individual feedstocks. This implies that the use of high flowrate of carbon dioxide does not promote synergy between biomass and polyethylene during the co- gasification process.

The general observation from Figure 4.3.11 to 4.3.13 shows that the oxygen as a gasifying agent provides a higher the Lower Heating Value (LHV) than the oxygen – steam and oxygen and carbon dioxide mixtures as a gasifying agent and the synergistic effect between biomass and polyethylene is attained only when oxygen – carbon dioxide mixture is used as a gasifying agent, through CO_2/C ratio equals to 0.6.

Table 4.3.5 shows different gasifying agents and operating conditions at which the maximum Lower Heating Value (LHV) of the syngas can be achieved, for the various blend ratios during the co- gasification of biomass and polyethylene. Table 4.3.5 depicts that the oxygen – carbon dioxide mixture as gasifying agent produces high LHV of the syngas, as compared to the other gasifying agents used on the blended fuels. It is also indicated from Table 4.3.5 that the high LHV can be attained at all ER values and low steam (SFR equals to 0.6) and carbon dioxide (CO_2/C ratio equals to 0.6) flowrates.

Table 4.3.5. Recommended operating conditions and gasifying agents for the co- gasification of biomass and polyethylene on the LHV of the syngas.

Lower heating value (LHV) of the syngas (MJ/Nm^3)				
Gasifying agent:	**oxygen**			
Blend ratio (BR)	**Recommended Value**	**ER**	**SBR**	**CO_2/C ratio**
25% PE + 75% BM		-	-	-
50% PE + 50% BM	-	-	-	-
75% PE + 25%BM	-	-	-	-
Gasifying agent:	**oxygen – steam mixture**			
25% PE + 75% BM	-	-	-	-
50% PE + 50% BM	9.6	0.22	0.6	-
75% PE + 25%BM	10.7	0.2	0.6	-
Gasifying agent:	**oxygen – carbon dioxide mixture**			
25% PE + 75% BM	9.2	0.1	-	0.6
50% PE + 50% BM	9.18	0.22	-	0.6
75% PE + 25%BM	9.19	0.28	-	0.6

*** BM – stand for biomass**

*** PE – stand for polyethylene**

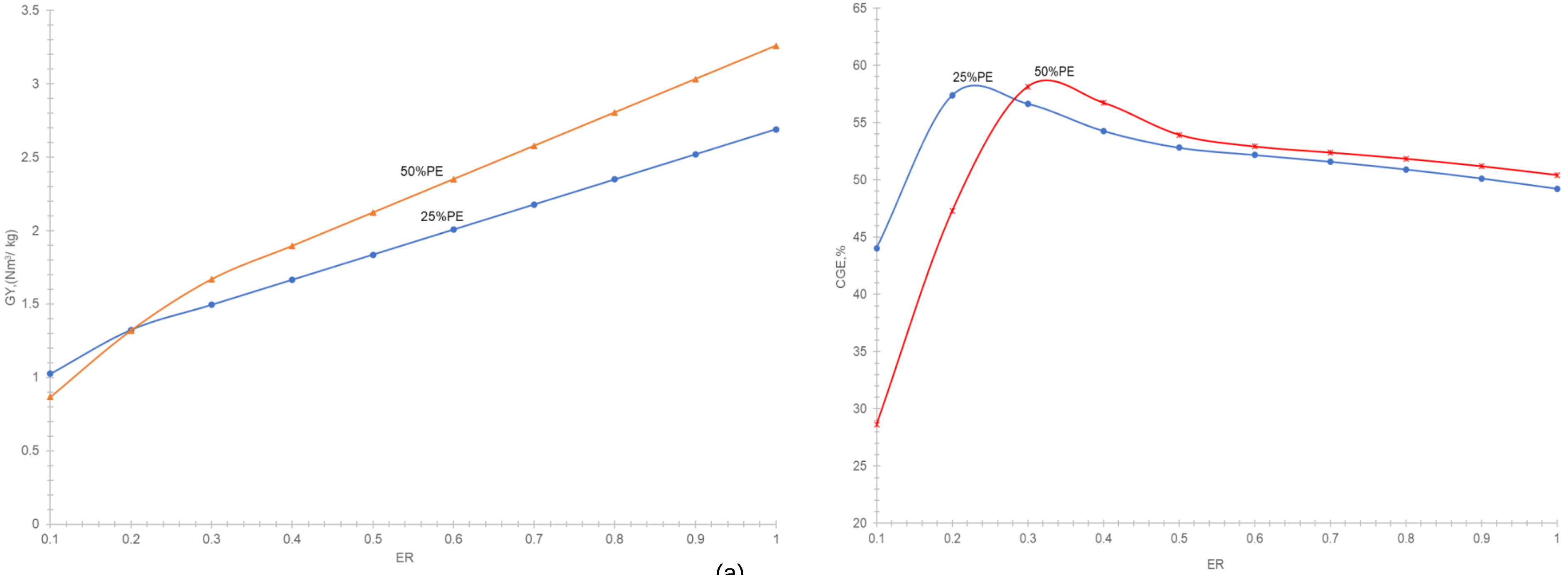
4.3.13. Effect of the equivalence ratio (ER) on the gas yield (GY) and cold gas efficiency (CGE) when oxygen is used as a gasifying agent.

This section discusses the gasifier performance indices such as the gas yield and the cold gas efficiency for the co- gasification of biomass and plastic waste in the presence of both single gasifying agent (oxygen) and combined gasifying agents (oxygen and steam mixture).

Figure 4.3.14 (a) shows the effect of the equivalence ratio (ER) on the gas yield (GY) at blend ratios of (25% PE + 75% biomass) and (50% PE + 50% biomass). It is observed that an increase in the ER increases the gas yield. The relationship between the equivalence ratio (ER) and the gas yield is positive. This can be attributed to the increase in the temperature in the gasifier. The temperature rise due to the increase in ER causes the char and volatiles produced from the feedstock during the devolatilization to react in the cracking, reforming of hydrocarbons and endothermic char gasification reactions thus resulting in an enhanced syngas production.

The reactions that are responsible for the increase in the gas yield during the co- gasification of biomass and plastic waste, when oxygen is used as a gasifying agent are the partial oxidation reaction, (R4) and partial methanation reaction (R13).

Figure 4.3.14 (a) shows that higher syngas yields from the blend ratio of (50% PE + 50% biomass) were obtained at different values of ER within the range between (0.2 – 1) in comparison with the syngas yields attained from the blend ratio of (25% PE + 75% biomass). The maximum yield from the blend ratio of (50% PE + 50% biomass) was found to be 3.2 Nm^3/ kg at ER equals to 1. Whereas, for the blend ratio of (25% PE + 75% biomass) a maximum syngas yield attained is 2.6 Nm^3/kg at ER equals to 1. This implies that when oxygen is used as a gasifying agent, the addition of plastic waste increases the syngas production. Furthermore, this can be attributed to the polymeric nature of plastic, which consists of high volatile matter, low fixed carbon content and low oxygen content, which during the co-gasification process results in high production of the combustible gases such as H_2, CO and CH_4, which subsequently increases the syngas yield.



(a)

(b)

Figure 4.3.14 Effect of the equivalence ratio (ER) on (a) gas yield (GY) and (b) cold gas efficiency (CGE) when oxygen is used a gasifying agent for the co- gasification of biomass and plastic waste.

Figure 4.3.14 (b) shows the effect of the equivalence ratio (ER) on the cold gas efficiency (CGE), when oxygen is used a gasifying agents, at blend ratios ratio of (25% PE + 75% biomass) and (50% PE + 50% biomass). Figure 4.3.14 (b) depicts that at lower ER values within the range of 0.1 – 0.5, an increase in ER causes the cold gas efficiency to increase. However, above ER of 0.5 the cold gas efficiency slightly decreased. This indicates that higher ER values has a negative effect on the cold gas efficiency.

This trend can be explained in that at low ER values, using oxygen as a gasifying agent, as the temperature in the gasifier increases, thus the partial oxidation reactions such as partial oxidation reaction, (R5) and partial methanation reaction (R13) are favoured, which tends to increase the composition of the combustible gases such as H_2, CO and CH_4 as well as the Lower Heating Value (LHV) of the syngas.

Figure 4.3.14 (b) indicates that the maximum cold gas efficiency of 59% was attained at ER equals to 0.32 from a blend ratio of (50% PE + 50% biomass) and from the blend ratio of (25% PE + 75% biomass) a maximum cold gas efficiency of 58% was obtained at ER equals to 0.22. This exhibits that an additional percentage of the plastic waste in the feedstock mixture slightly increases the cold gas efficiency of the system.

4.3.14. Effect of the equivalence ratio (ER) on the Gas yield (GY) and Cold gas efficiency (CGE) when oxygen- steam mixture is used as a gasifying agent.

Figure 4.3.15 (a) shows the effect of the equivalence ratio (ER) on the gas yield (GY) and cold gas efficiency (CGE) when oxygen-steam mixture (SFR =0.6) is used as a gasifying agent for the co-gasification of biomass and plastic waste. Figure 4.3.15 (a) exhibits that as ER increases from 0.1 – 1, the gas yield (GY) for the different blend ratios such as (25% PE + 75% biomass) and, (50% PE + 50% biomass) increases. The addition of steam at fixed SFR of 0.6 activates chemical reactions such as the partial methanation reaction (R13) and steam related reactions such as the steam reaction (R13), steam methane reforming reaction (R12) to produce more combustible gases, which subsequently increases the syngas production.

Figure 4.3.15 (a) shows that an increase in the plastic waste of the feedstock mixture has a positive influence on the production of syngas. Higher syngas yields were obtained from the blend ratio of (50% PE + 50% biomass) throughout the range of ER values as compared to the syngas yield obtained from the blend ratio of (25% PE + 75% biomass).

Figure 4.3.15 (b) shows the effect of the equivalence ratio (ER) at fixed SFR of 0.6 on the cold gas efficiency (CGE), when an oxygen- steam mixture is used as a gasifying agent for the co-gasification of biomass and plastic waste. Figure 4.3.15 (b) shows that for feedstock that contains a high percentage of the plastic waste in their mixture, such as the blend ratios of (50% PE + 50% biomass) the cold gas efficiency (CGE) increased as ER increased and reached a peak value of 61% at ER equal to 0.24 a (SFR fixed at 0.6) and thereafter decreased with an increasing ER. Whereas a blend ratio of (25% PE + 75% biomass) decreased with an increasing ER.

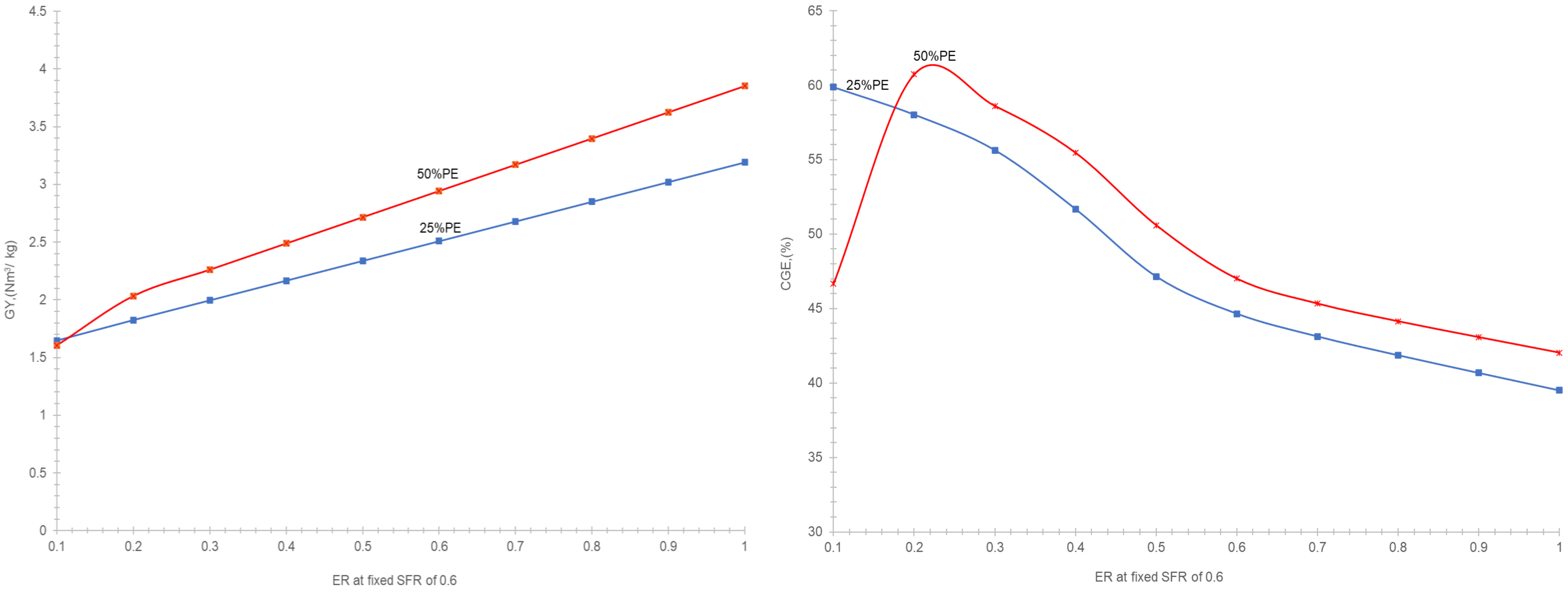
The reason this trend could be that at low ER values and fixed SFR of 0.6, there is a high production of the combustible gases such as H_2, CO and CH_4, which increases the Lower Heating Value of the syngas. The production of these combustible gases is enhanced by the activation of both the partial oxidation reaction (R4), and steam related reactions such as the steam reaction (R2), steam methane reforming reaction (R12) and partial methanation reaction (R13). Furthermore, the reason a higher cold gas efficiency has been observed at blend ratio of (50% PE + 50% biomass) instead of a blend ratio of (25% PE + 75% biomass) can be attributed to the plastic percentage in the feedstock mixture which increases the hydrogen composition in the product gas, due to its high volatile matter and no oxygen content. Thus, resulting in a high Lower Heating Value (LHV) of the syngas, which subsequently increases the cold gas efficiency (CGE).

At ER values above 0.3, the cold gas efficiency decreases since the temperature in the gasifier increases, and the oxidation reactions such as (R5) to (R8) are favoured which tend to oxidize H_2 ad CO into H_2O and CO_2 products. Therefore, resulting in a decrease in the heating value of the syngas, which negatively affects the cold gas efficiency (CGE) of the system.

A comparison of the use of oxygen and oxygen- steam mixture as a gasifying agent in Figure 4.3.14(b) and 4.3.15 (b), shows that the addition of steam at fixed SFR of 0.6, produced a maximum cold gas efficiency (CGE) of 61% for the blend ratio of (50% PE + 50% biomass) which is higher than that obtained when only oxygen was utilized as gasifying agent at which a cold gas efficiency (CGE) of 59% at ER equals to 0.32 for the same blend ratio of (50%PE + 50% biomass). A similar effect is observed even from the blend ratios with lower plastic waste percentage in the feedstock mixture such as the (25% PE + 75% biomass),

At which when oxygen - steam mixture was used as a gasifying agent a maximum cold gas efficiency (CGE) of 60% at ER equals to 0.1 and SFR of 0.6 was found, higher than that of

58% at ER equals to 0.22, obtained from the same blend ratio of (25% PE + 75% biomass) as well. Therefore, this implies that the use of oxygen-steam mixture as a gasifying agent increases the cold gas efficiency of the system for the co- gasification of biomass and plastic waste.



(a)

(b)

Figure 4.3.15 Effect of the equivalence ratio (ER) on (a) gas yield (GY) and (b) Cold gas efficiency (CGE) when oxygen – steam mixture (SFR=0.6) is used a gasifying agent for the co- gasification of biomass and plastic waste.

4.3.15. Quantitative synergistic effect analysis

Table 4.3.6 shows the components used to determine the extent of the synergistic effect, represented by ∆Y in equation 3.3, which is the difference between the model results and average of individual feedstocks results in terms of syngas yields for the blend ratio of (50% PE + 50% biomass). Equation 3.2 is used to calculate the average weighted syngas yields from the individual feedstocks. A positive ∆Y indicates that the synergistic effects between biomass and plastic waste and a negative ∆Y shows that there are antagonistic effects between biomass and plastic waste.

It is observed in Table 4.3.6 that varying the ER value affects the extent of the synergistic effect, for oxygen and oxygen – steam mixture as gasifying agents. It is observed that the maximum extent of the synergistic effect between biomass and plastic waste, indicated by syngas yield happens on ER equals 0.2. It is observed that the use of steam-oxygen mixture produces higher extent of synergistic effect of 7.4% as compared to when oxygen is used as a gasifying agent, with 6.5%.

However, as ER increases further, no synergy is observed. This trend is similar in both cases, when oxygen and oxygen-steam mixture are used as gasifying agents.

Table 4.3.6 Effect of equivalence ratio (ER) on the synergistic effect for the gas yield for the co-gasification of biomass and polyethylene at blend ratio of (50%PE + 50% biomass).

Oxygen used as a gasifying agent.					Oxygen-steam mixture as a gasifying agent			
ER	GY (50%PE)	GY, BM	GY, (PE)	∆Y (%)	GY (50%PE)	GY, BM	GY, (PE)	∆Y (%)
0.1	0.867	1.092	0.715	-4.052	1.606	1.502	1.716	-0.175
0.2	1.669	1.206	1.272	6.529	2.033	1.616	2.172	7.353
0.3	1.896	1.320	1.927	2.809	2.260	1.730	2.791	-0.008
0.4	1.896	1.434	2.358	-0.008	2.488	1.844	3.131	-0.006
0.5	2.124	1.549	2.699	-0.008	2.715	1.959	3.471	-0.006
0.6	2.351	1.663	3.039	-0.007	2.942	2.073	3.812	-0.005
0.7	2.578	1.777	3.379	-0.006	3.169	2.187	4.152	-0.005
0.8	2.805	1.892	3.719	-0.006	3.397	2.301	4.492	-0.005

0.9	3.032	2.006	4.059	-0.005	3.624	2.416	4.832	-0.004
1.0	3.260	2.120	4.399	-0.005	3.851	2.530	5.172	-0.004

*** BM – stand for biomass**

*** PE – stand for polyethylene**

***GY – stand for syngas yield**

REFERENCES

Al Amoodi. N, Kannan. P, Al. Shoaibi. A, Srinivasakannan. C, (2013), Aspen Plus Simulation Plus of Polyethylene Gasification Under Equilibrium Conditions, *Chemical Engineering Communications*, 200, 7, 977–992

Arena. U, Zaccariello. L, Mastellone. M. L, (2009) Tar Removal During the Fluidized Bed Gasification of Plastic Waste, *Waste Management*, 29,783 – 791.

Baloch. H. A, Yang. T, Li. R, Nizamuddin. S, Kai. X, Bhutto. A. W, (2016), Parametric Study of Co- gasification of Tenary Bends of Rice Straw, Polyethylene and Polyvinylchloride, *Clean Technology Environmental Policy*, 18, 1031 – 1042.

Barontini. F, Frigo. S, Gabrielli. R, Sica. P, (2021), Co-gasification of Woody Biomass with Organic and Waste Matrices in a Down-draft Gasifier: An Experimental and Modeling Approach, Energy Conversion and Management, 245, 114566.

Du. Y, Yang. Q, Berrouk. A.S, Yang .C, Al Shoaibi. A.S, (2014), Equivalent Reactor Network Model for Simulating the Air Gasification of Polyethylene in a Conical Spouted Bed Gasifier, *Energy Fuels*, 28, 6830 – 6840.

Deparrois. N, Singh. P, Burra. K.G, Gupta. A.K, (2019), Syngas Production from Co- pyrolysis and Co-gasification of Polyethylene and Paper with CO_2, *Applied Energy*, 246,1-10.

Erkiaga. A, Lopez. G, Amutio. M, Bilbao. J, Olazar. M, (2013), Syngas from Steam Gasification of Polyethylene in a Conical Spouted Bed Reactor, *Fuel*, 109, 461 – 469.

Franco .C, Pinto. F, Gulyurthu. I, Cabrita. I, (2003), The Study of Reactions Influencing the Biomass Steam Gasification Process, *Fuel*, 82, 835 – 842.

Islam. M.W, (2020), Effect of Different Gasifying Agents (Steam, H_2O_2, Oxygen, CO_2 and Air) on Gasifying Parameter, *International Journal of Hydrogen Energy*, 45, 31760 – 31774.

Li. J, Burra. K.R.G, Wang. Z.W, Liu. X, Gupta. A.K, (2021), Co- gasification of High Density Polyethylene and Pre-treated Pine Wood*, Applied Energy*, 285,116472.

Park. J.H, Park. H, Choi. S, Park. D, (2016), Effects of Blend Ratio between High Density Polyethylene and Biomass on Co- gasification Behaviour in a Two- Stage Gasification System. *International Journal of Hydrogen Energy*, 41,16813 – 16822.

Rosha. P, Kumar. S, Vikram. S, Ibrahim. H, Al-Muhtaseb. A. H, (2021), H_2 – enriched Gaseous Fuel Production via Co-gasification of an Algae-Plastic Waste Mixture using Aspen Plus, International Journal of Hydrogen Energy, 1-9.

Tavares. R, Monteiro. E, Tabet. F, Rouboa. A, (2020), Numerical Investigation of Optimum Operating Conditions for Syngas and Hydrogen Production for Biomass Gasification using Aspen Plus, *Renewable Energy*, 146, 1309 – 1314.

Tavares. R, Ramos. A, Rouboa. A, (2018), Microplastics Thermal Treatment by Polyethylene Terephthalate Biomass Gasification, *Energy Conversion and Management*,162,118 – 131.

Xiao. R, Jin. B, Zhou. H, Zhang. Z, Zhang. M, (2007), Air – gasification of Polypropylene Plastic Waste in Fluidized Bed Gasifier, *Energy Conversion and Management*, 48, 778 -786

Zheng. J, Zhu. M, Wen. J, Sun. R, (2016), Gasification of Bio – Oil: Effects of Equivalence Ratio and Gasifying Agent on Product Distribution and Gasification Efficiency, *Bioresource Technology*, 211,164 – 172.

Chapter 5: Conclusion

This chapter of the study summarizes the main findings of the research work, examines whether the main objectives of the dissertation have been met, and provides conclusions and recommendations based on the findings.

5.1. Summary of findings

- **Biomass and polyethylene (as individual feedstocks) on product gas composition**

There was no significant difference in the H_2 composition from single and mixed gasifying agents during the individual gasification of biomass and polyethylene. The use of oxygen and oxygen – steam have shown to be the suitable gasifying agents that can be used to produce a high H_2 composition in the product gas for both during biomass and polyethylene individual gasification. During the biomass gasification a high H_2 content of 44% at ER equals to 0.05 for oxygen use and 44% was attained at ER equals to 0.05 and SBR equals to 0.6 during the use of oxygen – steam mixture as a gasifying agent. Steam also appears to be a suitable gasifying agent for biomass gasification as a H_2 composition of 46% was achieved at SBR equals to 0.1. For polyethylene gasification a H_2 of 58.02% was attained at ER equals to 0.24 when oxygen was used as a gasifying agent and when oxygen – steam was used as a gasifying agent mixture a high H_2 composition of 57.8% was achieved at ER equals to 0.3 and SPR equals to 0.6.

The use of oxygen and steam as a gasifying agent for biomass gasification has shown a positive effect since a high CO composition of 56.1% at ER equals to 0.1 and 52.0% was achieved at SBR equals to 0.1. For polyethylene gasification a high CO composition of 45.0% was achieved at ER equals to 0.31 from the use of oxygen as a gasifying agent and also a high CO composition of 51.0% was achieved at ER equals to 0.36 and CO_2/C ratio of 0.6 when oxygen – carbon dioxide mixture was used as a gasifying agent. The use of oxygen – carbon dioxide mixture as a gasifying agent during the polyethylene has shown that mixing gasifying agents had a positive effect since it enhances CO composition in the product gas.

During the use of various gasifying agents, a high H_2 and CO composition were found at ER below 0.3 for biomass gasification and low ER values below 0.4 for polyethylene gasification. Low SBR of 0.6 and low SPR of 0.6 provided high H_2 and CO composition, as well as low CO_2/C ratio of 0.6 produced high H_2 and CO, for both when biomass and polyethylene were gasified individually. The increase in ER values above 0.4, SPR above 0.6, SBR above 0.6 and CO_2/C ratio above 0.6, reduces the H_2 and CO composition in the product gas (for biomass and polyethylene individual gasification).

- **Biomass and polyethylene (as individual feedstocks) on H_2/CO ratio of the syngas**

The use of oxygen – steam mixture as a gasifying agent, has shown to be the most suitable gasifying agent mixture that can be used for both biomass gasification and polyethylene gasification, since the recommended H_2/CO ratio of 2 was attained at both low and high ER values and both high and low SBR and SPR values. Steam as a gasifying agent, has shown positive results as the recommended H_2/CO ratio of 2 was attained, for both biomass and polyethylene gasification.

The biomass gasification results have shown that the use of oxygen and air-carbon dioxide and oxygen – carbon dioxide mixtures as gasifying agents, are not suitable for producing quality syngas, since the recommended H_2/CO ratio of 2 was not achieved. For polyethylene gasification the recommended H_2/CO ratio of 2 was obtained from the use of single and mixed gasifying agent (such as air, steam, oxygen, oxygen- steam, oxygen – carbon dioxide, air-carbon dioxide, and air- steam mixtures). Suitable operating conditions at which the recommended H_2/CO ratio of the syngas was attained was found to be ER values below 0.4, low CO_2/C ratio of 0.6 and low ER values below 0.4.

- **Biomass and polyethylene (as individual feedstocks) on Lower Heating Value (LHV) of the syngas**

High Lower Heating Values (LHV) of syngas from the use of various gasifying agents is favoured at low ER values below 0.3 and at low SBR of 0.6. Oxygen provides higher Lower Heating Value (LHV) of syngas as compared to air and its relative gasifying agent mixtures. This can be attributed to the nitrogen dilution in the air.

For polyethylene gasification, high Lower Heating Values (LHV) of the syngas were favoured from both the use single and mixed gasifying agents such as oxygen, steam and oxygen –

steam mixture. For instance, a Lower Heating Value (LHV) of 15.4 MJ/Nm^3 was found at ER equals to 0.1 in the presence of oxygen as a gasifying agent, and from the use of oxygen – steam mixture as a gasifying agent a Lower Heating Value (LHV) of syngas of 13.5 MJ/Nm^3 was attained at ER equals to 0.1 and SPR equals to 0.6. During the use of steam as a gasifying agent at fixed ER equals to 0.2 a high lower heating value of 13.2 MJ/Nm^3 was found at ER equals to 0.2 and SPR equals to 0.9.

Whereas for biomass gasification, a high Lower Heating Values (LHV) of syngas was favoured when there was no mixing of gasifying agents, the mixtures of gasifying agent are not suitable in biomass gasification as they produce syngas with low Lower Heating Value (LHV) of syngas. The Lower Heating Value (LHV) of the syngas of 11.8 MJ/Nm^3 at ER equals to 0.04 was obtained from the use of oxygen, Lower Heating Value (LHV) of 11.2 MJ/Nm^3 at SBR equals to 0.1 was obtained from the use of steam and a Lower Heating Value (LHV) of the syngas 11.0 MJ/Nm^3 was achieved at ER equals to 0.04 from the use of air as a gasifying agent.

In general, for biomass gasification, the use of the mixed gasifying agents did not show improved Lower Heating Values (LHV) of the syngas as compared to that attained from a single gasifying agent. Whereas, in the polyethylene gasification, the use of mixed gasifying agent has shown improved lower heating value as compared to that attained from the use of single gasifying agent.

- **Co- gasification of biomass and polyethylene on the product gas composition**

The increase in the polyethylene percentage in the blends, increased the H_2 composition in the product gas, however, it decreased the CO composition in the product gas. This can be attributed to the low fixed carbon of polyethylene materials and that it has no oxygen content. Furthermore, high H_2 composition was found from the blend ratio that contained high polyethylene percentage such as (75% PE + 25% biomass) and the high CO composition was found from the blend ratio of (25% PE + 75% biomass).

For the co- gasification of biomass and polyethylene, the use of both single and mixed gasifying agents such as oxygen and oxygen – steam mixtures as gasifying agents have a positive effect on the H_2 composition in the product gas, since a high H_2 composition was obtained from the blend ratios and not from the individual feedstocks. For instance, the use of oxygen – steam mixture as gasifying agents results in a high H_2 composition of 46.0% at ER equals to 0.1 and SFR equals to 0.6 was found from the blend ratios of (25% PE + 75% biomass), from a blend ratio of (50% PE + 50% biomass) a high H_2 composition of 49.0% was found at ER equals to 0.16 and SFR equals to 0.6 and from a blend ratio of (75% PE + 25% biomass) a high H_2 composition of 54.5% at achieved at ER equals to 0.34 and SFR equals to 0.6). When oxygen was used as a gasifying agent, a H_2 composition of 51.5% at ER equals to 0.1 was achieved from a blend ratio of (25% PE + 75% biomass), from a blend ratio of (50% PE + 50% biomass) a high H_2 composition of 54.0% was achieved at ER equals to 0.1 and from a blend ratio of (75% PE + 25% biomass) a high H_2 composition of 56.0% was obtained at ER equals to 0.1.

However, a high CO from the blended feedstocks was attained from both the use of single and mixed gasifying agents such as from oxygen and oxygen – carbon dioxide mixtures. The results have shown that during the use of oxygen as a gasifying agent the high CO composition of 54.2% at ER equals to 0.22 was found from the blend ratios of (25% PE + 75% biomass), from the blend ratio of (50% PE + 50% biomass) a high CO composition of 51.8% was achieved at ER equals to 0.32 and a high CO composition of 51.8% was achieved at ER equals to 0.32. from a blend ratio of (75% PE + 25% biomass).

During the use of oxygen – carbon dioxide mixtures as a gasifying agent a high CO composition of 52.0% was found at ER equals to 0.22 and CO_2/C ratio of 0.6, from the blend ratios of (50% PE + 50% biomass) and (75% PE + 25% biomass) a high CO composition of 50% was achieved at ER equals to 0.28 and CO_2/C ratio of 0.6.

The use of steam – oxygen mixtures as gasifying agent was found not to be suitable for obtaining a high CO composition for the co- gasification of biomass and polyethylene, since a high CO composition were not obtained from the blended feedstock, rather obtained from individual feedstocks.

The high H_2 and CO composition obtained from the blended feedstocks instead of the individual feedstocks have indicated that there is synergistic interaction between biomass and polyethylene feedstock during their gasification. Therefore, suitable operating conditions in addition to the use of a mixture of gasifying agents for high H_2 and CO composition were found to be ER values lower than 0.4 and low SFR values of 0.6 and low CO_2/C ratio of 0.6. The overall results have shown that the use of both single and mixed gasifying agents, have a positive effect on the product gas composition since a high H_2 and CO composition in the product gas were obtained and enhanced the synergistic effect between biomass and polyethylene feedstocks.

- **Co- gasification of biomass and polyethylene on the H_2/CO ratio of the syngas**

The use of both single and mixed gasifying agents such as oxygen and oxygen – steam mixtures have shown positive influence on the syngas quality as the recommended H_2/CO ratio of 2 was found from blended feedstocks from the blend ratios of (25% PE + 75% biomass), (50% PE + 50% biomass) and (75% PE + 25% biomass) instead of from the individual feedstocks.

The use oxygen – steam mixtures enabled the recommended H_2/CO ratio of 2 to be found both at low ER values below 0.4 and at high ER values above 0.4, at low SFR values of 0.6 and at high SFR values of 4. Whereas, with the use of oxygen the recommended H_2/CO ratio of the syngas was limited to lower ER values below 0.4 and low SFR values of 0.6.

- **Co- gasification of biomass and polyethylene on the Lower Heating Value (LHV) of the syngas**

The use of mixed gasifying agents such as oxygen – steam and oxygen – carbon dioxide mixtures have shown a positive effect on the Lower Heating Values (LHV) of the syngas, during the co- gasification of biomass and polyethylene. Higher Lower Heating Values (LHV) of syngas were found from the blended feedstocks instead of individual feedstocks. The use of oxygen – steam mixtures a high Lower Heating Value (LHV) of 9.6 MJ/Nm^3 was found at ER equals to 0.22 and SFR equals to 0.6 from the blend ratio of (50% PE + 50% biomass), a Lower Heating Value (LHV) of the syngas of 10.7 MJ/Nm^3 was achieved at ER equals to 0.2 and SFR equals to 0.6 from a blend ratio of (75% PE + 25% biomass).

During the use of oxygen – carbon dioxide mixtures as a gasifying agent, a Lower Heating Value (LHV) of the syngas of 9.2 MJ/Nm^3 was found at ER equals to 0.1 and CO_2/C ratio of 0.6, from a blend ratio of (50% PE + 50% biomass) a high Lower Heating Value (LHV) of the syngas of 9.18 MJ/Nm^3 was found at ER equals to 0.22 and CO_2/C ratio of 0.6 and from a blend ratio of (75% PE + 25% biomass) a Lower Heating Value (LHV) of the syngas of 9.19 MJ/Nm^3 was found at ER equals to 0.28 and CO_2/C ratio of 0.6. A high lower heating values (LHV) of syngas from the use of oxygen – steam and oxygen – carbon dioxide mixtures as gasifying agents was found at operating conditions such as low ER below 0.3 and low SFR of 0.6 and low CO_2/C ratio of 0.6.

The co- gasification of biomass and polyethylene on the Lower Heating Value (LHV) of the syngas has shown that an increase in the polyethylene in the blends enhanced the Lower Heating Value (LHV) of the syngas. The use of these operating conditions and in addition to the mixtures of gasifying agents have shown a positive effect on the Lower Heating Value (LHV) of the syngas and enhanced synergistic interaction between biomass and polyethylene material.

The positive outcome from the co- gasification of biomass and polyethylene will alleviate the challenges associated with the production of the syngas with low quality (with the H_2/CO ratio below the value of 2, syngas with low Lower Heating Value (LHV) of the syngas from biomass gasification.

- **Co- gasification of biomass and polyethylene on the gas yield (GY) and cold gas efficiency (CGE) and the extent of the synergistic effect.**

An increase in the equivalence ratio (ER) during the co- gasification of biomass and plastic waste, positively affect the gas production, since as ER increases the gas yield increases as well. The addition of plastic waste in the feedstock mixture also increases the gas yield (GY), irrespective of the values of ER used. In terms of the cold gas efficiency (CGE), the results indicates that at low ER values below 0.5, the cold gas efficiency is higher than at high ER values. Furthermore, the results indicates that the use of oxygen-steam mixture as gasifying agent produces high gas yield (GY) and high cold gas efficiency (CGE) as compared to only when oxygen is used as a gasifying agent, as well as the extent of the synergistic effect.

5.2. Recommendations

The following recommendations are made based on the finding of the co- gasification of the biomass and polyethylene feedstock:

Future studies on the co- gasification of biomass and polyethylene, should consider other forms of plastic wastes such as polyethylene terephthalate (PET), high density polyethylene (HDPE),polypropylene (PP) as a feedstock and other types of biomass such as agricultural waste, wood residues and solid waste as a feedstock, with the aim of determining the effect of mixing various plastic waste and biomass on the product gas composition, syngas quality and on the lower heating value of the syngas.

It would also be recommended that a parametric study be conducted using a kinetic model in Aspen Plus for a co- gasification of biomass and polyethylene, with the aim of improving the accuracy of the gasifier model by considering the geometry of the reactor and considering the kinetic expression for the various reactions involved. Such a model will allow the product gas composition to be determined along the length of the reactor and not only at the exit of the gasifier as with the equilibrium models.

It is recommended that the findings in this study can further be explored by conducting an experimental study evaluating the performance of different types of gasifiers such as fluidized bed gasifier, fixed bed gasifier or an entrained flow reactor. Furthermore, the addition of a catalyst such as Ni- Al should be considered. The effect of co- gasification of biomass and polyethylene on the product gas composition, syngas quality and on its Lower Heating Value (LHV) of the syngas can be experimentally evaluated.

APPENDICES

APPENDIX A

Biomass gasification

This appendix is divided into two sections, the section at which air and its relative mixtures such as air- steam and air- carbon dioxide mixtures are used as gasifying agent. The second section is for the use of oxygen and its relative mixtures as gasifying agents such as oxygen – steam mixture and oxygen – carbon dioxide mixtures as gasifying agent.

- **Effect of the equivalence ratio (ER) on the product gas composition when air is used as a gasifying agent.**

Figure A.1 shows the effect of equivalence ratio on the product gas composition, when air was used as a gasifying agent during the biomass gasification. The increase of the ER caused temperature to increase. The H_2 and CO composition decreased as ER increased. CO composition is higher than H_2 in the product gas. H_2O, N_2 and CO_2 increased with an increasing ER.

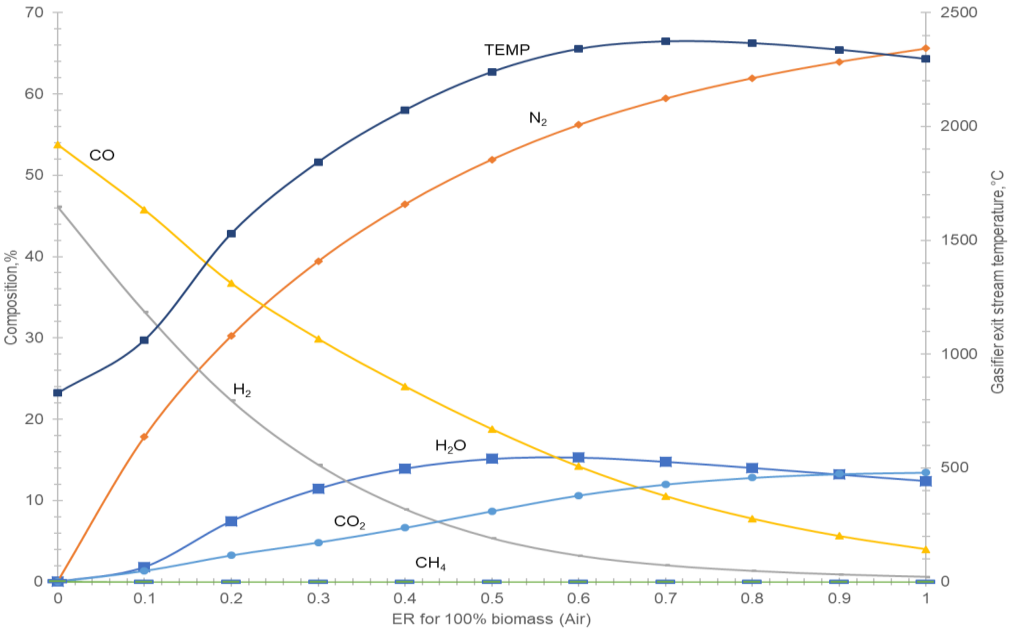
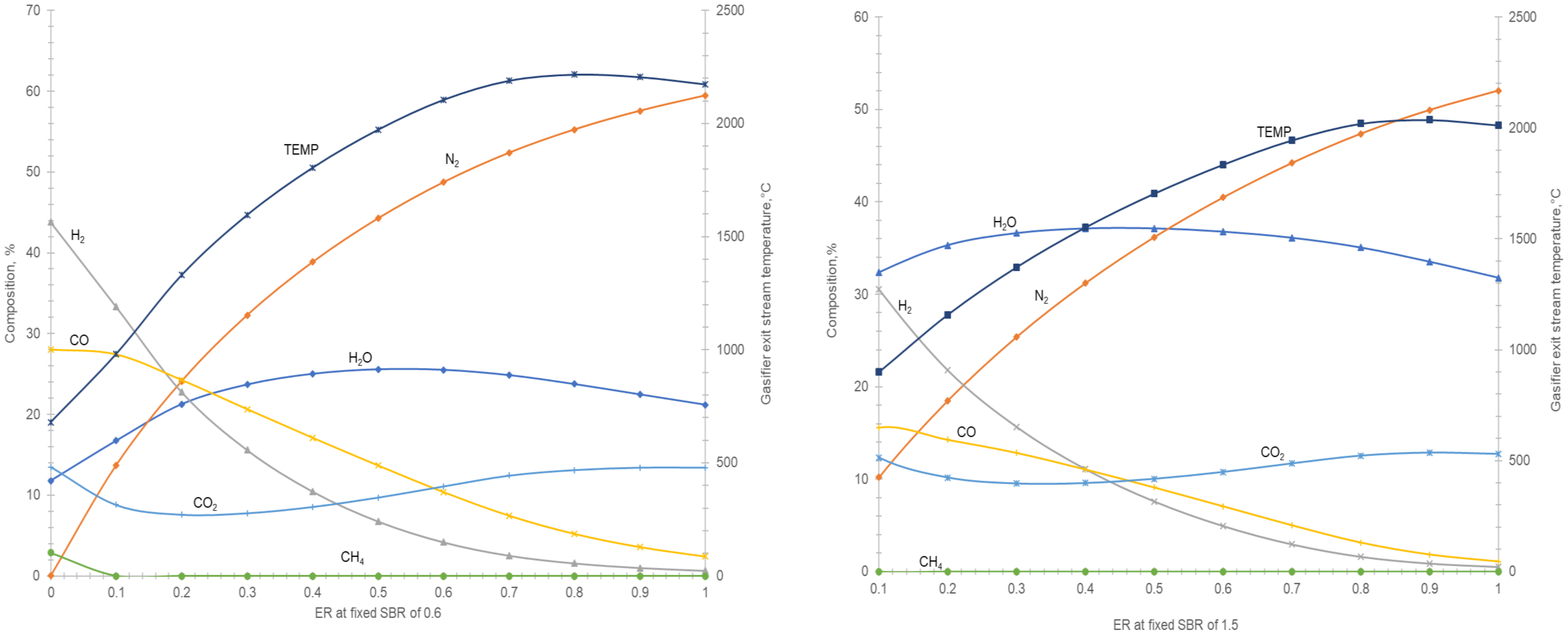


Figure A.1. Effect of the equivalence ratio on the product gas composition when air is used as a gasifying agent during biomass gasification.

- **Effect of the equivalence ratio (ER) at fixed SFR of 0.6 and 1.5 on the product gas composition.**

Figure A.2 shows the effect of the equivalence ratio (ER) at fixed SBR of 0.6 and 1.5 on the product gas composition, when air is used as a gasifying agent during the biomass gasification. It was found that the increase of the ER caused the H_2, CO, CH_4 composition in the product gas to decrease. The temperature increased as the ER increased. The increase of the steam flowrate from SBR of 0.6 to SBR of 1.5 increased the H_2O composition in the product gas

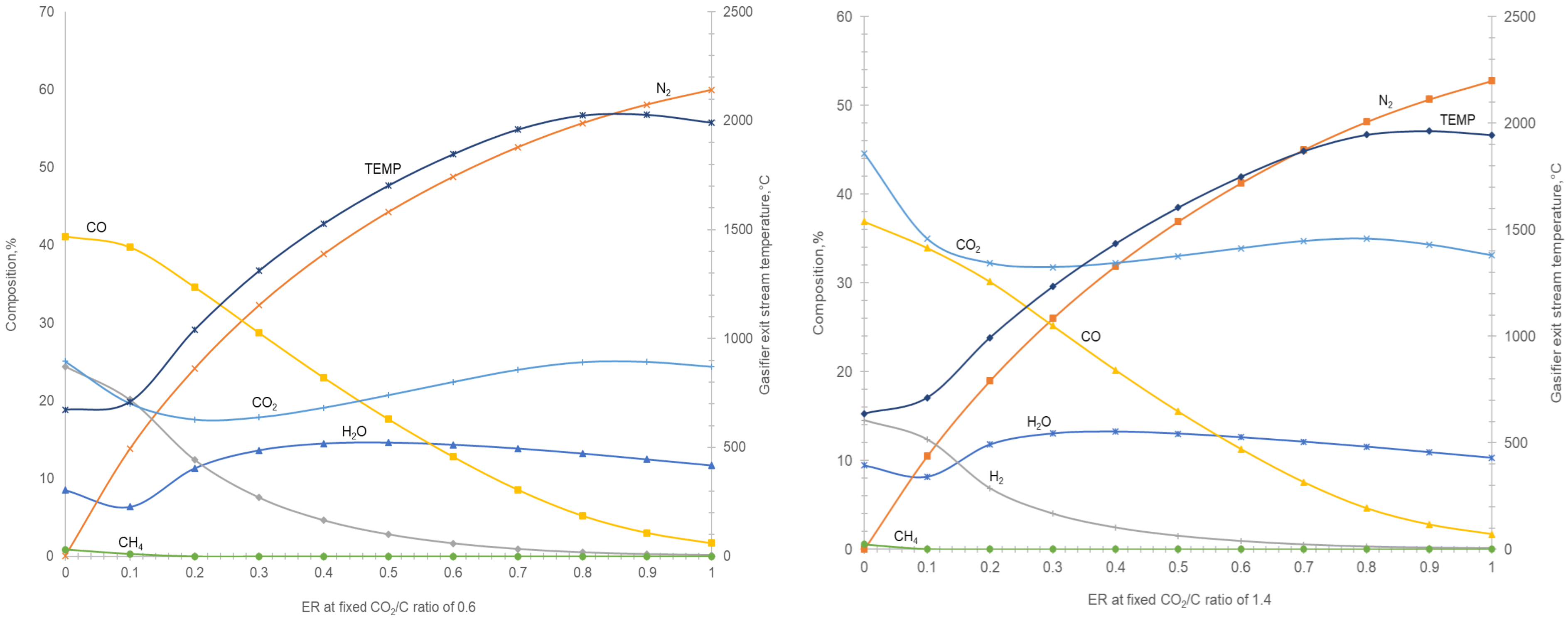


(a) (b)

Figure A.2. Effect of equivalence ratio at fixed (a) SBR of 0.6 and (b) 1.5 on the product gas composition, when air – steam was used as a gasifying agent during the biomass gasification.

- **Effect of the equivalence ratio (ER) at fixed CO_2/C ratio of 0.6 and 1.4 on the product gas composition.**

Figure A.3 shows the effect of the equivalence ratio (ER) at fixed (a) CO_2/C ratio of 0.6 and (b) CO_2/C ratio of 1.4 on the product gas composition, when air – carbon dioxide mixture was used as a gasifying agent. The increase of ER decreased the composition of H_2, CO and CH_4 in the product gas. However, increased the H_2O and CO_2. temperature in the gasifier also increase with the increasing ER. The increase of carbon dioxide flowrate from CO_2/C ratio of 0.6 to 1.4, increased the CO_2 in the product gas and decreased the CO composition.



(a) (b)

Figure A.3. Effect of equivalence ratio on the product gas composition, when air –carbon dioxide was used as a gasifying agent during the biomass gasification.

OXYGEN BIOMASS GASIFICATION

- **Effect of the equivalence ratio on the product gas composition.**

Figure A.4 shows the effect of the equivalence ratio (ER) on the product gas composition, when oxygen was used as a gasifying agent. The CO composition is higher than the H_2, in the product gas. These components are favored at low ER values below 0.3. Temperature in the gasifier increased with an increasing ER. CH_4 is negligible throughout the whole ER range. H_2O and CO_2 are favored at high ER values above 0.3.

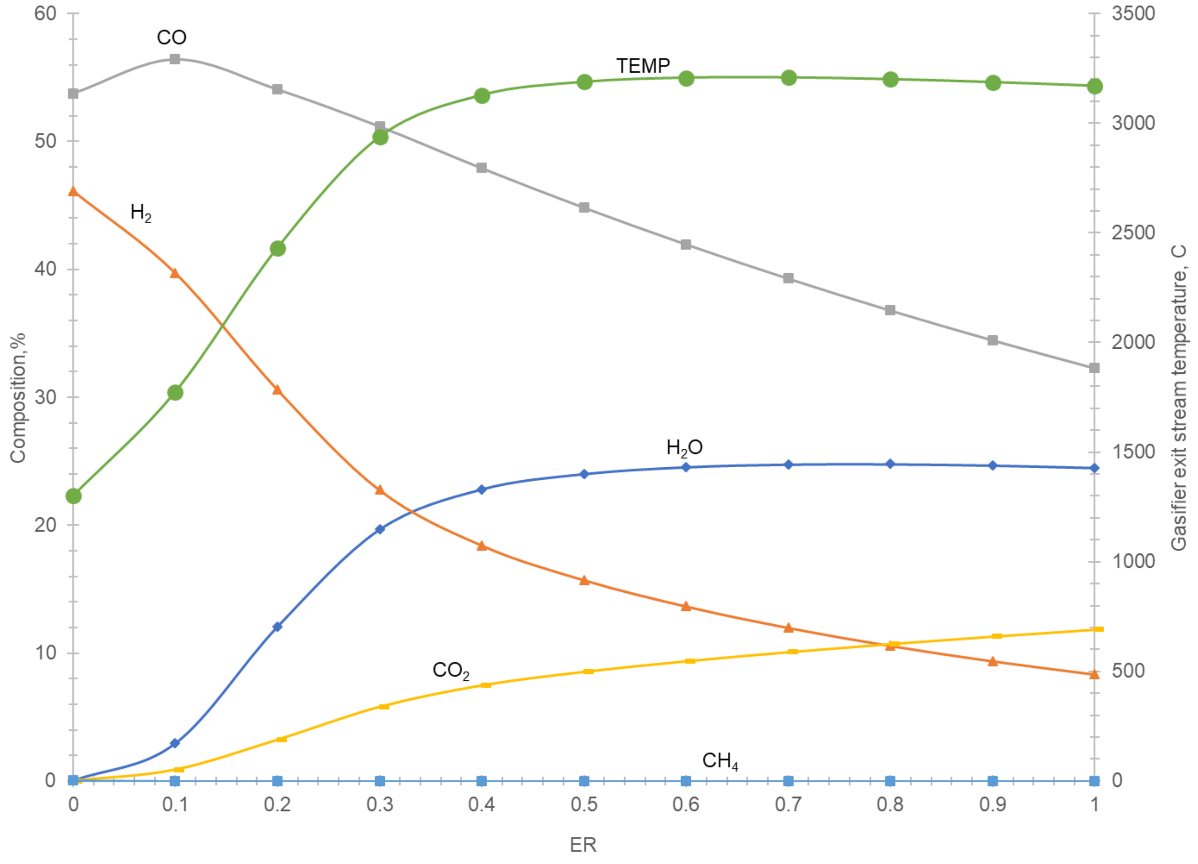
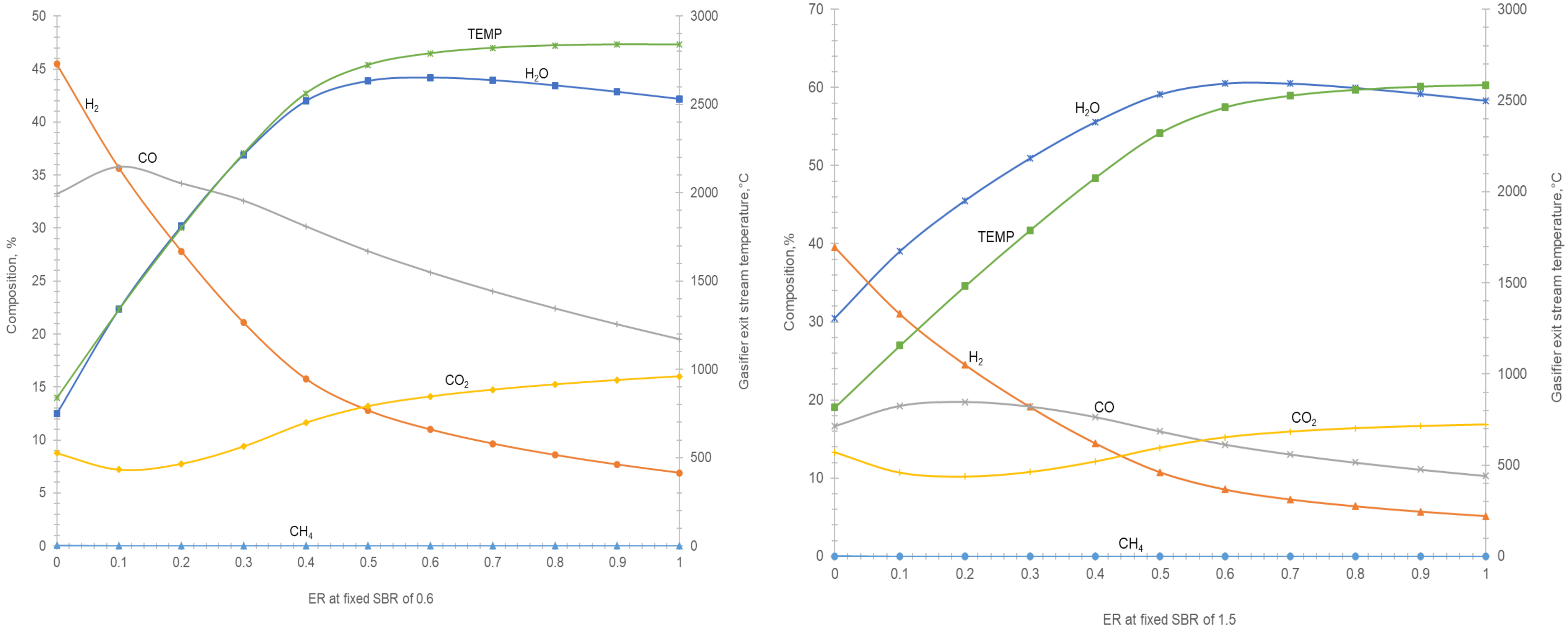


Figure A.4. Effect of equivalence ratio on the product gas composition, when oxygen was used as a gasifying agent during the biomass gasification.

- **Effect of equivalence ratio at fixed SFR of 0.6 and SBR of 1.5 on the product gas composition.**

Figure A.5 shows the effect of the equivalence ratio at fixed (a) SBR of 0.6 and (b) SBR of 1.5 on the product gas composition when oxygen – steam mixture as a gasifying agent. The addition of steam at low and high flowrate through SBR of 0.6 and SBR of 1.5, decreased the CO in the product gas as compared when only oxygen was used. The H_2 and CO composition were favored at low ER values below 0.3. The use of oxygen – steam as a gasifying agent, favored a high H_2O at high ER values. The CO_2 is also favored at high ER values. CH_4 is negligible throughout the range of ER. Temperature increased with the increasing ER values, regardless the type of gasifying agent used. SBR of 1.5 produced a low H_2 composition as compared to that of SBR of 0.6.



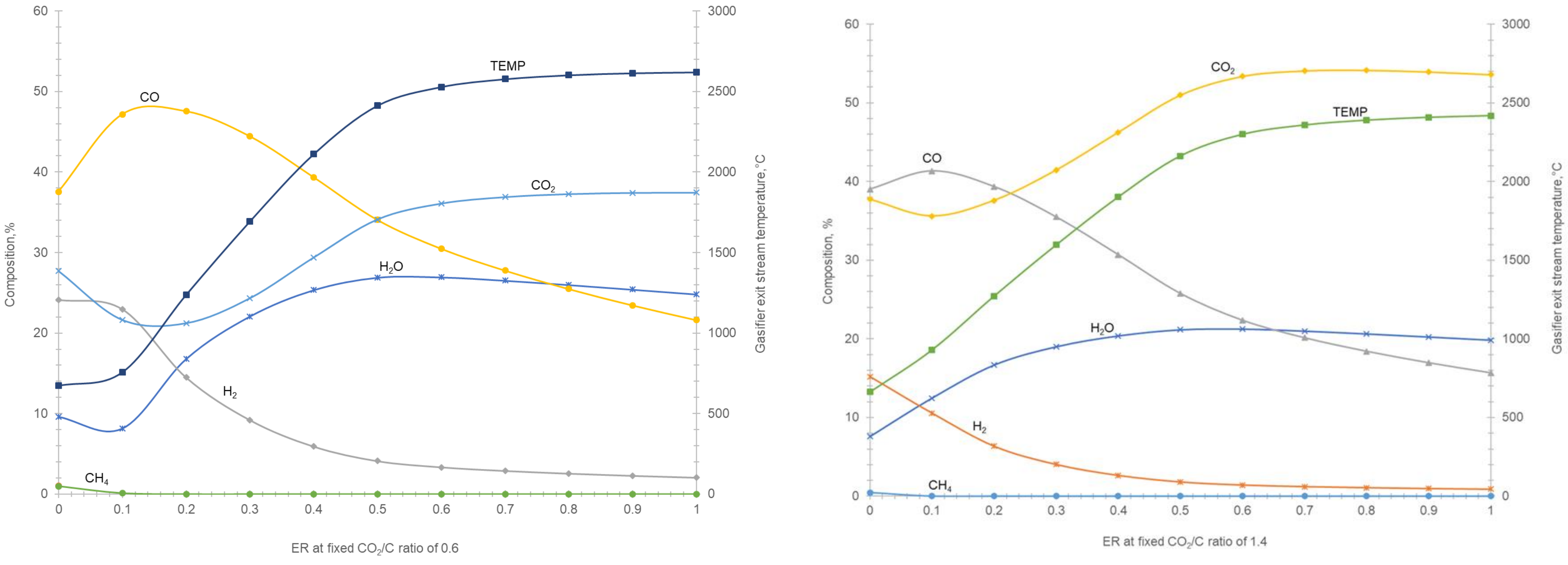
(a)

(b)

Figure A.5. Effect of equivalence ratio on the product gas composition at (a) fixed SBR of 0.6 and (b) fixed SBR of 1.5, when oxygen – steam mixture was used as a gasifying agent during the biomass gasification.

- **Effect of the equivalence ratio (ER) at fixed CO_2/C ratio of 0.6 and 1.4 on the product gas composition.**

Figure A.6 shows the effect of the equivalence ratio at (a) fixed CO_2/C ratio of 0.6 and (b) CO_2/C ratio of 1.4 on the product gas composition, when oxygen – carbon dioxide mixture was used as gasifying agent during the biomass gasification. It was found that the use of oxygen – carbon dioxide mixture as a gasifying agent reduced the H_2 composition in the product gas. The CO composition was favoured. However, both H_2 and CO were favoured at low ER values below 0.3. The increase in ER decreased the CH_4 in the product gas. The increase in ER increased the temperature in the gasifier and favoured H_2O and CO_2 in the product gas. The increase in carbon dioxide flowrate through CO_2/C ratio of 0.6 to 1.4, increased the CO_2 composition of the product gas and decreased the CO composition.



(a) (b)

Figure A.6. Effect of equivalence ratio on the product gas composition at fixed (a) CO_2/C ratio of 0.6 and (b) CO_2/C ratio of 1.4, when air –carbon dioxide was used as a gasifying agent during the biomass gasification.

APPENDIX B

Polyethylene gasification

This appendix is divided into two section, first section consists of air and its relative mixtures gasifying agents such as air- steam mixture and air- carbon dioxide mixtures. The second section oxygen and its relative mixtures of gasifying agents are used.

Air polyethylene gasification

- **Effect of the equivalence ratio on the product gas composition.**

Figure B.1 shows the effect of varying the equivalence ratio from 0.1 – 1 on the product gas composition when air is used as a gasifying agent in polyethylene gasification. N_2, CO_2 and H_2O are favoured at high ER values, while H_2 and CO composition were favoured at low ER values below 0.4. Temperature increased with increasing ER values.

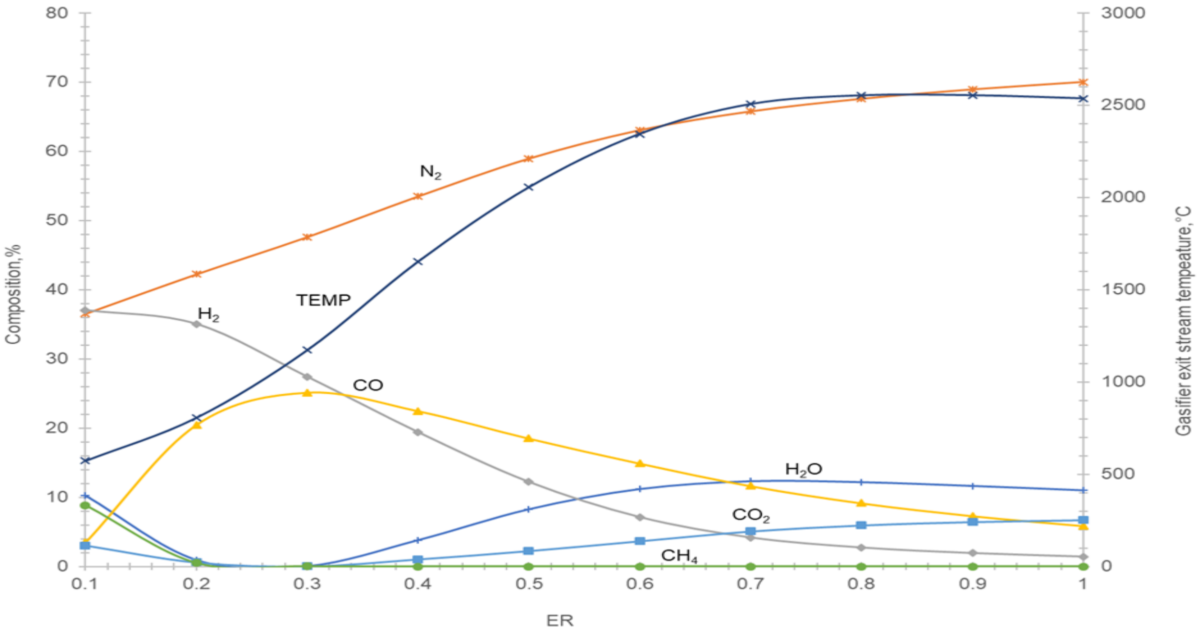
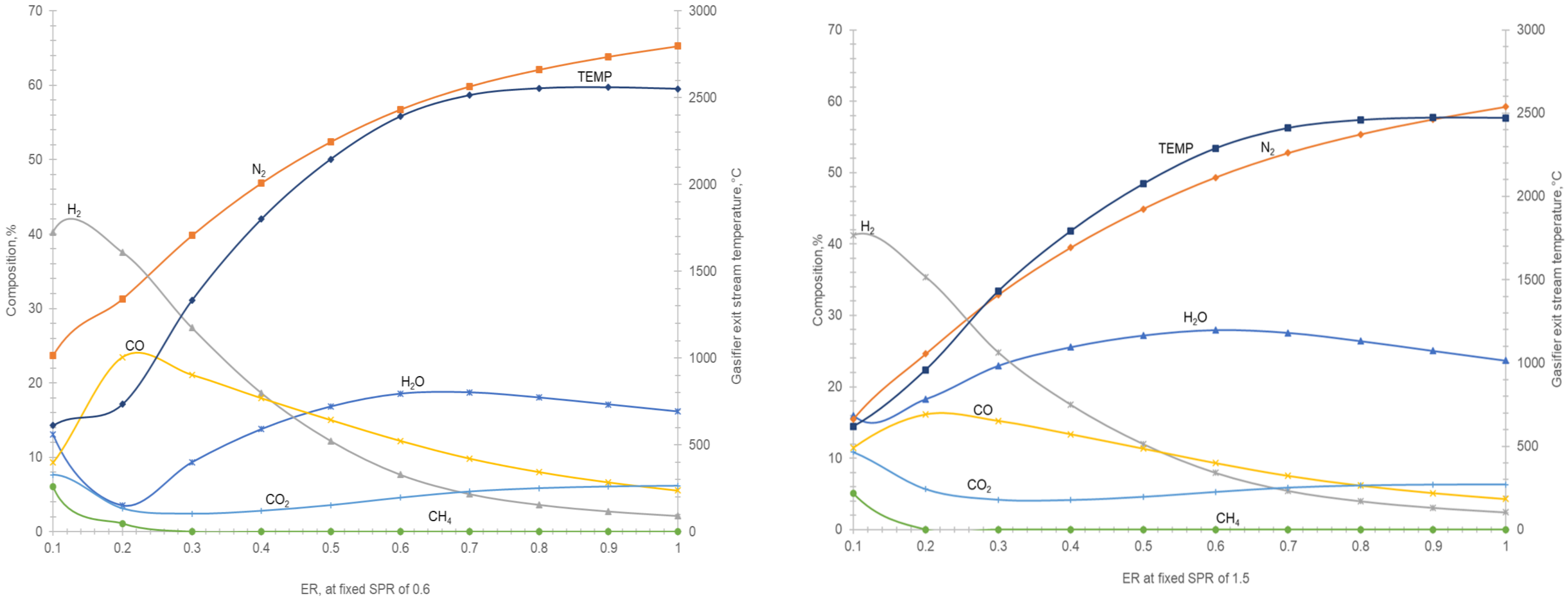


Figure B.1. Effect of the equivalence ratio on the product gas composition, when air is used as a gasifying agent during the polyethylene gasification.

- **Effect of the equivalence ratio at fixed SPR of 0.6 and 1.5 on the product gas Composition.**

Figure B.2 shows the effect of varying the equivalence ratio from 0.1 – 1 at fixed (a) SPR equals to 0.6 and (b) SPR equals to 1.5 on the product gas composition, in the presence of air and steam as gasifying agents in polyethylene gasification. The H_2 and CO composition are favoured at low ER values below 0.3. H_2 composition is higher than that of the CO in the product gas. The H_2 and CO composition produced at low steam flowrate at SPR of 0.6, is higher than that produced from high steam flowrate at SPR of 1.5. At high ER values for both at fixed SPR of 0.6 and 1.5, H_2O and CO_2 are favoured.



(a)

(b)

Figure B.2. Effect of equivalence ratio at fixed (a) SPR equals to 0.6 and (b) SPR equals to 1.5 on the product gas composition, when air- steam mixture is used as a gasifying agent during the polyethylene gasification.

Figure B.3 shows the effect of increasing the equivalence ratio from 0.1 – 1, at fixed SPR equals to 4 on the product gas composition, when air- steam mixture is used as a gasifying agent during the polyethylene gasification. The increase in SPR to 4, enhanced the H_2O in the product gas. H_2 and CO decreased, and CO_2 decreased.

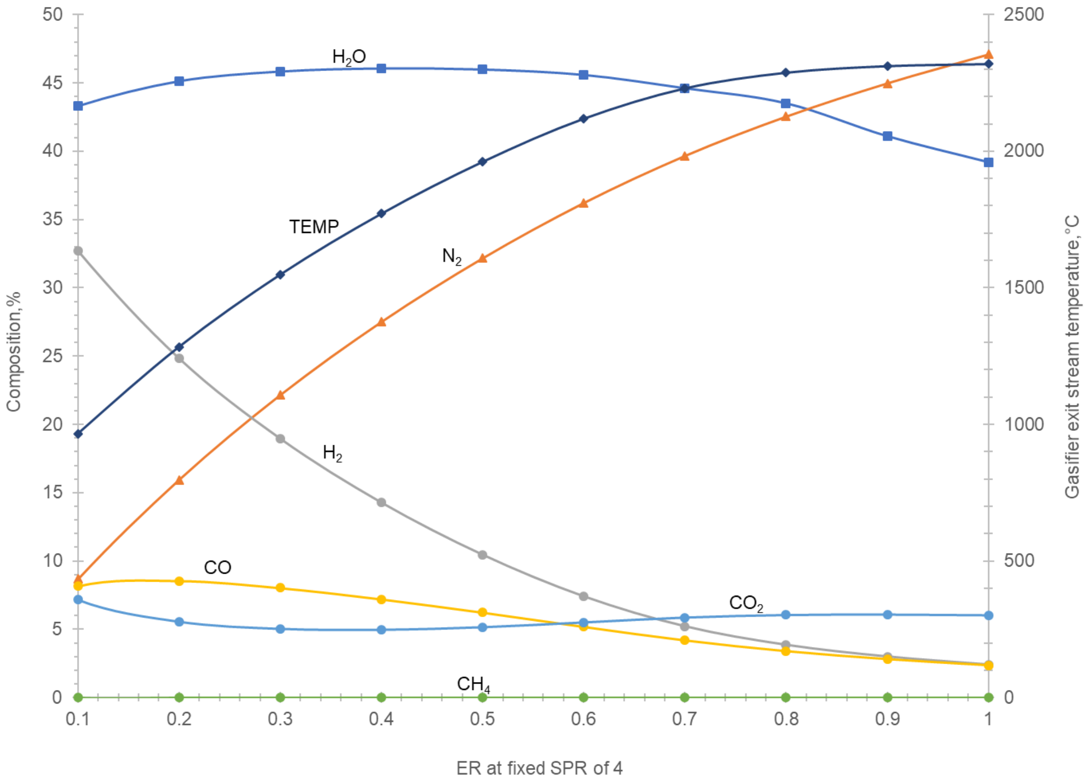


Figure B.3. Effect of equivalence ratio on the product gas composition, when air is used as a gasifying agent in polyethylene gasification.

- **Effect of the equivalence ratio at fixed CO_2/C ratio of 0.6 and 1.4 on the product gas composition.**

Figure B.4 shows the effect of the equivalence ratio, at fixed CO_2/C ratio of 0.6 and CO_2/C ratio of 1.4, on the product gas composition, when air- carbon dioxide mixture is used as a gasifying agent during the polyethylene gasification. The use of air- carbon dioxide mixture increased the CO composition in the product gas, however, decreased the H_2 composition. As ER increased, the H_2O, N_2 and CO_2 in the product gas increased.

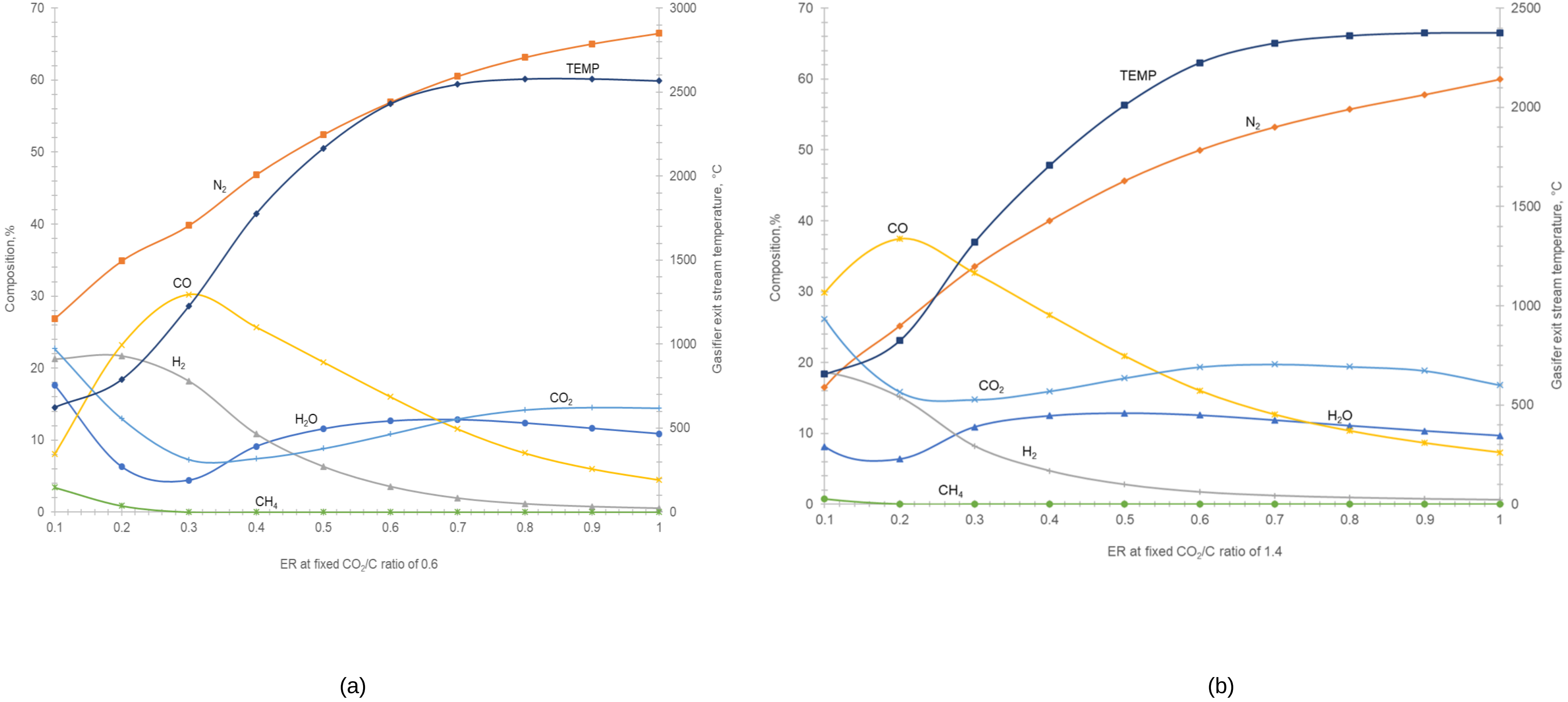


Figure B.4. Effect of equivalence ratio at fixed (a) CO$_2$/C ratio of 0.6 and (b) CO$_2$/C ratio of 1.4 on the product gas composition, when air – carbon dioxide is used as a gasifying agent mixture during the polyethylene gasification.

Oxygen polyethylene gasification

- **Effect of the equivalence ratio on the product gas composition**

Figure B.5 shows the effect of the equivalence ratio on the product gas composition when oxygen is used as a gasifying agent during the polyethylene gasification. For oxygen as a gasifying agent, the H_2 composition significantly increased as compared when air and its relative gasifying agent mixtures were used. H_2 and CO compositions are favoured at low ER values below 0.4. Temperature increased as ER increased. The amount of CO_2 is lower than that of H_2O at high ER values, however, these components are favoured at high ER values.

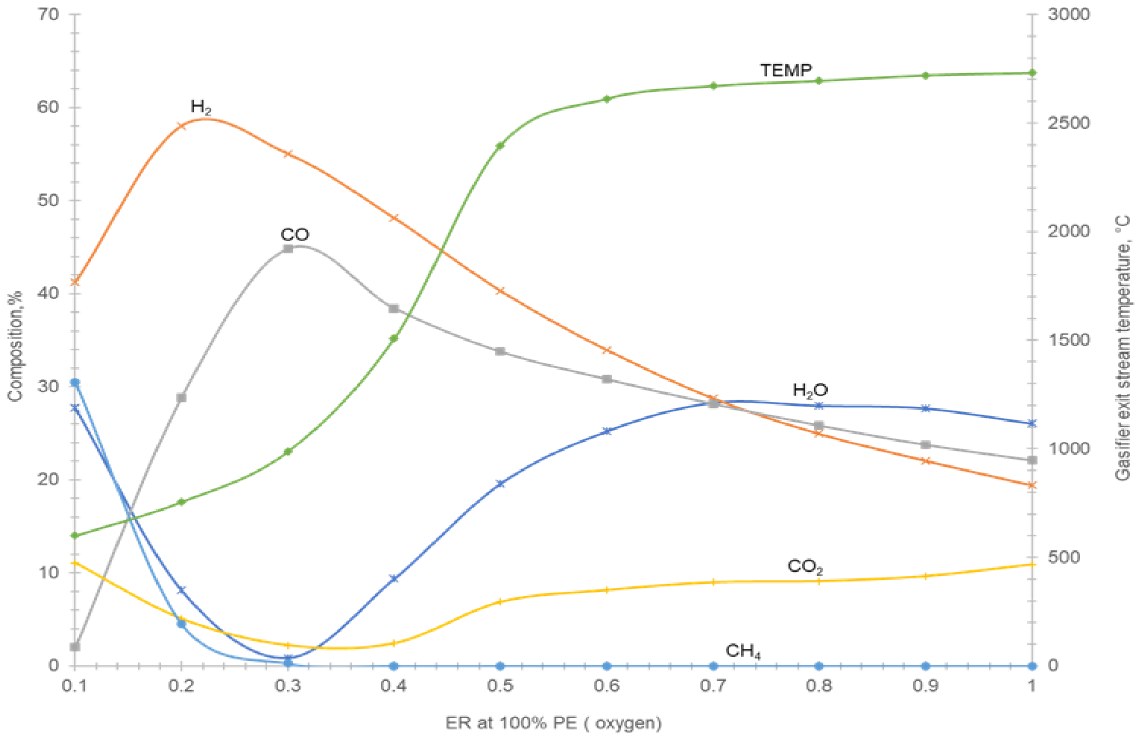
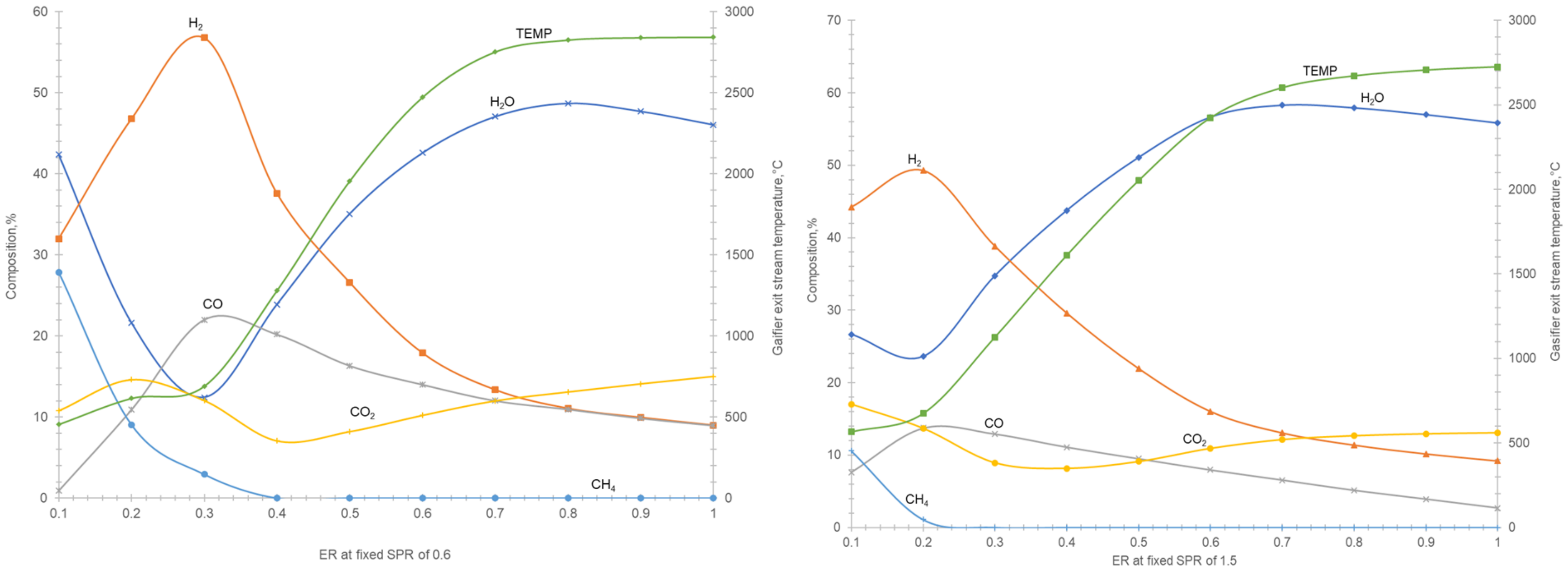


Figure B.5. Effect of equivalence ratio on the product gas composition, when oxygen is used as a gasifying agent in polyethylene gasification.

- **Effect of the equivalence ratio at fixed SPR of 0.6 and 1.5 on the product gas composition.**

Figure B.6 shows the effect of increasing the equivalence ratio from 0.1 – 1, at fixed (a) SPR equals to 0.6 and (b) SPR equals to 1.5, on the product gas composition, in the presence of oxygen – steam mixture as a gasifying agent during the polyethylene gasification. The increase in the steam flowrate from SPR of 0.6 to 1.5 decreased the H_2 and CO composition in the product gas. H_2 and CO composition were favoured at low ER values below 0.4, regardless of the steam flowrate used. The increase in the ER increased CO_2, N_2 and H_2O. Temperature is a function of ER, when ER increased, temperature also increased. The increase in SPR from 0.6 to 1.5, increased the H_2O in the product gas.



(a) (b)

Figure B.6. Effect of the equivalence ratio at fixed (a) SPR equals to 1.6 and (b) SPR equals to 1.5 on the product gas composition during the use of oxygen – steam mixture as a gasifying agent, in the polyethylene gasification process.

Figure B.7 shows the effect of the equivalence ratio at fixed SPR of 4, on the product gas composition when oxygen – steam mixture as a gasifying agent was used during the polyethylene gasification. The main effect caused by increasing SPR to 4, is the increase of the H_2O composition in the product gas. The increase of SPR to 4, significantly decreased H_2 and CO in the product gas.

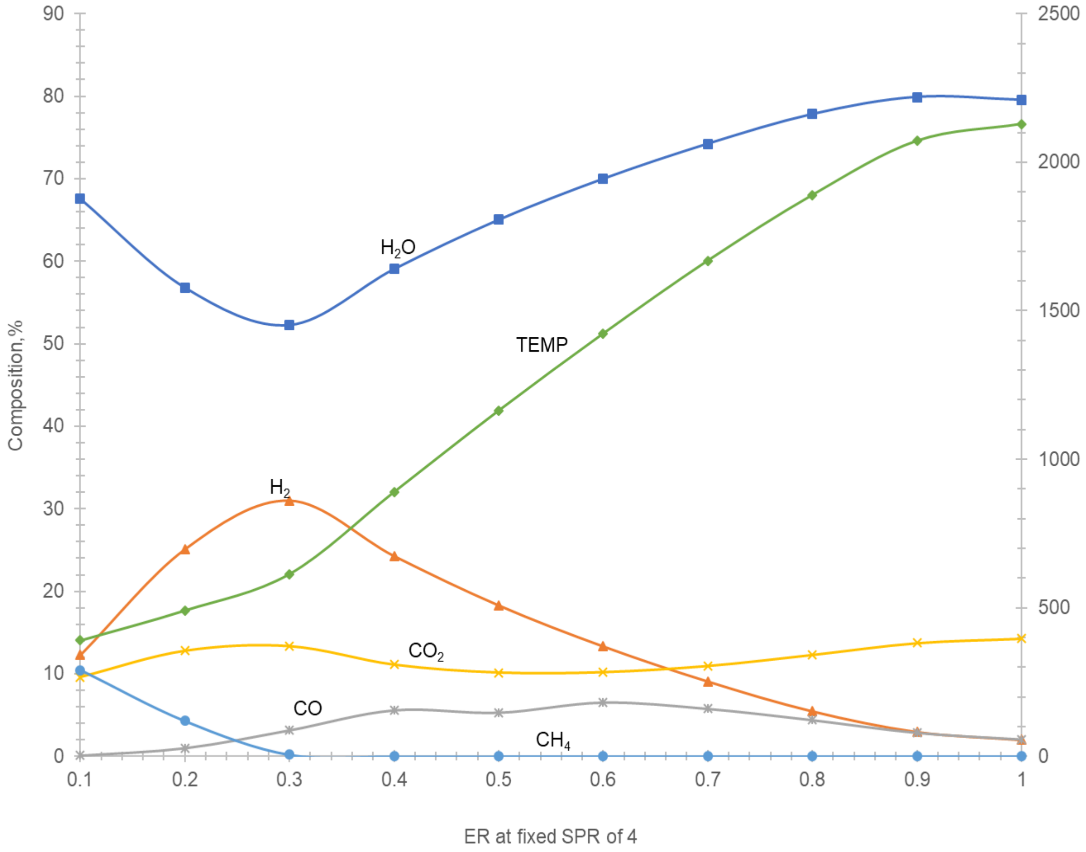


Figure B.7. Effect of equivalence ratio on the product gas composition, when oxygen- steam mixture is used as a gasifying agent in polyethylene gasification.

- **Effect of the equivalence ratio at fixed CO_2/C ratio of 0.6 and 1.5 on the product gas composition.**

Figure B.8 shows the effect of the equivalence ratio at fixed (a) CO_2/C ratio of 0.6 and (b) CO_2/C ratio of 1.4 on the product gas composition, when oxygen – carbon dioxide mixture is used as a gasifying agent during the polyethylene gasification. The use of oxygen – carbon dioxide enhanced the CO composition in the product gas.

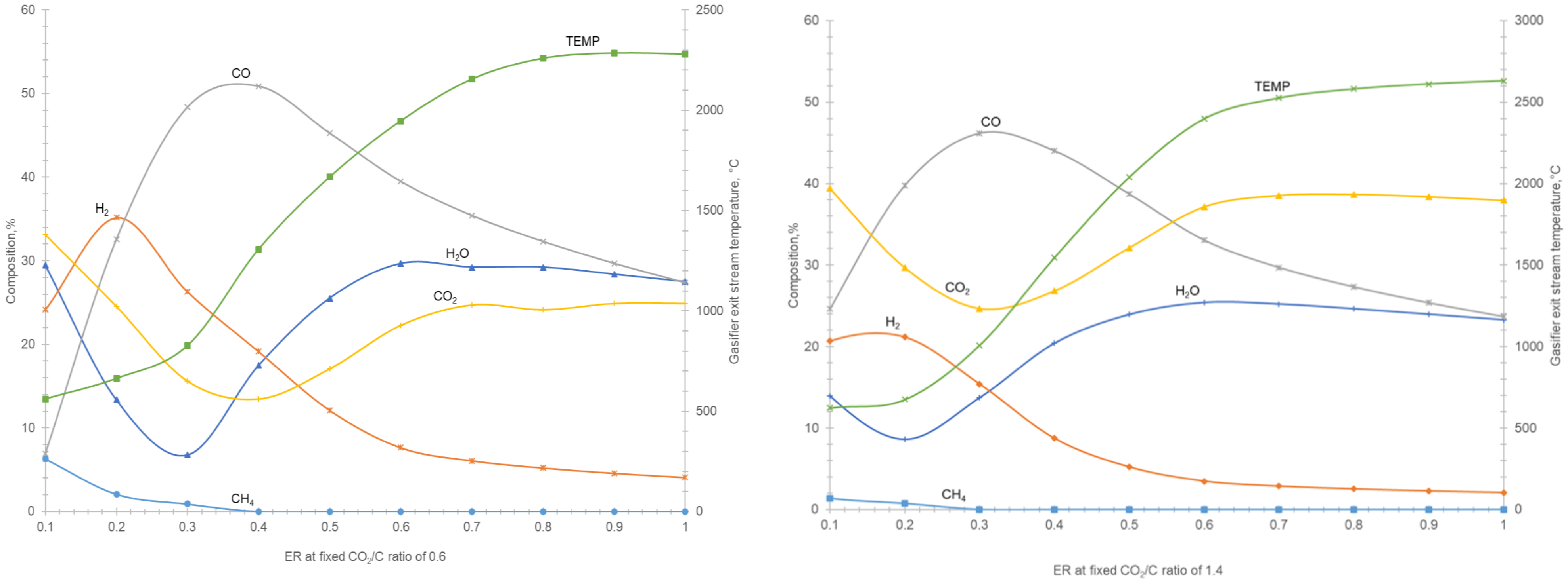


Figure B.8. Effect of equivalence ratio at fixed (a) CO_2/C ratio of 0.6 and (b) CO_2/C ratio of 1.4 on the product gas composition, when oxygen – carbon dioxide mixture is used as a gasifying agent during polyethylene gasification.

APPENDIX C

Co- gasification of biomass and polyethylene

- **Determining the product gas composition using oxygen only**

The effect of increasing the equivalence ratio from 0.1 – 1 in the presence of oxygen as a gasifying agent, at a blend ratio of (25%PE + 75% biomass) on the product gas composition, was evaluated and it was established that an increase in the ER, caused the H_2, CO and CH_4 to decrease, while the temperature, H_2O and CO_2 increased. The CO is higher than the H_2 composition in the product gas.

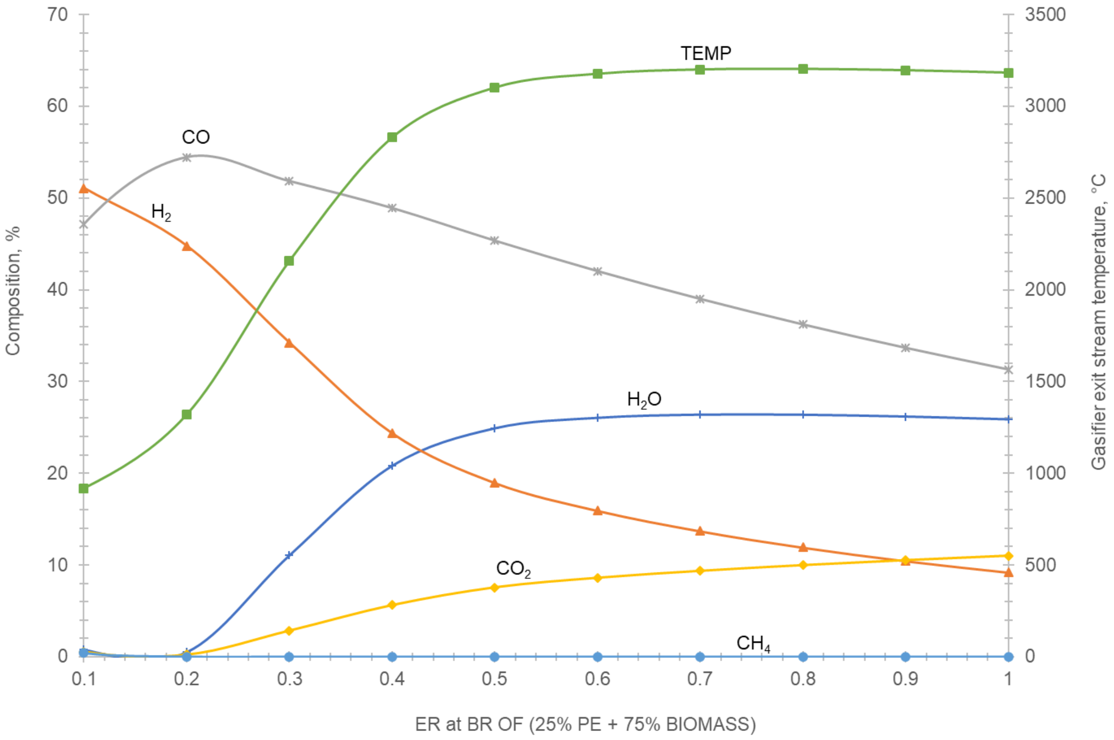
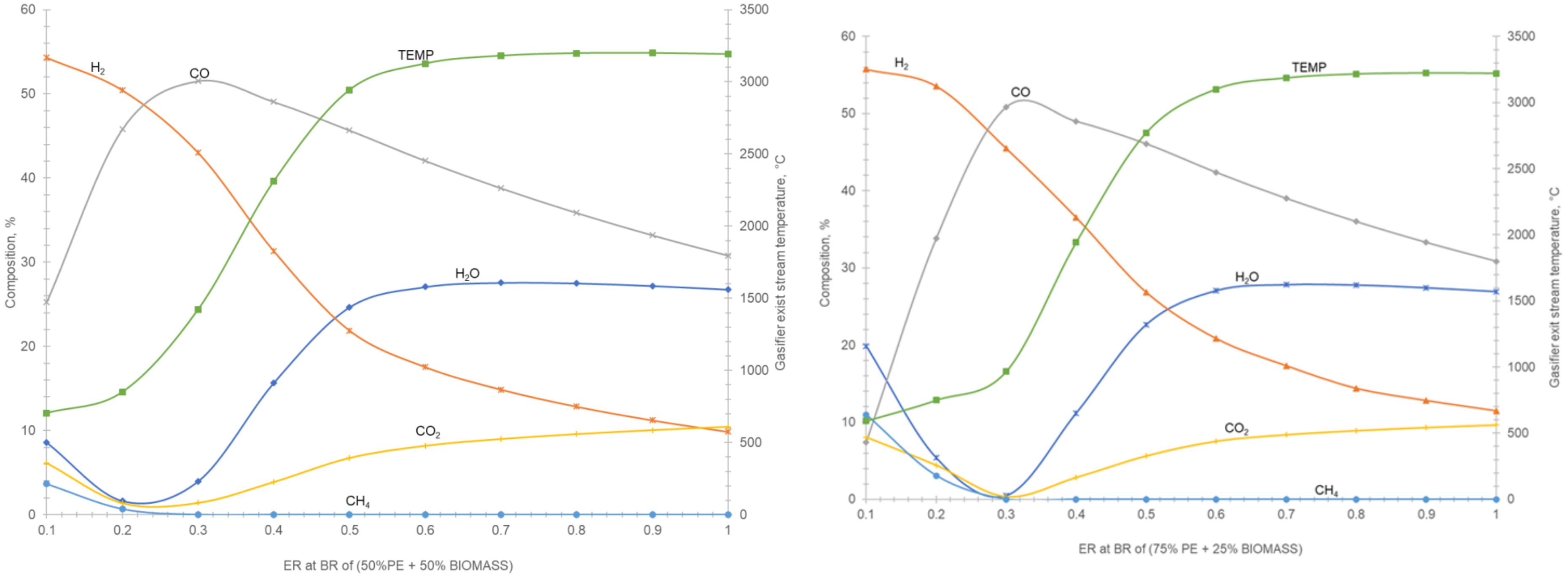


Figure C.1. Effect of the equivalence (ER) at blend ratio of (25% PE + 75% biomass).

Figure C.2 shows that when the equivalence ratio was increased from 0.1 – 1 in the presence of oxygen as a gasifying agent, and its effect on the product gas composition was evaluated from both the blend ratios of (50%PE + 50% biomass) and (75% PE + 25% biomass). Figure C.2 shows that an increase in the equivalence ratio, resulted in an increase in the gasifier temperature, and H_2O and CO_2. High H_2, CO and CH_4 (the combustible gases) are favoured at low ER values below 0.4. Figure C.2 shows that as the PE in the blend fuels increased the H_2 increased and CO decreased.



(a)

(b)

Figure C.2. Effect of the equivalence ratio (ER) on the product gas composition, in the presence of the oxygen as a gasifying agent for blend ratio of (a), (50% PE + 50% biomass) and (b), (75% PE + 25% biomass).

- **Effect of equivalence ratio (ER) on the product gas composition, at SFR of 0.6 on the product gas composition when oxygen – steam mixture was used as gasifying agent.**

The effect of varying the equivalence ratio (ER) from 0.1 -1 while keeping the SFR fixed at 0.6, on the product gas composition was evaluated for a blend ratio of (0% PE + 100% biomass) and (25% PE + 75% biomass). It was found that for biomass gasification, CO is higher than H_2, at low ER values, for the blend ratio of (25% PE + 75% biomass) the H_2 content at low ER values below 0.3 was higher than CO composition, this showed that the addition of 25% PE in the feedstock mixture increased the H_2 composition in the product gas.

However, the increase in the equivalence ratio decreased the H_2 and CO content in the product gas. The CH_4 composition is low throughout the variation of the equivalence ratio and H_2O is higher than CO_2. CO_2 and H_2O and the temperature increased as the ER increased. The temperature in the exit stream is a function of the equivalence ratio.

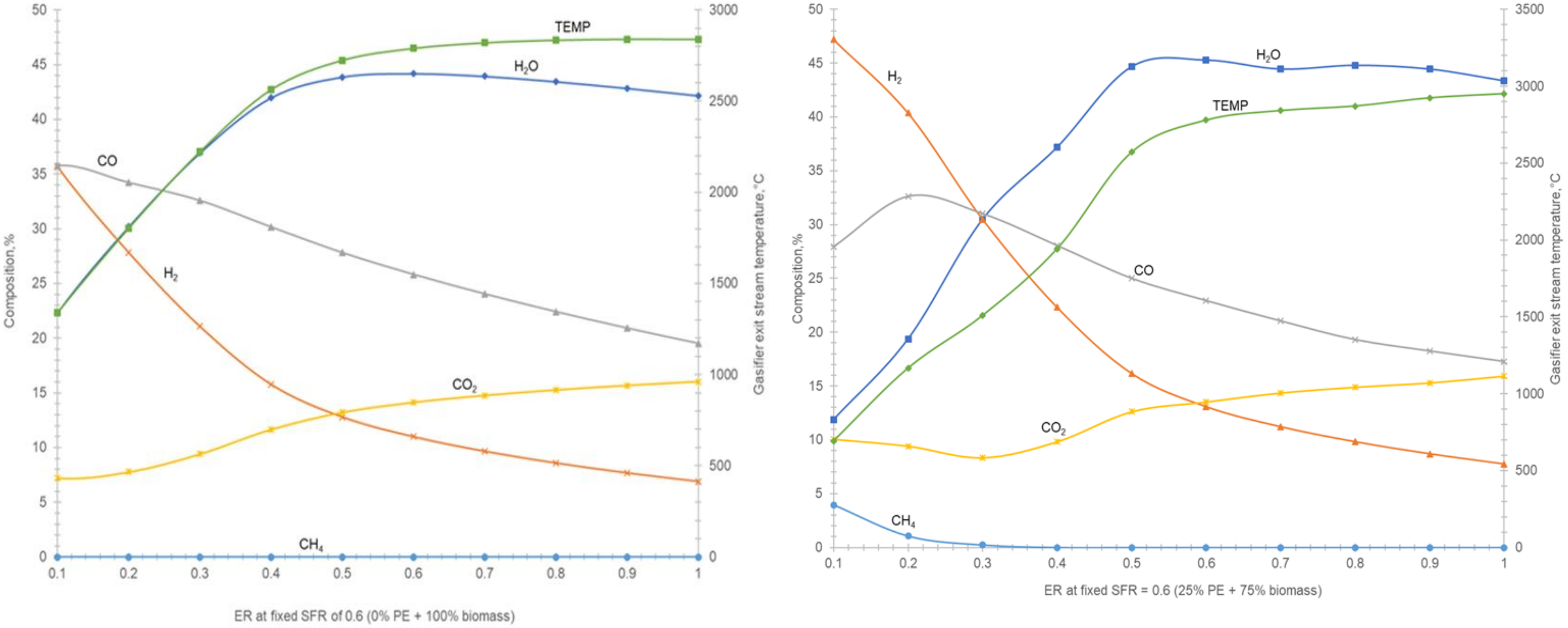
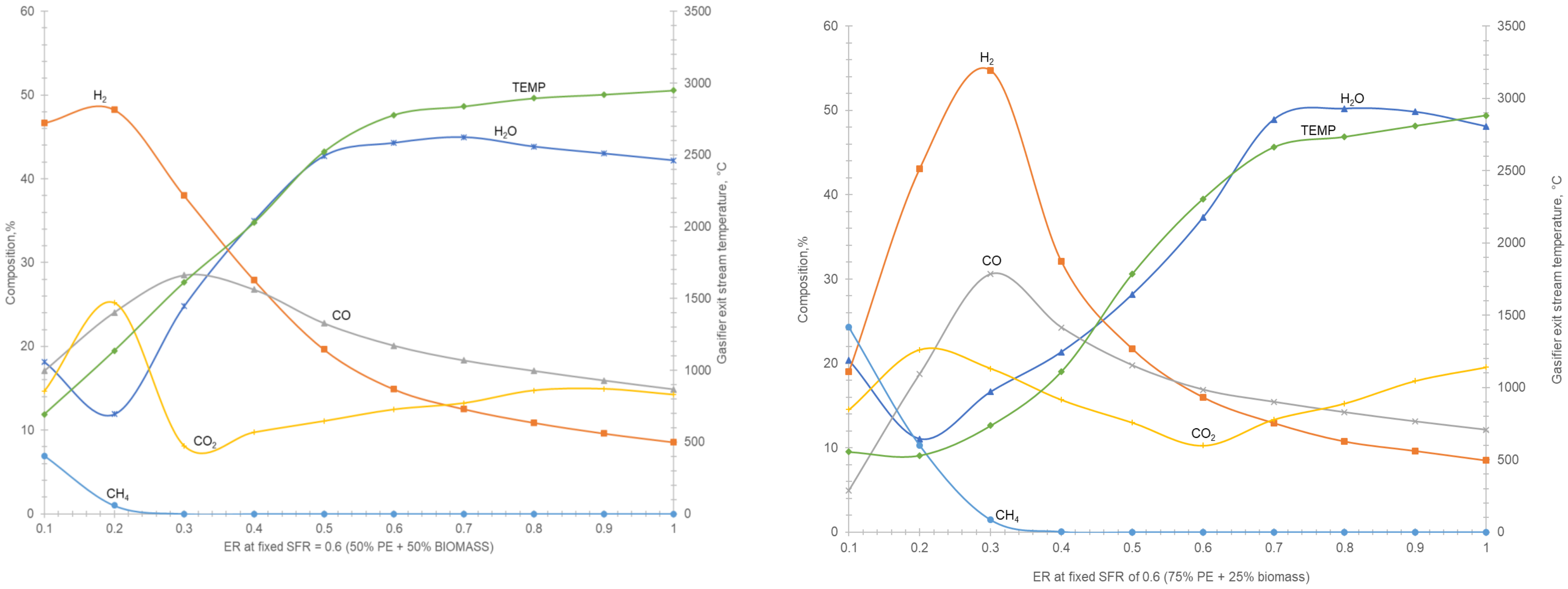


Figure C.3. Effect of the equivalence ratio at fixed SFR of 0.6 on the product gas composition, when oxygen – steam was used as a gasifying agent mixture for a blend ratio of (a), (0% PE + 100% biomass) and (b), (25% PE + 75% biomass).

The effect of varying the equivalence ratio from 0.1 -1 , in the presence of oxygen – steam mixture as a gasifying agent on the product gas composition was evaluated, for the blend ratios of (50% PE + 50% biomass) and (75% PE + 25% biomass). It was found that for these blend ratios that contains high percentage of the polyethylene the H_2 content is higher than the CO composition at low ER values below 0.4.

At low ER values below 0.4 the CO_2 and H_2 increased as the steam was introduced into the gasifier at low SFR of 0.6, and then as the ER increased, then the H_2 decreased so as the CO_2 decrease and thereafter start to increase with the increasing ER at higher ER values. The CH_4 composition, decreased as ER increased as well as the CO composition. The temperature, H_2O and CO_2 increased with an increasing ER values. The use of steam and high percentage of polyethylene in the mixtures increased the H_2 composition in the product gas.



(a)

(b)

Figure C.4. Effect of the equivalence ratio at fixed SFR of 0.6, on the product gas composition, when oxygen – steam mixture was used as a gasifying agent mixture for a blend ratio of (a), (50% PE + 50% biomass) and (b), (75% PE + 25% biomass).

Figure C.5 shows the effect of the equivalence ratio at fixed SFR of 0.6 on the product gas composition, when oxygen – steam mixture is used as a gasifying agent at a blend ratio of (100% PE + 0% biomass). At low ER values below 0.4 the composition of H_2 , CO and CH_4 are high, however an increase in the ER value results in a decrease in the composition of these gases and more of H_2O and CO_2 are favoured. The increase in ER increases the gasifier temperature.

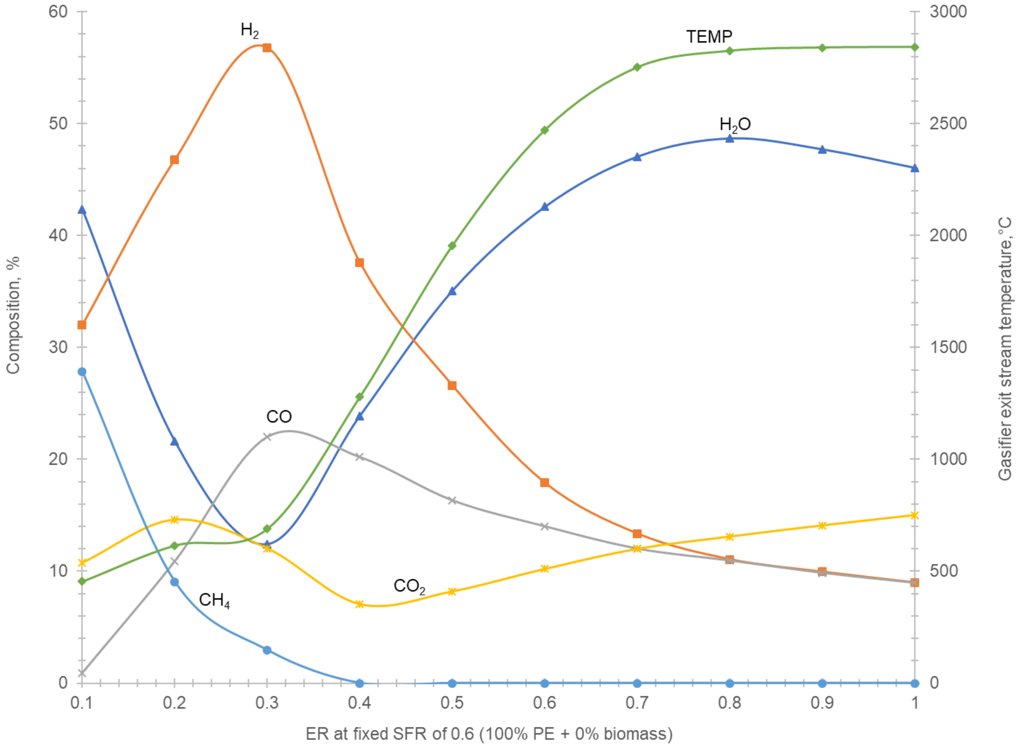
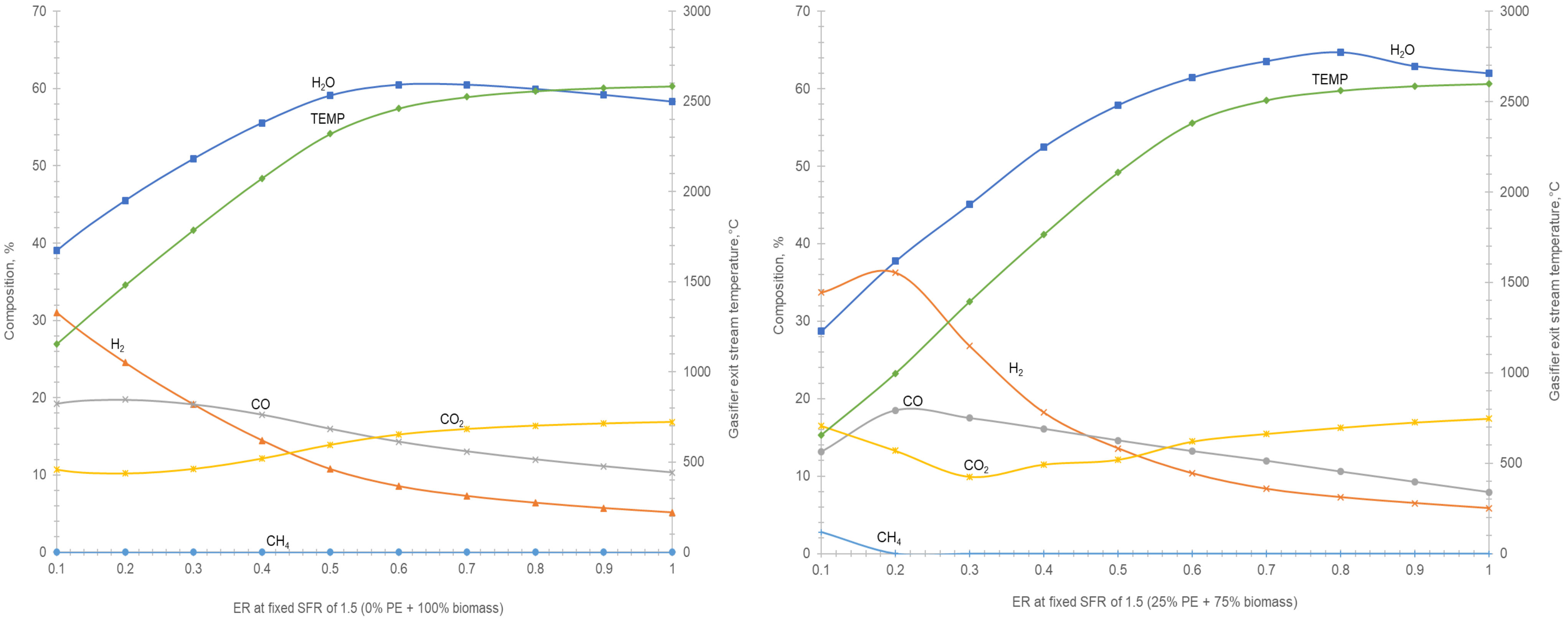


Figure C.5. Effect of the equivalence ratio at fixed SFR of 0.6 on the product gas composition, when oxygen – steam is used as a gasifying agent mixture for a blend ratio of (100% PE + 0% biomass).

- **Effect of equivalence ratio on the product gas composition, at SFR of 1.5 on the product gas composition when oxygen – steam mixture was used as gasifying agent.**

Figure C.6 shows the effect of increasing the equivalence ratio at fixed SFR of 1.5, on the product gas composition, when oxygen – steam mixture is used as a gasifying agent for a blend ratio of (0% PE + 100% biomass) and (25% PE + 75% biomass). It was found that increasing the steam flowrate from 0.6 to 1.5 increase the H_2O in the product gas. This trend is irrespective of the type of feedstock gasified. The H_2 is higher than CO at lower ER values, in both blend ratios. The increase in the ER decreases the H_2 and CO and favors the H_2O and CO_2. A fixed SFR of 1.5 resulted in a lower H_2 and CO composition as compared to that obtained from the fixed SFR of 0.6.

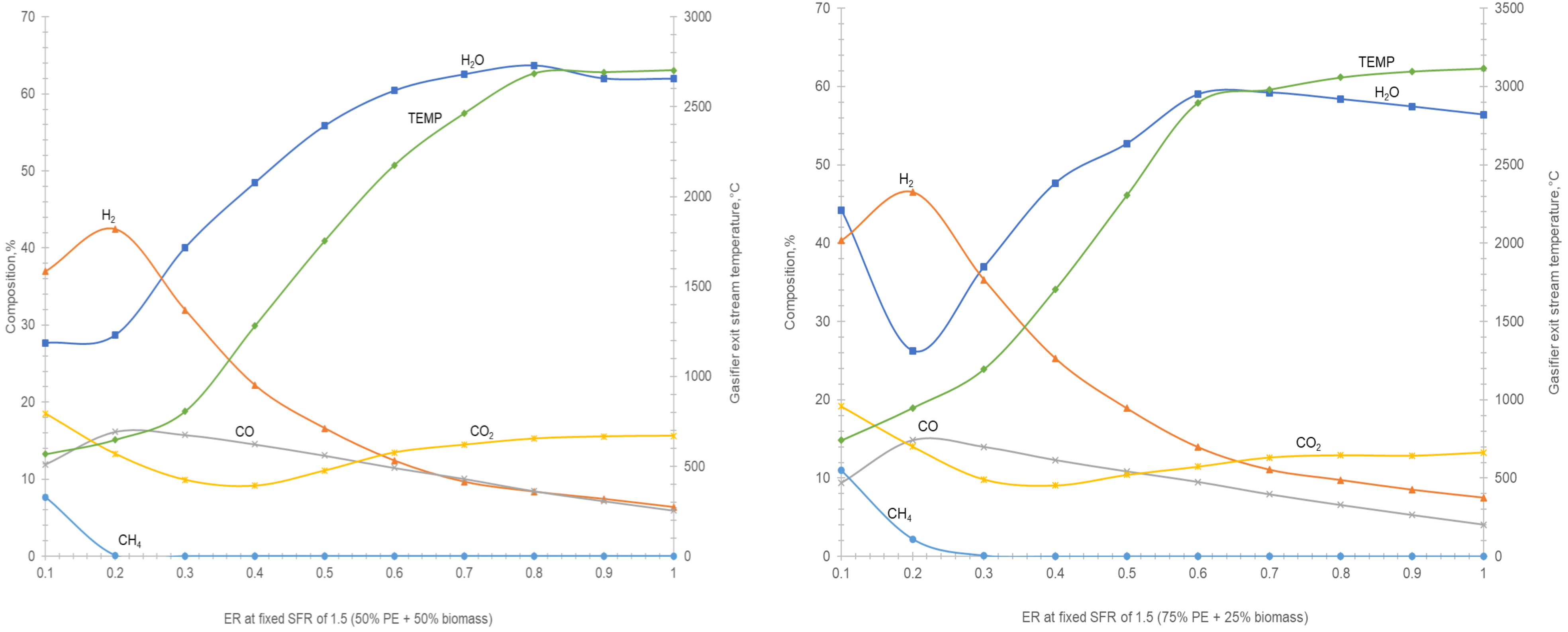


(a)

(b)

Figure C.6. Effect of the equivalence ratio at fixed SFR of 1.5 on the product gas composition, when oxygen – steam is used as a gasifying agent mixture for a blend ratio of (a), (0% PE + 100% biomass) and (b), (25%PE + 75% biomass).

Figure C.7 shows the effect of the equivalence ratio at fixed SFR of 1.5 on the product gas composition, when oxygen – steam mixture as a gasifying agent for the blend ratio of (50% PE + 50% biomass) and (75% PE + 25% biomass). The H_2 composition increases as the percentage of the polyethylene increases in the blended feedstocks. A high H_2 and CO composition are favoured at low ER values below 0.4. The increase in ER caused an increase of H_2O and CO_2 and an increase of temperature. The CH_4 decreased as the ER increased.



(a) (b)

Figure C.7. Effect of the equivalence ratio at fixed SFR of 1.5, on the product gas composition, when oxygen – steam is used as a gasifying agent mixture for a blend ratio of (a), (50% PE + 0% biomass) and (b), (75% PE + 25% biomass).

Figure C.8 shows the effect of the equivalence ratio at fixed SFR of 1.5 on the product gas composition, when oxygen – steam mixture as a gasifying agent was used. The H_2 and CO are high at low ER values below 0.4. The H_2 composition is higher than the CO composition in the product gas.

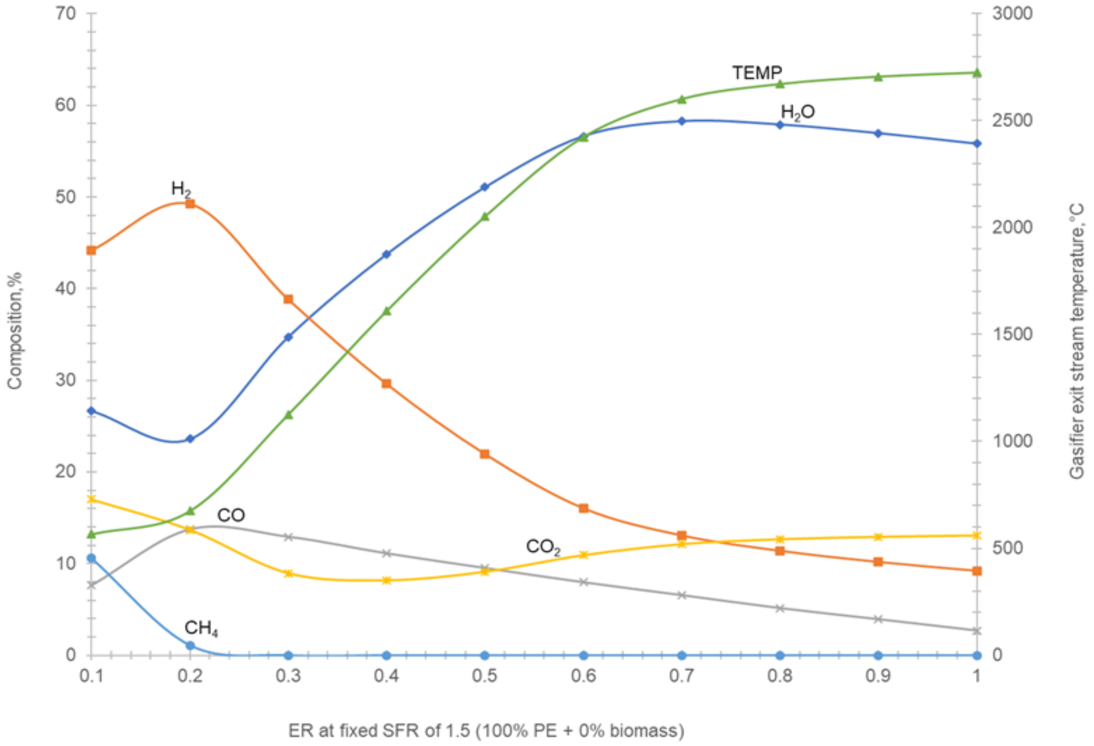


Figure C.8. Effect of the equivalence ratio at fixed SFR of 1.5 on the product gas composition, when oxygen – steam is used as a gasifying agent mixture for a blend ratio of (100% PE + 0% biomass).

- **Effect of equivalence ratio (ER) on the product gas composition, at CO_2/C ratio of 0.6 on the product gas composition when oxygen – carbon dioxide mixture was used as a gasifying agent.**

The effect of the equivalence ratio at fixed CO_2/C ratio of 0.6, on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent for a blend ratio of (0% PE + 100% biomass) was evaluated. It was found that an increase in the equivalence ratio increased the gasifier temperature and at low ER values below 0.4 a high CO composition was favoured. During the use of oxygen – carbon dioxide mixture as a gasifying agent, the CO composition was higher than the H_2 composition in the product gas.

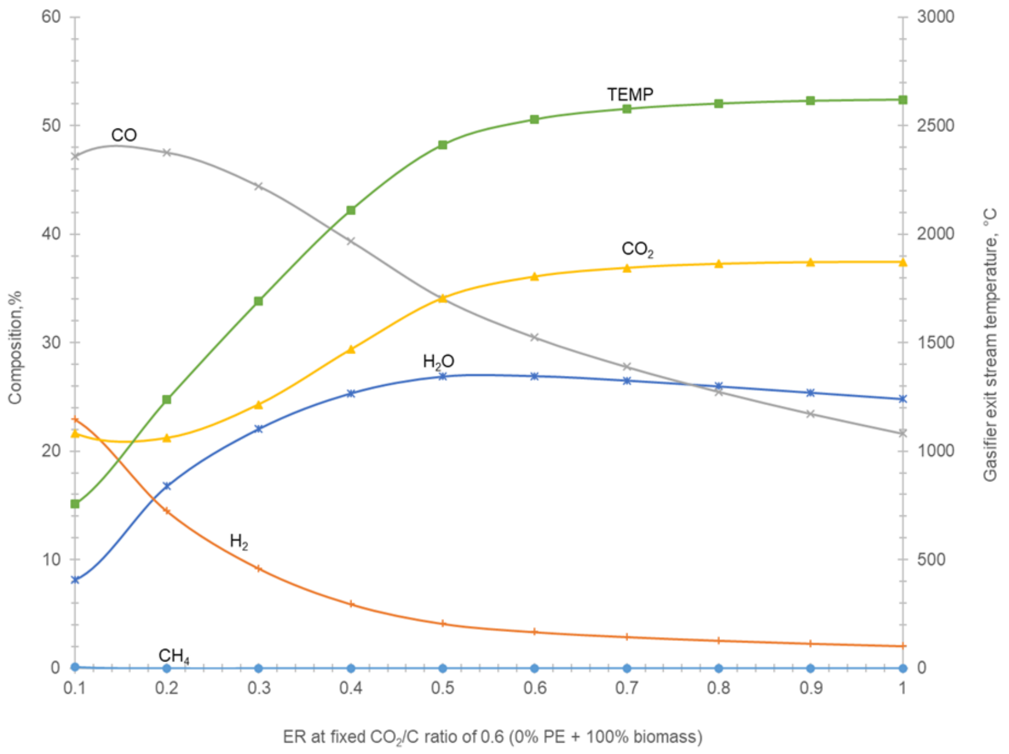
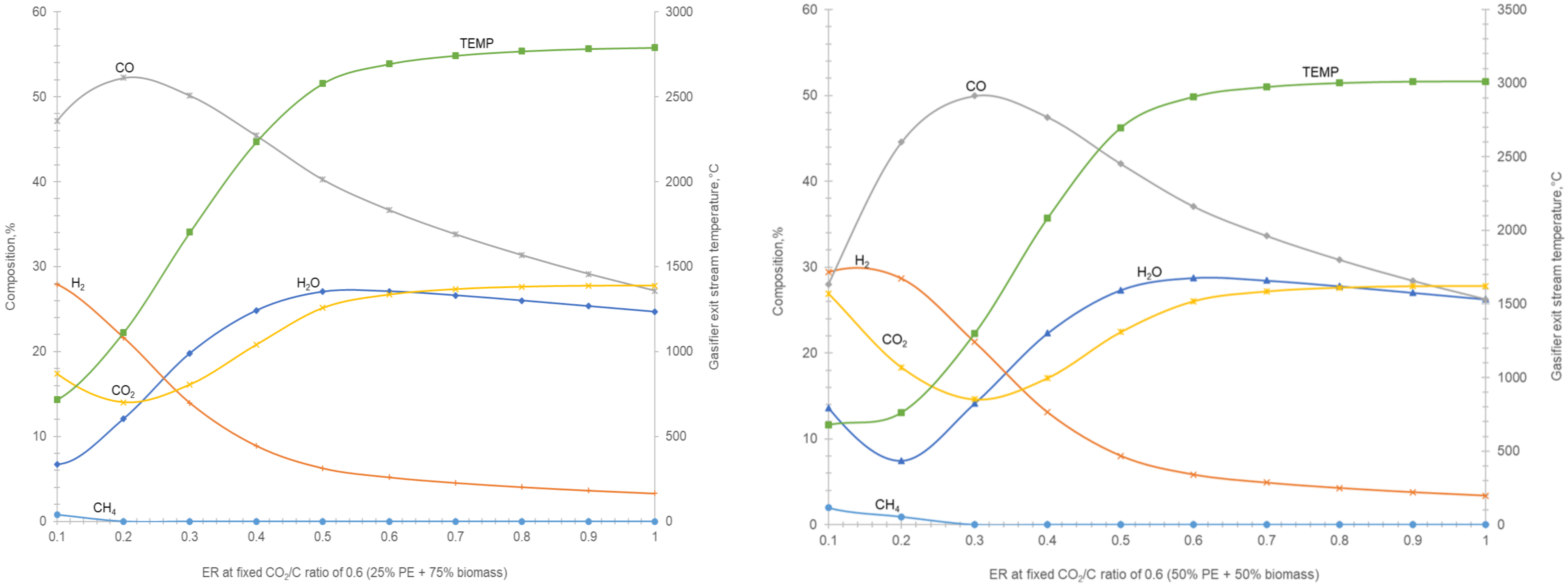


Figure C.9. Effect of the equivalence ratio at fixed CO_2/C ratio of 0.6 on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent was used as a gasifying agent mixture for a blend ratio of (0% PE + 100% biomass).

Figure C.10 shows the effect of the equivalence ratio at fixed CO_2/C ratio of 0.6 on the product gas when oxygen – carbon dioxide mixture was used as a gasifying as a gasifying agent for the blend ratio of (25% PE + 75% biomass) and (50% PE + 25% biomass). The use of oxygen - carbon dioxide mixture as a gasifying agent favoured a high CO composition in the product gas, at low ER values below 0.4. The H_2 is only higher at low ER between 0.1 -0.2 range. The increase in the ER increased H_2O and CO_2. Temperature in the gasifier also increased, as the ER increased.

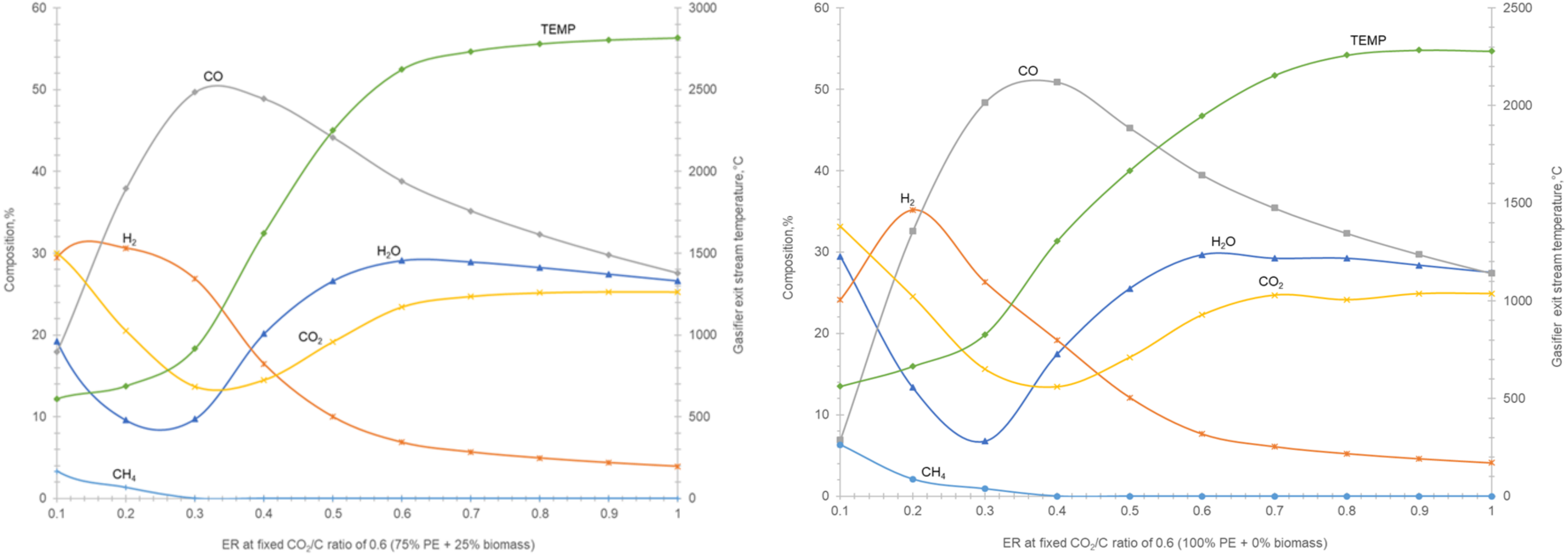


(a)

(b)

Figure C.10. Effect of the equivalence ratio at fixed CO_2/C ratio of 0.6, on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent was used as a gasifying agent mixture for a blend ratios of (a), (25% PE + 75% biomass) and (b), (50% PE + 50% biomass).

Figure C.11 shows the effect of the equivalence ratio at fixed CO_2/C ratio of 0.6 on the product gas composition, when oxygen - carbon dioxide mixture was used as a gasifying agent for the blend ratios of (75% PE + 25% biomass) and (100% PE + 0% biomass). The use of oxygen – carbon dioxide enhanced the CO composition in the product gas, and the H_2 was not that high. However, it was favoured at low ER values. The increase in the equivalence ratio caused the temperature in the gasifier and also the H_2O and CO_2 to increase.



(a) (b)

Figure C.11. Effect of the equivalence ratio at fixed CO_2/C ratio of 0.6, on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent was used as a gasifying agent mixture for a blend ratios of (a), (75% PE + 25% biomass) and (b), (100% PE + 0% biomass).

- **Effect of the equivalence ratio (ER) at fixed CO_2/C ratio of 1.4 on the product gas composition when oxygen – carbon dioxide mixture was used as a gasifying agent.**

Figure C.12 shows the effect of the equivalence ratio at fixed CO_2/C ratio of 1.4 on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent is used. It was found that the increase of CO_2/C ratio from 0.6 to 1.4, has cause the CO_2 in the product gas to increase, so as the CO composition. CO_2 increased with the increasing ER. High CO favoured at low ER values below 0.4. The H_2 composition is low, and only favoured at low ER values below 0.3. The increase of ER caused H_2O to increase.

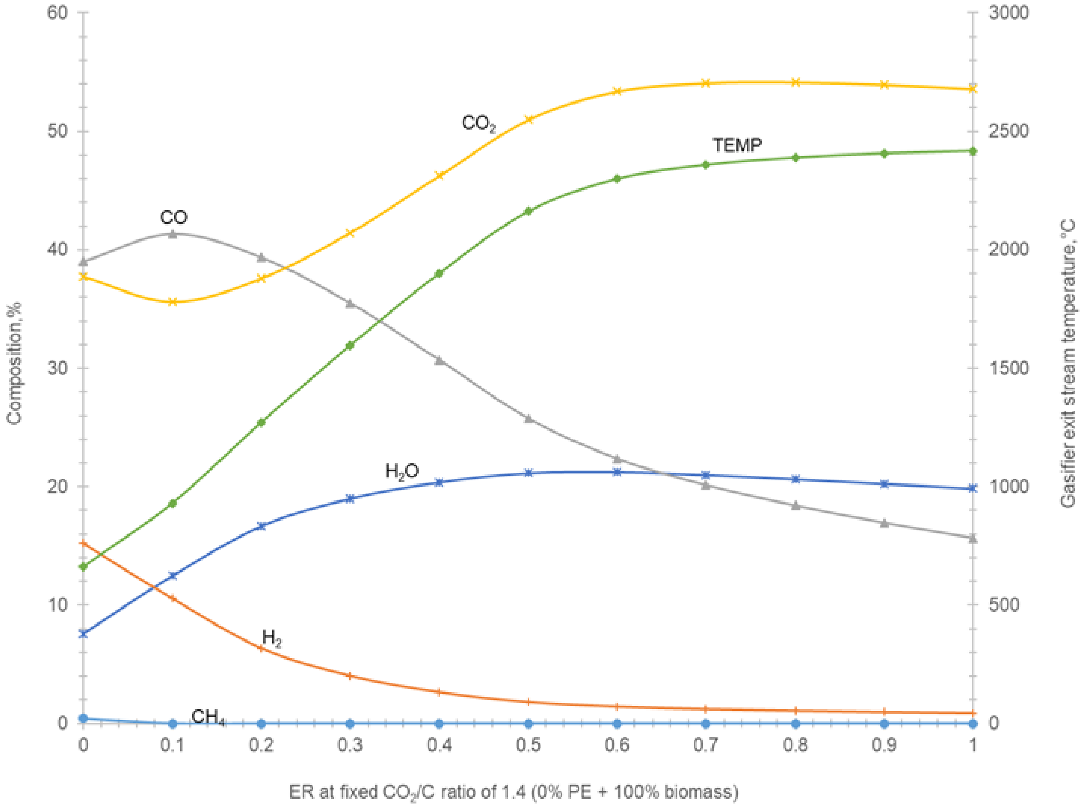


Figure C.12. Effect of the equivalence ratio at fixed CO_2/C ratio of 1.4, on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent was used as a gasifying agent mixture for a blend ratio of (0% PE + 100% biomass).

Figure C.13 shows the effect of the equivalence ratio at fixed CO_2/C ratio of 1.4 on the product gas composition, when oxygen – carbon dioxide mixture was used as a gasifying agent for the blend ratios of (25% PE + 75% biomass) and (50% PE + 50% biomass) was evaluated. It was found that the CO_2 composition is high and is mostly favoured at high ER values from the range of 0.4 – 1. The CO composition was favoured at low ER values below 0.4. The H_2 decreased as the ER increased. Temperature increased as the ER increased. CH_4 composition significantly decreased as ER increased. The trends of the different components follow the same pattern regardless of the type of feedstock used. H_2O increased as the ER increased.

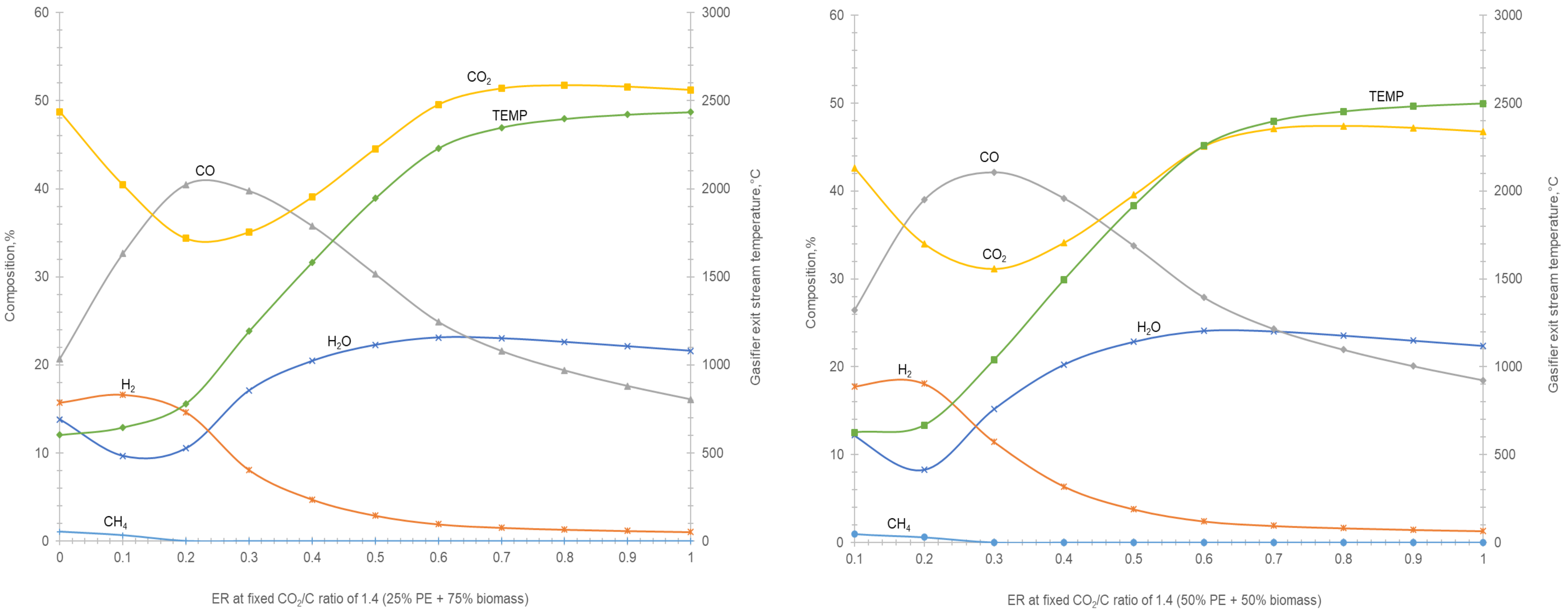
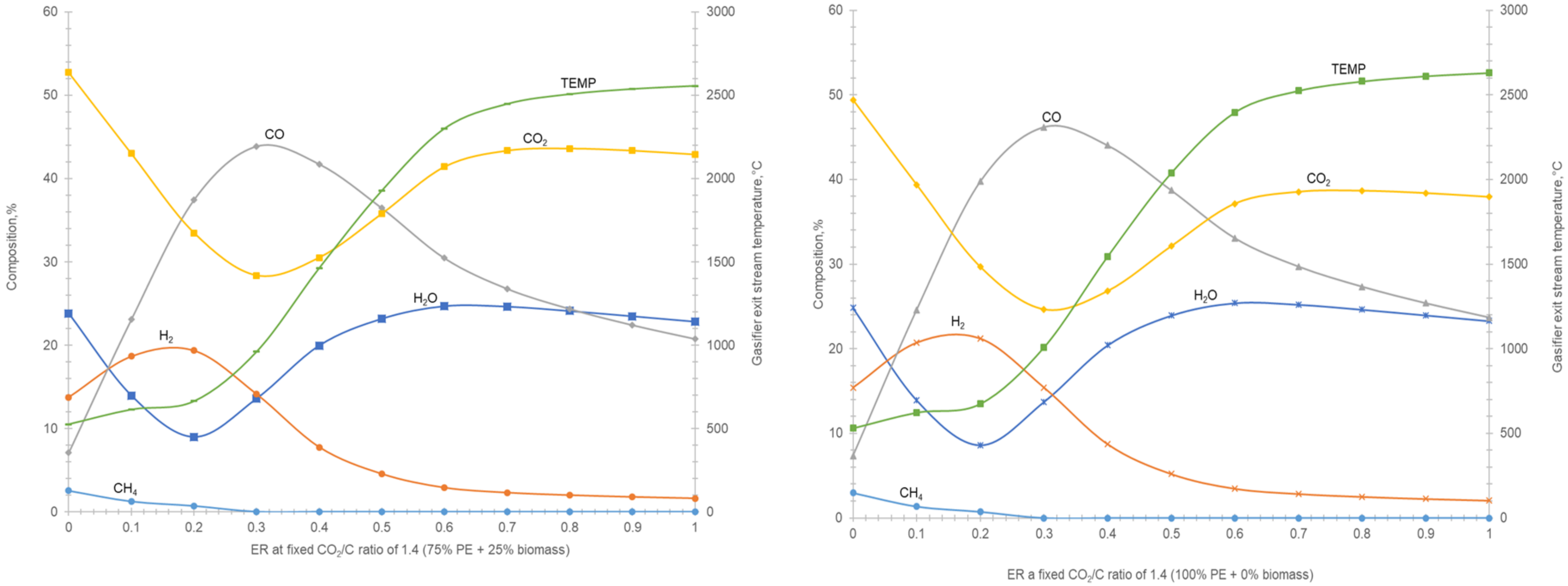


Figure C.13. Effect of the equivalence ratio at fixed CO_2/C ratio of 1.4, on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent was used as a gasifying agent mixture for a blend ratio of (a), (25% PE + 100% biomass) and (b) , (50%PE + 50% biomass).

Figure C.14 shows the effect of the equivalence ratio at fixed CO_2/C ratio of 1.4 on the product gas, when oxygen – carbon dioxide mixture was used as a gasifying agent for the blend ratios of (75% PE + 25% biomass) and (100% PE + 0% biomass). It was found that the increase of ER decreased the H_2, CH_4 and CO in the product gas and increased the CO_2 and H_2O. The increase of ER increased the temperature in the gasifier. High CO composition was favoured at low ER values below 0.4. The trends of the components show similar pattern as the ER increased, irrespective of the type of the feedstock composition used.



(a)

(b)

Figure C.14. Effect of the equivalence ratio at fixed CO_2/C ratio of 1.4, on the product gas composition, when oxygen – carbon dioxide mixture as a gasifying agent was used as a gasifying agent mixture for a blend ratio of (a), (75% PE + 25% biomass) and (b), (100% PE + 0% biomass).

APPENDIX D

D.1. Model description

The feedstock that is pre- treated is introduced into the simulation reactor called RYIELD, through stream FEED. The RYIELD reactor is used in the simulation as a pyrolyzer DECOMP, whereby the non- conventional feedstock, which is biomass (plastic waste) and plastic waste (polyethylene) are converted into conventional components, such as C, H, N, O and S. The pyrolyzer is set at 500˚C, with the aim to decompose the large molecules of the introduced feedstock into smaller molecules (Figure 3.1). The products from the DECOMP reactor are conveyed into the RGIBBS reactor GASIFIER, through the exit stream called CONV. The heat produced from pyrolyzer serves as the source of heat in the RGIBBS gasifier and goes through stream Q- DECOMP.

The pyrolyzed products enter into the RGIBBS reactor (GASIFIER) where they are converted into different product composition, however the syngas composition is the main product and the by- product being the ash. The gasifier was operated in an adiabatic mode, whereby its temperature was highly influenced by the input streams of the gasifying agents such as AIR, STEAM, CO_2 , Q- DECOMP and heat accompanying the products through CONVE.

This Aspen Plus software tool provides a mathematical modelling that enables the user to develop the model and run a simulation and be able to predict the yield of the product gas composition. The user can determine the suitable operating parameters that can be used to optimize the co- gasification system.

The assumptions on this simulation model for the co- gasification of biomass and plastic waste were based on the Aspen Plus V10 and thermodynamic equilibrium model and are as follows:

- All the gasifiers used are operating at steady state, and the operating pressure is kept constant at 1 atm, and there is no heat loss.
- The chemical reactions occur instantaneously, and equilibrium state is obtained rapidly.
- The particle size is not considered.

- Pressure drops are assumed to be small.
- The feedstocks temperature is kept constant at ambient temperature (25˚C).
- All elements that compose the non- conventional components yield into char, H_2, O_2, N_2, Cl_2, S.
- Cyclone efficiency is 100%.

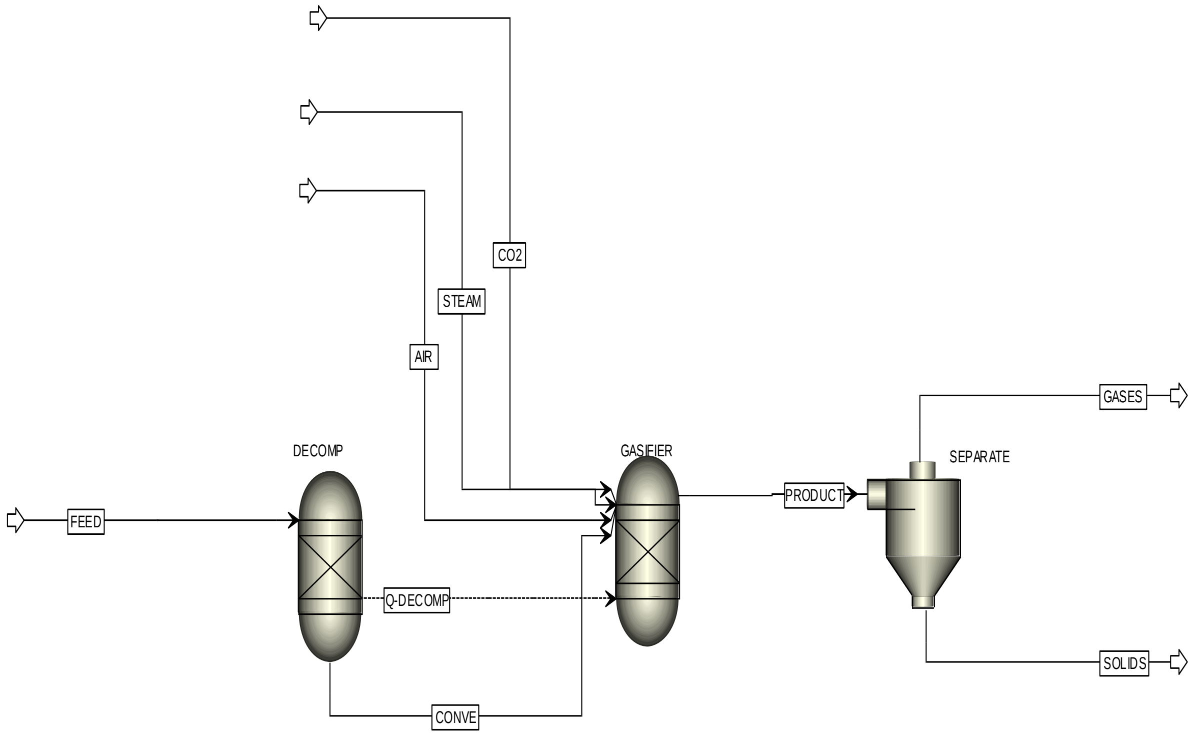


Figure 3.1. Aspen Plus Simulation model for co- gasification of biomass and plastic waste.

D.2. Components

The first step in the development of the simulation model was to specify all the components that were to be used in the process simulation (Table D1). The biomass, polyethylene and ash content were defined as non- conventional solid components, since the exact chemical formulas for these components are unknown. Their enthalpy and density were calculated using the simulation. The Aspen Plus software has property models that can be used to estimate both the enthalpy and density, using formulas derived for biomass and plastic waste.

they did not have exact formulas. Their enthalpy and density were calculated using the simulation. The ASPEN PLUS software has models that can estimate both the enthalpy and density, using the biomass and polyethylene derived materials. The details of the model are discussed later in the chapter, under thermodynamic properties.

Table D.1. Detail information of the components used for modeling of the simulation.

Component ID	**Type**	**Component name**	**Formula**
BIOMASS	Non- conventional	-	-
H_2O	Conventional	WATER	H_2O
O_2	Conventional	OXYGEN	O_2
N2	Conventional	NITROGEN	N_2
NO_2	Conventional	NITROGEN – OXIDE	NO_2
NO	Conventional	NITRIC – OXIDE	NO
S	Conventional	SULFUR	S
SO_2	Conventional	SULFUR – DIOXIDE	SO_2
SO_3	Conventional	SULFUR – TRIOXIDE	SO_3
H_2	Conventional	HYDROGEN	H_2
CL_2	Conventional	CHLORINE	Cl_2
HCL	Conventional	HYDROGEN-CHLORIDE	HCl
C	Solid	CARBON – GRAPHITE	C
CO	Conventional	CARBON - MONOXIDE	CO
CO_2	Conventional	CARBON - DIOXIDE	CO_2
ASH	Non- conventional		-
CH_4	Conventional	METHANE	CH_4
$(C_2H_4)_n$	Non- conventional		-

D.3. Physical property method

The property method chosen for the simulation of the model was Peng – Robinson equation of state with Boston – Mathias alpha function (PR – BM). This property method is chosen based on its ability to be able to facilitate the high temperatures in the gasifier for high carbon conversion efficiency, to be above 700˚C (Ramzan et al. 2011).

The biomass, polyethylene and ash were defined as non- conventional components; therefore, their density and enthalpy were calculated. During their calculation, HCOALGEN was selected as their enthalpy and DCOALIGT as their density model.

The components attributes consists of the ultimate, proximate and sulfur analysis, for biomass, polyethylene and ash, these attributes were required for the specification of enthalpy and density property models. The information of the composition of biomass and plastic waste is provided in Table D.2. The sulfur contained in the pine sawdust was specified as SULFATE, since the biomass used contained low content of sulfur, and does not affect the simulation results.

The stream class was chosen to be “MIXCINC”, since the simulation comprised of both conventional and non- conventional solids. The particle size distribution was not considered for the simulation. “MIXED” sub stream represented the gaseous stream, while “CI” represents the “CISOLID” sub stream for solids and “NC” represents the Non- conventional sub stream.

The biomass pine sawdust feed material was sourced in Mpumalanga, South Africa and the characterization in terms of ultimate and proximate analysis. The ultimate and proximate analysis data for the polyethylene was adopted from the reference of Al Amoodi et al. (2013).

Table D.2. Ultimate and Proximate analysis for the biomass and plastic feedstocks.

Ultimate analysis (Mass percent)	**Biomass**	**Polyethylene**
Carbon (C)	45.5	85.8
Hydrogen (H)	5	13.9
Oxygen (O)	47.1	0
Nitrogen (N)	0.05	0.12
Ash	5.76	0.02

Sulfur (S)	0	0.06
Proximate Analysis (Mass percent)	**Biomass**	**Polyethylene**
Fixed carbon, FC (dry basis)	18.45	0
Volatile matter, VM (dry basis)	79.2	99.85
Moisture content, MC	5.76	0.02
Ash (dry basis)	5.73	0.02
Sulfur analysis (dry basis)	**Biomass**	**Polyethylene**
Pyritic	0	0
Sulfate	0	0
Organic	0	0.06

D.4. Stream specification

The specifications of the streams for biomass, polyethylene, air, steam, carbon dioxide and "Q- DECOMP" are listed in Table D.3.

Table D.3. Specifications of the inlet streams.

Stream	**Component**	**Temperature**	**Pressure**	**Molar/ Mass flow rate**
FEEDSTOCK	Specified as its ultimate, proximate and sulfur analysis	25˚C	1 atm	2000 kg/hr
AIR	21% O_2 79% N_2 (Mole fraction)	500˚C	1 atm	Air to biomass ratio is varied between 0.15 – 0.27 for biomass and between 0.1 – 0.8 for the blend ratios including polyethylene.
Q- DECOMP	-	-	-	-

STEAM	H_2O	500˚C	1 atm	Steam to fuel ratio (SFR) is varied between 0.5 – 3
CARBON DIOXIDE	CO_2	500˚C	1 atm	Carbon dioxide to carbon ratio (CO_2/C) is varied between 0.5 – 1.5

The mole flow rate of air, carbon dioxide and steam were calculated by setting calculator blocks. The air to feedstock ratio is defined as:

$$\text{Air to feedstock ratio} = a_{ir}/\ f_{uel} \qquad (3.1)$$

The steam to fuel ratio (SFR) is defined as:

$$\text{SFR} = (m_{\text{oisture content in fuel}} + s_{\text{team}})/\ d_{\text{ry fuel}} \qquad (3.2)$$

Carbon dioxide to carbon of the fuel ratio is defined as:

$$CO_2/C = (\text{carbon}_{\text{ dioxide}})/c_{\text{arbon in fuel}}) \qquad (3.3)$$

The heat required for the gasifier, from the decomposer was calculated by adding the heat stream.

Table D.4. Operating parameters for the unit blocks.

BLOCK ID	**Temperature (˚C)**	**Pressure (atm)**	**Specification**
DECOMP	500˚	1	Components yields are determined using a calculator block.
GASIFIER	Adiabatic system (Temperature influenced by Q-DECOMP, AIR< STEAM and CO_2/C streams).	1	Calculate the phase equilibrium and chemical equilibrium. Products are determined by

			RGibbs model. RGibbs considers all components as products.
SEPARATE	-	-	The cyclone separation efficiency was assumed to be 1. Therefore, the split fraction was specified as 1.

D.5. Calculator specification

Three calculators were used in the simulation. Each calculator requirements were defined, and FORTRAN statements were used.

D.5.1. Calculator 1

Calculator 1 was used to determine the product composition after the decomposition reactor. Table D.5 shows the definition of the import variables using category streams created in calculator 1.

Table D.5. Definition of the import variables for the Calculator 1.

Variable Name	**Type**	**Stream**	**Sub - stream**	**Component**	**Attribute**	**Elements**
ULT	Compattr-Vec	BIOMASS	NC	BIOMASS/BLEND RATIOS/POLYETHYLENE	ULTANAL	
WATER	Compattr - Var	BIOMASS	NC	BIOMASS/BLEND RATIOS/POLYETHYLENE	PROXANAL	1

ULT is the vector defined for accessing the values in the ultimate analysis of the fuel. Water is the variable corresponding to the first element in the proximate analysis of the feedstocks (biomass/blend ratios/polyethylene), which represents moisture content. The ULTANAL and PROXANAL represent the ultimate and proximate analysis.

Table D.6. The export variables used in the block's category.

Variable Name	**Type**	**Block**	**Variable**	**ID1**	**ID2**
H_2O	Block Var	DECOMP	MASS - YIELD	H_2O	MIXED
ASH	Block Var	DECOMP	MASS - YIELD	ASH	NC
CARB	Block Var	DECOMP	MASS - YIELD	CARB	CISOLID
H_2	Block Var	DECOMP	MASS - YIELD	H_2	MIXED
N_2	Block Var	DECOMP	MASS - YIELD	N_2	MIXED
CL_2	Block Var	DECOMP	MASS - YIELD	CL_2	MIXED
SULF	Block Var	DECOMP	MASS - YIELD	SULF	MIXED
O_2	Block Var	DECOMP	MASS - YIELD	O_2	MIXED

ID 1 stands for the corresponding components. ID 2 stands for the classification of the component.

The Fortran statements was entered as below:
FACT = (100 - WATER) / 100
H_2O = WATER / 100
ASH = ULT (1) / 100 * FACT
C = ULT (2) / 100 * FACT
H_2 = ULT (3) / 100 * FACT
N_2 = ULT (4) / 100 * FACT
CL_2 = ULT (5) / 100 * FACT
S = ULT (6) / 100 * FACT
O_2 = ULT (7) / 100 * FACT

Here FACT is the factor to convert the ultimate analysis to a wet basis. This calculator block was executed before the GASIFIER block operation.

D.5.2. Calculator 2:

Table D.7. Calculator 2

Variable Name	**Variable Classification**	**Type**	**Stream**	**Subtream**	**Variable**
BIOMASS/BLEND RATIOS/POLYETHYLENE	Import	Stream - Var	BIOMASS/BLEND RATIOS/POLYETHYLENE	NC	MASS - FLOW
AIR	Export	Stream - Var	AIR	MIXED	MOLE - FLOW

The Fortran statements was entered as below:

AIR = 1.12 * BIOMASS/BLEND RATIOS/POLYETHYLENE

D.5.3. Calculator 3

Calculator 3 was used to determine the steam and carbon dioxide mole flow rate. Table D.8 shows the definition of the variables using category Streams created in the Calculator 3.

Table D.8. Definition of the variables for the Calculator 3.

Variable Name	**Variable Classification**	**Type**	**Stream**	**Sub - stream**	**Variable**	**Component**
BIOMASS/BLEND RATIOS/POLYETHYLENE	Import	Stream - Var	BIOMASS/BLEND RATIOS/POLYETHYLENE	NC	MASS FLOW	**-**
MOISTURE	Import	Mole - Flow	AFT-DECOMP	MIXED	-	**H_2O**
STEAM	Export	Stream - Var	STEAM	MIXED	MOLE FLOW	**-**

The Fortran statements was entered as below:

STEAM=0.6*(BIOMASS-MOISTURE)-MOISTURE

D.6. Validation of model

The capabilities of the model was then tested for validation, using a reference from an experimental data from Lv et al. (2003) for syngas components such as CO, H_2, CO_2 and CH_4. In the experiment, pine sawdust, which is the same material as used in this study for biomass feedstock was used. However, the operating conditions were different as shown in Table D.9.

Table D.9. Operating conditions.

Conditions	**Experiment (Lv et al.2003)**	**Co- gasification simulation**
Air flow kept fixed	0.5 Nm^3/h	51.27 kmol / hr
Steam to biomass ratio (SBR)	0 - 4	0 - 3
Temperature	800˚	1043 - 1650˚C

Therefore, the results of the experimental data and simulation data were compared. The results displayed in Table D.10 between the experimental data and simulation are mostly in agreement with each other, however only the CO_2 composition that shows a huge difference of 16%, therefore this percentage gas can be justified by highlighting that the air flow rates, are measured differently, with different units used, that might have an impact on the carbon dioxide yield.

Table D.10. The difference of syngas composition between the experimental data and simulation data.

Syngas composition, %	**Experimental data**	**Simulation data**	**Difference**
CO	38%	40%	-2%
H_2	33%	27%	3%
CO_2	18%	2%	16%
CH_4	7%	7%	0%

REFERENCES

(1) Al – Amoodi. N, Kannan. P, Al Shoaibi. A, Srinivasakannan. C, (2013), Aspen Plus Simulation of Polyethylene Gasification under Equilibrium Conditions, *Chemical Engineering Communications*, 200, 7 - 9.

(2) Lv. P. M, Xiong. Z. H, Chang. J, Wu.C. Z, Chen.Y, Zhu. J.X, (2004), An Experimental Study on Biomass Air- Steam Gasification in a Fluidized Bed, *Bioresource Technology* 95, 95 – 101.

(3) Ramzan. N, Ashraf. A, Naveed. S, Malik. A, (2011), Simulation of hybrid biomass gasification using Aspen Plus: A Comparative Performance Analysis for Food, Municipal Solid and Poultry Waste, *Biomass and Bioenergy*, 35, 3962 – 3969.