INVESTIGATION of DIOXIN FORMATION in CONVENTIONAL GASIFICATION PROCESS with MODELED HAZARDOUS WASTE

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Submitted to the Institute of Environmental Sciences in partial fulfillment of the requirements for the degree of

Doctor

of

Philosophy

Boğaziçi University

2015

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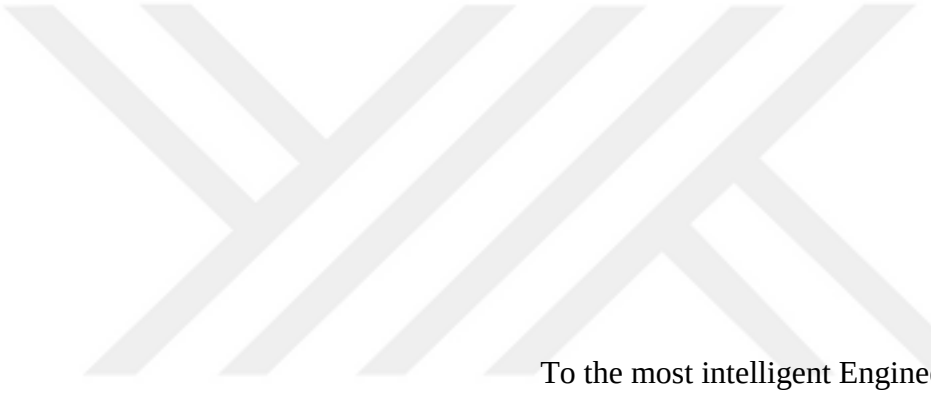
DATE OF APPROVAL: 06/11/2015



To the most intelligent Engineer I have ever met,

ACKNOWLEDGMENTS

I would like to express my deep thanks to my thesis supervisor Prof. Dr. Orhan YENİGÜN, for giving me the opportunity to continue my PhD education in Boğaziçi University and his endless support during my study.

The financial support provided by the Boğaziçi University Research Fund to the project 5728D is greatly acknowledged.

I would like to thank to my dearest friends Mrs. Işıl ÇOŞKUN and Mr. Emin KAYALI, for providing me the activated carbon and the virgin PVC materials to use in my experiments.

My great thanks go to the researchers, Berrin Bay Engin, Ufuk Kayahan, and all others, staff and technicians of the Biomass and Coal Gasification and Combustion Laboratory of Energy Institute at TUBITAK- Marmara Reseach Center (MRC). I would like to thank to Dr. Özgen ERCAN, Dr. Mehmet ÜNSAL, Dr. Sönmez DAĞLI and the sampling and analysing team of the Environment Institute of MRC for their great support and help during dioxin sampling and analysing.

I want to gratefully thank to Assoc. Prof. Fehmi AKGÜN for giving me this research opportunity for performing my experiments in Tubitak-MRC facilities.

Last but definitely not least, I would like to thank to two special people. This research project would not have been possible without the leadership and support of Prof. Dr. Hayati OLGUN and technician support of Mr. Erdal GÜGÜK during my experiments.

INVESTIGATION of DIOXIN FORMATION in CONVENTIONAL GASIFICATION PROCESS with MODELED HAZARDOUS WASTE

The hazardous waste incineration has significant environmental concern due to its potential to produce dioxin and furan emissions. Thus, the gasification which is a mature technology used to produce energy and chemicals more than 100 years may be used as an alternative to hazardous waste disposal. However, waste gasification has been studied for just decades with refused derived fual (RDF) and municipal solid waste. Therefore, the hazardous waste gasification is completely new research area.

The aim of this study was to investigate the applicability of gasification to hazardous waste disposal from the dioxin/furan formation point of view. For this reason, gasification experiments were conducted with modeled hazardous waste which was created by mixing the hazelnut shell and virgin polyvinylchloride (PVC) due to its chlorine content. The factors that effect the dioxin/furan formation were examined and the formation mechanism of dioxins was explained as the result of the research study. The investigation of the results focused mainly on the effect of the operating parameters on dioxin formation and the distribution of dioxin congeners in different sampling points.

It was found that the congener distribution in all measurement points showed strong similarity. Whether it was in syngas or in the bottom ash the dominant congeners have similar sequence. This similarity was an indicator that the dioxins were formed from the same macromolecular carbon structure which widely exists as tar form in gasification. Also gasification periods, Equivalence Ratio (ER), temperature and hyrogenchloride (HCl) have direct effect on dioxin formation. The dioxin analysis results also showed that the formation mechanism of dioxins was de novo synthesis which is occurred at the post-combustion zone of the plants in the existing study.

MODELLENMİŞ TEHLİKELİ ATIK İLE KONVANSİYONEL GAZLAŞTIRMADA DİOXİN OLUŞUMUNUN İNCELENMESİ

Tehlikeli atıkların yakılması, dioxin ve furan emisyonları oluşturması sebebiyle çevresel açıdan önemli bir endişe taşımaktadır. Bu sebeple, 100 yıldan fazla süredir enerji ve kimyasalların üretilmesinde kullanılan olgunlaşmış bir proses olan gazlaştırma tehlikeli atıkların bertarafında bir alternatif olarak kullanılabilir. Ancak atıkların gazlaştırılması sadece 10 yıllardan beri atıktan türetilmiş yakıt (RDF) ve evsel atık üzerinde çalışılmaktadır. Bu nedenle tehlikeli atıkların gazlaştırılması tamamı ile yeni bir araştırma alanıdır.

Bu çalışmanın amacı gazlaştırmanın tehlikeli atıkların bertarafına uygulanabilirliğini dioxin/furan oluşumu açısından değerlendirmektir. Bu sebeple, fındıkkabuğuyla klor içeriği sebebi ile PVC hammaddesinin karıştırılmasıyla elde edilmiş tehlikeli atık kütlesi ile deneyler gerçekleştirilmiştir. Sonuç olarak, dioxin/furan oluşumunu etkileyen faktörler incelenmiş ve dioxinlerin oluşum mekanizması tanımlanmıştır. Sonuçların incelenmesi temel olarak, işletme parametrelerinin dioxin oluşumu üzerindeki etkilerine ve farklı numune alma noktalarındaki dioxin congenerlerinin dağılımı üzerine odaklanmıştır.

Dioxin ölçümü yapılan bütün noktalarda, dioxin congenerlerinin kuvvetli bir benzerlik gösterdiği bulunmuştur. Syngazda veya dip külünde olsun konsantrasyon açısından baskın congenerler benzer bir sıralamaya sahip omuşlardır. Bu benzerlik dioxinlerin gazlaştırmada geniş bir şekilde yer alan tar formunda var olan aynı makromoleküler karbon yapısından oluştuklarının bir göstergesidir. Ayrıca, gazlaştırma periyotları, kullanılan hava/yakıt oranı, sıcaklılk ve hidrojen klorür, dioxin oluşumu üzerinden direkt olarak etkili olmuştur. Dioxin analiz sonuçları ayrıca mevcut çalışmada dioxinlerin oluşum mekanizmasının proseslerin yanma bölgesi sonrasında gerçekleşen “de novo” sentezi olduğunu göstermiştir.

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LIST OF ABBREVIATIONS

Symbol	Explanation
PCDD	Polychlorinated dibenzo-p-dioxins
PCDF	Polychlorinated dibenzofurans
AC	Activated Carbon
PAH	Polycyclic Aromatic Hydrocarbons
TEF	Toxic Equivalency Factors
TEQ	Toxic Equivalency

1. INTRODUCTION

Gasification process has gained interest since 1970s for energy production due to the growing concern about the estimations for fossil fuels reserves would be depleted and demand would exceed reserves by the 1980s and 1990s. Therfore, the research studies are mainly focused on biomass gasification for energy production. However, waste gasification has shorter research history and most particularly the hazardous waste gasification has limited research data in conventional gasification process. In this research study, it is intended to investigate the applicability of gasification process to hazardous waste disposal. The evaluation of the dioxin formation mechanism and the effecting factors were tried to be understood.

According to the Turkish Statistical Institute 806 thousands tons of hazardous waste has been generated in 2012 based only on manufacturing industry self-declaration in Turkey. Ministry of Environment and Urban Planning survey has established that 629,029 tons hazardous waste was processed in 2009 in Turkey. The actual hazardous waste volume is estimated as 5-6 million tons per year. Turkey also has a growing concern about hazardous waste since the buried abandoned hazardous waste drums were found in an empty area in Tuzla, Istanbul in 2006. This was the first public awareness about hazardous waste in Turkey. Thus, proper management of hazardous waste is a curicial step for a healty environment.

One of the important steps of waste management is the waste disposal. Thermal treatment methods- mainly incineration- to dispose of the hazardous wastes have been used for more than 100 years. The most used thermal treatment technique is incineration. Incineration is a combustion process which is applied to both municipal and hazardous wastes in order to minimize the volume of the waste and to destroy the hazardous components. This destruction capability of incineration makes it favorable for waste disposal. Although incineration eliminates the hazardous constituents of the waste and decreases the waste volume; the process has potential to form one of the most toxic compounds, dioxins. Dioxins which are the general name of 75 polychlorinated dibenzo-para dioxin and 135 polychlorinated dibenzo furan compounds are formed during thermal

processes. The individual compounds within the groups are often referred to as congeners and congeners with the same number of chlorine substituents are called homologues. Hazardous waste incineration is generally accepted as the primary source of dioxin formation. Due to the incineration is a controversial process about dioxin formation, there is a need to find an alternative thermal process to dispose the hazardous waste.

Gasification is also a well-known mature thermal conversion process which has been commercially applied for more than a century in production of both fuels and chemicals. Gasification converts carbonaceous material into combustible gases in a reducing atmosphere with sub-stoichiometric air supply. The produced gas is called synthetic gas (syngas) or producer gas and consists of mainly CO, H_2, CH_4 and inert gases. The main difference between incineration and gasification is the supplied air amount inside the reactor. Incineration uses excess amount of air to convert the carbonaceous material to CO_2 and H_2O in an oxidative medium while gasification uses starved air to convert the carbon-containing feedstock into a combustible gas in a reducing medium. Incineration produces non-combustible flue gas which has to be treated prior to discharge to the atmosphere; however, gasification produces combustible synthetic gas which can be used to produce energy and/or chemicals.

Dioxin formation mechanisms were excessively studied in incineration process. Unlike in the industrial combustion processes, formation and emission of dioxins from processes based on the gasification technologies have so far not been studied in detail (Cieplik and Kamp, 2009). Few studies which mentioned about dioxin concentrations in gasification process have measurements in syngas and/or ash. Dioxin congener distribution was only examined in 2 studies with addition sub-stoichiometric air to pyrolysis process not in a gasifier.

The research study was performed at the Biomass and Coal Gasification and Combustion Laboratory of Energy Institute at TUBITAK-MRC with financial support from Bogazici University. The financial support was used for the dioxin samplings and measurements which can only be carried out by Tubitak in Turkey. Tubitak-Energy Institute Management allowed using the existing gasification set-up for the research study and provided technician support during the experiments. A conventional down-draft

gasifier with gas cleaning unit were used to perform the experiments. Modeled hazardous waste was used as feedstock. Formation of dioxins was investigated by examination of the distribution of total dioxin concentrations as well as the congener concentrations within the experimental set-up. The effects of gasification process features such as operating conditions, reducing medium, and tar formation on dioxin formation mechanism are evaluated.

The set-up configuration consists of gasifier, cyclone, dolomite column, heat exchanger, water scrubber, perlite column, ID fan, activated carbon filter, and stack respectively. Two different feedstock menus were prepared with hazelnut shell and virgin PVC. Hazelnut shell was used as biomass feedstock in order to maintain gasification reactions properly according to the wide usage in gasification. Virgin PVC was used to create representative hazardous waste mixture because of its chlorine (Cl) content. There are many processes that deal with PVC waste aim to recover chemicals such as HCl gas or produce energy. It is pointed again that virgin PVC is only used as chlorine source to create hazardous waste feedstock in order to observe the dioxin formation during gasification in this research study. Eventually, a modeled hazardous waste feedstock was created with the mixture of hazelnut shell and virgin PVC. Virgin PVC has been mixed with 1% and 2% (w/w) Cl concentrations into the hazelnut shell in order to maintain the halogen content of the hazardous waste feedstock. In general, chlorine content of the feedstock should be kept less than 2% by weight in the feedstock menu during thermal processes to avoid corrosion and generation of harmful chemicals such as dioxins. As a result of PVC thermal degradation, the hydrochloric acid gas (HCl) was released in the gasifier and participated to the dioxin formation. Dioxin formation was evaluted according to the operating conditions, total concentration distribution with in the set-up, and congener distribution. It was observed that the operating conditions are the main effecting factor on dioxin formation in the research study as well as in the literature. The obtained data could be used as basic information prior to using gasification processes for hazardous waste disposal in the future.

The dioxin formation mechanism is suggested as “de novo synthesis” for the existing research study. The congener distribution which were examined in all mediums throughout the system was revealed that the similar carbonaceous materials which have similar

morphology and chemical properties, participated to the dioxin formation altough the sampling points has different temperature ranges. This carbonaceous material comes from the tar formation in gasification and provides the main carbon structure for dioxin formation via fly ash catalytic effect. The tar production is the most important issue has to be solved in gasification process whether it will be used to dispose hazardous waste. Thus, the existing study is important about understanding the dioxin formation mechanism in gasification process and the effect of gasification features on dioxin formation. The findings are also important for future works to be able to design the suitable configuration for dioxin-free hazardous waste gasification and suggest the gasification as an alternative to incineration.

The investigation of the results was done from environmental engineering view point. Energy production part of gasification process has not been included within the scope of this research study. The process design, air pollution control, feedstock preparation, operation conditions should be considered for hazardous waste gasification. Fly ash treatment and control methods such as melting should be applied in gasification process if the hazardous waste will be disposed by gasification.

Chapter 2 presents the theoretical background about gasification process and dioxin. History of gasification, process principles, reactor types, and the gasification applications in the world were introduced. Dioxin definition, dioxin compounds, congeners, and dioxin formation mechanisms were also represented in this chapter.

Chapter 3 represents the previous gasification research studies which dioxin measurement had been performe. There are limited studies and limited data about dioxin concentrations in gasification process. Comments about those dioxin concentrations which have been determined at those gasification research studies were made in the discussion chapter.

Chapter 4 explains the materials and methods which have been used and applied in research study. The experimental set-up consists of a down-draft gasifier, cyclone, dolomite column, heat exchanger, water scrubber, perlite column, ID fan, activated carbon

filter, and stack with flare. System parts, materials and methods used in the experiments were explained.

Chaper 5 explains the start-up preparations and research experiments. Prior to the research experiments system was checked and modified. After system modifications were carried out, the research experiments were performed. The operation preparation steps and the experiemnts were explained in this chapter.

Chapter 6 is the discussion part of the thesis. In this chapter, temperature, ER, and chlorine effect on dioxin formation in conventional down-draft gasification process are investigated. Dioxin formation mechanism in the existing study is discussed not only with dioxin analyses results in different sampling points and mediums, but also with comparison with the other similar research studies'.

Chapter 7 gives the conclusion and recommendations.

Chapter 8 gives the future works and follows with the References.

1.1. Aim of The Study

The research idea was created in 2005. During my biomass gasification studies in Newcastle University Upon Tyne in England, I decided to apply gasification process to hazardous waste disposal. After the return to Turkey from England, I started to look for a suitable set-up for my experiments. However, there was no opportunity to find and use a gasification set-up in Turkey. Also, there is not much gasification research laboratory to study with waste and/or hazardous waste. I tried to look for the foreign-based opportunities for a long time. One was found in a private research company in Italy, but the communications could not reach the desired result. Secondly, almost a perfect set-up was discovered in a University in Greece. However, in spite of tens of calls, the related person has rejected to answer the calls every time via her secretary. Another very good set-up was found in a University in Russia. Also that person has rejected to answer the calls. Even once, I visited to Royal Institute of Technology with my Supervisor in order to negotiate about establishing a laboratory scale set-up in Boğazici University Laboratory.

Unfortunately, this communication was interrupted surprisingly. Consequently, it took more than 3 years to find a gasifier for the research study. Finally in 2010, the experiments with modelled hazardous waste were begun in Tubitak-MRC.

The aim of the study was to investigate the applicability of gasification process to hazardous waste disposal from the dioxin/furan formation point of view. To realize this aim, the investigation was performed with a series of gasification experiments in order to observe the dioxin concentrations. The gasification experiments were conducted with modeled hazardous waste feedstock which was synthetically prepared by mixing the common gasification biomass hazelnut shell and virgin polyvinylchloride (PVC). PVC was specially chosen due to its chlorine content to maintain the chlorine source in order to observe whether if dioxin will form or not. Chlorine was added to the feedstock with the common proportions which are used in the incineration plants to investigate the chlorine rate effect on dioxin formation. In other words, the question “Can the gasification process be an alternative to incineration for hazardous waste disposal from the dioxin formation point of view?” was tried to be answered with this study.

On the other hand, although the virgin PVC was used as a chlorine source in order to create a synthetic hazardous waste, the study may give idea about the disposal options for PVC containing waste. From the literature, the virgin PVC is commonly used in coatings for swimming pools, shoe soles, hoses, diaphragms tunnel, coated fabrics, PVC sheets, and building applications (Ref: https://en.wikipedia.org/wiki/Polyvinyl_chloride). Thus, those types of waste materials may be gasified for disposal while recovering their energy content and converting their carbon into useful gases.

2. THEORETICAL BACKGROUND

2.1. Gasification Process

2.1.1. Gasification History

Gasification technologies have been commercially applied for more than a century for the production of both fuels and chemicals. The basic principles of gasification have been known since the late 18th century. The earliest practical production of synthetic gas is reported to have taken place in 1792 when Murdoch, a Scottish engineer, pyrolyzed coal in an iron retort and then used the product, coal gas, to light his home. Later on, Murdoch built a gas plant for James Watt, the inventor of the steam engine, and applied the technology to lighting one of Watt's foundries.

The first gas company was established in 1812 in London to produce gas from coal and to light the Westminster Bridge. In 1816, the first gas plant for the manufacture of syngas from coal was built in the United States to light the streets of the city of Baltimore. By 1826, gas plants were also built to manufacture gas for lighting the streets of Boston and New York City. Soon thereafter, gas plants and distribution Networks were built to light the streets of most major cities throughout the world. In 1855, the invention of the Bunsen burner premixed air and gas, allowing it to burn more economically, at very high temperatures, and without smoke. This invention added impetus to the further use of gas. In the latter half of the 19th century coal gasification became a commercial reality.

By 1875, manufactured gas was being widely used for home lighting, and by the end of the century it was applied to domestic and industrial applications. By the 1920s, producer gas systems for operating stationary engines as well as trucks, tractors, and automobiles were demonstrated in Europe and elsewhere. In the United States more than 1200 gas plants were in operation by the late 1920s. In early 1900s, gasification processes which use biomass such as agricultural waste materials as feedstock were also widely used to manufacture synthetic gases for production of fuels, chemicals, and hydrogen (Rezaiyan and Cheremisinoff, 2005).

During World War II, biomass power gasifiers reappeared in force in Europe, Asia, Latin America, and Australia. The cause was the general scarcity of petroleum fuels. Gasification was used as energy production process while convert the carbonaceous material to syngas. In Europe alone, almost a million gasifier-powered vehicles helped to keep basic transport systems running. In most cases, the gasifiers were fueled by charcoal or wood. However, most of the systems mobilized by the exigencies of war were readily abandoned with the return of peace and the renewed availability of relatively inexpensive petroleum fuels (Stassen, 1995).

After World War II, the discovery of large quantities of low-cost natural gas with heating values of about 37 MJ/m^3 led to the demise of the synthetic gas manufacturing industry. The energy crises of the 1970s and 1980s appear to have rekindled interest in biomass gasification. Again, a primary attraction has been the potential of biomass gasification to substitute for petroleum products. Another factor in the renewed interest in biomass gasification has been the increased energy demand of developing countries.

Throughout the 1980s, researchers and industry came to recognize some of the environmental benefits of gasification technology. More restrictive and stringent environmental standards aimed at controlling power plant emissions, and domestic and industrial waste landfills, and an increased emphasis on greenhouse gas reductions provided incentives for both government and industry stakeholders to explore and promote the commercialization of gasification technologies (Rezaiyan and Cheremisinoff, 2005).

2.1.2. Gasification Process Description

Gasification is a thermochemical process which uses starved air in order to convert the carbon-containing feedstock such as coal, biomass or waste, into a combustible gas containing mainly CO, H_2, and CH_4 and inert gases, in a reducing medium (Erlich, 2009). The produced gas is called synthetic gas, syngas, which can be used not only to produce energy via turbines or engines but also chemicals such as methanol and hydrogen.

Gasification process takes place mainly in five steps. Those are explained in the following and the shematic illustrations are shown in Figure 2.1.

1. Drying : In drying step, feedstock loses its moisture content with the heat comes from oxidation step. In other words, as every beginning step of thermal processes, the gasification process begins with drying. Drying occurs at temperatures between 100-150^{o}C. There is no decomposition reaction in this step. The lower the moisture content, the more heat is available for pyrolysis and gasification steps. Generally, gasifiers usually handle up to 30% moisture content of the feedstock.

2. Pyrolysis: Pyrolysis is the thermal decomposition of feedstock fuels in the absence of oxygen. In pyrolysis step, according to the heating the feedstock in the range of 200-500^{o}C, volatile compounds of carbonaceous material are released. The products from pyrolysis are combustible and inert gases, such as CO, CO_2, H_2 liquids and solid reside such as char, tars, oils, and hydrocarbons.

3. Oxidation: The partial of the volatile products of pyrolysis involves a series of highly exothermic reaction which generate the thermal energy is needed to initiate and sustain pyrolysis and also dry the feedstock in the drying zone. In other words, oxidation is the heat source in the gasifier. The step takes place at the temperature of 700-2000^{o}C. The products are CO_2, CO, H_2, H_2O, hydrocarbon gases, residual tars and char. The first oxidation reactions involve combustion of volatiles from the pyrolysis step; secondly, some of the char is oxidized.

4. Reduction: In reduction zone, chemical reactions take place in the absence of oxygen. Heat is required during this step; therefore, the temperature of gas goes down during reduction. If complete gasification takes place, all the carbon is burned or reduced to carbon monoxide, a combustible gas and some other mineral matter is vaporized. The remains are ash and some char.

2.1.2.1. Reactor Types. Three main reactor types which are used in gasification are briefly described below.

Up-Draft Gasifier.

An updraft gasifier has zones for partial combustion, reduction, and pyrolysis. Air is introduced at the bottom and acts as countercurrent to feedstock/fuel flow.

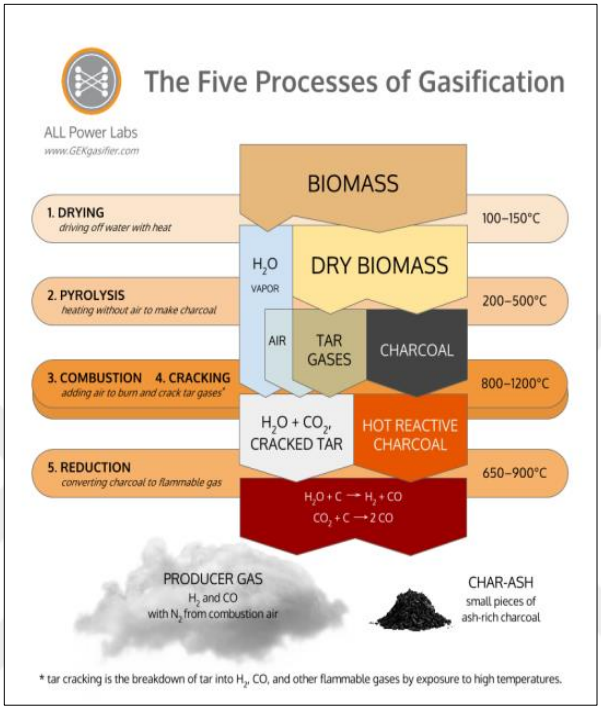


Figure 2.1. Shematic illustration of gasification process.
(Source: http://www.allpowerlabs.com/gasification-explained)

The gas is drawn at higher location. The updraft gasifier achieves the highest efficiecy as the hot gas passes through feedstock bed and leaves the gasifier at low temperature. The heat given by gas is used to preheat and dry the feedstock. Excessive amount of tar in raw gas and poor loading capability are the disadvantages of updraft gasifier. Shematic illustration of up-draft gasifier can be seen in Figure 2.2.

Down-Draft Gasifier.

In down-draft gasifier, feedstock is introduced from the top of the reactor and the air is fed into the lower section of the gasifier. The pyrolysis and ombustion products flow downward. The hot gas then moves downward over the remaining hot char, where gasification takes place. A lower overall efficiency and difficulties in handling higher moisture and ash content are common problems in small downdraft gas producers. The time (20-30 minutes) needed to ignite and bring plant to working temperature with good

gas quality is shorter than updraft gas producer. It has low tar content but has low energy output. Shematic illustration of down-draft gasifier can be seen in Figure 2.3.

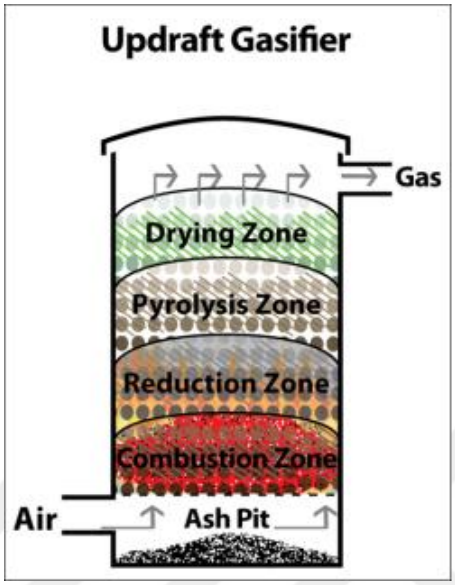


Figure 2.2. Up-draft gasifier.

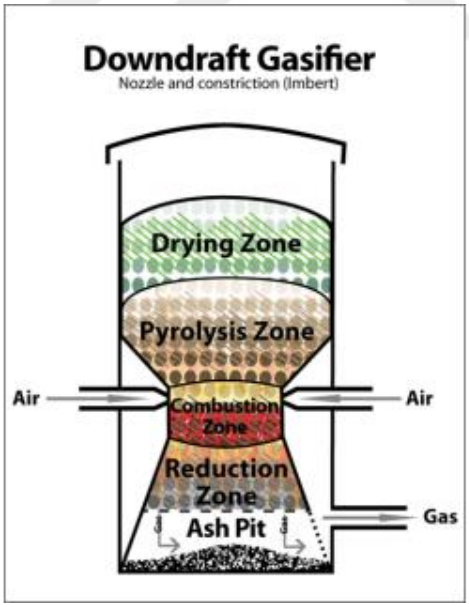


Figure 2.3. Down-draft gasifier.

Cross-Draft *Gasifier*.

Crossdraft gasifiers, although they have certain advantages over updraft and downdraft gasifiers, they are not of ideal type. The disadvantages such as high exit gas

temperature, poor CO_2 reduction and high gas velocity are the consequence of the design. Unlike downdraft and updraft gasifiers, the ash bin, fire and reduction zone in crossdraft gasifiers are separated. These design characteristics limit the type of fuel for operation to low ash fuels such as wood, charcoal and coke. Start up time (5-10 minutes) is much faster than that of downdraft and updraft units. The relatively higher temperature in cross draft gas producer has an obvious effect on gas composition such as high carbon monoxide, and low hydrogen and methane content when dry fuel such as charcoal is used. Crossdraft gasifier operates well on dry air feeding and dry fuel. Shematic illustration of cross-draft gasifier can be seen in Figure 2.4.

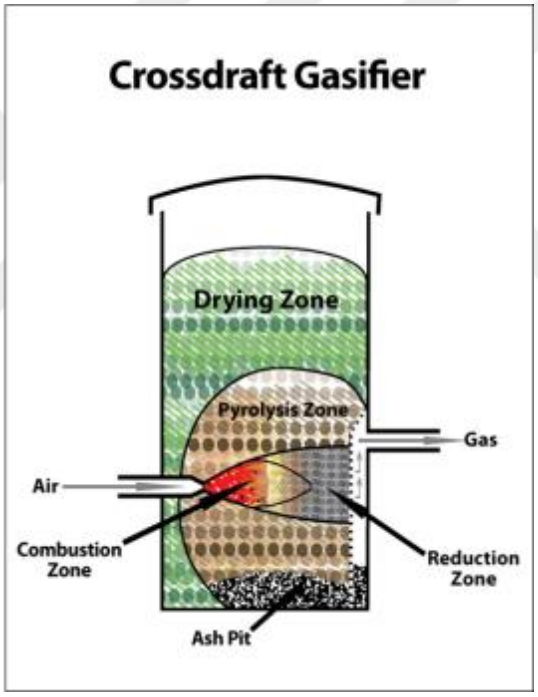


Figure 2.4. Cross-draft gasifier.

Fluidized Bed Gasifier.

Fluidized-bed gasifiers which an illustration can be seen in Figure 2.5., suspend feedstock particles in an oxygen rich gas so the resulting bed within the gasifier acts as a fluid. Fluidized bed gasifiers offer load flexibility and high heat transfer rates, however, lower temperature operation limits feedstock to reactive and low rank coals. Bubbling Fluidized-Bed (BFB) gasifiers are the most demonstrated of the biomass gasification technologies reviewed. The BFB technology has been operated over a wide range of

temperatures, pressures, throughput, and a variety of biomass types. Fuel, chemicals, and hydrogen production benefits from high temperatures, like those seen in coal gasification, because at temperatures over 1200-1300 °C little or no tar, methane, or higher hydrocarbons are formed, while hydrogen and carbon monoxide production in syngas is maximized.

Circulating Fluidized-Bed (CFB) gasifiers have not been demonstrated to quite the extent of BFB. In fact, the literature surveyed showed very few tests at elevated pressure and all with temperatures below 1000 °C. While Bubbling Fluidized-Bed gasifiers have been tested (at the time of the article) up to 35 bar, CFBs have only been tested up to 19 bar. Like BFB gasification, particle sizes would need to be reduced and feedstock dried. Probably the biggest issue with CFB is the lack of demonstrations with pure oxygen and/or steam, which greatly limits the confidence in the technology for synthesis applications. From the information available, CO2 levels in the syngas are low, as are H2/CO ratios, because the lack of steam means the water-gas-shift reaction is suppressed.

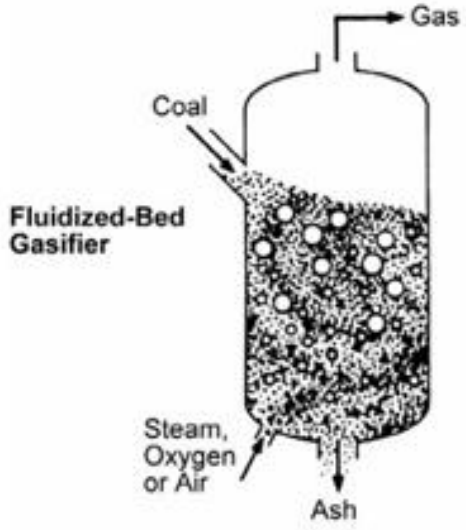


Figure 2.5. Fluidized bed gasifier (Source: Electric Power Research Institute USA).

2.1.2.2. Chemistry of Gasification. It can be viewed as consisting of a few major reactions which can progress to different extents depending on the gasification conditions (like temperature and pressure) and the feedstock used. Combustion reactions take place in a gasification process, but, in comparison with conventional combustion which uses a stoichiometric excess of oxidant, gasification typically uses one-fifth to one-third of the

theoretical oxidant. At that moment to define “The Equivalence Ratio (ER)” would be necessary that the ER is defined as the actual air fuel ratio/the air fuel ratio for complete combustion by Reed and Desrosiers (1979). This only partially oxidizes the carbon feedstock. As a ”partial oxidation” process, the major combustible products of gasification are carbon monoxide, CO, and hydrogen, H_2, with only a minor portion of the carbon completely oxidized to carbon dioxide, CO_2. The heat produced by the partial oxidation provides most of the energy required to drive the endothermic gasification reactions. The major chemical reactions within a gasification process are those involving carbon, CO, CO_2, hydrogen, water /steam and methane, are shown from Equation (2.1) to (2.8) as follows:

The combustion reactions:

$C + ½\ O_2 \rightarrow CO$ (-111 MJ/kmol) (2.1)

$CO + ½\ O_2 \rightarrow CO_2$ (-283 MJ/kmol) (2.2)

$H_2 + ½\ O_2 \rightarrow H_2O$ (-242 MJ/kmol) (2.3)

Other important gasification reactions include:

$C + H_2O \leftrightarrow CO + H_2$ (+131 MJ/kmol) “The Water-Gas Reaction” (2.4)

$C + CO_2 \leftrightarrow 2CO$ (+172 MJ/kmol) “The Boudouard Reaction” (2.5)

$C + 2H_2 \leftrightarrow CH_4$ (-75 MJ/kmol) “The Methanation Reaction” (2.6)

With the above, the combustion reactions are essentially carried out to completion under normal gasification operating conditions. And, under the condition of high carbon conversion, the three heterogeneous reactions in the equilibrium 2.4 to 2.6 can be reduced to two homogeneous gas phase reactions of water-gas-shift and steam methane-reforming reactions shown in the equlibrium 2.7 and 2.8 which collectively play a key role in determining the final equilibrium syngas composition.

$CO + H_2O \leftrightarrow CO_2 + H_2$ (-41 MJ/kmol) “Water-Gas-Shift Reaction” (2.7)

$CH_4 + H_2O \leftrightarrow CO_2 + 3H_2$ (+206MJ/kmol) “Steam-Methane-Reforming Reaction” (2.8)

Under the sub-stoichiometric reducing conditions of gasification, most of the feedstock's sulfur is converted to hydrogen sulfide, H_2S, and, to a lesser degree, carbonyl sulfide, COS. Nitrogen in the feed is converted to nitrogen N_2, with some ammonia NH_3 and a small amount of hydrogen cyanide HCN. Chlorine in the feed is primarily converted to hydrogen chloride, HCl. In general, the quantities of sulfur, nitrogen, and chloride in the feedstock are sufficiently small that they have a negligible effect on the main syngas components of hydrogen H_2 and CO.

Trace elements associated with both organic and inorganic components of the feedstock, such as mercury and other heavy metals, appear in various ash fractions as well as in gaseous emissions, which can be removed from the syngas prior to its final application (http://www.netl.doe.gov/).

2.1.2.3. Syngas Characteristics. Syngas is the mixture of combustible and non-combustible gases. The quantity of gas constituents of syngas depends upon the type of feedstock and operating conditions. The heating value of the gas varies from 4.5 to 6 MJ/m^3 depending upon the quantity of it´s constituents. Carbon monoxide is produced from the reduction of carbon dioxide and it´s quantity varies from 15 to 30 % by volume basis within the syngas. This gas is toxic in nature. Hence, operators need to be careful while handling gas.

Hydrogen is also a product of reduction process in the gasifier. Methane and hydrogen are responsible for higher heating value of producer gas. Amount of methane present in syngas is very less as up to 4%. Carbon dioxide and nitrogen are non-combustible gases present in the syngas. Compared to other gas constituents, syngas contains highest amount as 45-60% of nitrogen. The amount of carbon dioxide varies from 5 to 15%. Higher percentage of carbon dioxide indicates incomplete reduction. Water vapours in the syngas occur due to moisture content of air introduced during oxidation process, injection of steam in gasifier or moisture content of the feedstock. Average syngas composition can be seen in Figure 2.6.

2.1.2.4. Impact of Feedstock/Fuel Properties on Gasification. A wide range of biomass such as wood, charcoal, wood waste, maize cobs, coconut shells, hazelnut shells, cereal straws, and rice husks can be used as feedstock for gasification. Theoretically, almost all

kinds of biomass with moisture content of 5-30% can be gasified; however, not every biomass leads to the successful gasification. Most of the gasification works are carried out with common fuels such as coal, charcoal and wood. Feedstocks have different properties which may influnce the gasification efficiency.

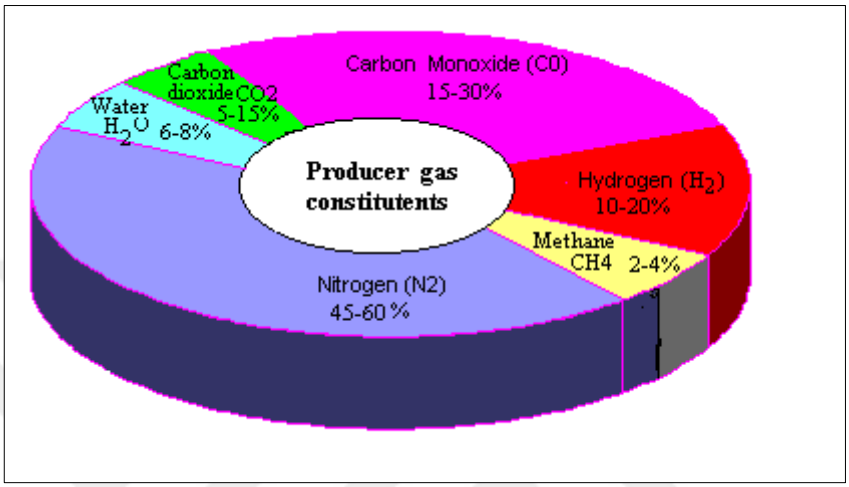


Figure 2.6. Average syngas composition.

(Source: http://www.nzdl.org/gsdlmod?a=p&p=about&c=envl)

Heating value is the amount of heat produced by a complete combustion of fuel and it is measured as a unit of energy per unit mass or volume of substance (e.g., kcal/kg, kJ/kg, J/mol and Btu/m³). The heat of combustion of fuels is expressed by the higher and lower heating values (HHV and LHV). The higher heating value is also known as the gross calorific value. The higher heating value (HHV) is measured using a bomb calorimeter; and defined as the amount of heat released when fuel is combusted and the products have returned to a temperature of 25°C. The heat of condensation of the water is included in the total measured heat. The lower heating value (LHV) is defined as the net calorific value and is determined by subtracting the heat of vaporization of water vapor (generated during combustion of fuel) from the higher heating value. Same types of fuels can usually be compared according to their HHV, whereas the different types of fuels are usually compared according to their LHV. Because hydrogen contents of the different types of fuels are different from each other (e.g. oil and coal); therefore, it is necessary to determine the hydrogen content of the fuel for calculating the LHV. The most of the biomass such as wood and straw have heating value in the ragne of 10-16 MJ/kg, whereas liquid fuels such as diesel and gasoline have higher heating values.

Higher moisture contents reduce temperature and the thermal efficiency of the gasifier and results in low gas heating values. Igniting the feedstock with higher moisture content becomes increasingly difficult, and the gas quality and the yield are also poor. Biomass usually contains a high percentage of moisture; however, moisture content below 15% by weight is desirable for trouble free and economical operation of the gasifier. Therefore, many biomass gasification technologies require that the biomass be dried to reduce the moisture content prior to feeding it into the gasifier.

The feedstock size affects the pressure drop across the gasifier and power that must be supplied to draw the air and gas through the gasifier. Large pressure drops will lead to reduction of the gas load in downdraft gasifier, resulting in low temperature and tar production. Excessively large sizes of particles give rise to reduced reactivity of fuel, causing start-up problem and poor gas quality. Thus, the biomass which can come in a range of sizes may have to be processed to a uniform size or shape to feed into the gasifier at a consistent rate and to ensure that as much of the biomass is gasified as possible in many biomass gasification systems.

Also the form in which feedstock is fed to gasifier has an economical impact on gasification. Densifying biomass has been practiced in the US for the past 40 years. Pelletizers densify all kinds of biomass and municipal waste into "energy cubes". These cubes are available in cylindrical or cubic form and have a high density of 600-1000 kg/m^3. The specific volumetric content of cubes is much higher than the raw material from which they are made.

Another property, the bulk density is defined as the weight per unit volume of loosely tipped feedstock. Bulk density varies significantly with moisture content and particle size of feedstock. Volume occupied by stored feedstock depends on not only the bulk density of feedstock, but also on the manner in which feedstock is piled. It is also recognised that bulk density has considerable impact on gas quality, as it influences the feedstock residence time in the fire box, feedstock velocity and gas flow rate.

Volatile matter in the feedstock and the remaining water content after drying step are given up in pyrolyis zone at the temperatures of 200-500^oC forming a vapour consisting of

water, tar, oils and gases. Feedstock with high volatile matter content produces more tar, causing problems to internal combustion engine. Volatile matters in the feedstock determine the design of gasifier for removal of tar.

Mineral content of feedstock which remains in oxidized form after combustion of feedstock is called ash. In practice, ash also contains some unburned feedstock. Ash content and ash composition have impact on smooth running of gasifier. Melting and agglomeration of ashes in reactor causes slagging and clinker formation. If no measures are taken, slagging or clinker formation leads to excessive tar formation or complete blocking of reactor. In general, no slagging occurs with feedstock having ash content below 5%. Ash content varies feedstock to feedstock. Wood chips contain 0.1% ash, while rice hust contains high amount of ash as 16-23%.

Fuel reactivity determines the rate of reduction of carbon dioxide to carbon monoxide in the gasifier. Reactivity depends upon the type of fuel. For example, it has found that wood and charcoal are more reactive than coal. There are number of elements which act as catalyst and influence the gasification process. Small quantities of potassium, sodium and zink can have large influence on reactivity of the fuel.

Organic constituents of biomass may exhibit different thermal properties leading different reactions during the conversion processes. Thus, tar compounds produced during gasification can differ from biomass to biomass. The biomass which is composed of cellulose, hemicellulose, and lignin is called lignocellulosic biomass (Wikipedia-lignocellulosic biomass). Pyrolysis of lignocellulosic materials results various and complex products with different volatility such as chars, gases and tars. The major components, lignin, cellulose and hemicellulose mainly react independently and produce primary tars (Balcı, 1992).

2.1.2.5. Tar Formation in Gasification Process. Thermochemical biomass conversion processes produce complex mixture of organics such as tar which is formed as an unwanted by-product from the pyrolysis of the solid carbonaceous material during biomass gasification (Morf, 2001). Tar has been operationally defined in gasification work as the material in the product stream that is condensible in the gasifier or in downstream

processing steps. Tar is a mixture of mainly aromatics such as benzene, toluene, phenol, pyridines, thiophenes and 2-4 ring PAHs such as naphtalene and anthracene. These are formed during pyrolysis or gasification of solid fuels. Depending on the fuel and the process conditions (temperature and gas phase) and reactor type the amounts of tar compounds can vary widely; thus, producer gases can contain considerable amounts of tars. The amount of tar in the gas depends very much on the air factor (stoichiometry) (Zevenhoven and Kilpinen, 2001), fuel, the operating conditions and the secondary gas phase reactions (Klein, 2002) during gasification. The tar content varied from 0.1 and 10% of the product gas (Milne and Evans, 1998).

At temperatures below their dew point (200-600^{o}C) and/or at elevated pressures, tars condense causing operational problems due to the formation of droplets which accumulate to sticky films on cold surfaces of e.g. pipes and other equipment. Besides the condensation related issues, tars may cause carbon deposition problems at very elevated temperatures (Nagel, 2008). Elliot (1988) classified tars into three primary categories based on the reaction temperature ranges in which they form. Also the tar maturation sheme proposed by Elliot are shown in Figure 2.7.

1. Primary Tars, which are formed at 400-600^{o}C and contains mixed oxygenates and phenolic ethers;
2. Secondary Tars, which are formed at 600-800^{o}C and contains alkyl phenolics and heterocyclic ethers;
3. Tertiary tars, which are formed at 800-1000^{o}C and contains polycyclic aromatic hydrocarbons (PAHs).

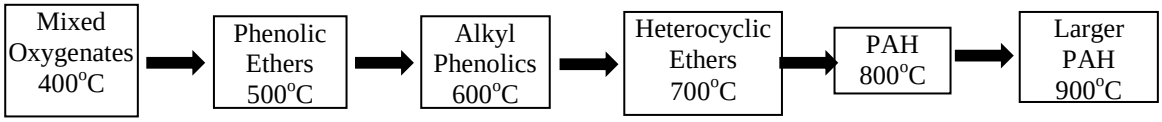


Figure 2.7. Tar maturation sheme proposed by Elliot, 1988.

The primary tar formation is not avoidable. However, after their evolution from the solid phase, tar vapors are subject to secondary tar reactions which occur immediately after the primary reactions and alter both mass and composition of the tar. Tar conversion by secondary tar reactions already occurs in the pores of the “mother” fuel particle as well as

in the gasphase and on surfaces outside the particle which are shown in Figure 2.8 (Morf, 2001).

While the primary tars thermally crack to CO, H_2, and other light gases with temperature which has a major impact on tar formation and conversion, tertiary products grow in molecular weight with increasing temperature. The primary products are destroyed before the tertiary products appear (Milne and Evans, 1998).

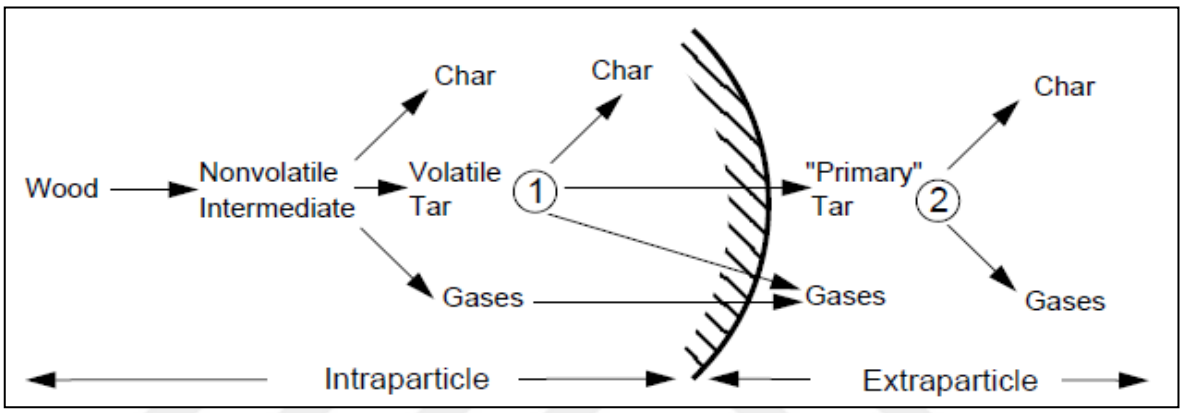


Figure 2.8.Intraparticle and extraparticle tar formation and conversion (Morf, 2001).

Simell (1997) distinguishes “low temperature tar” which is formed at temperatures below 650^{o}C and consists mainly of the primary decomposition products of the fuel, and “high temperature tar”, mainly mono- and polycyclic aromatic compounds, formed by secondary reactions between primary pyrolysis products. Considering then different gasification reactors, low temperature tar is obtained from updraft gasifiers, whilst high temperature tar is produced in downdraft, fluidized bed and entrained flow gasifiers.

Polycyclic aromatic hydrocarbons (PAHs) which are hydrocarbon compounds composed of several aromatic rings are typical products of the pyrolysis and gasification processes as tertiary tars. PAHs are formed in almost all high temperature processes, even in the presence of oxygen. Typical PAHs found in flue gases or in pyrolysis or gasification product gases are those composed of 2 to 7 aromatic rings (Zevenhoven and Kilpinen, 2001). Once these compounds are formed, they are very difficult to destroy because of their high thermal stability due to the presence of aromatic rings. Formation of PAHs in

the gas phase has been extensively studied in combustion science because of their role in soot formation. Although extensive work has been done to understand PAH and soot formation, several key PAH reactions are not well understood (Fullana and Sidhu, 2005).

Unlike in the industrial combustion processes, formation and emission of dioxins from processes based on the gasification technologies have so far not been studied in detail. Nonetheless, evidence has also been gathered proving that the probable formation mechanisms and the corresponding dioxin levels in the product gas are closely related to tar formation and thus fairly comparable for all gasifiers in which organics (tars) are incompletely converted into product gas (Cieplik and Kamp, 2009).

2.1.3. Gasification Applictions

2.1.3.1. Coal Gasification. Coal can be used as a feedstock to produce electricity via gasification, commonly referred to as Integrated Gasification Combined Cycle (IGCC). This particular coal-to-power technology allows the continued use of coal without the high level of air emissions associated with conventional coal-burning technologies. IGCC uses syngas and steam turbines to generate electricity. Most investigations of IGCC have focused on coal as feedstock, but it is possible to gasify most carbonaceous fuels (like petcoke, refinery bottoms, biomass, waste, etc). Gasification can handle different coal ranks, but most IGCC applications have focused on high calorific-value coals for efficiency reasons. In gasification power plants, the pollutants in the syngas are removed before the syngas is combusted in the turbines. In contrast, conventional coal combustion technologies capture the pollutants after combustion, which requires cleaning a much larger volume of the exhaust gas.

2.1.3.2. Biomass Gasification. Biomass includes a wide range of materials such as switch grass, micanthus, corn husks, wood pellets, and biosolids. Gasification helps to recover the energy locked in these materials with converting it into electricity and products, such as ethanol, methanol, fuels, fertilizers, and chemicals. The biomass is first gasified to produce the synthetic gas, and then converted via catalytic processes to these downstream products.

The gasification of biomass differs in many ways from the gasification of coal, petrocoke, or natural gas. The gasification technologies used with biomass are fairly standard; performance depends greatly on the unique characteristics of the biomass. Biomass as feedstock has much higher moisture content and less heating value by volume than coal. In addition, the non-uniformity of the feedstocks and the variability of the specific compositions over time require flexible and robust gasifiers. Also, biomass gasification plants differ in several aspects from the large-scale gasification processes typically used in major industrial facilities such as power plants, refineries, and chemical plants. In general, biomass gasification plants are much smaller than the typical coal or petroleum coke gasification plants used in the power, chemical, fertilizer and refining industries. While a large industrial gasification plant may process 2500-15000 tons per day of feedstock such as coal or petroleum coke, the smaller biomass plants typically process 25-200 tons of feedstock per day.

2.1.3.3. Waste Gasification. Waste is a type of biomass in gasification literature; thus, waste gasification can be imagined as a biomass gasification application. However, gasification and melting systems which gasifies waste and smelts the gasification residue began to be used in waste gasification to be able to handle the large variety of waste. The molten residue obtained by smelting is called slag, and it can be used in construction works. In a typical process, waste is thermally decomposed to syngas and mainly char and ash residue in the gasifer. The residue is burned and incombustible material, the ash, in the residue then smelts to slag in a smelting furnace at a temperature of about 1200^{o}C. Though the waste gasification and smelting process supports both gas recovery and generation of electricity, it is mostly used for generation of electricity. In many cases the fuel gas is burned in a melting furnace and the resulting hot gas then passes to a gas clean-up unit through a heat recovery boiler where steam is formed. Electrical energy is produced by the steam in a steam turbine equipped with a power generator.

At the present, the gasification and smelting furnace developed and operated in Japan and overseas can be divided into two types: one is called a shaft furnace (straight-standing type) in which waste is melted and gasified in one process with coke, and the other is the combination of a thermal decomposition furnace (fluidized bed or rotary kiln) and a rotary smelting furnace, which consists of two processes. The most known GSP is patented

Thermoselect Process which was developed in Switzerland between 1985 and 1992. A schematic illustration of Thermoselect Process can be seen in Figure 2.9.

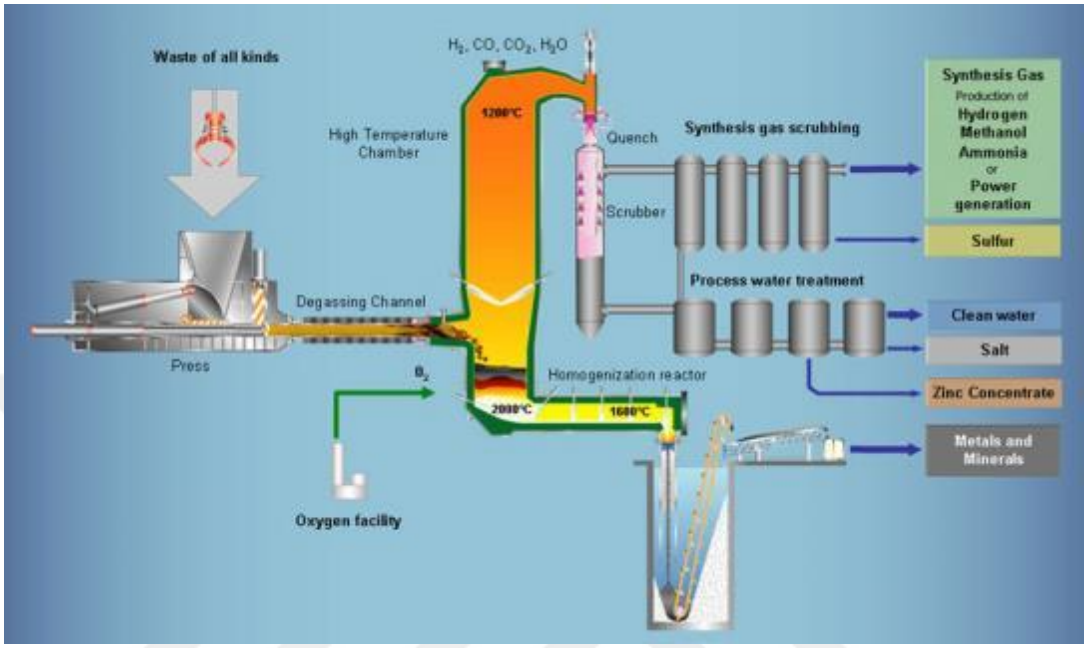


Figure 2.9. The Thermoselect resource recovery facility.

2.3.1.4. Plasma Gasification. Plasma is an ionized gas that is formed when an electrical discharge passes through a gas. The resultant flash from lightning is an example of plasma found in nature. Plasma torches and arcs which can generate heat up to 5000-7000^{o}C convert electrical energy into intense thermal /heat energy. When used in a gasification plant, plasma torches and arcs generate this intense heat, which initiates and supplements the gasification reactions, and can even increase the rate of those reactions, making gasification more efficient. Inside the gasifier, the hot gases from the plasma torch or arc contact the feedstock, such as municipal solid waste, auto shredder wastes, medical waste, biomass or hazardous waste, heating it to more than 1800^{o}C. This extreme heat maintains the gasification reactions, which break apart the chemical bonds of the feedstock and converts them to a synthesis gas. The syngas can be used to produce chemicals and can also be sent to gas turbines or reciprocating engines to produce electricity, or combusted to produce steam for a steam turbine-generator. Because the feedstocks reacting within the gasifier are converted into their basic elements, even hazardous waste becomes a useful syngas. Inorganic materials in the feedstock are melted and fused into a glassy-like slag,

which is nonhazardous and can be used in a variety of applications, such as roadbed construction and roofing materials.

Plasma technologies have been used for over 30 years in a variety of industries, including the chemical and metals industries. Historically, the primary use of this technology has been to decompose and destroy hazardous wastes, as well as to melt ash from mass-burn incinerators into a safe, non-leachable slag. Use of the technology as part of the waste-to-energy industry is much newer. There are currently plasma gasification plants operating in Japan, Canada and India. For example, a facility in Utashinai, Japan has been in commercial operation since 2001, gasifying municipal solid waste and auto shredder waste to produce electricity. Shematic illustration of the most known commercial plasma gasification process, Westinghouse Plasma Gasifier, can be seen in Figure 2.10. Also the main advantages of plasma gasification among other gasification process types are given below:

- greater feedstock flexibility;
- high conversion ratio of organic matter to synthesis gas (>99%);
- no tar in syngas;
- no char, ash or residual carbon; only producing a glassy slag;
- higher thermal efficiency;
- lower carbon dioxide emissions;
- low estimated capital and operations and maintenance costs.

Significantly low dioxin concentrations as low as 0.01 ng-TEQ/Nm^3 can be obtained in waste plasma gasification process applications.

According to the Gasification Technologies Council (GTC) records by 2014, the gasification database now includes a total of 862 projects, consisting of 2378 gasifiers (excluding spares), of which 272 projects with 686 gasifiers are active commercial operating projects. It covers 82 projects with 262 gasifiers under construction and a further 133 projects with 735 gasifiers in the planning phase. The output of operating gasifiers is 116.6 MW_{th} (up from 104.7 last year) with 82,8 and 109,2 MW_{th} in the construction and

planning phases respectively (http://www.gasification.org/). Summary of worldwide gasification ındustry is given in Table 2.1.

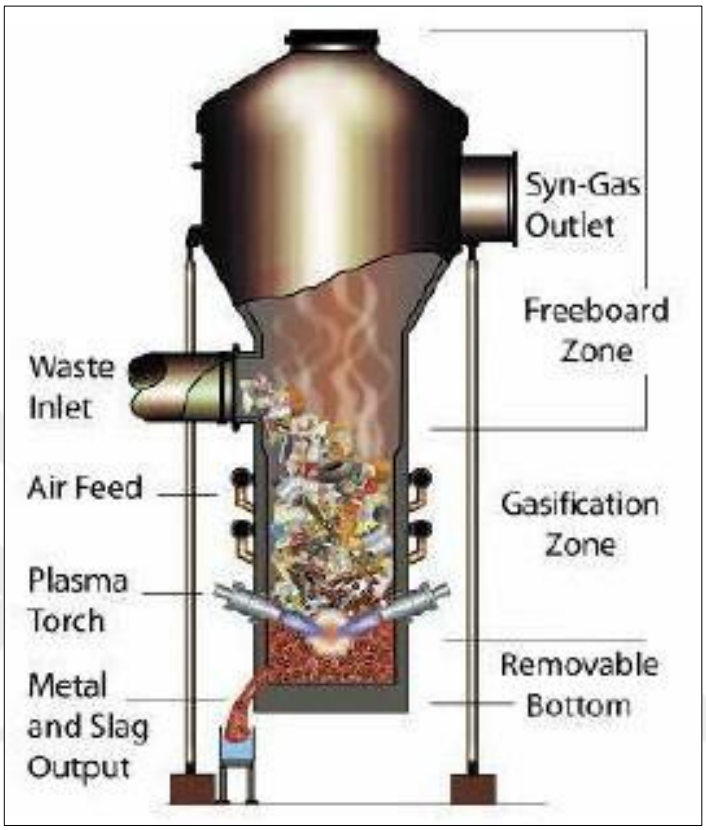


Figure 2.10. Schematic illustration of Westinghouse plasma gasifier.

Table 2.1. Summary of worldwide gasification industry.

Update Year	Total Projects	Total Gasifiers	Real-Active Projects/ Gasifiers	Construction Projects/ Gasifiers	Planned Projects/ Gasifiers
1999	329	754	128/366	n/a	33/48
2001	350	800	131/409	n/a	32/59
2004	391	841	117/385	n/a	38/66
2007	408	891	144/427	n/a	10/34
2010	463	990	192/505	11/17	37/76
2013	747	1741	234/618	61/202	98/550
2014	862	2378	272/686	82/262	133/735

Source: http://www.gasification.org/

2.2. Dioxin

2.2.1. Dioxin Structure and Composition

The term "dioxin" is often used to denote a family of compounds known chemically as polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). Each compound comprises two aromatic -benzene- rings interconnected by oxygen atoms. In the case of PCDDs, the rings are joined by two oxygen bridges, whereas in the PCDFs, the rings are connected by a carbon bond and an oxygen bridge. Figure 2.11 shows the basic structures of PCDDs and PCDFs, together with the numbering convention at the positions on the benzene rings where chlorine or other halogen atoms can be substituted.

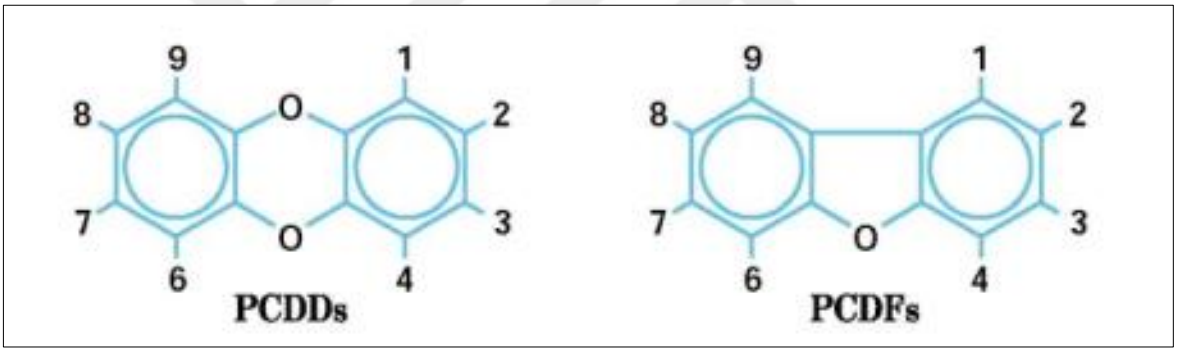


Figure 2.11. Chemical structures of PCDDs and PCDFs.

PCDDs consist of 75 species while PCDFs consist of 135 species. The structures of the species within each group differ in terms of the number and spatial arrangements of chlorine atoms. The individual compounds within the groups are often referred to as congeners and congeners with the same number of chlorine substituents are called homologues. The distribution of congeners within each homologue is referred to as an isomer distribution pattern. The substitution sites adjacent to the oxygen bridges (1-, 4-, 6-, and 9-) are referred to as α-positions, and the lateral (2-, 3-, 7-, and 8-sites) as β-positions. Among those 210 PCDD/PCDF congeners, the most toxic 17 ones are subject to interested mostly. The most toxic dioxin congener is 2,3,7,8-tetrachlorodibenzoparadioxin (2,3,7,8-TCDD) which was released from the ICMESA plant at Seveso in 1977. Numbers of homologue groups which have same chlorine atoms are shown in Table 2.2.

Table 2.2. Numbers of homologue groups with same chlorine atoms.

No. of Cl atoms in molecule	Dioxin (PCDDs)	No. of Isomers		Furan (PCDFs)	No. of Isomers	
		Total	Toxic		Total	Toxic
1	Mono - chloro dibenzo-para dioxin	2	-	Mono - chloro dibenzo furan	4	-
2	Di - chloro dibenzo-para dioxin	10	-	Di - chloro dibenzo furan	16	-
3	Tri - chloro dibenzo-para dioxin	14	-	Tri - chloro dibenzo furan	28	-
4	Tetra - chloro dibenzo-para dioxin	22	5	Tetra - chloro dibenzo furan	38	8
5	Penta - chloro dibenzo-para dioxin	14	7	Penta - chloro dibenzo furan	28	14
6	Hexa - chloro dibenzo-para dioxin	10	7	Hexa - chloro dibenzo furan	16	12
7	Hepta - chloro dibenzo-para dioxin	2	1	Hepta - chloro dibenzo furan	4	2
8	Octa - chloro dibenzo-para dioxin	1	-	Octa - chloro dibenzo furan	1	-
Total PCDDs		**75**	**20**	**Total PCDFs**	**135**	**36**

Source: Central Pollution Control Board, Government of India

Dioxins are chemically stable and, like many other chlorinated organic compounds, are included in a group given the generic term Persistent Organic Pollutants (POPs). However the PCDFs are more stable than PCDDs. Because of their highly lipophilic character they tend to accumulate in fat and, thus, throughout the food chain. The highest levels are often found in fatty tissues of animals at the top of the chain (Hedman, 2005).

2.2.2. Toxic Equivalency Factors

A toxicity equivalence procedure has been developed by researchers to describe the cumulative toxicity of complex mixtures of the compounds. The procedure involves assigning individual toxicity equivalency factors (TEFs) to the PCDD and PCDF congeners in terms of their relative toxicity to 2,3,7,8-TCDD. Because of the 2,3,7,8-TCDD is the most toxic congener, its TEF is assigned 1.0. Three sets of generally accepted

TEF values are shown in the Table 2.3 that the factors endorsed by the United States Environmental Protection Agency (USEPA), those accepted by the North Atlantic Treaty Organisation (NATO) and those accepted by the World Health Organization (WHO). Calculating the toxic equivalency (TEQ) of a mixture involves multiplying the concentrations of individual congeners by their respective TEF, then adding the individual TEQ's to obtain a total TEQ concentration for the mixture (https://www.pacelabs.com/). The NATO/ CCMS (1988) scheme has been adopted internationally. These TEFs are termed as International TEFs, of I-TEFs. The summation of individual TEQs for a mixture of PCDDs and PCDFs is termed the International Toxic Equivalent or I-TEQ of the mixture (Quass et al. 2000). The results of this study were given in I-TEQ scheme. In other words, each congener was multiplied by its TEF and individual TEQ was found. Then those individual TEQs were added together in order to obtain the total TEQ of the mixture which comprices of the 17 most toxic dioxin and furan congeners. The provided concentrations reflect the total dioxins (dioxin and furan) in TEQ.

Table 2.3. Toxic equivalency factors (TEFs) for PCDD/Fs.

Congeners	**WHO Factors**	**NATO Factors /International (I-TEF)**	**EPA Factors**
2,3,7,8 -TeCDD	1	1	1
1,2,3,7,8 -PeCDD	1	0.5	0.5
1,2,3,4,7,8 -HxCDD	0.1	0.1	0.1
1,2,3,6,7,8 -HxCDD	0.1	0.1	0.1
1,2,3,7,8,9 -HxCDD	0.1	0.1	0.1
1,2,3,4,6,7,8 -HpCDD	0.01	0.01	0.01
OCDD	0.0001	0.001	0.001
2,3,7,8 -TeCDF	0.1	0.1	0.1
1,2,3,7,8 -PeCDF	0.05	0.05	0.05
2,3,4,7,8 –PeCDF	0.5	0.5	0.5
1,2,3,4,7,8 -HxCDF	0.1	0.1	0.1
1,2,3,6,7,8 -HxCDF	0.1	0.1	0.1
1,2,3,7,8,9 -HxCDF	0.1	0.1	0.1
2,3,4,6,7,8 –HxCDF	0.1	0.1	0.1
1,2,3,4,6,7,8 -HpCDF	0.01	0.01	0.01
1,2,3,4,7,8,9 -HpCDF	0.01	0.01	0.01
OCDF	0.0001	0.001	0.001

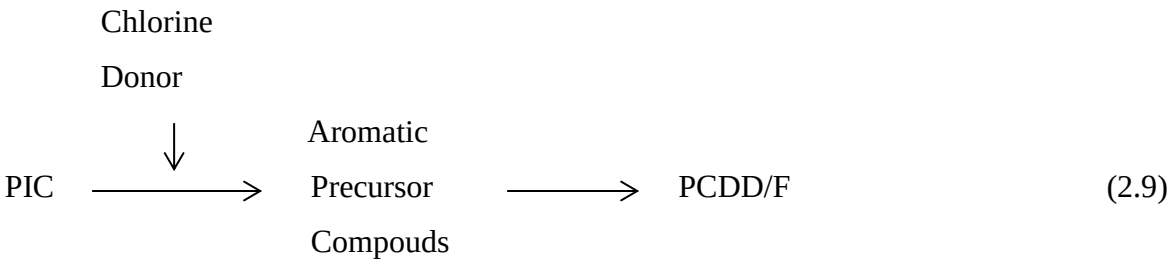
Source: Hedman, 2005.

2.2.3. Dioxins Formation Mechanisms

Formation of polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) in waste combustion was first reported in 1977 by Olie et al. PCDD/Fs are mainly formed in the temperature window of 250-450°C by reactions of unburned or incompletely oxidized hydrocarbons escaping the high-temperature region of the combustion chamber and Cl containing species such as Cl_2 (Anthony et al., 2001). In addition, the presence of catalysts (especially Cu) and oxygen is essential for the formation of PCDD/Fs (Saeed, 2004). The formation of dioxins can occur either in the gas-phase (homogenous reactions) or via gas phase-solid surfaces interaction (heterogeneous reactions). Although three mechanisms have been identified for dioxin formation via those homogenous and heterogeneous reactions, the two of them, precursor mechanism and the de novo synthesis, are the most accepted theories. Both reactions are heterogeneous, catalytic and post-combustion formation mechanisms which both occur on surfaces (Environment Australia (1999). The three dioxin formation mechanisms are as follows:

1. Pyrosynthesis: Pyrosynthesis which occur at high temperatures like 500-700°C, is homogenous gas phase reaction. According to the literature, gas-phase reactions only produce very low levels of PCDD/Fs.
2. Precursor Mechanism (heterogeneous): The precursor mechanism is the result of the polycondensation of precursors (e.g. polychlorophenols, polychlorobenzenes, PCBs). This gas phase synthesis occurs at temperatures between 300°C and 600°C. Precursor mechanism can be explained in 2 steps. The first one is the formation of aromatic precursor compounds such as benzene, chlorobenzene, phenol, chlorophenol from the chlorination of products of incomplete combustion (PIC) via a chlorine donor in high temperature gas-phase. However, formation can take place either from pre-existing precursor molecules like polychlorinated benzenes (PCBz) and polychlorinated phenols (PCPh) or from newly formed precursors originating from aliphatic hydrocarbons. The second step is combination of these precursors heterogeneously and catalytically with the fly ash surface and finally formation dioxin. The catalysts which may participate to precursor reactions are primarily copper then iron, nickel, zinc, chromium and their water insoluble salts. Precursor mechanism is considered to

mainly produce PCDD. The schematic precursor mechanism can be seen in Equation 2.9.



(2.9)

3. De novo synthesis (heterogeneous): De novo formation is a surface mediated catalytic reaction which occurs on fly ash surface with the presence of macromolecular carbon. The 'de novo' route has been defined as the breakdown reactions of a carbon matrix and the formed carbon containing structure can be further chlorinated in the following steps. The requirements for de novo synthesis are a chlorine source, a metal catalyst, oxygen, suitable temperature range, macromolecular residual carbon, and fly ash. The fly ash acts as a catalytic surface during the formation process (Addink et al., 1990) and also possesses all the necessary components for dioxin formation such as carbon, small organic compounds, metal ions and inorganic chloride. Chlorine may be incorporated into dioxins through elemental Cl_2 or acid (HCl) form (Unilabs Environmental, 1999). The most favorable temperature range is 200-450^{o}C for de novo mechanism (Everaert and Baeyens, 2002; Dickson et al., 1989). Incomplete combustion products are the carbon sources for dioxin formation as well as precursors. Also, de novo synthesis can use carbon structures such as PAHs as carbon source.

Certain metals act as catalysts for dioxin formation on the fly ash, providing a surface for dioxins formation. Copper (Cu) is the most potent catalyst for dioxin formation, but Iron (Fe), Zinc (Zn), Potassium (K) and Sodium (Na) have also been found in multiple studies to be correlated with increased dioxin/furan formation. Some studies have also indicated that Manganese (Mn), Magnesium (Mg) and Nickel (Ni) may also serve as catalysts for dioxin formation. Studies have conflicted on whether Aluminum (Al) encourages or inhibits dioxin formation (www.ejnet.org).

De novo mechanism is much faster than precursor mechanism (Everaert and Baeyens, 2002) both mechanisms can occur simultaneously and/or independently. PCDD/Fs in flue gas can exist in either the gaseous form or the particle-bound form (Yokohama et al. 2008).

At the same time that PCDD/Fs are formed they are also degraded. The rate of their degradation increases with increasing temperature (Pakarek et al. 2001). Thus, the emission levels found in the flue gases are the net results of both formation and degradation reactions (Vogg et al. 1987). The formation and degradation temperatures of dioxin were shown in Figure 2.12. (Erlich, 2009).

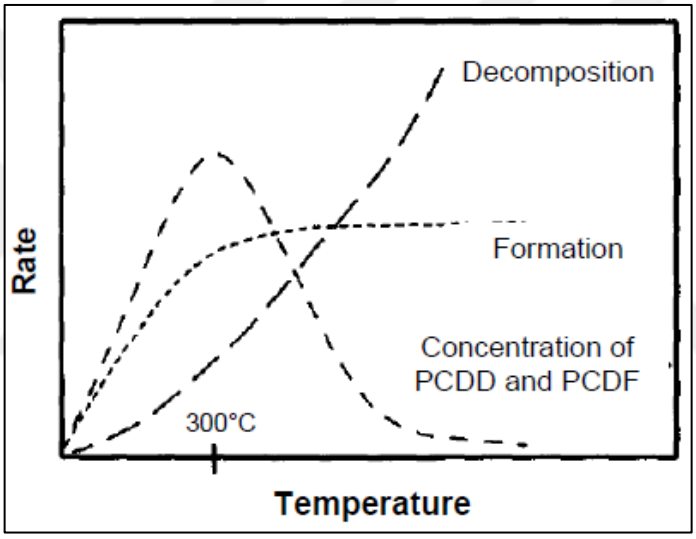
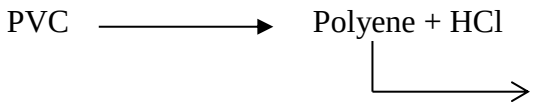


Figure 2.12. Formation and degredation temperatures of dioxin, Erlich, 2009.

PCDF/PCDD ratio has been used as an indicator of the dominating reaction; a ratio of less than 1 is being regarded as a sign of precursor predominance, and the PCDF/PCDD ratio greater than 1 as de novo mechanism (Erlich, 2009). Therefore, de novo mechanism is believed that has more suitable conditions for PCDF formation.

All PCDDs and PCDFs are organic solids with high melting points and low vapour pressures. They are characterised by extremely low water solubilities, and have a tendency for being strongly adsorbed on surfaces of particulate matter. The water solubility of dioxin and furans decreases and the solubility in organic solvents and fats increases with increasing chlorine content (McKay, 2002).

2.2.3.1. Chlorine Source and PVC Thermal Decomposition. PVC thermal decomposition releases HCl, some hydrocarbons and a coke-like residue at a 200-400°C temperature range (Shigaki et al., 1973; Cullis and Hirschler, 1981; Bockhorn et al., 1999; Bockhorn et al., 1996; Zevenhoven et al., 1997). First of all, chlorine is released as gas-phase HCl. The degradation occurs in two steps. The first step corresponds to dehydrochlorination and polyene chain formation, while the second to the degradation of the polyene chain (Wu et al., 1994) into volatile aromatics and solid residue. The PVC thermal decomposition can be seen in Equation 2.10.



(2.10)

According to the pyrolysis tests on PVC, 90% or more of the chlorine was released as HCl at a temperature between 350 and 400°C (Oudhuis et al., 1991; Wu et al., 1994; Zevenhoven et al., 2002). If the pyrolysis temperature rises above 400°C, there will be a second stage of degradation that will further break down the hydrocarbon intermediates produced after dehydrochlorination (Saeed, 2004). Part of HCl dissociates after 400^{o}C to aromatic hydrocarbons and some of them are dioxin formation precursors such as chlorobenzene. The remaining HCl fraction leaves the stack. In 1968, Boettner and co-workers published on the thermal decomposition of PVC by using thermal gravimetric analysis. In that work, PVC was heated from ambient to 600°C at 3°C per minute and polymer weight loss was recorded. At approximately 275°C, sudden weight loss occurred for approximately 60% of the initial weight. During this loss, 95% hydrogen chloride and 5% benzene were released according to the byproduct analyses (O'Mara, 1977).

Also, Figure 2.13 illustrates PVC decomposition between the temperature range 50-900°C. According to the information from the virgin PVC manufacturer; "PETVİNİL S 39/71" long-term degradation begins at 120^{o}C, and short-term at 250^{o}C. It decomposes totally at 650^{o}C.

2.2.3.2. Deacon Process. The oxidation of hydrochloric acid gas by atmospheric oxygen in the presence of a catalyst is called Deacon Process. Deacon is a fast, exothermic, and reversible process which produces Cl_2 from gaseous HCl**.** At the first chloridizing step,

HCl contacts with catalyst at around 100-250^{o}C. Thus, the transition metal oxide is converted to a transition metal chloride with water. At the second oxidizing step, the transition metal chloride is contacted with a source of oxygen. Cl_2 is produced and the transition metal chloride is reconverted to a transition metal oxide at temperature range between 300-375^{o}C. The overall Deacon Process reaction is shown in Equation (2.11).

$$\begin{aligned} CuO + 2\,HCl &\longrightarrow CuCl_2 + H_2O \\ CuCl_2 + \tfrac{1}{2}\,O_2 &\longrightarrow CuO + Cl_2 \\ \hline 2\,HCl + \tfrac{1}{2}\,O_2 &\leftrightarrow H_2O + Cl_2 \end{aligned} \qquad (2.11)$$

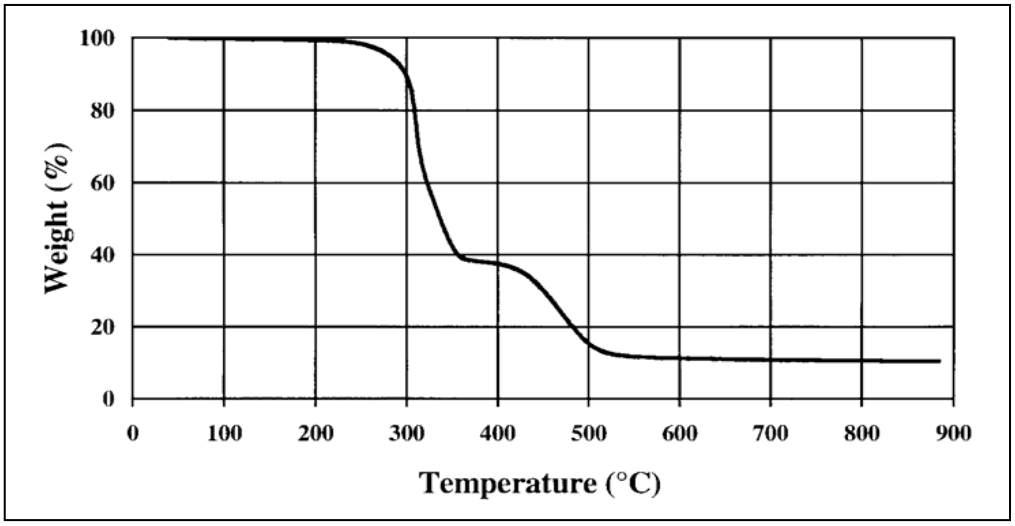


Figure 2.13. PVC thermal decomposition (Saeed, 2004).

3. LITERATURE REVIEW ON DIOXIN AND GASIFICATION

In this section the research studies which measured and evaluated the dioxin concentrations during gasification process were given as literature review in order to present the research status of the subject and have an idea about dioxin formation during gasification process. Unlike in the industrial combustion processes, formation and emission of dioxins from processes based on the gasification technologies have so far not been studied in detail (Zwart et al., 2009).

Joung et al. studied with Automobile Shredder Residue (ASR) to observe the yields of gas, oil and char from pyrolysis and gasification process in different conditions in 2006 and 2009. Effect of oxygen, catalyst and PVC on the process products were investigated in 2006 with simulated ASR while the effect of oxygen was investigated with commercial ASR in 2009. Both studies were carried out in stainless steel 300 mm in height and 100 mm in inner diameter laboratory scale set-up which is shown in Figure 3.1.

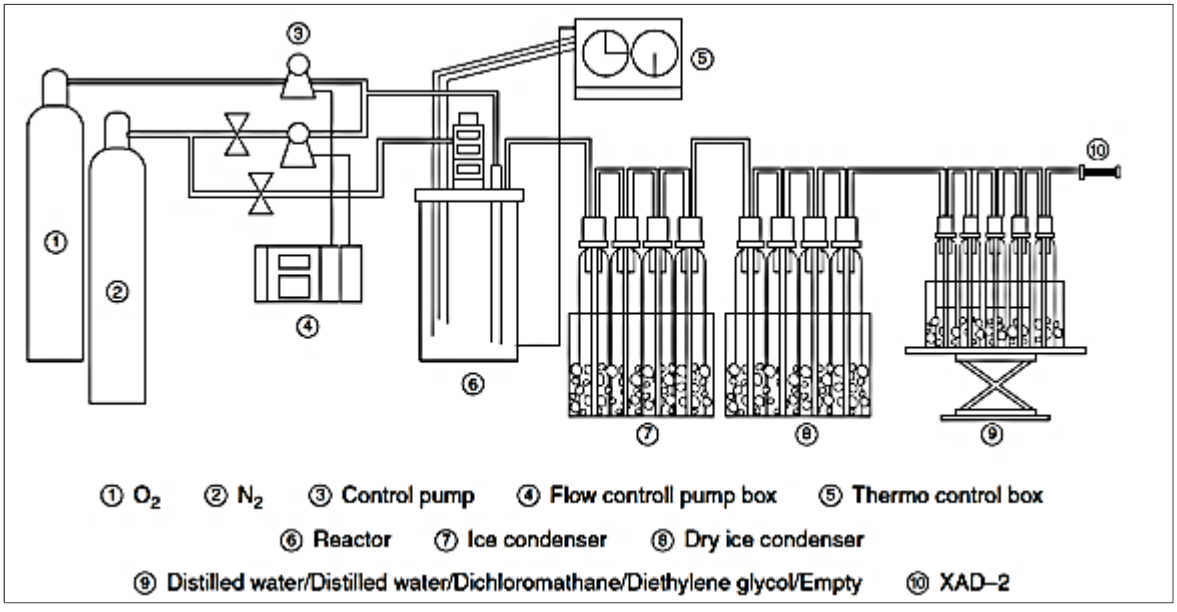


Figure 3.1. Joung et al. laboratory scale experimental set-Up (Joung et al., 2006).

In 2006, the scientists performed the tests with simulated ASR with 3,89% (w/w) PVC means approximately 2% (w/w) chlorine at ER=0 and ER=0.5 conditions with and

without catalyst in order to evaluate the oxygen and catalyst effect on dioxin formation in process byproducts during pyrolysis and gasification at 400-800^{o}C. Preliminary experiments showed that no dioxins were detected when the chlorine source, PVC, was removed from experiments regardless of oxygen or the existence of other catalysts. Catalyst and oxygen effects on dioxin formation were tested with PVC feedstock. After addition of oxygen to the pyrolysis of PVC, the process became gasification and the dioxins increased in gas phase by 360 times with the oxygen effect. Also the ratio of PCDFs/PCDDs increased from 3.5 to 10.9 with oxygen addition and 3.5 to 18.9 with catalyst addition, respectively. The oxygen feed dramatically enhanced the furan concentrations. Scientists stated that the oxygen was a more effective factor in dioxin formation in gas byproducts. Joung et al. have the following analysis results in gas, char, and oil which were shown in Table 3.1, Table 3.2., and Table 3.3., respectively. Dioxins distributions in all mediums were characterized by applying WHO-TEF to PCDDs and PCDFs concentrations.

Table 3.1. Dioxin concentrations in gas in Joung et al. study in 2006.

	PVC Only	PVC+O_2	PVC+ Catalyst	PVC+ O_2+ Catalyst
PCDFs, pg-TEQ/g (%)	0.243 (77.9)	102.008 (91.6)	4.601 (93.3)	92.651 (95.0)
PCDDs, pg-TEQ/g (%)	0.069 (22.1)	9.395 (8.4)	0.332 (6.7)	4.899 (5.0)
PCDFs/PCDDs	3.529	10.869	13.867	18.913
Total, pg-TEQ/g (%)	0.312 (100.0)	111.393 (100.0)	4.933 (100.0)	97.550 (100.0)

Ref: Joung et al., 2006.

Table 3.2. Dioxin concentrations in char in Joung et al. study in 2006.

	PVC Only	PVC+O_2	PVC+ Catalyst	PVC+ O_2+ Catalyst
PCDFs, pg-TEQ/g (%)	0.449 (54.7)	1.022 (66.8)	1.543 (77.0)	76.560 (73.1)
PCDDs, pg-TEQ/g (%)	0.371 (45.3)	0.509 (33.2)	0.460 (23.0)	28.182 (26.9)
PCDFs/PCDDs	1.209	2.010	3.357	2.717
Total, pg-TEQ/g (%)	0.820 (100.0)	1.531 (100.0)	2.002 (100.0)	104.742 (100.0)

Ref: Joung et al., 2006.

Table 3.3. Dioxin concentrations in oil in Joung et al. study in 2006.

	PVC Only	PVC+O_2	PVC+ Catalyst	PVC+ O_2+ Catalyst
PCDFs, pg-TEQ/g (%)	3.900 (65.6)	1141.195 (92.0)	12.915 (89.4)	1081.464 (95.0)
PCDDs, pg-TEQ/g (%)	2.045 (34.4)	99.653 (8.0)	1.526 (10.6)	57.162 (5.0)
PCDFs/PCDDs	1.907	11.452	8.464	18.919
Total, pg-TEQ/g (%)	5.945 (100.0)	1240.848 (100.0)	14.441 (100.0)	1138.626 (100.0)

Ref: Joung et al., 2006.

Figure 3.2, Figure 3.3, and Figure 3.4 show the distribution of dioxin congeners in gas, char, and oil byproducts for applied experimental conditions. PCDFs were dominant in all mediums but there are slight differences in congener distribution.

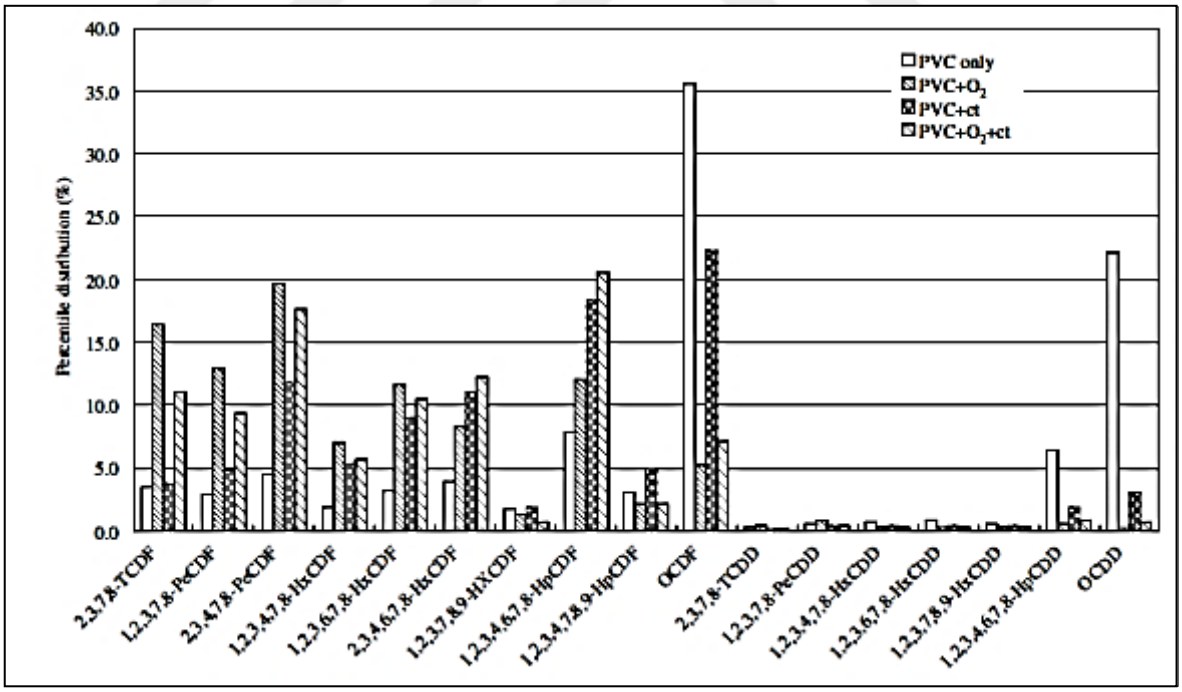


Figure 3.2. Percentile distribution of PCDDs/PCDFs in gas byproducts at different conditions, Joung et al., 2006.

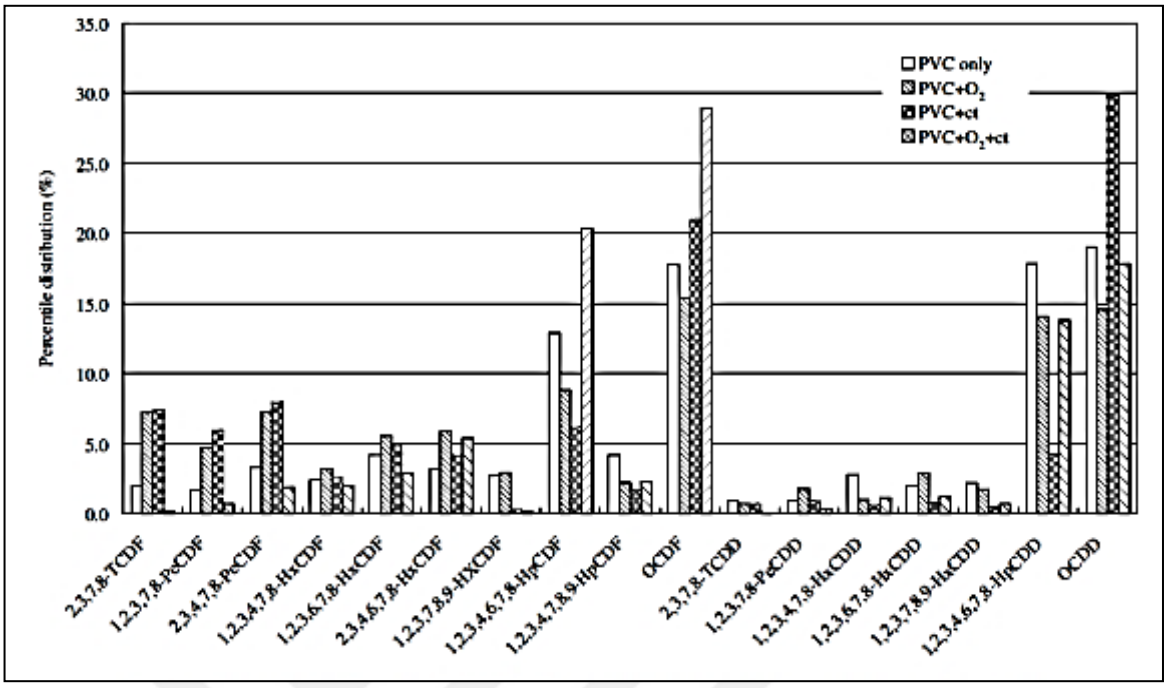


Figure 3.3. Percentile distribution of PCDDs/PCDFs in char byproducts at different conditions, Joung et al., 2006.

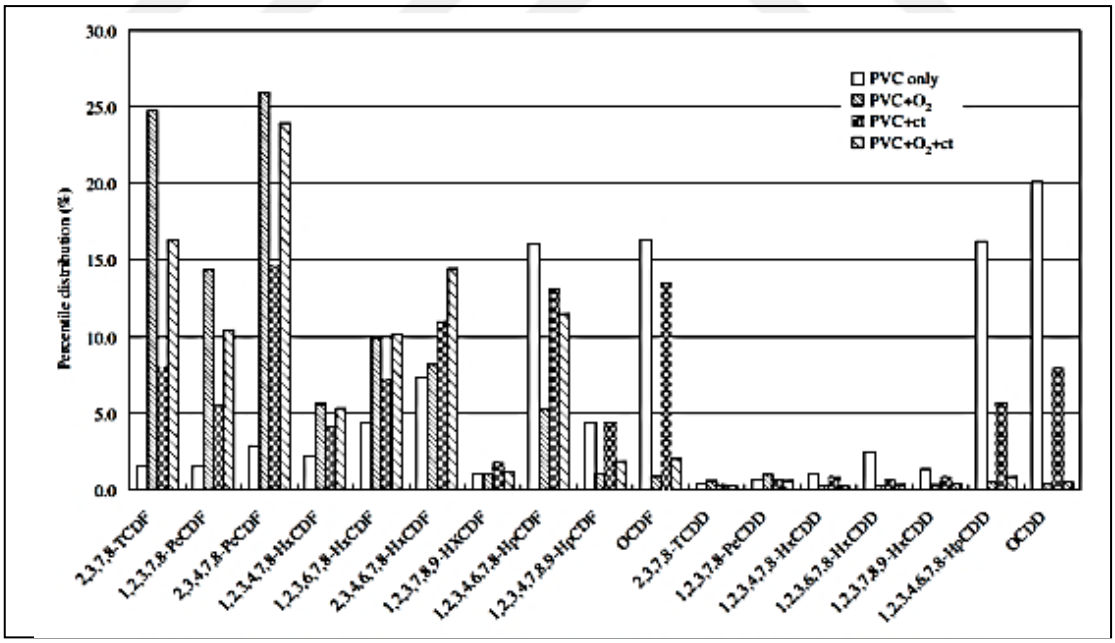


Figure 3.4. Percentile distribution of PCDDs/PCDFs in oil byproducts at different conditions, Joung et al., 2006.

Joung et al. investigated the dioxin congener distribution in commercial Automobile Shredder Residue (ASR) dust pyrolysis/ gasification process gas, char, oil, and melted char

slag by-products at ER=0 and ER= 0.5 conditions in 2009. The slag was prepared by melting the char provided from ER=0 operation. ASR dust is consists of shredded 24.3% fiber, 22.6% plastic, 16.9% sponge, 16.0% soil/sand, 6.3% rubbers, 5.2% paper and woods, 2% wire, 1.1% metals including copper and iron, and 3.8% others. The chlorine content of the mixed sample was 2.2% and the proximate and elemental analyses of the feedstock can be seen in Table 3.4.

Table 3.4. Proximate and elemental analysis of automobile shredder residue dust.

	Moisture	Volatile	Ash	C	H	O	N	S	Cl
Light fluff	0.14	80.80	19.06	61.68	8,96	22.48	4,74	0.00	—
Heavy fluff	1.23	76.47	22.30	64.75	10.07	12.06	0.13	0.14	—
Glass/soil/sand	0.89	43.68	55.43	17.23	1.94	7.56	0.63	0.00	—
Mixed sample	0.38	75.39	24.23	56.24	8.18	19.21	3.62	0.02	2.2

Ref: Joung et al., 2009.

Pyrolysis was performed with 10–20g samples at 600°C. Tests were conducted at oxygen-free (ER=0) and oxygen deficient conditions (ER=0.5) in order to analyze the oxygen dependency of dioxin congeners. Toxicity equivalents (TEQ) were calculated with International Toxicity Equivalent Factor (I-TEF).

As can be seen from the Table 3.5., the TEQ level of PCDD/Fs in gas-phase at ER=0 condition was 82.65 pg I-TEQ/g with 92.8% PCDFs and 7.2% PCDDs ratios. At ER=0.5 condition, the concentration was 6,251.07 pg TEQ/g with 97.8% PCDFs and only 2.2% PCDDs. The amount of PCDD/Fs at 0.5 air/fuel ratio was 75 times higher than PCDDs/PCDFs at 0 air/fuel ratio. PCDFs were dominant both in pyrolysis and gasification conditions.

Other than gas phase, dioxin concentrations were also measured in char. The concentration of dioxins in char at the 0 air/fuel ratio was 71.546 pg-TEQ/g while the concentration was 5,332.685 pg-TEQ/g at the 0.5 air/fuel ratio. In the same way, dioxin

concentrations were almost 75 times higher at 0.5 air/fuel ratio than dioxins at 0 air/fuel ratio in char. PCDFs were dominant both in pyrolysis and gasification conditions.

Table 3.5. Concentrations of congeners in process byproducts.

Congeners, pg/g (%)	**Gas Phase**		**Oil Phase**		**Char**	
	ER=0	**ER=0.5**	**ER=0**	**ER=0.5**	**ER=0**	**ER=0.5**
Total PCDFs %	514 (92.8)	64105 (97.8)	15077 (99.0)	1117 (97.6)	500.79 (92.4)	41031.59 (97.0)
Total PCDDs %	40 (7.2)	1469 (2.2)	148 (1.0)	28 (2.4)	41.09 (7.6)	1258.12 (3.0)
PCDFs/PCDDs	12.85	43.64	101.87	39.89	12.19	32.61
Total PCDD/Fs, pg/g	554	65574	15225	1145	541.88	42289.71
Total PCDD/Fs, pg-TEQ/g	82.65	6251.07	2458.45	111.58	71.55	5332.69

Ref: Joung et al., 2009.

The concentrations of PCDDs/PCDFs in oil phase were 2,458.45 pg-TEQ/g and 111.58 pg-TEQ/g at ER=0 and ER=0.5 conditions, respectively. Opposite of to the gas and char results, the dioxins were more than 20 times higher in pyrolysis conditions than gasification conditions. This may be explained with the contribution effect of the oily tar compounds on dioxin formation which form during pyrolysis.

The PCDD/Fs in melted slag showed much lower concentrations than in char because of the destruction capability of the melting process. The total concentrations of PCDDs/PCDFs in melted slag which was quenched by water, cooled by air, and cooled slowly were 1.51, 1.38, and 2.32 pg-TEQ/g, respectively.

Moreover the overall dioxin concentrations related with the ER effect, the furan congeners were dominant in all mediums. However, the PCDDs congeners which did not form in gas-phase at the 0 air/fuel ratio, formed at the 0.5 air/fuel ratio in the range of 41.0–526.0 pg/g. The congener distributions in gas, oil, char and slag can be seen in Figure 3.5, Figure 3.6, Figure 3.7, and Figure 3.8 respectively.

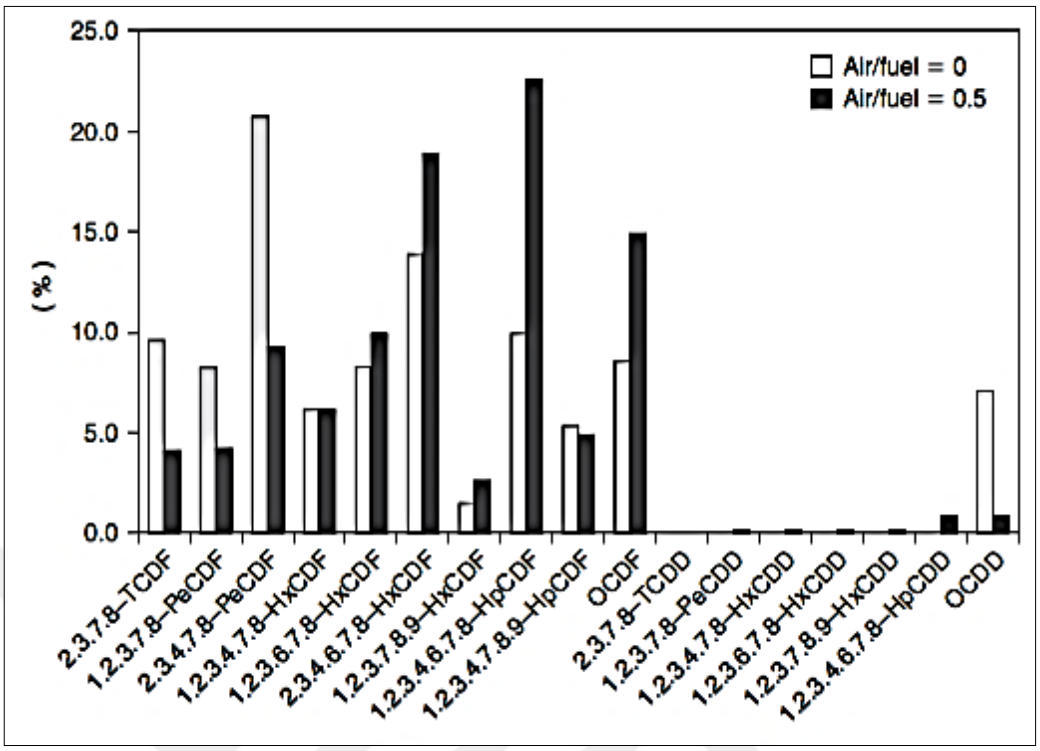


Figure 3.5. The distribution characteristics of PCDD/PCDF congeners in gas, Joung et al., 2009.

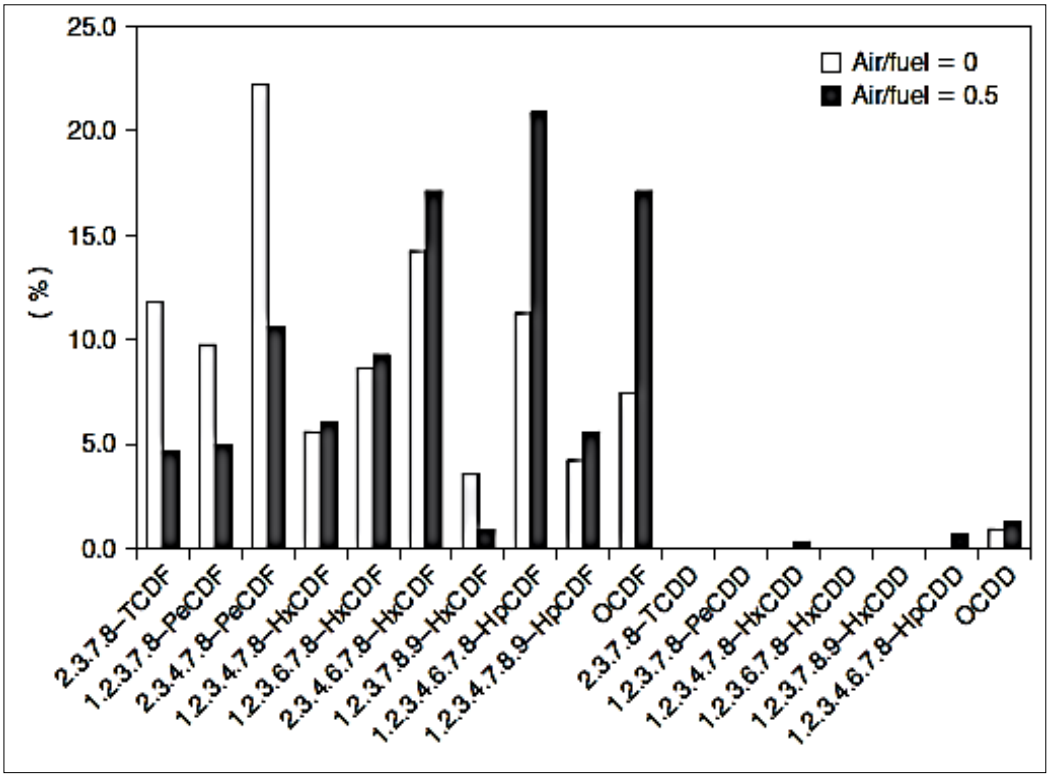


Figure 3.6. The distribution characteristics of PCDD/PCDF congeners in oil Joung et al., 2009.

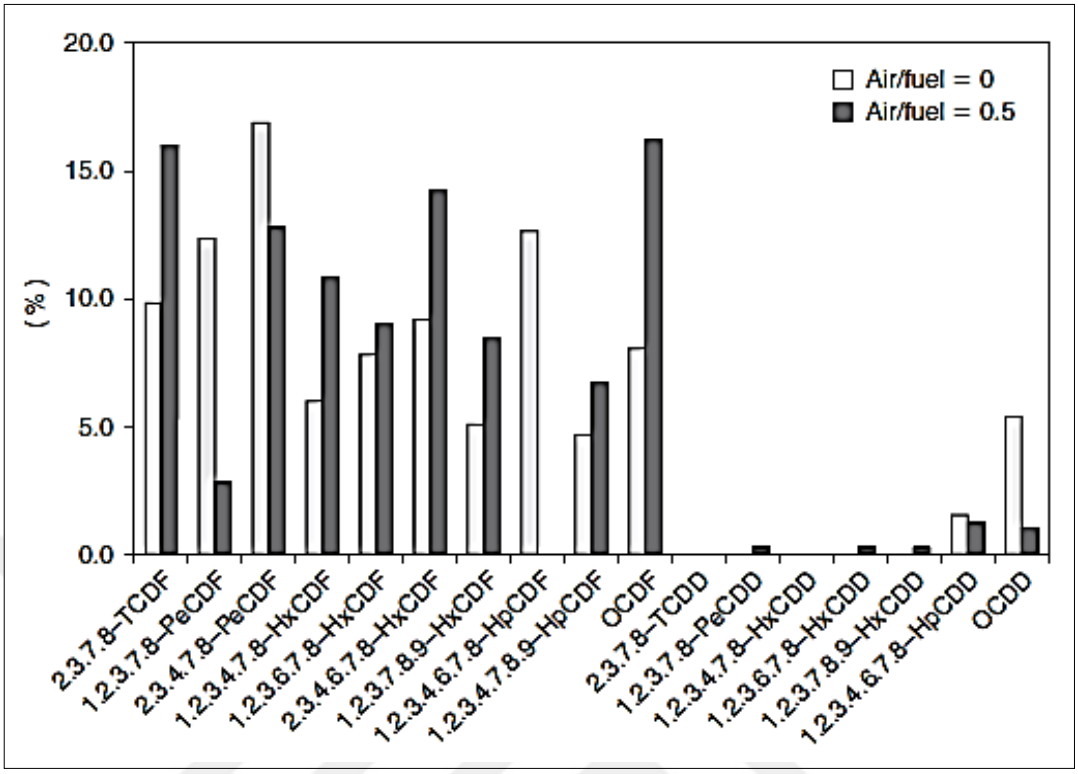


Figure 3.7. The distribution characteristics of PCDD/PCDF congeners in char, Joung et al., 2009.

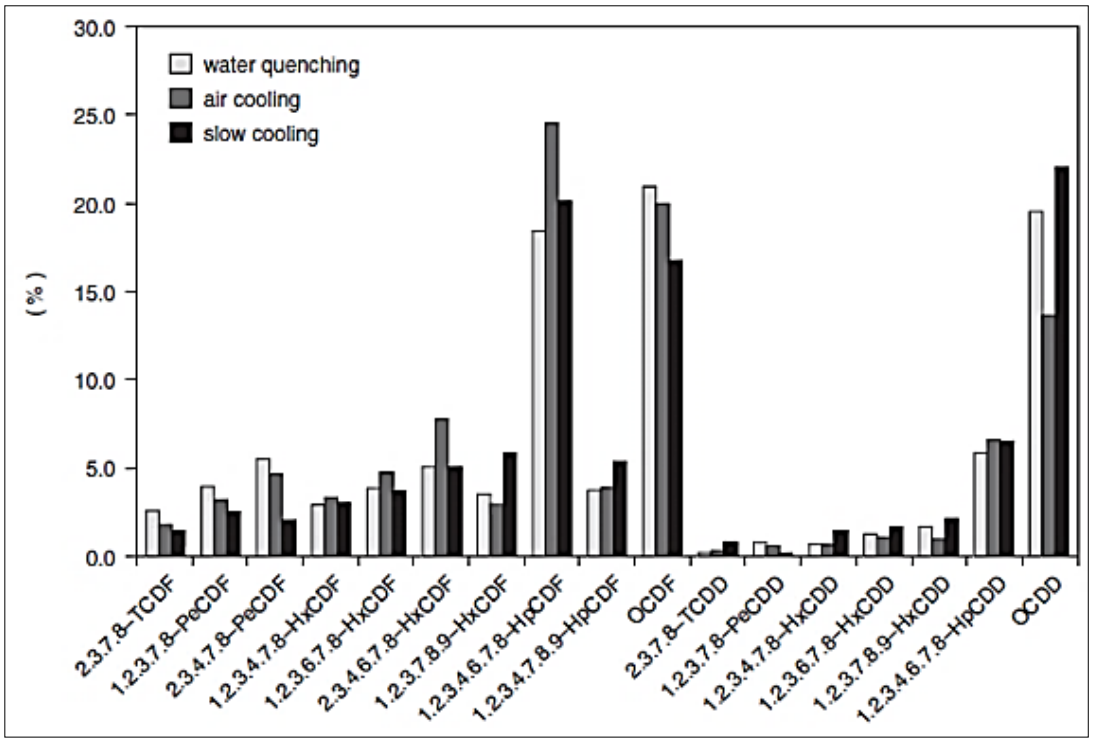


Figure 3.8. The distribution characteristics of PCDD/pcdf congeners in melted slag, Joung et al., 2009.

Mendoza et al. in 2006, was conducted gasification tests in a semi-industrial scale set-up in order to thermally treat mixtures of spent oil and PCB containing oil at a concentration of 50.000 ppm and 100.000 ppm of polychlorinated biphenyls (PCBs). The spent oil and the contaminated oil with PCBs were mixed together in order to prepare the feedstock. The characterization of this mixture was given in Table 3.6.

Table.3.6. Feedstock analysis of Mendoza et al. Study.

Parameter	**Units**	**0% PCBs**	**5% PCBs**	**10% PCBs**
Heating value	kcal/kg	10710	10280	9850
Chlorine	%	0.05	3.23	5.28
Cu	mg/kg	23	18	16
Water	%	0.6	0.54	0.53

Ref: Mendoza et al. 2006

The vertical carbon steel cylindrical gasification reactor which marked with R-1, has 3.8m^3 volume, 7.35 m. total length, 4.20 m main body length, 0.89 m in inner diameter was used in the experiments and can be seen in Figure 3.9.

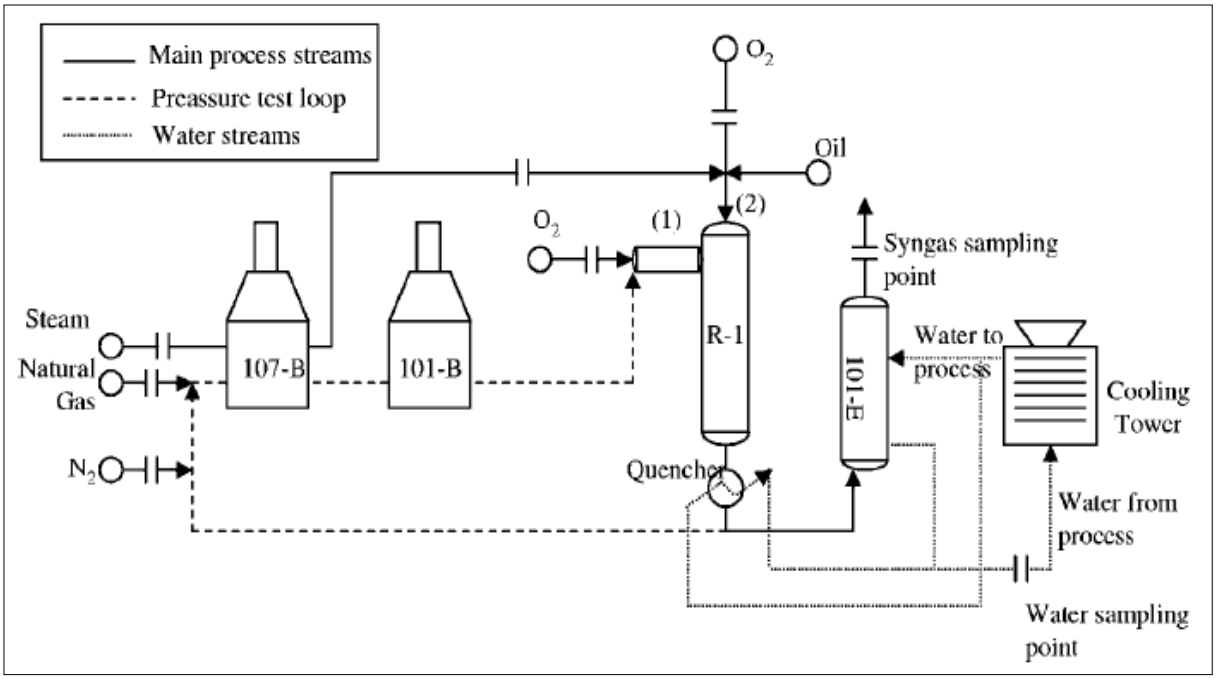


Figure 3.9. Gasification set-up used by Mendoza et al.

The steady state temperature in the reactor was recorded as ~1140 °C. The syngas was cooled to 40°C and 35°C after quencher and scrubber, respectively. The residence time of the gas in the reactor was estimated as ~42 second to give enough time to the gasification of the feedstock and reduce the possibility of releasing undestroyed PCBs.

Dioxin sampling and analyses were implemented with an isokinetic source sampling system as described in EPA Method 5 and EPA Method 23, respectively. Dioxins congeners were analyzed in syngas and water used in the scrubber/quencher.

According to the analysis results, octachloro-dibenzo-p-dioxin (OCDD) was the only detected congener in syngas. Only 2,3,7,8-tetra-chloro-dibenzofuran was detected in used scrubber water. HCl stayed lower than the detection limit of the method (<0.03 mg/m^3). Dioxins and chlorine species analysis results for 0%, 5%, and 10%PCBs concentrations were shown in Table 3.7. Volumetric percentage measurements of syngas constituents are given on dry basis.

Table 3.7. Dioxin and chlorine concentrations in syngas and scrubber water.

Parameter		0% PCBs	5%PCBs	10%PCBs
Syngas	HCl, mg/m^3	< 0.03	< 0.03	< 0.03
	OCDD, ng-TEQ/m^3	$6.5x10^{-6}$	$8.1 x10^{-6}$	$7.1 x10^{-6}$
Scrubber Water	Chlorides, mg/l	74	756	1850
	2378-TCDF, ng-TEQ/m^3	$9.4x10^{-5}$	$1.5 x10^{-4}$	$8.4 x10^{-3}$

Ref: Mendoza et al. 2006

Kawamoto and Mabuchi, 2001, extensively examined the formation behavior of PCDDs/Fs in the municipal solid waste fly ash (Ash A) of a gasification–melting process in order to understand their formation potential. Ash samples were fixed in a laboratory-scale heating apparatus with carrier gases to investigate the effects of the type and composition of the ash, temperatures, gas residence time, and organic precursors. The results were compared with those of fly ash from a conventional incinerator (Ash B). Gasification and melting process ash and conventional incinerator ash compositions can be seen in Table 3.8.

The ash samples are not directly subjected to gasification process, the study is important to represent the dioxin formation behavior of gasification process ashes. The aim to refer this study is to better understand the behavior of the gasification process ash on dioxin formation. Main differences between Ash A and Ash B are that the carbon content, concentration of copper, chloride ions, and the PCDDs/DFs concentrations. Ash B was treated for 2h at 600°C in order to decrease the carbon content; thus the organic carbon content of the Ash B was reduced to 0.01% from 3.4% by volatilization. Also Ash A was impregnated with copper and then the copper content was increased to 1.5% from 0.1%. Moreover, a solid model ash sample was prepared that contained no organic carbon, chlorine, or catalyst metals as a reference. According to allow to the gas flow inside these very fine particulated ashes inside the reactor, the ash was mixed with distilled water and pelletized. Carrier gas which the composition was selected as a typical value based on information about the actual values in several types of gasification–melting plants contained 1% HCl besides N_2, O_2, and CO_2. Kawamoto and Mabuchi's experimental set-up were given in Figure 3.10.

Table 3.8. Elemental composition and dioxin concentrations in ash A and ash B.

Component	Ash A	Ash B
Si (%)	14	13
Al (%)	7	11
Ca (%)	13	14
Mg (%)	2.1	2.1
Na (%)	3.8	4.8
K (%)	3.2	1.8
Cu (%)	0.10	0.052
Fe (%)	1.7	3.8
C (%)	<0.01 *(1.5)**	3.4
T-S (%)	2.9	1.5
T-Cl (%)	5.5	1.5
PCDDs/PCDFs, (ng-TEQ/g)	0.0072	0.12 *(0.0085)**

**After Treatment*
Ref: Kawamoto and Mabuchi, 2001

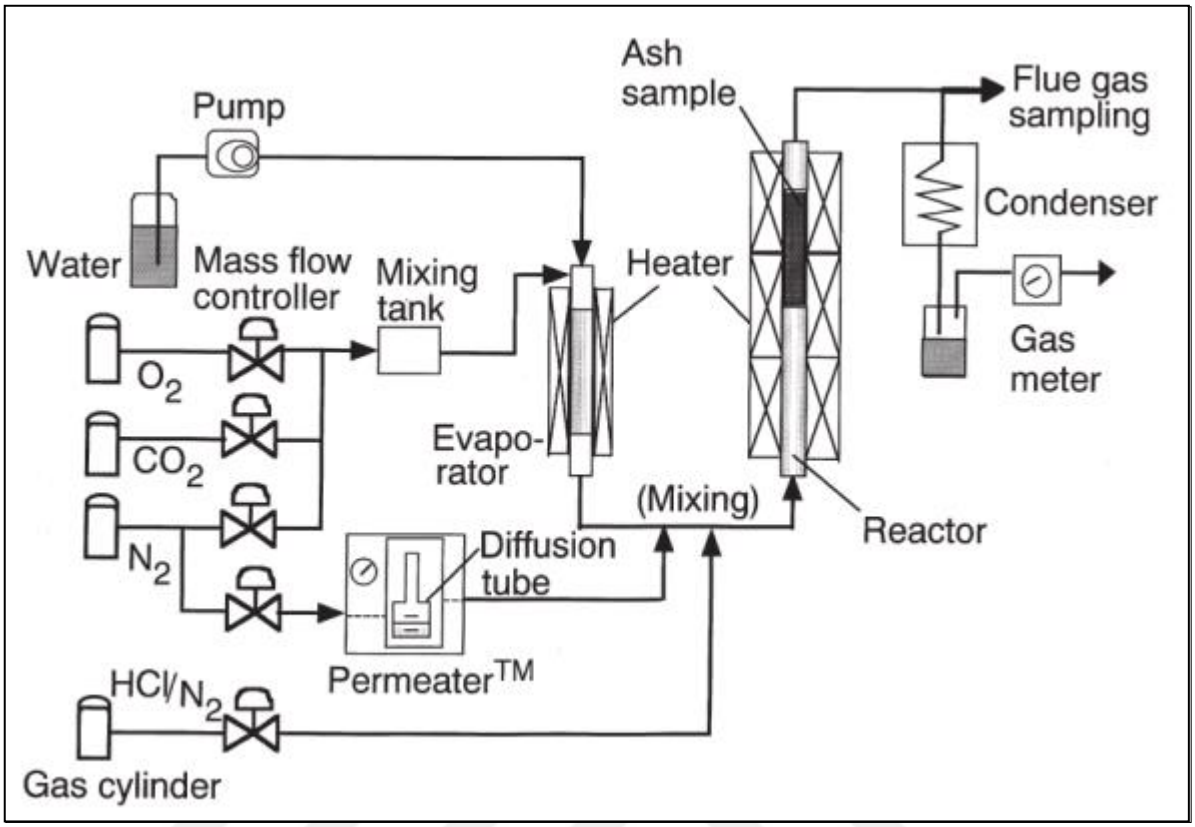


Figure 3.10. Experimental set-up for Kawamoto and Mabuchi ash heating study (Ref: Kawamoto and Mabuchi, 2001).

The experiments were carried in the following manner. First, carrier and organic gases were introduced into the reaction tube and the reaction tube was heated. The organic compounds which were fed into the reactor were o-chlorophenol, benzene, chlorobenzene, n-Octane in order to investigate precursor effect. The average concentration of the o-chlorophenol at the reactor inlet was 145mg/m^3 which was high enough to supply the amount of organic compound required for the formation of PCDDs/DFs. When the evaporator temperature reached 200°C, distilled water was introduced into the system. When the temperatures reached the designated values about 1h later, HCl gas was introduced into the system and it was operated for about 3h to ensure that the system was stabilized. About 4h after starting the experiment, the measurement of dioxins was initiated. Measurements were taken for 4h, following the Standard Manual for Determination and Analysis of Dioxins in Waste Treatment Process. The total volume of the gas sampled was 2m^3, which corresponded to about half of the flue gas in the experimental apparatus. After dioxin measurements were completed and the experimental run had finished, a fly ash sample was taken from inside the reactor and 50g was tested to determine PCDD/F. The

overall experiment conditions and dioxin concentrations in flue gas and ash can be seen in Table 3.9.

Table 3.9. Experiment conditions and dioxin concentrations in flue gas and ash.

Run No.	Fly Ash	^{o}T	Retention Time (s)	Organic Compound Fed	HCl (ppm)	Dioxins in Flue Gas, ng-TEQ/Nm^3	Dioxins in Ash, ng-TEQ/g
1	Ash A	350	1.5	o-Chlorophenol	1000	8.7	0.026
2	Ash A	200	1.5	o-Chlorophenol	1000	0.21	0.033
3	Ash A	275	1.5	o-Chlorophenol	1000	0.71	0.071
4	Ash A	420	1.5	o-Chlorophenol	1000	1.4	0.0029
5	Ash A	550	1.5	o-Chlorophenol	1000	0.20	0.000046
6	Ash A	350	0.15	o-Chlorophenol	1000	0.23	0.019
7	Ash A	350	0.75	o-Chlorophenol	1000	2.1	0.033
8	Ash A	350	3	o-Chlorophenol	1000	13	0.025
9	Ash B	350	1.5	o-Chlorophenol	1000	7.6	4.3
10	Ash B[b]	350	1.5	o-Chlorophenol	1000	0.19	0.013
11	Ash A+ $CuCl_2$	350	1.5	o-Chlorophenol	1000	28	0.029
12	Synthetic Ash	350	1.5	o-Chlorophenol	1000	0.23	<0.0016
13	Ash A	350	1.5	o-Chlorophenol[c]	1000	4.8	0.013
14	Ash A	350	1.5	None	1000	8.5	0.049
15	Ash B	350	1.5	None	1000	3.1	6.2
16	Ash A	350	1.5	n-Octane	1000	4.7	0.018
17	Ash A	350	1.5	Chlorobenzene	1000	10	0.018
18	Ash A	350	1.5	Benzene	1000	14	0.059
19	Ash A	350	1.5	o-Chlorophenol	0	5.9	0.038
20	Ash A	350	1.5	Benzene	0	2.6	0.064

Ref: Kawamoto and Mabuchi, 2001

Yamamoto et al., 2000, have carried out basic function tests of new concept shaft-type gasification and smelting process by a 2 tons/day capacity bench furnace and 20 ton/day capacity demonstration plant with raw and dried municipal waste. The chemical compositions of the wastes are shown in Table 3.10. The basic flow of this system is shown in Figure 3.11.

Table 3.10. Chemical composition of wastes.

%, w/w	Combustibles						Total	Ash	Moisture	Total
	C	H	O	N	S	Cl				
Municipal waste	22.5	3.4	17.9	0.5	0.07	0.94	45.3	5.2	49.5	100
Dried waste	40	6.3	32.2	0.9	0.12	1.7	81.2	9.8	9	100

Ref: Yamamoto et al., 2000.

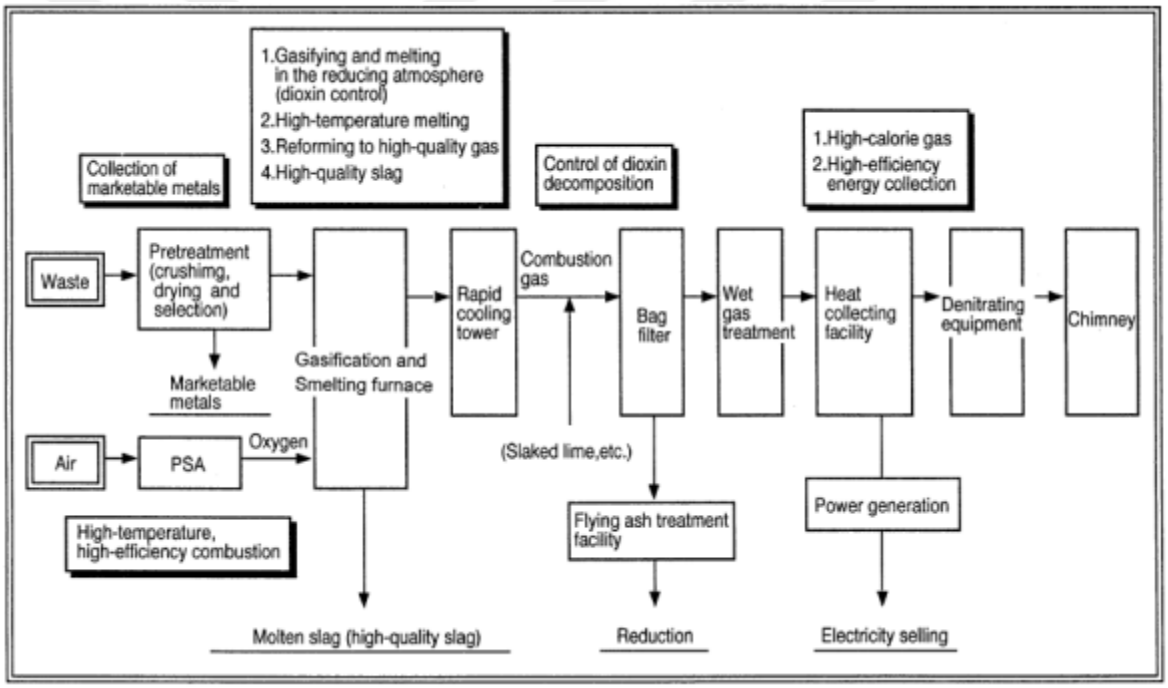


Figure 3.11. The basic flow of the waste gasification and smelting system, Yamamoto et al., 2000.

The concept has waste gasification and smelting system in high-temperature reduction atmosphere, high temperature gas reforming and rapid gas cooling for reduction of dioxins emissions. The ashes are smelted in high-temperature reduction atmosphere to reduce the final waste. The produced high calorie gas is maintained by combining oxygen blowing and waste drying. The furnace consists of three zones, a combustion and smelting zone in the packed bed, a thermal decomposition zone on the top of the packed bed, and a free board to reform the gas maintained at 1070^{o}C or more above the top of the packed bed.

Exhaust gas discharged from the furnace is cooled down to 170^{o}C through the cooling tower in order to control the decomposition of dioxins and containment in gas or dust. The bench type set-up schematic illustration can be seen in Figure 3.12.

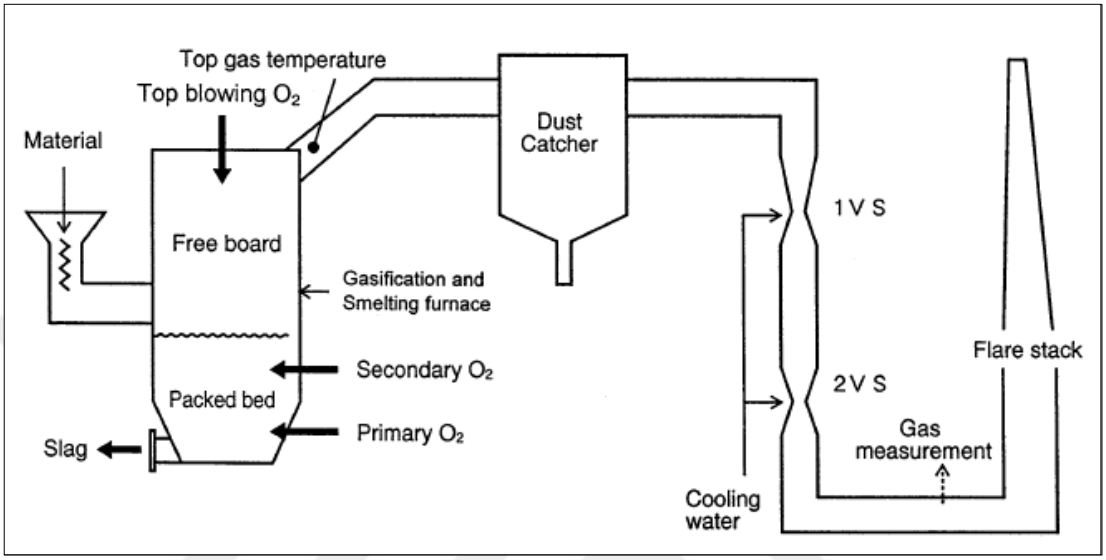


Figure 3.12. 2 ton MW/day bench furnace, Yamamoto et al., 2000.

Two runs were performed in 2 tons/day capacity bench furnace with municipal waste and dried waste. The dioxins concentrations were measured less than 0.01 ng-TEQ/Nm^3 in syngas after venturi scrubber in all runs. Dioxins concentrations in the dust were also less than 0.01 ng-TEQ/g. Another 2 runs were performed in 20 tons/day capacity demonstration plant and the dioxin concentration results at the exit of the stack were less than 0.01 ng-TEQ/Nm^3. The results were reported according to 12% O_2. The dioxin measurement results both in bench-scale furnace and the demonstration plant were given in Table 3.11. The demonstration plant schematic illustration can also be seen in Figure 3.13.

Table 3.11. Dioxin results in Yamamoto et al.'s Study.

	2 t/d Capacity Bench System		20 t/d Capacity Demonstration Plant
	Dried Municipal Waste	Wet Municipal Waste	Dried Municipal Waste
Dioxins in syngas, ng-TEQ/Nm^3	<0.01	<0.01	0.0002 (run1) 0.0011 (run2)
Dioxins in dust, ng-TEQ/Nm^3	<0.01	<0.01	-

(Ref: Yamamoto et al., 2000)

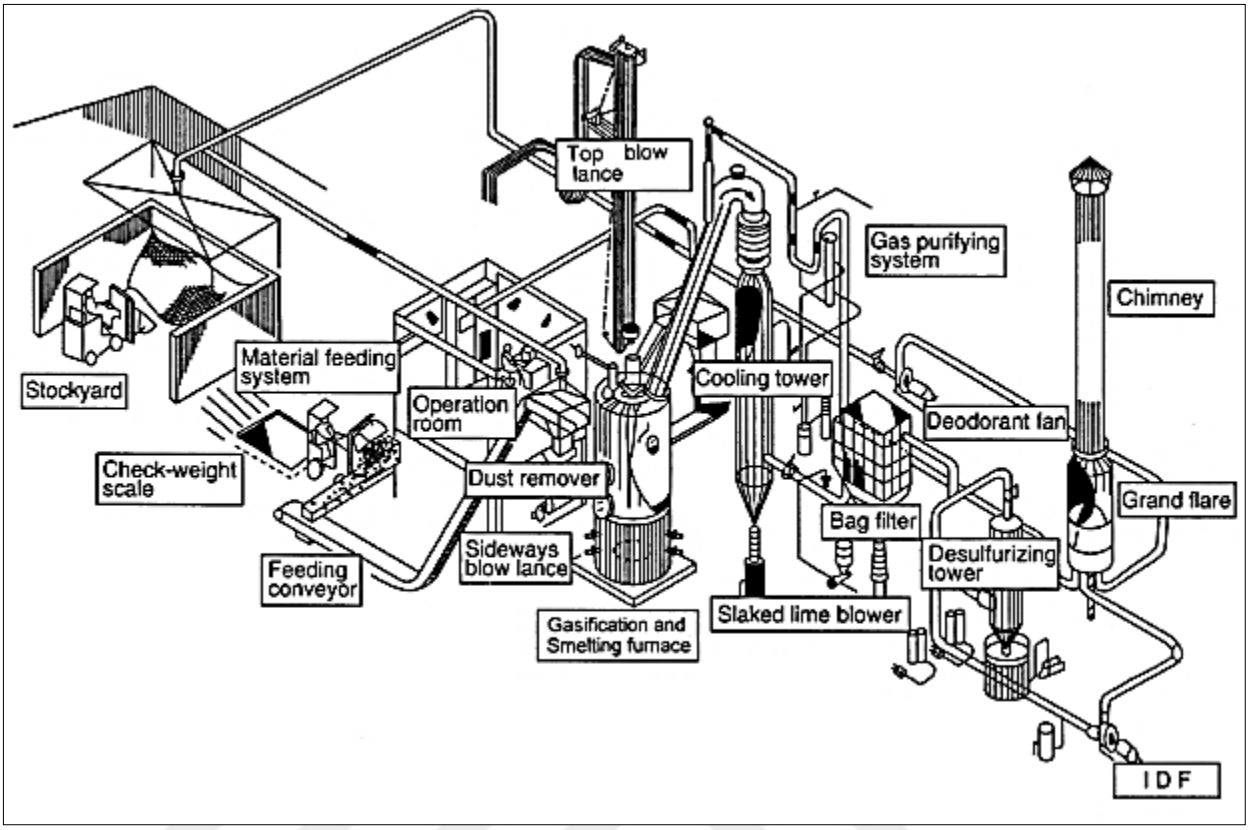


Figure 3.13. demonstration plant, Yamamoto et al., 2000.

In 2005, same reactor type of Yamamoto et al.'s study was used by Kikuchi et al. for making clean fuel gas from various wastes rather than burn the fuel gas at high temperature and produce steam. The furnace is a shaft type in which waste is gasified and smelted in one process using a top-blow lance together with side-blow oxygen lances. The designed reactor has two main functions that the first one is gasification which takes place at the upper part of the reactor and the second is smelting combustion that takes place at the lower part of the reactor in an oxygen-rich environment. In that multifunctional reactor, 7 reactions such as thermal decomposition of waste, combustion of volatile matter, combustion of char, smelting of ash (incombustible matter), 2 different types of gasification, and CO reforming by the shift reaction take place. The reactor can be seen in Figure 3.14. The expected functions and reactions in the reactor are summarized in Table 3.12.

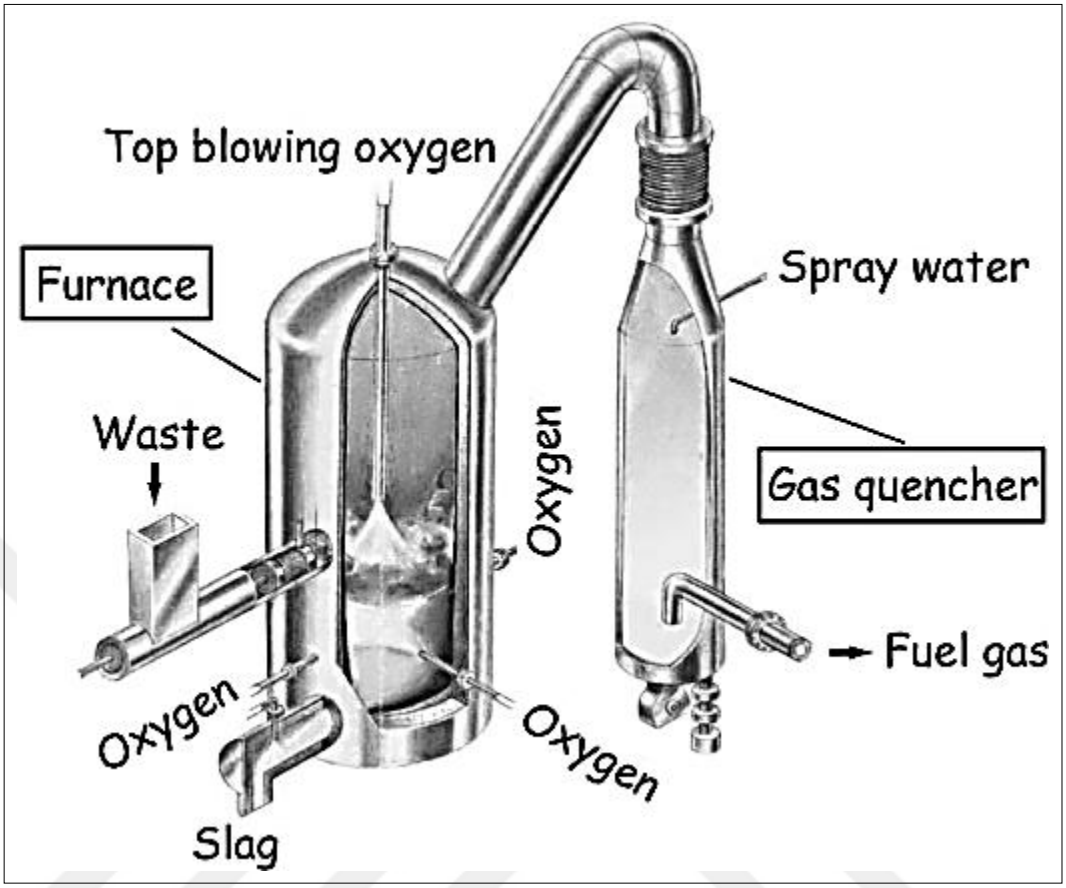


Figure 3.14. Kikuchi et al. gasification and smelting furnace design (Ref: Kikuchi et al. 2005).

Table 3.12. Kikuchi et al. gasification and smelting process reactions.

Furnace Part	**Function**	**Reactions**
Upper Part (reductor)	Gasification	$Char + CO_2 = CO$
		$Char + H_2O = CO + H_2$
	Reforming	$CO + H_2O = CO_2 + H_2$
Lower Part (combustor)	Thermal decomposition	Waste = Volatile matter + Char + Ash
	Combustion	$Volatile\ Matter + O_2 = CO_2 + H_2$
		$Char + O_2 = CO_2 + CO$
	Smelting	Ash (non-combustible matter) = Slag

Ref: Kikuchi et al. 2005.

At first step of the reactor, waste is burned and decomposed to syngas and a residue as char and ash in an oxygen-rich environment. The ash melts at a temperature of about 1400^{o}C, flows down to the lower part of the furnace and is removed as slag. The formed gas and some of the char rise upwards into the upper part, where they are gasified and reformed to fuel gas containing H_2, CO and CO_2 at a temperature of about 1000^{o}C. Top blowing oxygen lance prevents the mixing of dust with fuel gas. The overall concept aimed to control 3T parameters, temperature, time and turbulence, in order to prevent dioxin formation.

During the experiments, three different type of waste such as municipal solid waste, plastic waste, and PVC refuse have been tested separately with 70kg/h feed rate. The feeded chlorine rates within the waste types were 1,7% in municipal waste, 3,2% in plastic waste, and 47,8% in PVC waste. The HCl, accordingly Cl was recovered by greater than %95 in all waste type experiments. The top-blowing oxygen lance eliminated the fly ash entrance to the fuel gas pathway. Thus, dioxins formation via de novo synthesis with the important role of fly ash was eliminated. Another prevention of dioxin formation is quick quenching. High temperature fuel gas with fly ash passes toward to the quencher which uses water spray and rapidly cools the gas from about 1000^{o}C to about 200^{o}C. This quick quenching also prevents PCDD/F formation. At this time, some of the fly ash was scrubbed in the quencher are collected and treated in the residue stabilizer using cement solidification. The process flowchart can be seen in Figure 3.15.

Fly ash remaining in the fuel gas was captured in the bag filter, and PCDD/F concentrations in the fly ash were measured between 0.0035 and 0.014 ng TEQ/g in ash. Both the fly ash separated in the quencher and that collected in the bag filter were properly solidified in the residue stabilizer. It is considered that these combined techniques (quenching, filtration and solidification) enabled the fly ash to be thoroughly controlled. As a result of these intensive ash control applications, the concentration of dioxins did not exceed the target limit 0.01 ng TEQ/Nm^3 in fuel gas although dioxins increased with an increase in the chlorine content in the feed stock. The overall dioxin results with chlorine rates were given in Table 3.13.

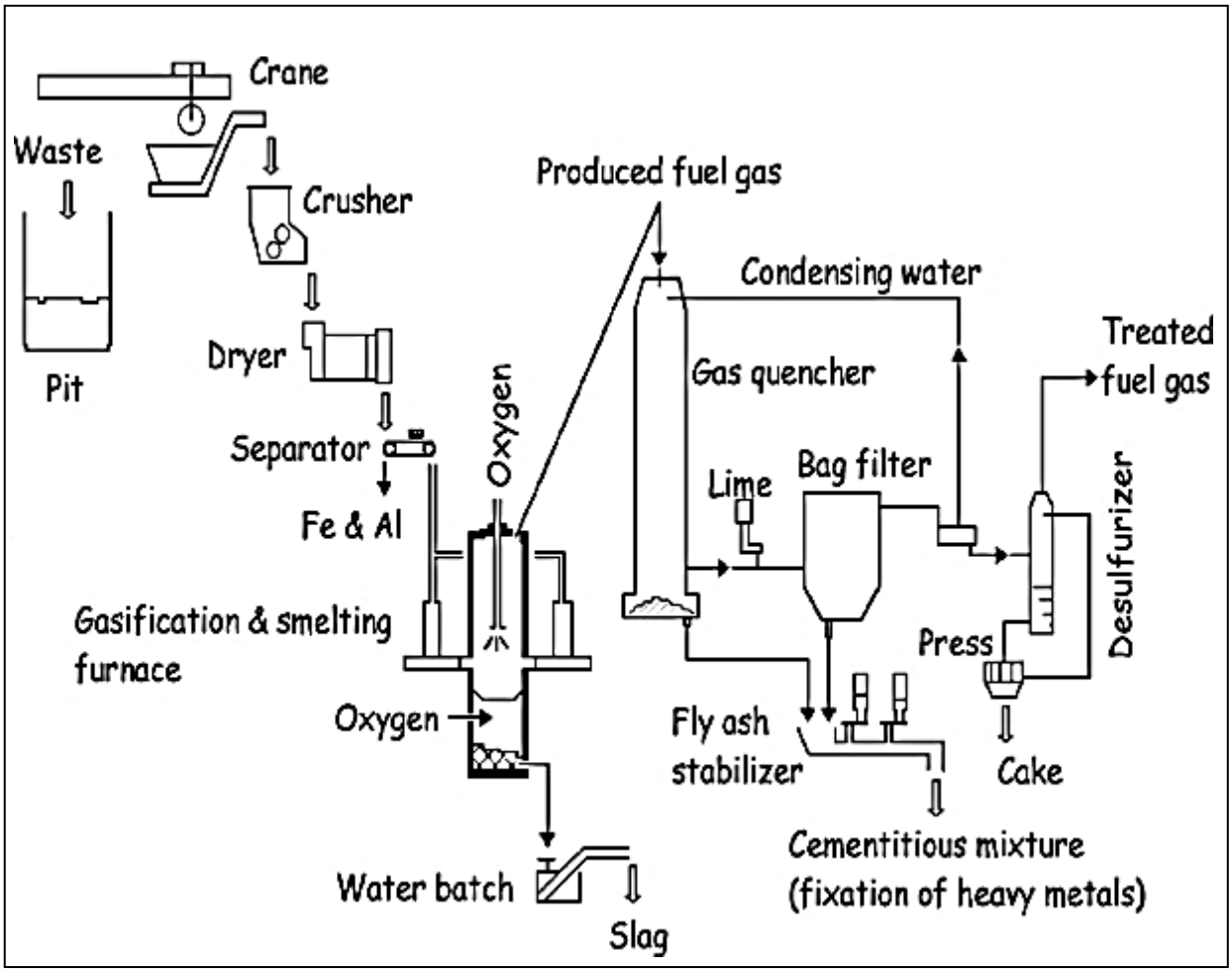


Figure 3.15. The process flowchart for Kikuchi et al. study,
Kikuchi et al. 2005.

Table 3.13. Chlorine species and dioxin results Kikuchi et al.'s study.

Feedstock	Chlorine rate, %	HCl, ppm	Dioxins in Fuel Gas, ng-TEQ/Nm^3	Dioxins in Fly Ash, ng-TEQ/gr ash	Dioxins in condensate water, ng-TEQ/lt
MSW	1.7	975	< 0.001	0.0035 0.014	0.024
Plastic waste	3.2	-	< 0.002	-	-
PVC	47.8	-	< 0.01	-	-

Ref: Kikuchi et al. 2005.

Gang et al. fulfilled a series of experiments in order to develop municipal solid waste (MSW) gasification and melting technology in 2007. According to the first MSW gasification experiments at 500–750°C with ER= 0.19–0.5, scientists found that the LHV of syngas increases with increasing temperature or decreasing ER. They also commented

that when ER is lower than 0.15, gasification can hardly be completed in time and the gasifier will be jammed by reactants.

However, the second experiment which is more related to the dioxin formation, were carried out in a fixed-bed melting furnace with fly ash samples from a commercial incineration plant. The fly ash was melted and the resulted slag was analyzed for dioxin content. The results showed that more than %99 of dioxins were decomposed when temperature was over 1100^{o}C, and when temperature achieved 1460°C, no dioxins can be detected by the instrument. The dioxin concentrations with decomposition ratios in the original fly ash and melted slag can be seen in Table 3.14.

This study has a meaning from the point of view of fly ash melting after gasification step in order to control and eliminate dioxin formation at the post-combustion zones of the experimental set-ups with de novo formation mechanism.

Table 3.14. Dioxin concentrations and decomposition ratios.

Ash/Slag	Dioxins, ng-TEQ/kg	Decomposition Ratio, %
Original Fly Ash	275	-
Slag from 1100^{o}C	0.042	99.968
Slag from 1300^{o}C	0.026	99.990
Slag from 1460^{o}C	0	100.000

Ref: Gang et al., 2007.

Jiao et al. 2012, were carried out an experimental research on gasification of simulation garbage containing-high-PVC on a special designed integrated experimental platform for fluidized-bed gasification. Scientists examined the effects of PVC content and equivalent air ratio (ER) on dioxins formation. The results show that when PVC content is 20% and ER decreases from 1.2 to 0.4, the yield and TEQ of dioxin produced per gram of PVC are decreased from 146.53 ng/g and 20.71 ng I-TEQ/g to 2.07 ng/g and 0.31 ng I-TEQ/g, respectively. For the same ER 0.4 and PVC decreased from 20% to 1%, the yield and TEQ of dioxin produced per gram of PVC reduced from 23.54 ng/g and 3.49 ng I-

TEQ/g to 2.07 ng/g and 0.31 ng I-TEQ/g. Jiao et al.'s study has indicated the ER has direct effect on dioxin formation during gasification of chlorine containing material.

Other than the studies which investigate the effects of operating parameters and PVC on dioxin formation, Tanigaki et al. (2013) investigated the gas components from the waste gasification and melting technology in two plants with different flue gas cleaning systems. First plat, the plant A, has wet-scrubber system while the second one, the plant B, has dry cleaning system both with selective catalytic reduction (SCR) reactors for gas treatment. The researchers measured the gas parameters such as hydrogen chloride, sulfur dioxide and nitrogen oxides at the inlet and outlet of the baghouse (BF), and the stack. The removal efficiencies of dioxins and furans, and other flue gas components in different flue gas cleaning systems were evaluated. The ER used in the experiments was 0,33 and 0,35 for the plants, recpectively. The chlorine contents of the feedstock were 0.6 and 0.2 for the plant A and B, respectively. The ER values and the chlorine rates in Tanigaki et al.'s study are different than the existing research study. However, the treatment detailes are important to control the dioxin emissions in a gasification process. Researchers determined significant reduction for the dioxins concentrations with SCR both at plant A and B. The SCR reactor can be considered as a gas treatment component for further gasification studies with hazardous wastes.

Lopes et al. (2015) operated a moving grit gasifier which they designed for that study, to evaluate dioxin and furan emissions during municipal solid waste (MSW) gasification. The produced syngas subsequently was burned during the study. Similar with the existing study, Lopes et al. controlled the system manually. This manual control resulted with the instability at their study. Reserachers determined high amount of chlorine on to the fly ash that supports the fly ash role on dioxin formation. However the dioxin results are below the National limits (0.5 ng TEQ /Nm^3) that the mean dioxin and furan emission from the gasification in the mobile grit reactor was 0.28 ng TEQ/Nm^3. Researchers suggested that gasification followed by combustion releases significantly less PCDDs and PCDFs than the usual MSW incineration. The findings of this study can also be used for decision-making of the further process configurations.

4. MATERIALS AND METHODS

4.1. Materials

4.1.1. Pilot Gasification Set-Up

The Pilot Gasification Set-Up was designed by the Biomass and Coal Gasification and Combustion Laboratory Research Team after a series of experiments. At the beginning, the team used an existing system which was designed and manufactured previously, in order to increase the knowledge on gasification process. Afterwards, the pilot gasification set-up was designed which was used forthis PhD thesis.

The reactor of the set-up is a throat type down-draft gasifier which was designed according to the design steps given below:

1. Selection and analysis of biomass,
2. Determination of fuel feeding rate (kg/h),
3. Selection of the optimum hearth load,
4. Calculation of the diameter of the throat,
5. Determination of the height of the throat,
6. Determination of the diameter of bunker,
7. Selection of the optimum ER for gasification,
8. Calculation of the required air for woodchips gasification at selected ER,
9. Selection of the air velocity,
10. Selection of the number of nozzles and calculation of the diameter of nozzles,
11. Estimation of the gas flow rate,
12. Calculation of the gasifier efficiency,
13. Making the mass and energy balance, and
14. Design of the cyclone.

The set-up mainly consists of the gasifier, a cyclone and a gas cleaning system. The diameter and the length of the gasifier are 300 mm and 1095 mm, respectively. Feedstock

feeding capacity is 10kg/h and the maximum thermal capacity of the gasifier is 50kW. The main body of the gasifier and the all tube in the system were made from 3 mm thick AISI 310S quality stainless steel. The throat diameter is 100 mm and it was designed like a cone which has 5 mm holes. The cone structure was desinged with 300 mm high and inclined at 72^{o} the horizontal below the hopper section. Air jacket was formed between the outside the reactor and the cone part. The ignition port and the air inlet nozzle were desined at the same level. The level of gas outlet is in the middle of the throat. The char and ash are removed from the bottom of the gasifier after the experiments using a globe valve with 80 mm diameter mounted with a flange. The shematic illustration of the gasifier can be seen in Figure 4.1a. Overall set-up diagram can be seen in Figure 4.1b.

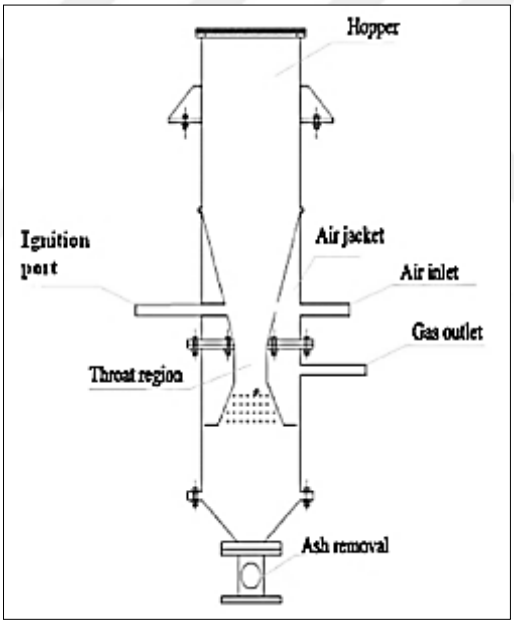


Figure 4.1a. Throat type down-draft gasifier, Olgun et al. 2011.

Gas which is produced by gasifier enters the cyclone and goes through the gas cleaning system. After the cleaning system, the gas enters the on-line gas analyzer to be analysed for the gas composition. A cyclone is used to remove the particulates in the gas stream at the gasifier exit. For high temperature gas cleaning purpose, a Lapple type cyclone was chosen and designed by the Tubitak Team based on the inlet producer gas temperature of $500^{o}C$, gas flow rate of 25 Nm^{3}/h and gas inlet velocity of 20m/s. AISI 310S quality stainless steel was used with 2 mm thickness for the cyclon construction. After the cyclone, the heat exchanger (the cooler) which is composed of one inner and one

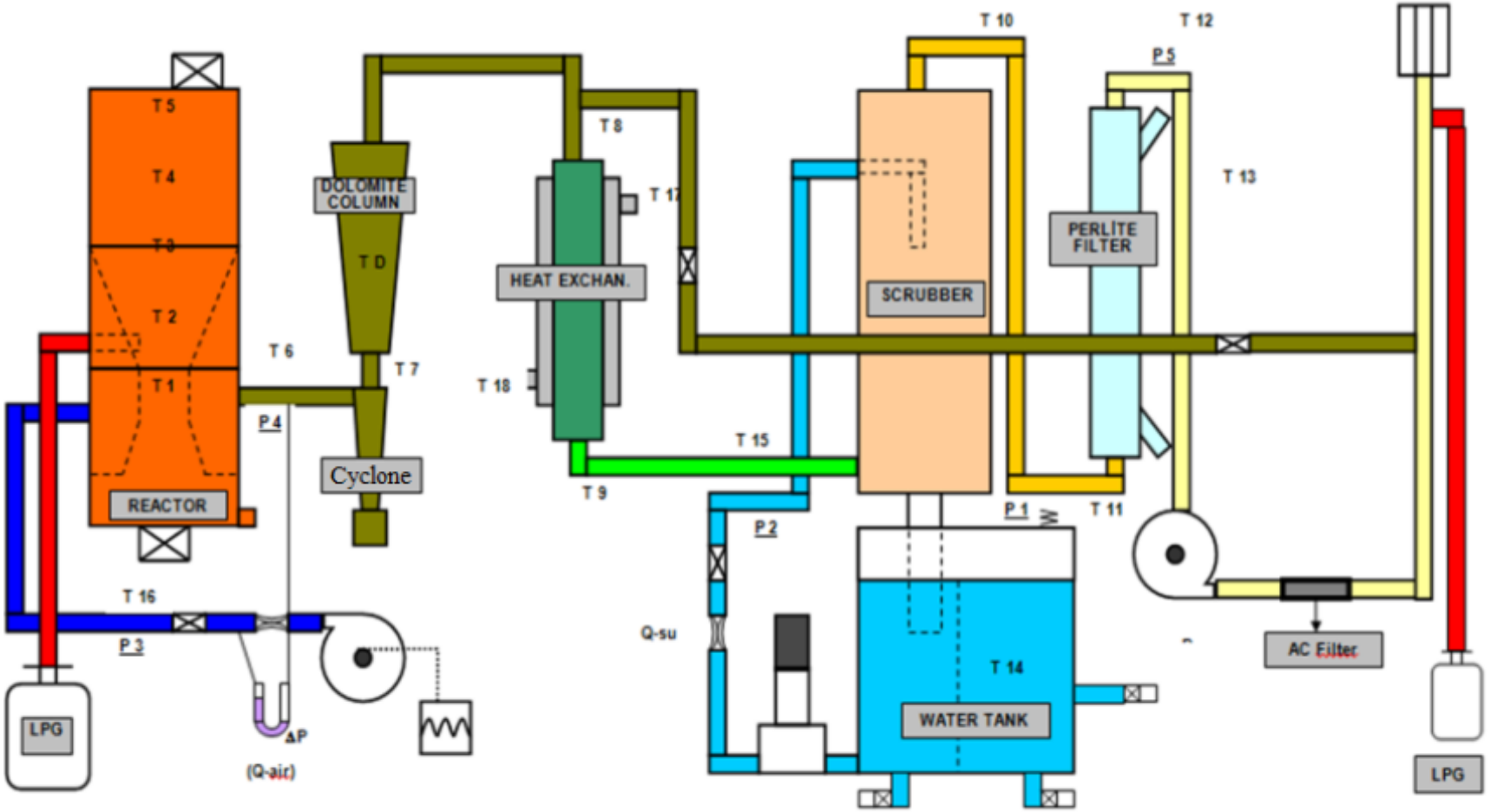


Figure 4.1b. Pilot gasification set-up.

outer tube is used to cool the syngas. The heat exchanger was designed to reduce the gas temperature from 400°C at the inlet to 45°C at the outlet. The cooling water flows in outer tube in reverse direction to the hot syngas which flows in the inner tube. The cooler also removes some of the tar in the syngas by condensation. The gas cleaning system follows the heat exchanger with water scrubber, perlite column, and activated carbon filter. Water scrubber is used to remove the acidic gases from the syngas while perlite column is used to adsorb the remaining tar and moisture content of the gas. Activated carbon filter was installed specifically for this research study to remove dioxin and furan compounds.

Secondary air is fed by an air-blower. Air flow rate is adjusted with changing the motor speed manually with frequency converter motor driver. ID fan draws the syngas from the system to the flare. All components and pipes are isolated with glass wool to prevent heat loss.

4.1.2. Frequency Converter

Frequency Converter (FC) is a power electronic device, which transforms DC voltage to AC voltage of desired frequency and magnitude. Secondary air blower already has an FC. However ID fan had constant speed. Siemens Micromaster 420 Frequency Converter with 50Hz maximum frequency was adapted to the ID fan in order to change and control the speed of the fan. The FC can be seen at Figure 4.2.

Figure 4.2. Siemens frequency converter.

4.1.3. Ignition System

The system consists of mainly a burner with an igniter in order to ignite the fuel, an LPG cylinder as fuel supply, a blower as air supply for burning, and an electronic control panel. The system has also control valve and a pressure gauge for LPG flow control. System is not a stationary system, it is moveable. After ignition the feedstock with burner flame it is shuted down and moved away from the pilot plant. Ignition system photografh can be seen at Figure 4.3.

Figure 4.3. Ignition system.

4.1.4. Thermocouples

Thermocouples are junctions between two different metals that produce a voltage related to temperature difference. The most common type of thermocouples is K-type thermocouples for general purposes. At the experimental pilot plant 17 K-type thermocouples were used in order to able to control the reactor and overall operation temperatures. Five-type K thermocouples put in the tube with 22mm diameter 310 stainless steel and plug into the reactor bed at the lip along the height of the gasifier. T5 and T4 measure the temperature of the drying zone, T3 measures the temperature of the pyrolysis

zone, T2 measures the temperature of the oxidation zone and T1 measures the temperature of the reduction zone. Thermocouple locations can be seen in Figure 4.1. Figure 4.4. shows a set of thermocouples and the shematic locations illustration used in the set-up.

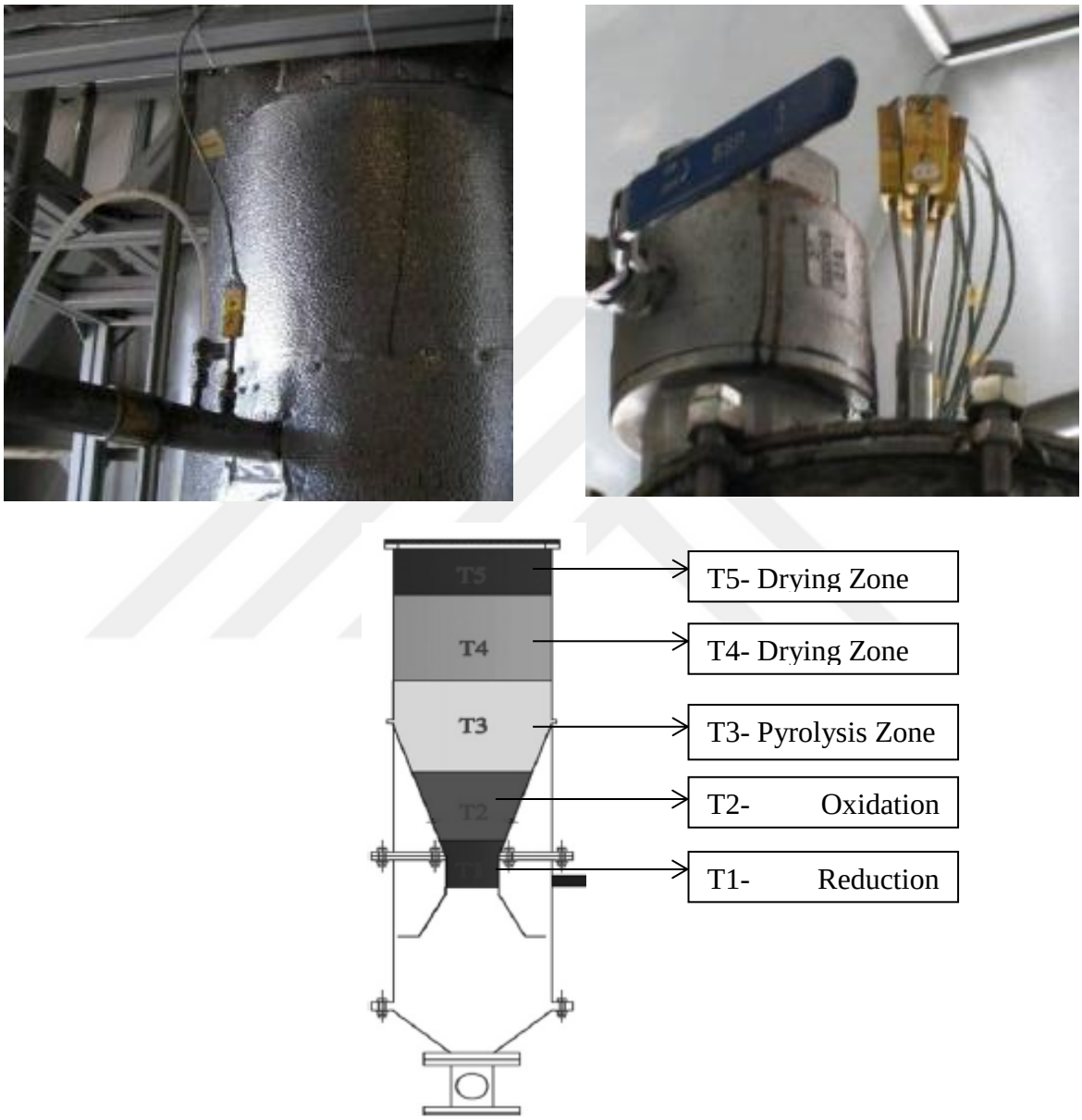


Figure 4.4. Thermocouples.

4.1.5. ABB On-line Gas Analyzer

ABB On-line Gas Analyzer is gas measurement equipment which is capable to measure large number of gas components. The composition of producer gas is measured by

using ABB AO2000 on-line gas analyzer. The gas analyzer consists of three types of detectors. CO, CO_2, CH_4 are measured by an infrared analyzer module. H_2 is measured by a thermal conductivity analyzer module. O_2 is measured by a paramagnetic online analyzer module. The system has its own gas cooling and filters. The gas cooled up to 5°C also there is a moisture sensor which cuts the line if feels the moisture. All the measurements are in volume fraction**.** Analyzer has integrated ethernet port for network communication; therefore, the gas concentrations were observed and recorded via releated data program installed to the PC that can be seen at Figure 4.5.

Figure 4.5. On-line gas analyzer PC.

Analyzer was calibrated prior to beginning the experiments. The equipment has 3 connection line means that it can be possible to connect 3 different set-ups at the same time and switch the lines between each other. However, it is not possible to analyse all 3 different gases at the same time. The ABB On-line gas analyzer is shown at Figure 4.6.

Figure 4.6. On-line gas analyzer.

4.1.6. Data Logger, Wincontrol Program and Laptop

Data Logger is a device that can read various types of electrical signals via built in instrument or sensor or external instruments and sensors and store the data in internal memory for later download to a computer. In this study data logger red the signals via thermocouples which is located critical points in the system and recorded these temperature data every 3 minutes. Additionally to thermocouples, secondary flow rate was red with data logger with electrical connection.

Thermocouples was connected to data logger ports, and the data logger was connected to laptop which has the Wincontrol program which enables to see the readings in a spread sheet at the screen and download as Excel file. Laptop with Wincontrol program and the data logger can be seen in Figure 4.7.

Figure 4.7. Data logger and laptop.

4.1.7. Dolomite

Dolomite is the name of a sedimentary carbonate rock and a mineral, both composed of calcium magnesium carbonate $CaMg(CO_3)_2$ found in crystals. Dolomite was used in a column in order to adsorb the excess amount of tar which is produced during gasification process. The spent dolomite which was used in the experiments can be seen in Figure 4.8.

Figure 4.8. Used dolomite in the column.

4.1.8. Activated Carbon

Activated Carbon (AC) is a form of carbon that has been processed to make it extremely porous and thus to have a very large surface area available for adsorption or chemical reactions. AC is manufactured as powder activated carbon, granular activated carbon, and pelletized activated carbon.

Pellet type DioxSorb-BXB activated carbon was used in the AC Filter of the gasifier syngas cleaning part. DioxSorb-BXB is a very high activity pellet shaped activated carbon manufactured by steam activation from select grades of anthracite coal. This activated carbon is exceptionally hard and resistant to mechanical breakdown due to a unique binding and extrusion process used during manufacturing. DioxSorb® BXB has been specifically developed for the removal of dioxins and furans from waste incineration flue gases in fixed bed configurations. It exhibits a high adsorption capacity giving prolonged adsorption cycles, which coupled with low steam consumption rates during the regeneration cycle, results in a low total operating cost.

DioxSorb-BXB CTC activity is min. 60%, moisture content is (as packed) max. 5% and total ash content is max. 12%. Its properties such as surface area, butane activity, apparent density, and pellet diameter tolerance are 1000 m^2/g, 25%, 470 - 530 kg/m^3, and

± 10% respectively. The technical specifications of the AC are obtained from the Technical Data Sheet of the material which is provided by the Jacobi the Carbon Company. DioxSorb-BXB activated carbon filled into the AC filter can be seen in Figure 4.9.

Figure 4.9. Activated carbon filled in the filter.

4.1.9. Water

Potable water was used as circulating agent in the scrubber. Water is reserved in water tank and circulated via pump. Prior to beginning the operation scrubber water was renewed. Altough the circulated scrubber water was sampled, it could not be analysed. Morover, the cooling water used in the the heat exchanger was provided and adjusted via running tap.

4.1.10. Hazelnut Shell

Hazelnut shell is the main feedstock which helps to feed Virgin PVC as chlorine source of the representative hazardous waste.

4.1.11. Virgin PVC

Virgin PVC, PETVİNİL S 39/71, was obtained from PETKİM Petrokimya Holding A.Ş. Aliağa Plant. PETVİNİL S 39/71 is used to manufacture cables, soft products, and pipes. Its particule size is approximately 0,063 mm and bulk density is 0,44-0,53 gr/cm^3

(Petkim A.Ş.-PETVİNİL MSDS). It has 55% chlorine content without additives. Virgin PVC can be seen in Figure 4.10.

Figure 4.10. Virgin PVC.

4.1.12. Screen

Five mm sieve size screen was used to eliminate the sawdust from hazelnut shells stock. Screen can be seen in Figure 4.11.

Figure 4.11. Screen.

4.1.13. Scale

Scale is used to prepare the feeding menu. It has digital screen. Scale can be seen in Figure 4.12.

Figure 4.12 Scale.

4.1.14. Dioxin and Furan Sampling Set and Probes

The dioxin and furan sampling set and probes which can be seen in Figure 4.13 and 4.14, were provided by TUBITAK- Environmental Institute (EI) sampling team. All the equipments are suitable for the related sampling methods.

Figure 4.13. Dioxin and furan sampling set.

Figure 4.14. Dioxin and furan sampling probes.

4.1.15. Volatile Organic Compounds Sampling Bags and Box

Volatile Organic Compounds was sampled between ID fan and activated carbon filter via gas bag. Gas bag sampling box can be seen in Figure 4.15.

Figure 4.15. Gas bag sampling box.

4.1.16. Sample Containers and Plastic Drums

Gasification process bottom ash/char, spent activated carbon, spent hazelnut shell used in the perlite column, spent dolomite, spent scrubber water, and heat exhanger condense water are sampled in containers. Plastic drums were used to prepare feeding menu with mixing hazelnut shell and Virgin PVC. Containers and drums can be seen in Figure 4.16.

Figure 4.16. Sample containers and plastic drums.

4.2. Methods

4.2.1. Dioxin and Furan Sampling and Analysis Method

Dioxins sampling from syngas and analysis were carried out by Environmental Institute of TUBITAK-MRC according to TS EN 1948-1, 2, 3 methods. All results are calculated in dry basis, at 1013 mbar and 273^{o}K. Sampling points were detected according to the EPA Method 1. Gas velocity, temperature, and pressure were measured with TS ISO 10780 and the moisture was measured according to the EPA Method 4. Environmental Institute is accredited for all methods except EPA Method 1.

Adsorbent beds materials for dioxin analyses were sampled by the researcher and analysed by the EI team also according to the TS EN 1948-1, 2, 3 methods.

All dioxin and measurements were performed by the EI team as service procurement with the financial support provided by the Boğaziçi University Research Fund. Sampling aparatures are suitable to apply the TS EN 1948-1,2, 3 methods.

4.2.2. Volatile Organic Compounds Sampling and Analysis Method

Volatile Organic Compounds which included the HCl and some tar compounds sampling and analysis were carried out according to EPA Method 26 by also the Environmental Institute.

5. EXPERIMENTS

5.1. Start-up Preparations of the Experimental Set-Up

The set-up was in shut-down mode for a long time at Biomass and Coal Gasification and Combustion Laboratory. The pre-designed set-up had constituted of only gasifier at the early stages. The gas cleaning unit which has cyclone, heat exchanger, venture scrubber, and perlite column had been added to the system after a series of experiments by MRC researchers. However, no experiment had been carried out after those installations. Existing experiments were the first operations with the modified system after adding the gas cleaning unit.

Prior to the beginning the preparation experiments system was checked for valve positions, line connections, gas measurement connections to the ABB on-line gas analyzer, and the all other appropriate parts. ABB on-line gas analyzer was calibrated prior to the preparation experiments. Unfortunately, the analyzer had not been connected to a program loaded computer which allowed reading the syngas composition on-line. Afterwards the connection was made by an authorized service person and the device was calibrated. Additionally inlet of the gasifier was checked visually if any blockage or material retained in the system from the previous experiments. Firstly cold start-up was performed in order to check the initial conditions of the system. Subsequently, preparation experiments were performed to control the modified set-up for proper operation capability.

Preparation Experiment 1: Ten kilograms of hazelnut shell was fed to the reactor as biomass feedstock and ignited with the ignition system. After ignition the feedstock temperature rose up gradually and the system was observed for the equipment runnings. After a short time ID fan overheating was observed and the system was shut down for the next start-up.

Preparation Experiment 2: Possible causes for overheating of the ID fan were evaluated. It was seen that, while the secondary air flow rate, the incoming air feeding, was controlled via frequency converter, the ID fan flow rate, the outgoing gas flow, was not controlled

during operation. In other words, the ID fan speed was constant. It was thought that the overheating of the ID fan caused by the constant motor speed. Having with all these in mind, the system was started up one more time with same specifications but with slower seconder air feeding than the first time to be able to ensure the conclusion. However the ID fan overheated again and the system was shut down step by step.

System Modification: After the overheating problem of the ID fan, a new induced draft fan with 450 mbar pressure, 650 m^3/h maximum flow rate, and 4kV power supply was replaced with the old one. In other words, the ID fan capacity was increased in order to draft the syngas properly.

Preparation Experiment 3: Set-up was started-up after the modifications have been completed. However, prior to the experiment, during system preparation, it was observed that the data logger was malfunctioning. The temperature values from the connected thermocouples could not be read. Despite this undesirable situation, the system was started-up in order to test the new ID fan. Fan overheating was not observed at that time; however, being unable to monitor the temperature, the temperature increased excessively in the reactor and a valve melted down.

As a result of this experiment it was decided that the new ID fan was sufficient to be used for the upcoming research experiments.

System Clean-up: Pilot plant was dissembled in order to clean and make a visual check inside the equipments. While the system was dissembled, excessive tar production was observed inside the ID fan. It is known fact that the most limiting factor is tar production in gasification process. Excessive tar production was also observed inside the perlite column on the hazelnut shells. Hazelnut shells were filled into the perlite column instead of perlite to adsorb the excessive tar and moisture from the syngas. Tar contaminated ID fan body can be seen in Figure 5.1. Tar contaminated hazelnut shells filled in the perlite column and the column itself can also be seen in Figure 5.2. Naturally the hazelnut shells at the gas inlet end of the column contained more tar than the gas outlet end.

Figure 5.1. Tar in ID fan.

Figure 5.2. Perlite column and hazelnut shells.

A new adsorbant material column which was installed after the cyclone was filled with dolomite in order to adsorb tar and prevent the system contamination. Additionally, the diameter of the pipelines was increased to 2 inch from 1 inch to maintain steady gas

flow. And frequency converter was connected to the ID fan in order to control the speed of the fan.

Preparation Experiment 4: Following the last modifications such as dolomite column installation and piping modification, cold start-up was performed in order to check the system and it was not observed any problem.

Preparation Experiment 5: Pilot plant was prepared for the operation. Perlite column was emptied, cleaned and refilled with clean hazelnut shells. 10.75 kg hazelnut shell was filled to the reactor hopper as feedstock. In this run, possible heating in the ID fan and dolomite column tar removal performance were observed. At the end of the run, it is experienced that dolomite adsorbed significant amounts of tar. Eventually, tar contamination was not observed inside the ID fan.

Concludingly, the modified set-up consists of gasifier, cyclone, dolomite column, heat exchanger, water scrubber, perlite column, ID fan, activated carbon filter, and stack respectively after the preparation experiments.

5.2. Gasification Experiments with Modelled Hazardous Waste

After modification of the system, research experiments were conducted in order to investigate the dioxin formation during gasification with modeled hazardous waste feedstock. Prior to the experiments system was checked for all operational requirements.

System Preparation: Perlite column, dolomite column and activated carbon filter were filled with fresh hazelnut shell, dolomite, and pelletized activated carbon materials. All valves were controlled for proper positions. ABB On-line Gas Analyzer was zero-calibrated and the gas lines were checked. A dedicated computer program on the desktop computer was started in order to read the syngas composition coming from the ABB On-line Gas Analyzer. All thermocouples were checked for proper connection and connected to the data logger. Data logger channels were controlled in the program installed in laptop computer for correct reading. Water tank for scrubber circulation was filled with fresh water. The ignition system was controlled and tested. Heat exchanger cooling water valves were opened and flow was adjusted.

Feedstock Preparation: Two diffent feedstock menus were prepared with hazelnut shell and virgin PVC. Hazelnut shell was used as biomass feedstock in order to maintain gasification reactions properly according to the wide biomass usage in gasification. Virgin PVC was used to create representative hazardous waste mixture because of its chlorine content. In other words, a modeled hazardous waste feedstock was created with the mixture of hazelnut shell and virgin PVC. Virgin PVC has been mixed with the hazelnut shell in order to obtain 1% and 2% chlorine concentrations by weight within the feedstock. 180gr. and 360 gr. virgin PVC have been added respectively to the hazelnut shell in order to maintain the c_1= 1% and c_2 = 2% chlorine concentrations in the feedstock. The proximate analysis of hazelnut shell and the ultimate analysis of hazelnut shell and the virgin PVC can be seen in Table 5.1 and Table 5.2, respectively. Results of the proximate and ultimate analysis of hazelnut shell belong to previous studies by the Tubitak-MRC Laboratory team. The data belong to the same feedstock with the hazelnut shell which was used during the experiments.

Table 5.1 Proximate analysis of hazelnut shell*.

	Volatile Matter, %	Fixed Carbon, %	Moisture Content, %	Ash, %	Higher Heating Value, MJ/kg	Lower Heating Value, MJ/kg
Hazelnut Shell	68.2	18.2	12.4	1.1	19.5	17.4

Source: Literature of the Biomass and Coal Gasification and Combustion Laboratory

Table 5.2 Ultimate analysis of hazelnut shell and virgin PVC.

	C, %	H, %	O, %	S, %	N, %	Cl, %
Hazelnut Shell	45.9	5.7	48.2	0.0721	<1	-
Virgin PVC	40.1	5.1	0.5	-	-	54.4

Source: Literature of the Biomass and Coal Gasification and Combustion Laboratory

The prepared mixture then was manually loaded to the feeding hopper which is connected to the top of the reactor. Hopper was unloaded by opening the globe valve and the feedstock was filled in the reactor. Feedstock preparation, scale, hopper, and the globe valve can be seen in Figure 5.3.

Start-Up: The ID fan and the air fan were started-up in order to maintain the gas flow within the system. The burner was ignited and inserted into the reactor to ignite the feedstock. Within the first seconds flue gas was observed by visually from the stack to ensure about the reaction begun. In the following minutes experiments was observed from the temperature recordings.

Operation and Sampling: Five runs were performed. The first 3 runs were operated with c_1 concentration menu and the last two runs were operated with c_2 concentration menu. Activated carbon, perlite column filling material, and water scrubber circulating water have been changed with fresh ones between run2 and run3 (before chlorine concentration changings). Dolomite has not been changed between the runs.

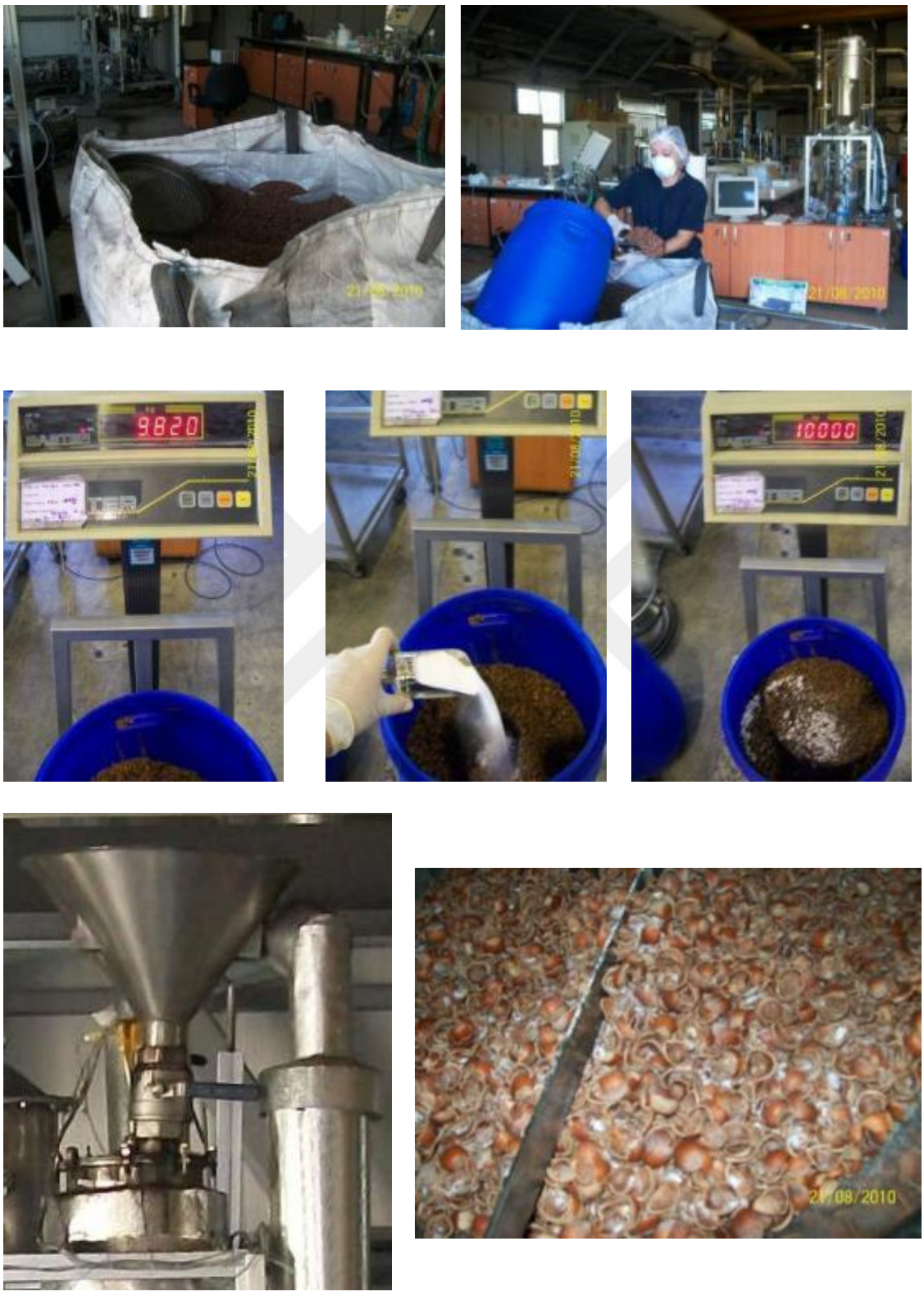


Figure 5.3. Feedstock preparation, scale, hopper, and the globe valve.

After the ignition of the feedstock, temperatures increased gradually and gasification reaction begun. The gasification reaction beginnings and endings were recognized by syngas composition which was measured by ABB on-line gas analyzer, recorded by the computer program, and observed from the desktop computer. Operation temperatures and seconder air flowrate were measured online, recorded by the wincontrol program, and observed from the laptop computer.

Syngas and bottom ash samplings for dioxin measurement were performed at each run. Syngas was also sampled for volatile organic compounds measurement at each run. All syngas samplings were performed during the gasification periods of the runs. Bottom ash samplings were performed at the end of the runs after a certain time for cooling with opening the globe valve at the bottom of the reactor. Activated carbon and the perlite bed filling material were sampled for dioxin measuring at the end of each concentration changing. The dolomite was sampled at the end of run5 which means that dioxin concentration in the dolomite measurement has reflected the total accumulated concentration for 5 Runs. Dioxin sampling points were given in Figure 5.4.

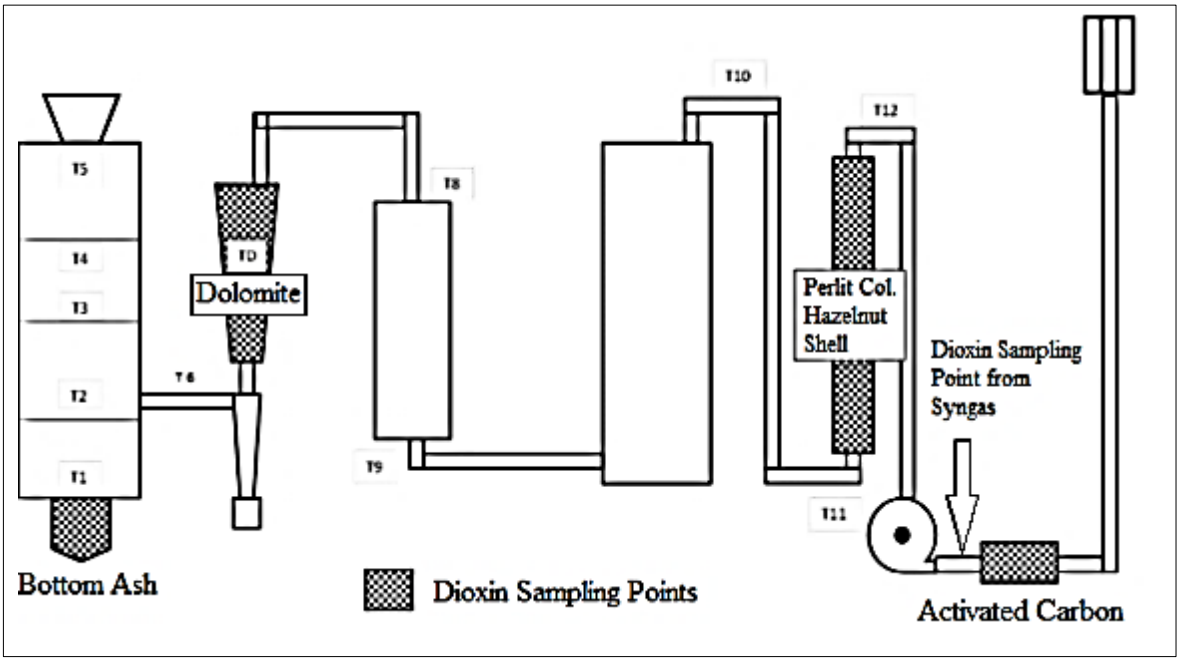


Figure 5.4. Dioxin sampling points.

Cooling: After the gasification reactions terminated, the gasifier temperatures and syngas compositions began to decrease. Cooling was supported with the seconder air feeding. Overall experiment plan was given in Table 5.3.

Table 5.3. Experiment plan.

RUNS	OPERATING CONDITIONS					BOTTOM ASH ANALYSES	SYNGAS ANALYSES	FEEDSTOCK ANALYSES		PERLIT COLUMN ANALYSES	ACTIVE CARBON FILTER ANALYSES	DOLOMITE COLUMN ANALYSES
	Chlorine, % w/w gr	Hazelnut Shell, gr.	PVC, gr.	T_1-T_2, T^oC	$Q_{air,}$ m^3/h		After ID Fan	Hazelnut Shell	PVC			
RUN1	%1 100	9820 gr.	180 gr.	947-1036	7	Dioxin-Furan	CO, CO_2, O_2, CH_4, H_2 Dioxin-Furan HCl	Proximate and Ultimate Analysis	Ultimate Analysis	Dioxin-Furan	Dioxin-Furan	Dioxin-Furan
RUN2	%1 100	7364 gr.	136 gr.	833-798	6	Dioxin-Furan	CO, CO_2, O_2, CH_4, H_2 Dioxin-Furan HCl					
RUN3	%1 100	7364 gr.	136 gr.	805-840	6,4	Dioxin-Furan	CO, CO_2, O_2, CH_4, H_2 Dioxin-Furan HCl					
RUN4	%2 200	9640 gr.	360 gr.	846-922	4,75	Dioxin-Furan	CO, CO_2, O_2, CH_4, H_2 Dioxin-Furan HCl			Dioxin-Furan	Dioxin-Furan	
RUN5	%2 200	9640 gr.	360 gr.	669-777	5	Dioxin-Furan	CO, CO_2, O_2, CH_4, H_2 Dioxin-Furan HCl					

6. RESULTS AND DISCUSSION

Gasification operations were evaluated Run by Run according to the syngas composition, gasification periods, temperature profiles, and ER values. The effect of operation parameters such as ER, temperature, and feedstock halogen ratio, on dioxin formation and congener distribution in all mediums was evaluated in order to better understand the dioxin formation mechanism during the study. In the light of the findings, the dioxin formation mechanism was discussed.

6.1. Gasification Operation Results and Conditions

The gasification periods were determined by beginning of the increase and decrease of CO and H_2 concentrations. In other words, at the beginning of the gasification period, CO and H_2 concentrations started to increase and at the end of the gasification period the concentrations began to decrease.

Generally, the ABB on-line gas analyser measurements showed that efficient gasification was maintained at the higher temperature Runs. Syngas composition, especially CO and H_2, remained stable for 20-30 minutes at a steady-state level and then started to decrease in response to the consumption of the feedstock in the gasifier. This also means that the gasification process has ended (Yinesor, 2008). During experiments the syngas flow rate was measured 1-1.5 m/sn at ID fan downstream by the sampling Team.

The feedstock was 10 kg and the chlorine concentration was %1 (w/w) durig the Run1. The maximum reactor temperatures were 1024^{o}C and 1180^{o}C at reduction zone and oxidation zone, respectively. The syngas composition reached %20.93 CO, %10.33 H_2, and %2.07 CH_4 at maximum levels by volume and %6.81 CO_2 and %1.93 O_2 at minimum levels by volume. The remaining portions of the syngas mainly consist of nitrogen and water wapor. The average seconder air flow rate during operation was 7 m^3/h. The reactor temperatures and syngas composition for Run1 can be seen at Figure 6.1. and Figure 6.2., respectively.

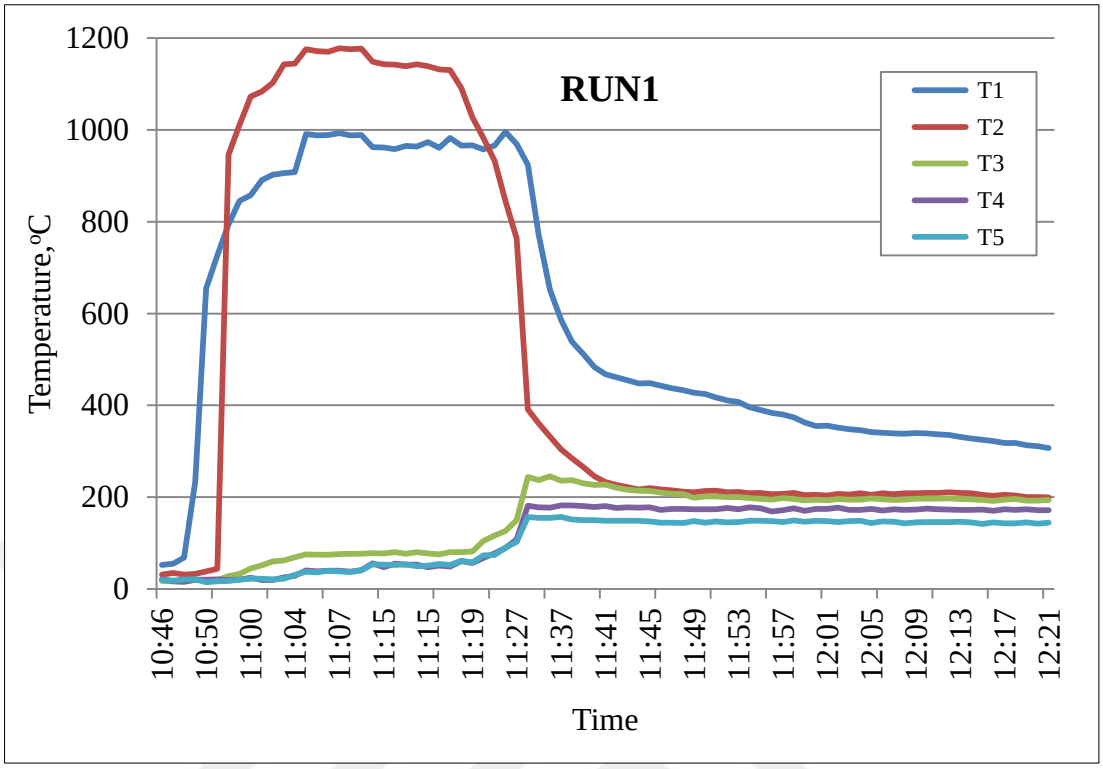


Figure 6.1. Run1 reactor temperatures.

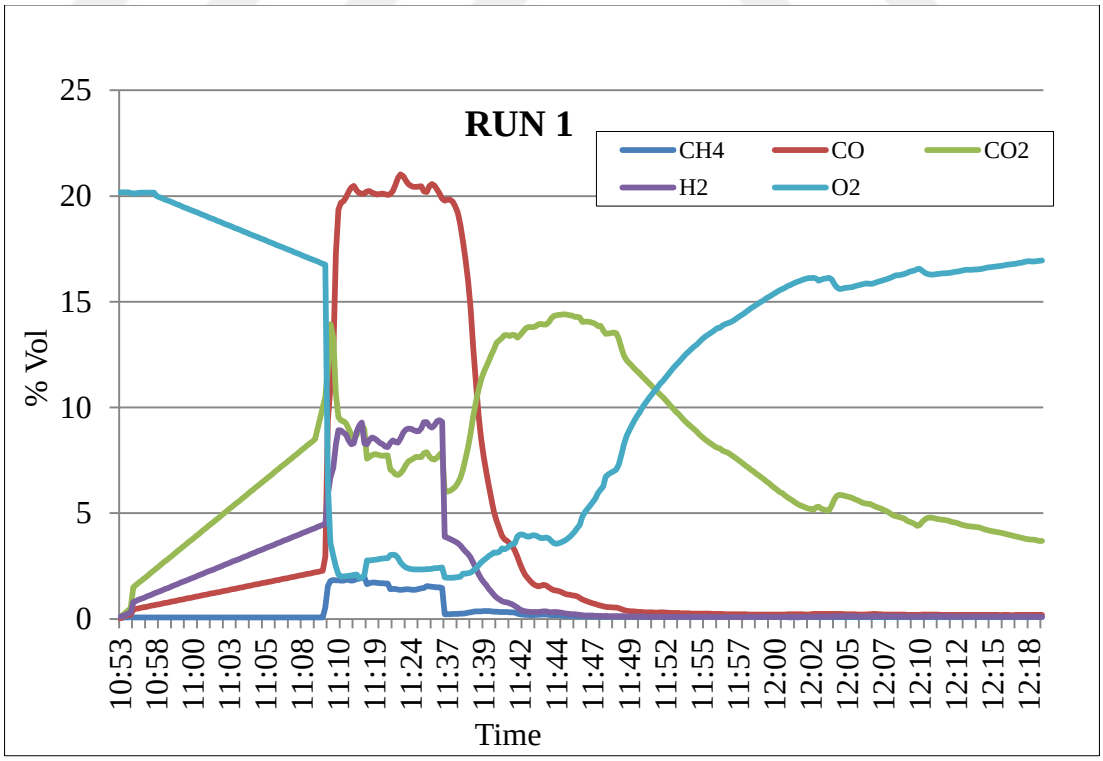


Figure 6.2. Run1 syngas composition.

The feedstock was 7.5 kg and the chlorine concentration was %1 (w/w) during the Run2. The maximum reactor temperatures were 860°C and 906°C at reduction zone and oxidation zone, respectively. The syngas composition reached %16.45 CO, %7.50 H_2, and %2.32 CH_4 at maximum levels by volume and %10.71 CO_2 and %2.97 O_2 at minimum levels by volume. The average seconder air flow rate during operation was 6 m^3/h. The reactor temperatures and syngas composition for Run2 can be seen at Figure 6.3. and Figure 6.4., respectively.

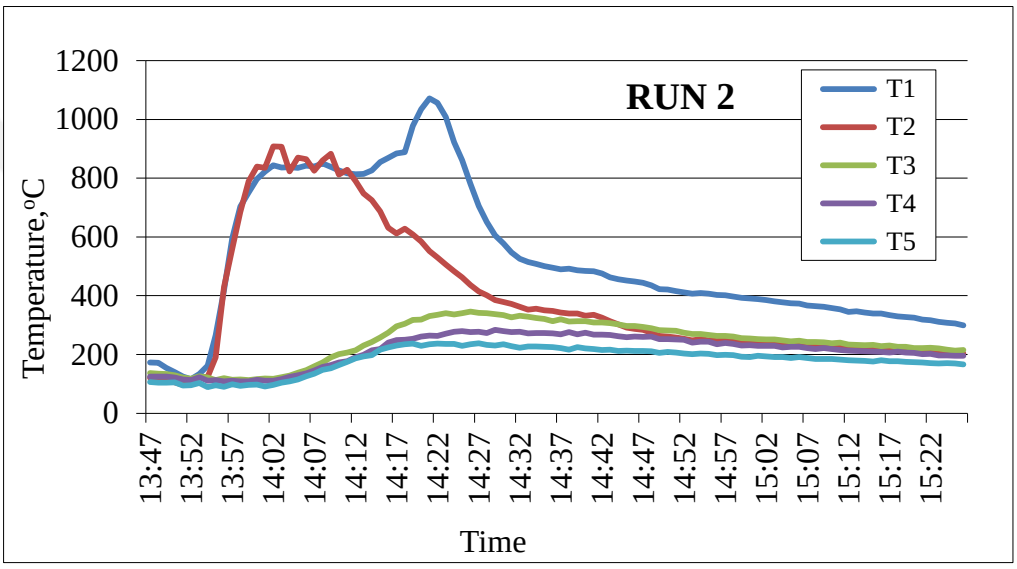


Figure 6.3. Run2 reactor temperatures.

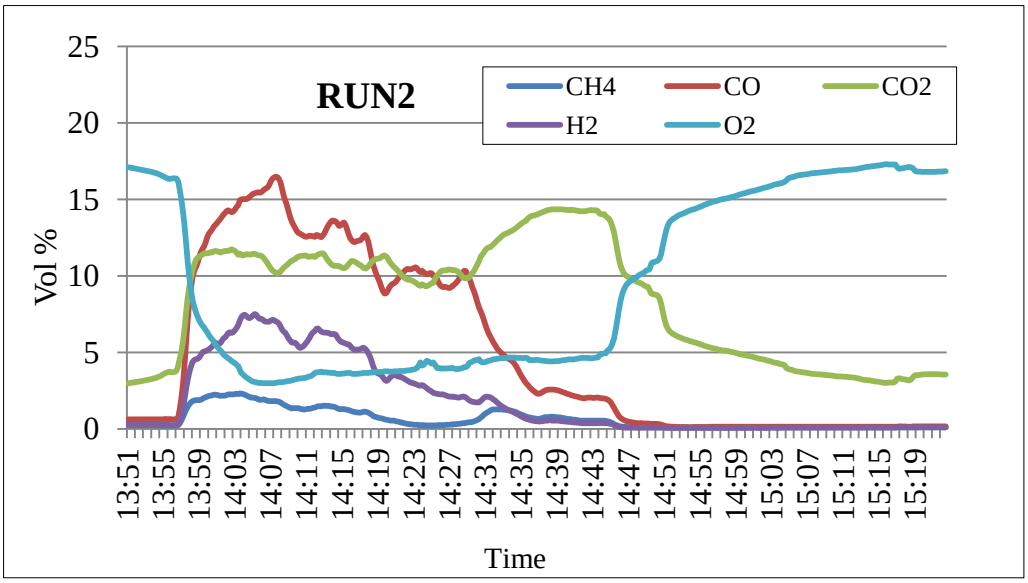


Figure 6.4. Run2 syngas composition.

The feedstock was 7.5 kg and the chlorine concentration was %1 (w/w) during the Run3. The maximum reactor temperatures were 820°C and 965°C at reduction zone and oxidation zone, respectively. The syngas composition reached %12.35 CO, %6.,15 H_2, and %2.08 CH_4 at maximum levels by volume and %8 CO_2 and %5.8 O_2 at minimum levels by volume. The average seconder air flow rate during operation was 6.4 m^3/h. Reactor temperatures and syngas composition for Run3 can be seen at Figure 6.5. and Figure 6.6., respectively.

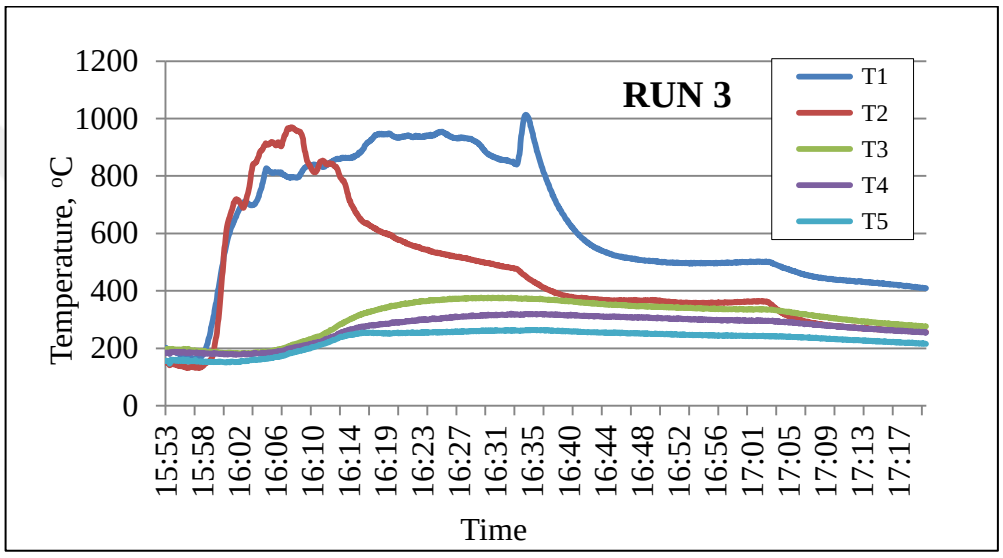


Figure 6.5. Run3 reactor temperatures.

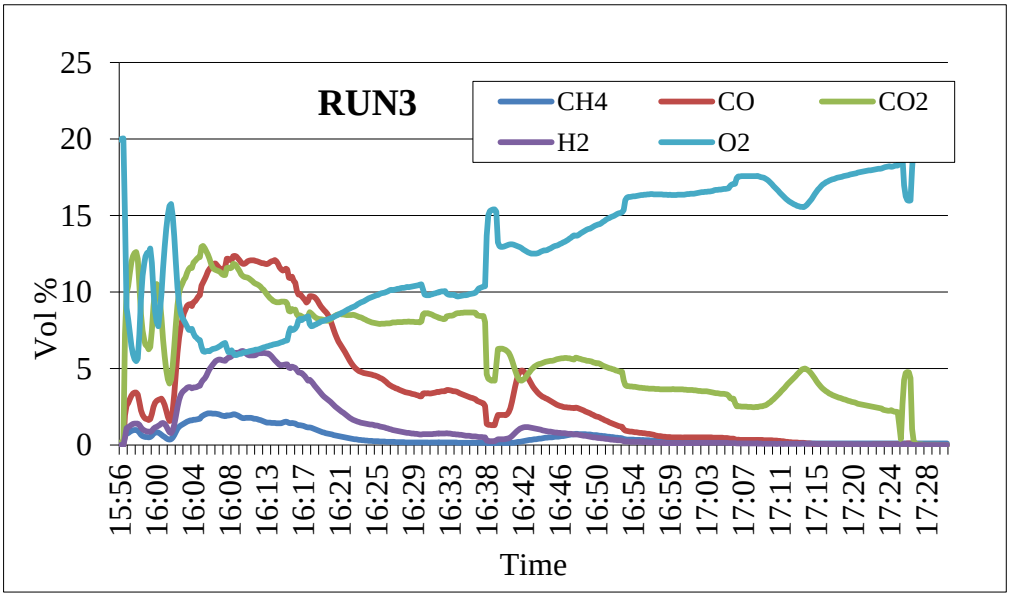


Figure 6.6. Run3 syngas composition.

The feedstock was 10 kg and the chlorine concentration was %2 (w/w) during the Run4. The maximum reactor temperatures were 918°C and 1095°C at the reduction zone and the oxidation zone, respectively. The syngas composition reached %15.82 CO, %8.27 H_2, and %1.48 CH_4 at maximum levels by volume and %6.87 CO_2 and %5.093 O_2 at minimum levels by volume. The average seconder air flow rate during operation was 4.75 m^3/h. Reactor temperatures and syngas composition for Run4 can be seen at Figure 6.7. and Figure 6.8., respectively.

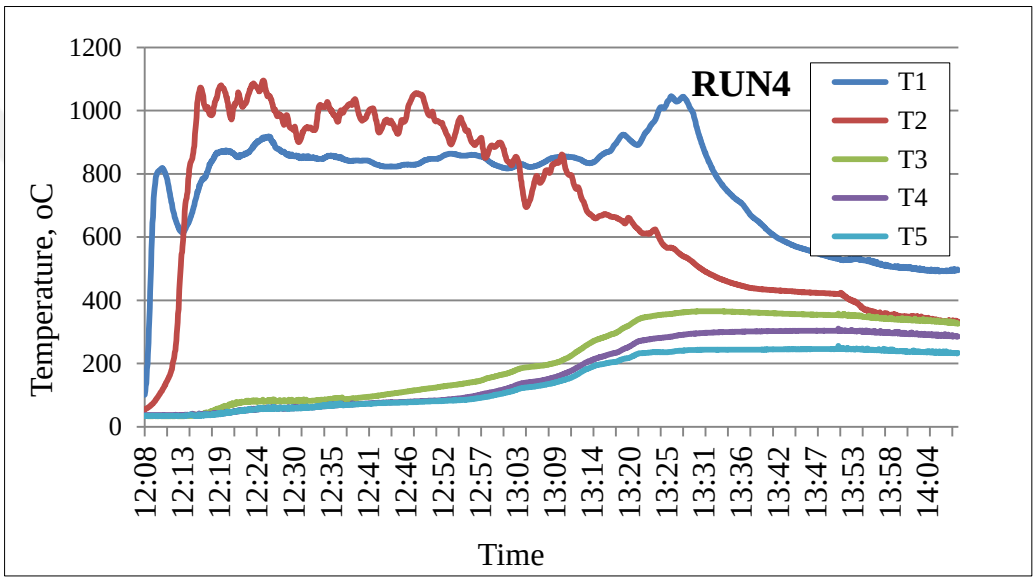


Figure 6.7. Run4 reactor temperatures.

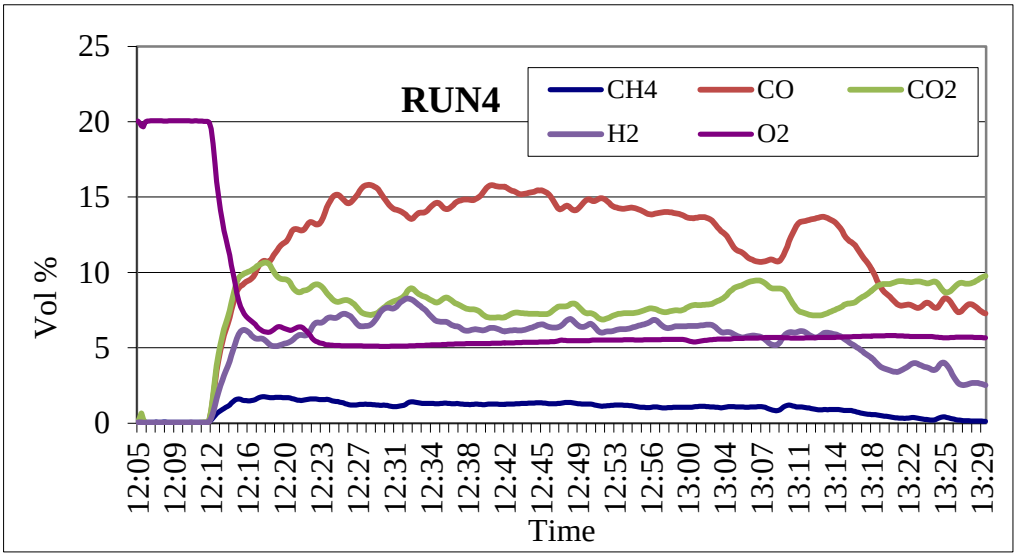


Figure 6.8. Run4 syngas composition.

The feedstock was 10 kg and chlorine concentration was %2 (w/w) during the Run5. The maximum reactor temperatures were 716°C and 991°C at the reduction zone and the oxidation zone, respectively. The syngas composition reached %14.54 CO, %5.96 H_2, and %2.46 CH_4 at maximum levels by volume and %8.32 CO_2 and %5.30 O_2 at minimum levels by volume. The average seconder air flow rate during operation was 5 m^3/h. Reactor temperatures and syngas composition for Run5 can be seen at Figure 6.9. and Figure 6.10., respectively.

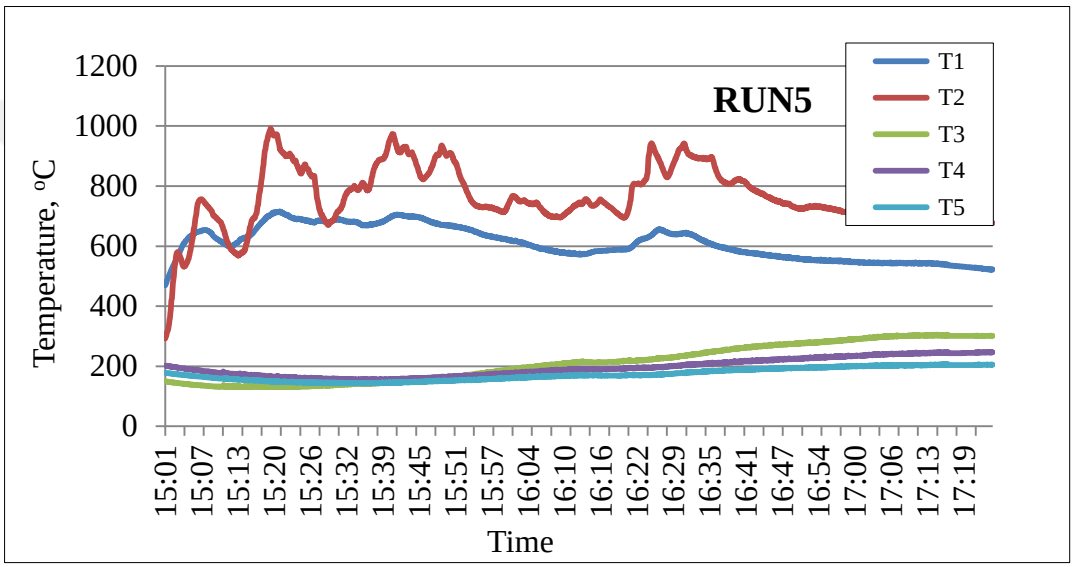


Figure 6.9. Run5 reactor temperatures.

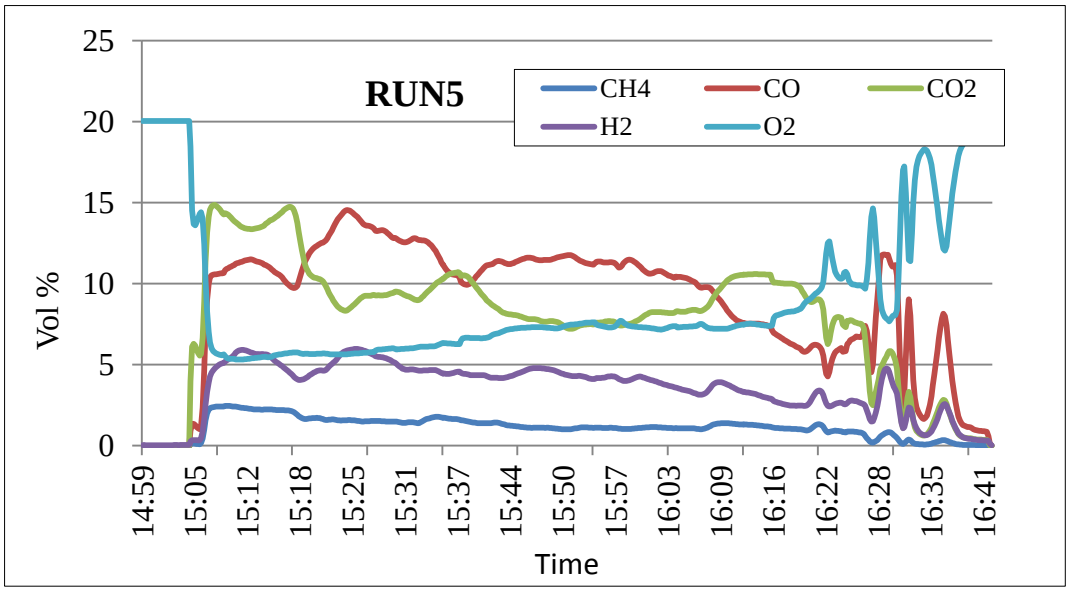


Figure 6.10. Run5 syngas composition.

Overall Operating Conditions: The overall operating conditions of 5 Runs were evaluated according to the gasification periods, temperature profiles, syngas compositions, ER values, lower heating values of syngas, and chlorine content in the feedstock. Additionally, relationships between temperature and CO, temperature and ER, and CO and ER were evaluated in order to better understand the process behavior and the conditions related with the dioxins formation.

All experiments almost lasted in 1.5-2 hours. Gasification periods of each Run which differed from each other according to the feedstock amount and operation conditions, were 30, 20, 14, 48, and 32 minutes from Run 1 to Run 5, respectively. Gasification periods were shown in Figure 6.11.The remaining time after the gasification was cool-down period of the Runs. Cooling lasted approximately one hour after the feedstock and the gasification reactions ended. However, it should be remembered that the cooling had not been waited till the temperatures reached to the room temperature. The following Runs were started-up after a certain cooling period of the previous Run. At that moment, the reduction zone temperature was almost 300^{o}C, while the drying zone temperature was 140^{o}C. Cooling times can also be checked in the Figure 6.1, 6.3., 6.5., 6.7., and 6.9. at the previous pages.

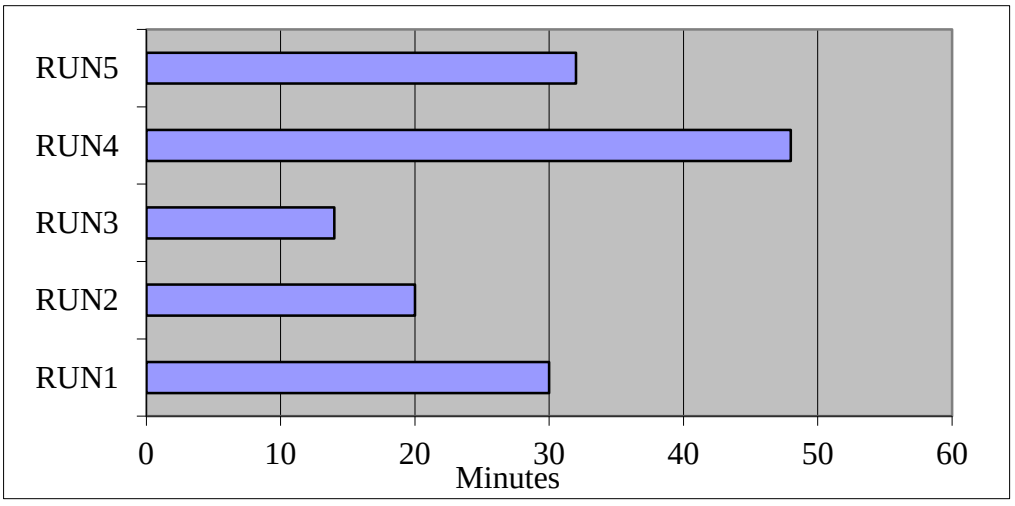


Figure 6.11. Gasification period of runs.

Run 1 was the best operation between all Runs according to both the syngas composition and the temperature profile. Combustible gases CO, H_2 and CH_4 and the reactor temperatures reached their maximum values during gasification period of Run1.

Run 4 was the second best operation according to the syngas composition and the temperature profile. The sequence regarding the syngas composition from the best to the poorest operation was Run1, Run4, Run2, Run5 and Run3 respectively. However, the sequence regarding the temperature profile was Run1, Run4, Run2, Run3 and Run5 respectively. Run2 and Run3 had lesser amount of feedstock than other runs; thus, temperature profiles stayed lower than Run1. Moreover, more tar compounds produced and the accumulation of tar and condensate occurred during Run2 and Run3. Lower temperature profile, poor syngas quality and tar formation affected each other negatively. It should be remembered that Run1, Run2, and Run3 were operated with 1% chlorine content by weight while the Run4 and Run5 were operated with %2 Cl content.

After Run3 was completed, the system was shut down in order to to check the set-up visually, clean and remove the tar and condensate accumulation, and refresh the adsorbent materials. As reminder, the set-up was not shut down from Run 1 to Run 3. System has been waited to cool down, and then another Run began to be operated. Meanwhile system has not been cleaned between Runs. The same tar formation and condensate accumulation affected the system prior to Run5. Run1 is better than Run2 and Run2 is better than Run3 in terms of syngas composition. After cleaning and re-preparing the system for new Runs, syngas composition of Run 4 reached better than Run3. However, Run4 reached a much lower CO concentration than Run1. It is a well-known fact that the presence of chlorine slows down the thermal reaction (Borgianni et al., 2002). Even though Run4 is a totally cleaned new run, its performance increased after system cleaning however stayed lower than Run1. Finally, Run2 is better than Run5. The syngas composition of each run can be seen in Table 6.1.

Table 6.1. Average syngas composition of each run.

	RUN1	RUN2	RUN3	RUN4	RUN5
CO	19.56	13.38	10.67	14.02	11.90
H_2	8.7	5.93	5	6.45	5.04
CO_2	8.4	11	10.47	7.8	11.10
CH_4	1.69	1.67	1.63	1.18	1.80
O_2	2.54	4.29	7.1	5.4	5.80

The calculated ER values, experiment and gasification periods, reactor temperatures at critical points, and the lower heating values which are calculated from the concentration of the combustible components such as CO, H_2, CH_4 - of each Run were given as the overall operating parameters in Table 6.2.

Table 6.2. Overall operating parameters.

Parameter	Unit	RUN1	RUN2	RUN3	RUN4	RUN5
ER	-	0.16	0.18	0.19	0.1079	0.1136
$t_{exp.}$	minute	~ 90	~ 90	~ 90	~ 90	~ 90
$t_{gasf.}$	minute	30	20	14	48	32
T^{o}_{oxid}	^{o}C	1036	788	840	922	777
T^{o}_{red}	^{o}C	947	833	805	846	669
T^{o}_{exit}	^{o}C	360	348	402	358	412
LHV_{mean}	MJ/Nm^3	4.01	2.92	2.47	2.89	2.48

The ER values showed that the gasification process has acted as “Flaming Pyrolitic Gasification” which uses smaller amounts of air/oxygen passing through a bed of biomass to generate gas. Figure 6.12 shows the Equivalence Ratio and Air/Fuel Diyagram for biomass fuel such as hazelnut shell. The P point at the diagram shows the equivalence ratio for pyrolysis, the G point in the diagram shows the equivalence ratio for gasification and the C point in the diagram shows the equivalence ratio for combustion. The FP area shows the Flaming Pyrolitic Gasification. Operations within the FP area, means ER<0.25, produce more tar due to its nature (Reed and Desrosiers, 1979).

ER is a significant parameter in gasification and can be compared with other operation conditions such as temperature, CO concentration, and syngas composition in order to investigate the gasification process. This gives a better understanding to the reader for evaluating the gasification process according to the basic operationg parameters.

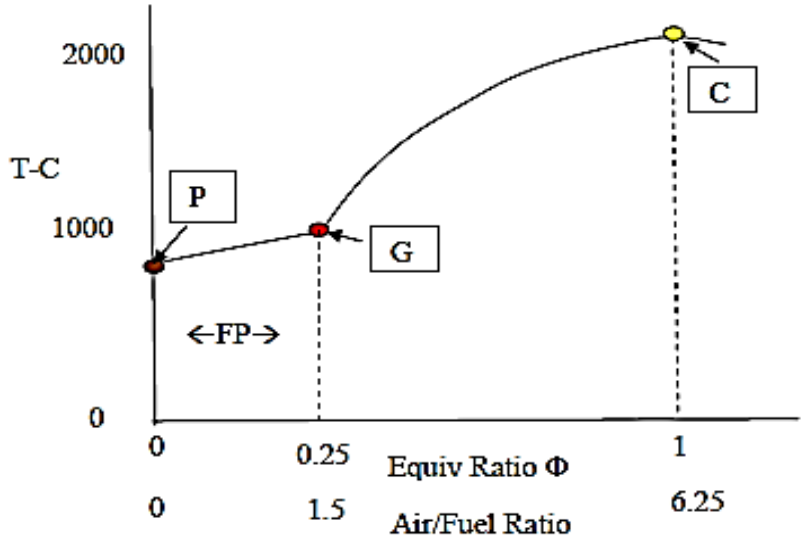


Figure 6.12. Equivalence ratio and air/fuel diyagram.

Relationship between temperature and ER values was given in Figure 6.13. It can be clearly seen that the temperature decreased with the increasing ER means that the temperature decreased with the cooling effect of air. Seconder air may be heated prior to the feeding in order to avoid the cooling effect. Consequently, it can be clearly seen that the termperature is inversely proportional with ER. Additionally, it should be remembered that the temperature stayed lower due to the lower amount of feedstock feeding in Run2 and Run3.

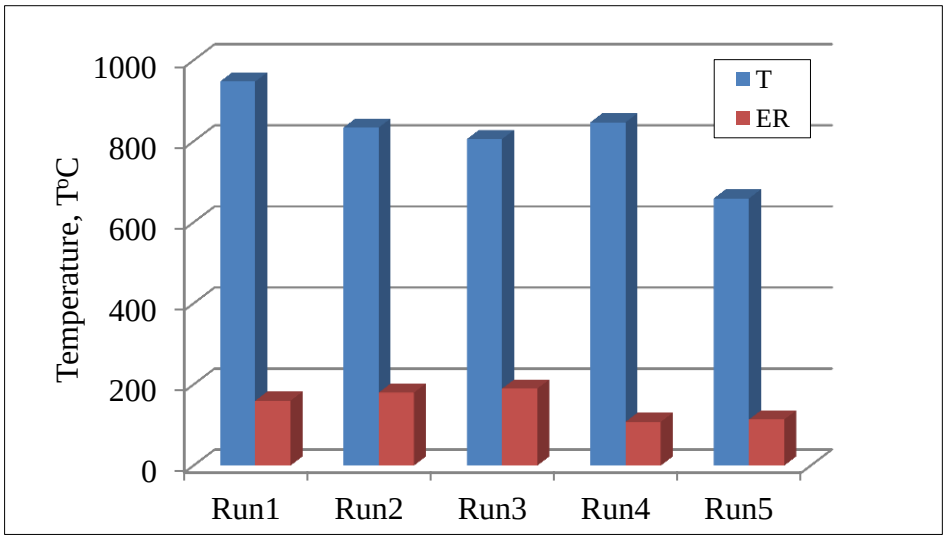


Figure 6.13. Relationship between ER and temperature.

Additionally, the ER and CO are inversely proportional with each other. When the ER increases, carbon compounds tend to produce carbon dioxide rather than to produce carbon monoxide. The ER and CO values can be seen in Figure 6.14. The ER values were multiplied with one thousand in order to magnify the bars in the figure.

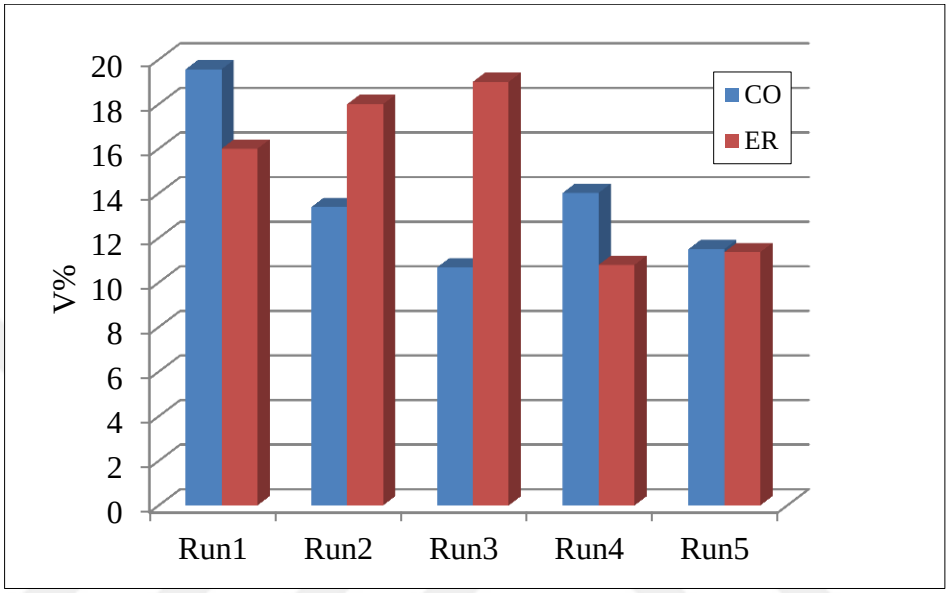


Figure 6.14. Relationship between carbonmonoxide and ER.

Temperature and CO concentrations are directly proportional. Higher CO concentrations were obtained at higher gasification temperatures. The relationship between temperature and carbonmonoxide can be seen in Figure 6.15. CO values were multiplied with ten in order to magnify the bars in the figure.

Consequently, overall gasification experiments were evaluated according to the operating parameters. Thus, it is obvious that ER has significant affect on process efficiency. Temperature is an important parameter to provide ghigh HV and efficient gasification process with high quality gas composition.

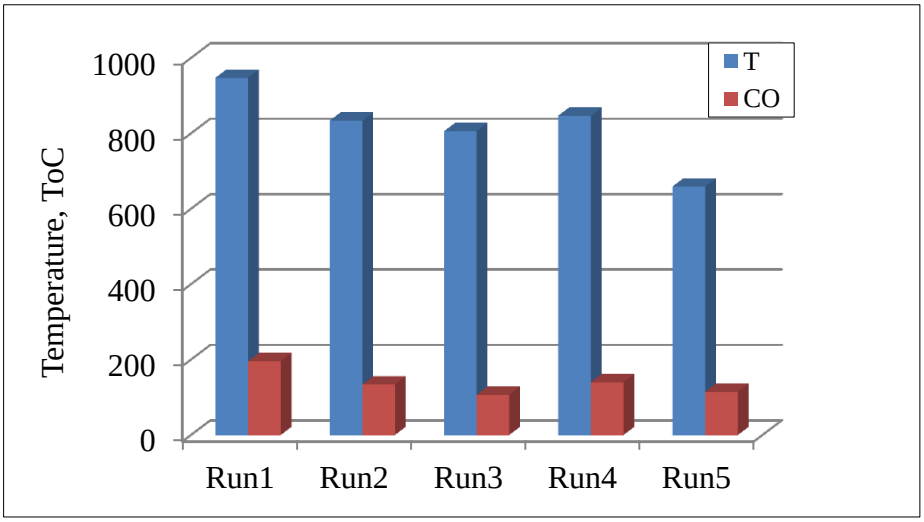


Figure 6.15. Relationship between temperature and carbon monoxide.

6.2. Dioxin Concentrations

The overall dioxin and furan concentrations as TEQ, percentages, the PCDF/PCDD ratios, and total dioxins concentrations in syngas were shown in Table 6.3. for each Run. The mass concentrations of dioxins as ng/Nm^3 were given in Table 6.4. However, the evaluation of dioxin results was made in TEQ values in this study.

According to the test results, Run 4 has the lowest dioxin concentration with 60.3 ng I-TEQ/Nm^3. Run 4 was followed by Run5 with 115.5 ng I-TEQ/Nm^3, Run1 with 131.7 ng I-TEQ/Nm^3, Run2 with 468.7 ng I-TEQ/Nm^3, and Run3 with 519.7 ng I-TEQ/Nm^3, respectively. When the dioxin concentrations were compared to each other it can be seen that not only the operating parameters but also the gasification periods played a significant role on dioxin formation. Gasification periods of each Run affected the magnitude of the dioxin concentrations as can be seen in Table 6.5. The effect of operating parameters such as ER, temperature, and chlorine rate on dioxin concentrations were also discussed at the following sections.

Table 6.3. Total Dioxin concentrations in syngas.

	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
PCDFs, ng I-TEQ/Nm^3 (%)	115.6 (87.7)	401.1 (85.6)	463.6 (89.2)	52.9 (87.7)	101.4 (87.8)
PCDDs, ng I-TEQ/Nm^3 (%)	16.1 (12.3)	67.6 (14.4)	56.1 (10.8)	7.4 (12. 3)	14.1 (12.2)
PCDF/PCDD	7.2	6	8.2	7.1	7.2
TOTAL Dioxins, ng I-TEQ/Nm^3 (%)	131.7 (100)	468.7 (100)	519.7 (100)	60.3 (100)	115.5 (100)

Table 6.4. Dioxin mass concentrations in syngas.

	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
Total PCDFs, ng/Nm^3	942.22	3749.47	4334.39	347.73	668.96
Total PCDDs, ng/Nm^3	101.67	435.48	361.44	21.76	37.82
PCDF/PCDD	9.27	8.61	11.99	15.98	17.69
TOTAL, PCDD/Fs, ng/Nm^3	1043.89	4184.94	4695.83	369.49	706.78

Table 6.5. Dioxin concentrations vs. gasification periods of runs.

	Unit	RUN 1	RUN 2	RUN 3	RUN 4	RUN 5
Dioxin	ng I-TEQ/Nm3	131.7	468.7	519.7	60.3	115.5
$t_{gasification}$	minute	30	20	14	48	32

The dioxin concentrations and percentage profiles were also given as bar graph in Figure 6.16. It can be seen that the PCDF concentrations are significantly dominant in all runs. Approximately 85-89% of total dioxins was PCDFs and the rest 11-15% was PCDDs. The PCDD/Fs congener distributions in syngas were also given in Table 6.6.

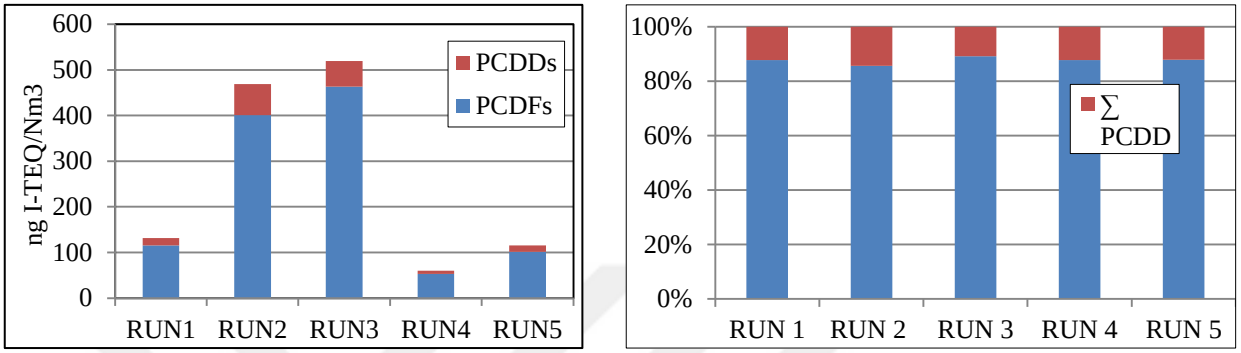


Figure 6.16. PCDD/PCDF concentrations and percentage profile in syngas.

In Run1, the 2,3,4,7,8 PeCDF has the highest concentration. The 2,3,7,8 TCDF has second highest concentration. In Run2, the 2,3,4,7,8 PeCDF has the highest concentration. The 123478-HxCDF has second highest concentration. Run3 has the highest dioxin concentration amoung all Runs. According to the decreasing gasification efficiency, very short gasification time and temperature profile, dioxin concentrations reached their highest values in Run3. However, congener ratios are almost same in all Runs. The 2,3,4,7,8 PeCDF has the highest concentration. The 123478-HxCDF has second highest concentration. In Run4, the 2,3,4,7,8 PeCDF has the highest concentration. The 2,3,7,8 TCDF has second highest concentration. In Run5, the 2,3,4,7,8 PeCDF has the highest concentration. The 2,3,7,8 TCDF has second highest concentration. TEQ concentrations and mass percentage distributions of PCDD/F congeners in Run1, Run2, Run3, Run4, and Run5 are given between Figure 6.17. and Figure 6.26., respectively.

Table 6.6. Overall congener TEQ levels in syngas.

CONGENERS, ngI-TEQ/Nm^3	**RUN 1**	**RUN 2**	**RUN 3**	**RUN 4**	**RUN 5**
2378-TCDF	21.55	47.86	55.32	13.28	26.08
12378-PeCDF	4.78	14.43	16.68	2.26	4.11
23478-PeCDF	59.18	202.12	233.65	26.27	50.01
123478-HxCDF	13.69	65.50	75.72	6.04	11.66
123678-HxCDF	7.43	32.67	37.77	3.01	5.83
234678-HxCDF	6.08	24.11	27.88	1.84	3.39
123789-HxCDF	0.66	1.88	2.17	0.20	0.36
1234678-HpCDF	1.97	11.47	13.26	0.00	0.00
1234789-HpCDF	0.21	0.91	1.05	0.00	0.00
OCDF	0.02	0.10	0.11	0.01	0.01
Total PCDF	**115.6**	**401.1**	**463.6**	**52.9**	**101.4**
2378-TCDD	5.46	20.94	17.38	3.64	7.32
12378-PeCDD	7.42	33.18	27.54	2.92	5.36
123478-HxCDD	0.67	2.94	2.44	0.21	0.35
123678-HxCDD	0.74	2.69	2.23	0.22	0.35
123789-HxCDD	1.41	6.01	4.99	0.42	0.70
1234678-HpCDD	0.43	1.83	1.52	0.00	0.00
OCDD	0.01	0.05	0.04	0.00	0.01
Total PCDD	**16.1**	**67.6**	**56.1**	**7.4**	**14.1**
Total-TEQ	**131.7**	**468.7**	**519.7**	**60.3**	**115.5**

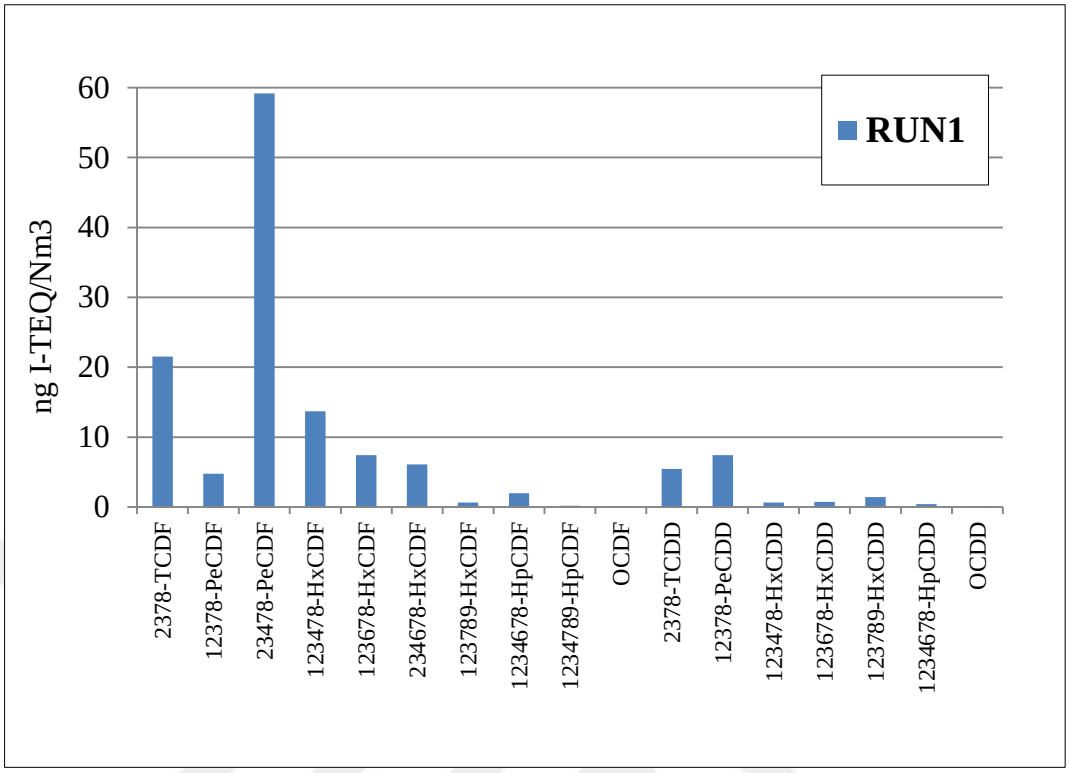


Figure 6.17. Congener distribution in Run1.

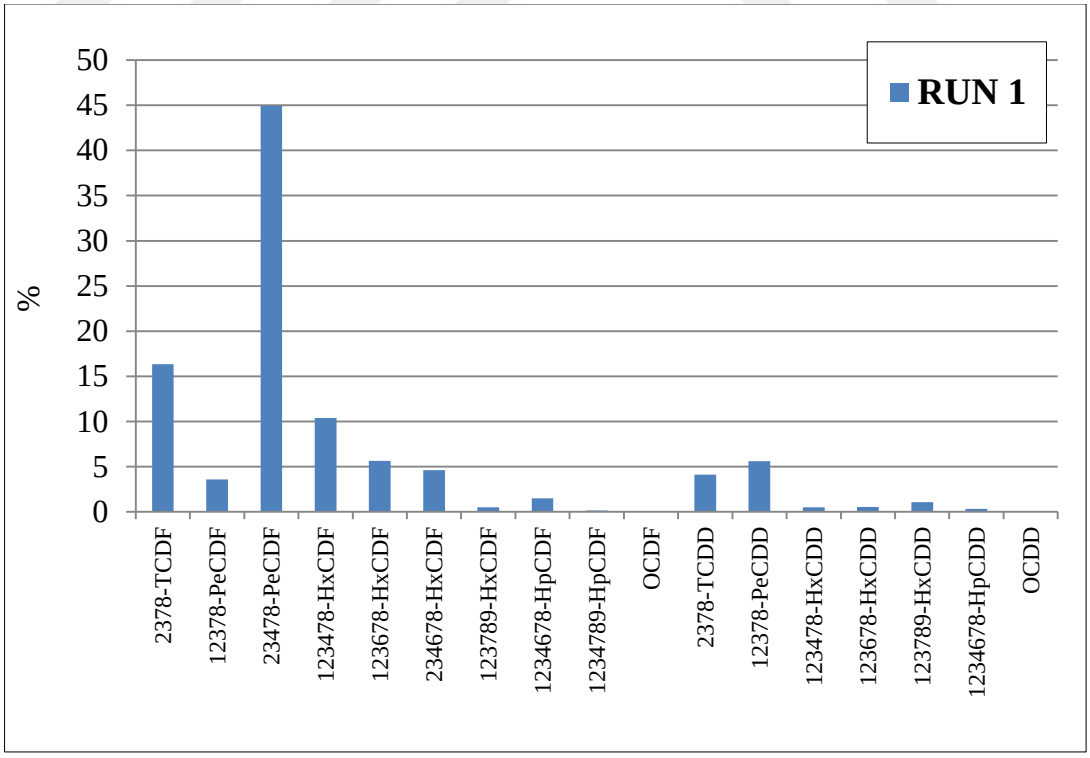


Figure 6.18. Congener percentage distribution in Run1.

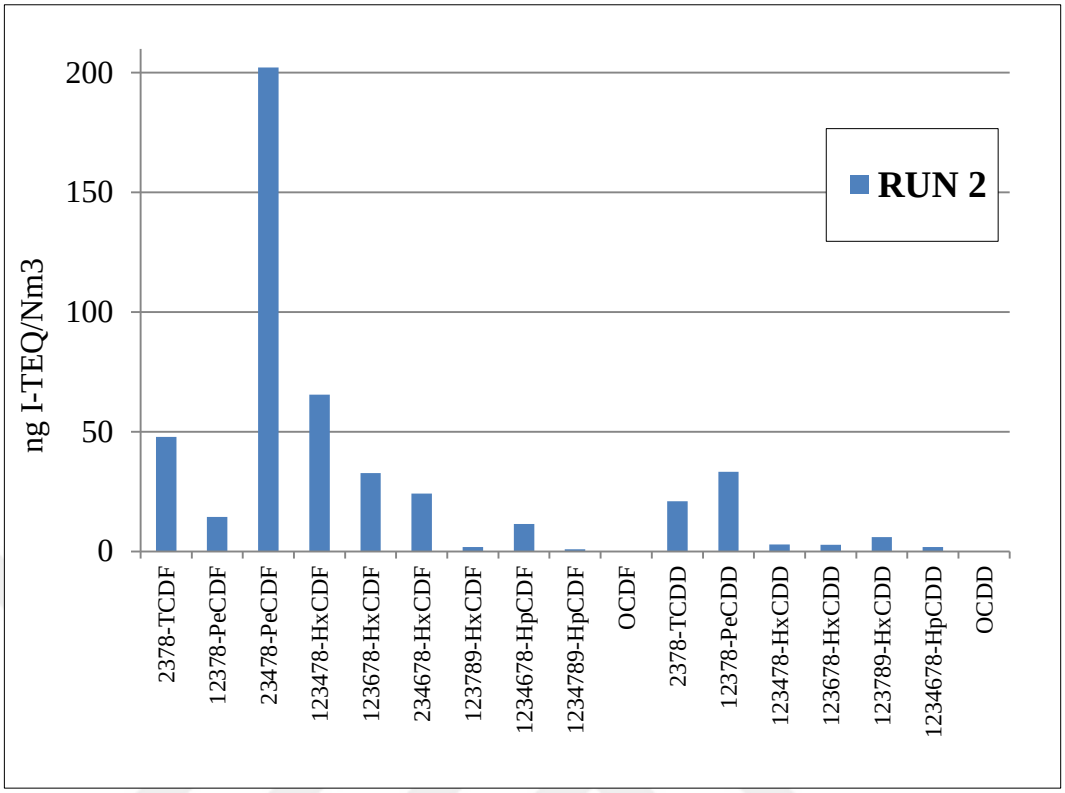


Figure 6.19. Congener distribution in Run2.

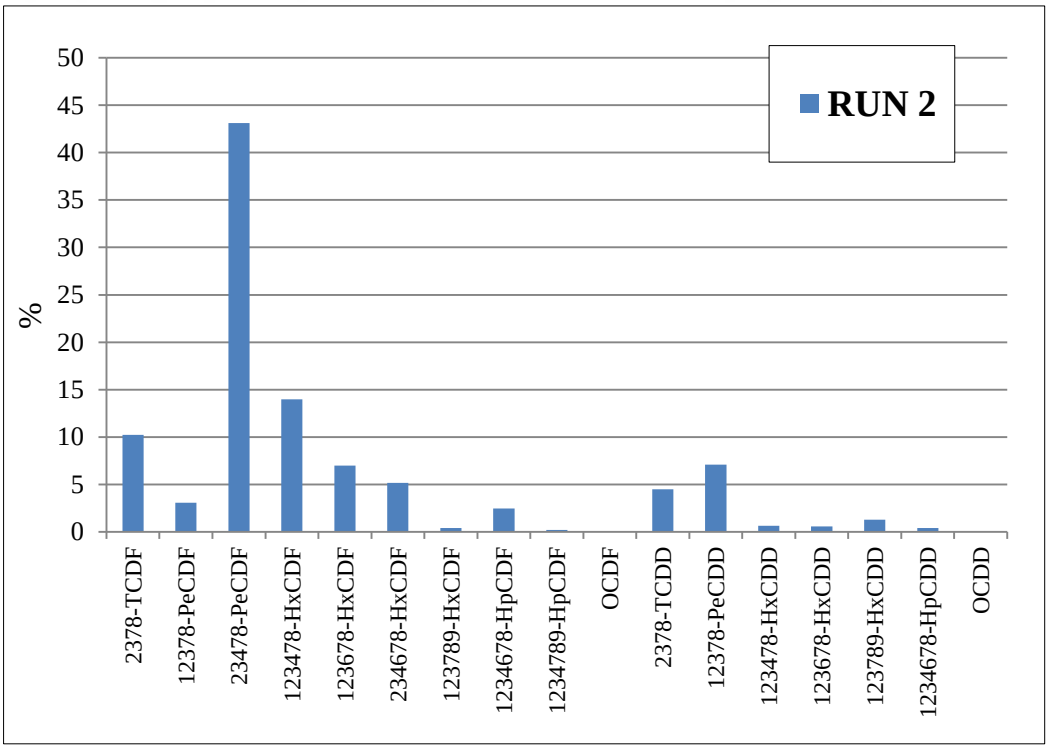


Figure 6.20. Congener Percentage Distribution in Run2.

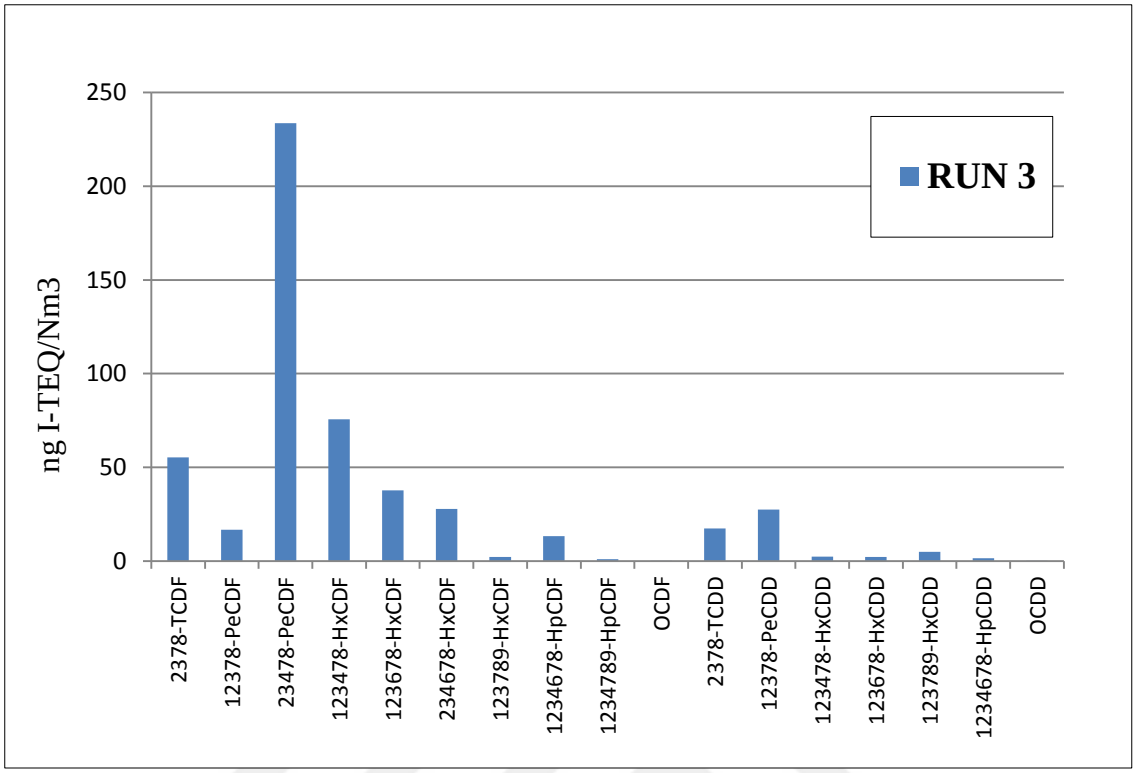


Figure 6.21. Congener distribution in Run3.

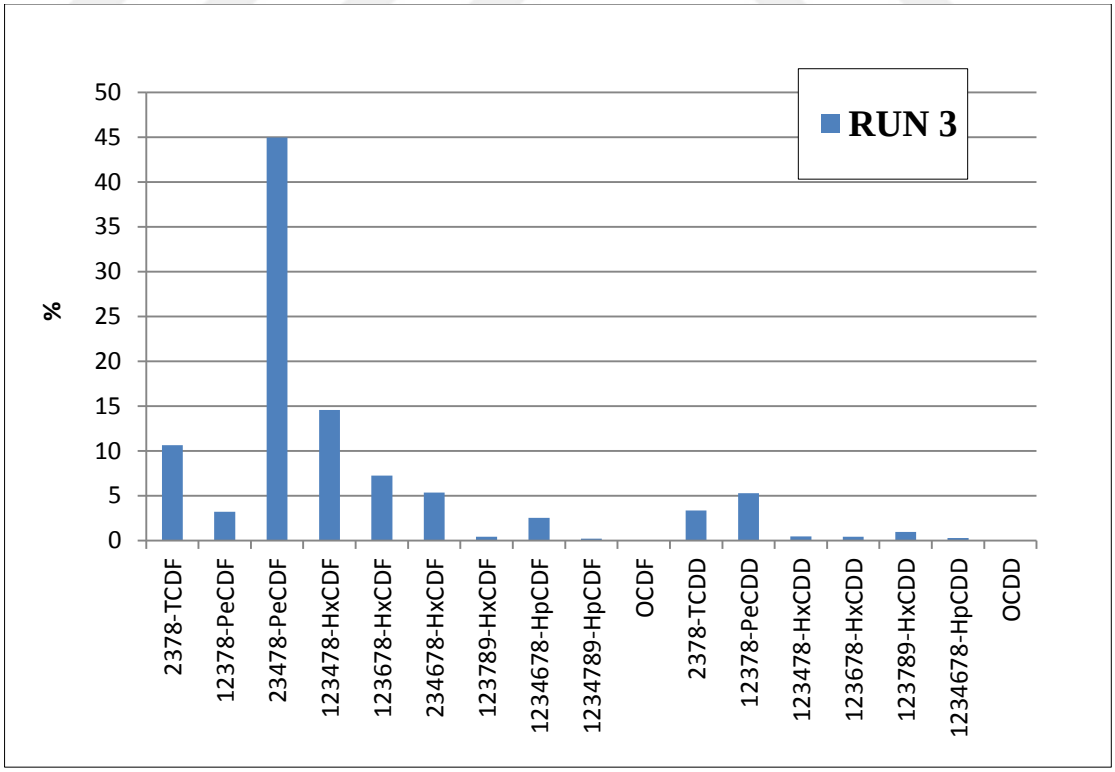


Figure 6.22. Congener Percentage Distribution in Run3.

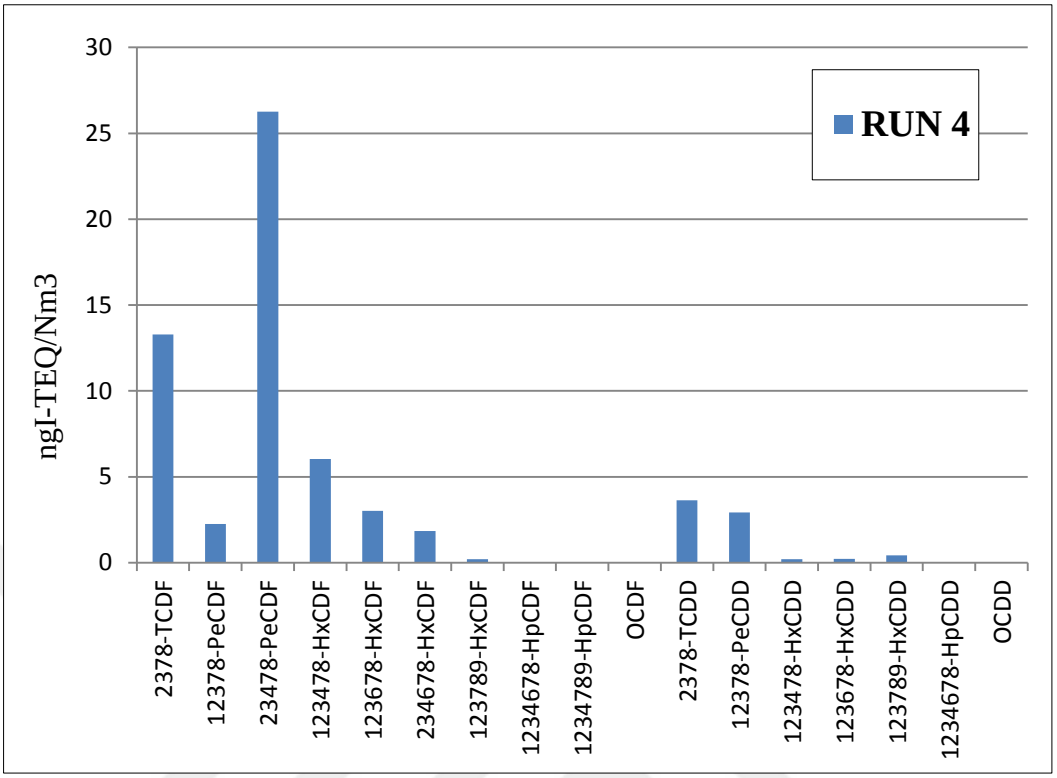


Figure 6.23. Congener distribution in Run4.

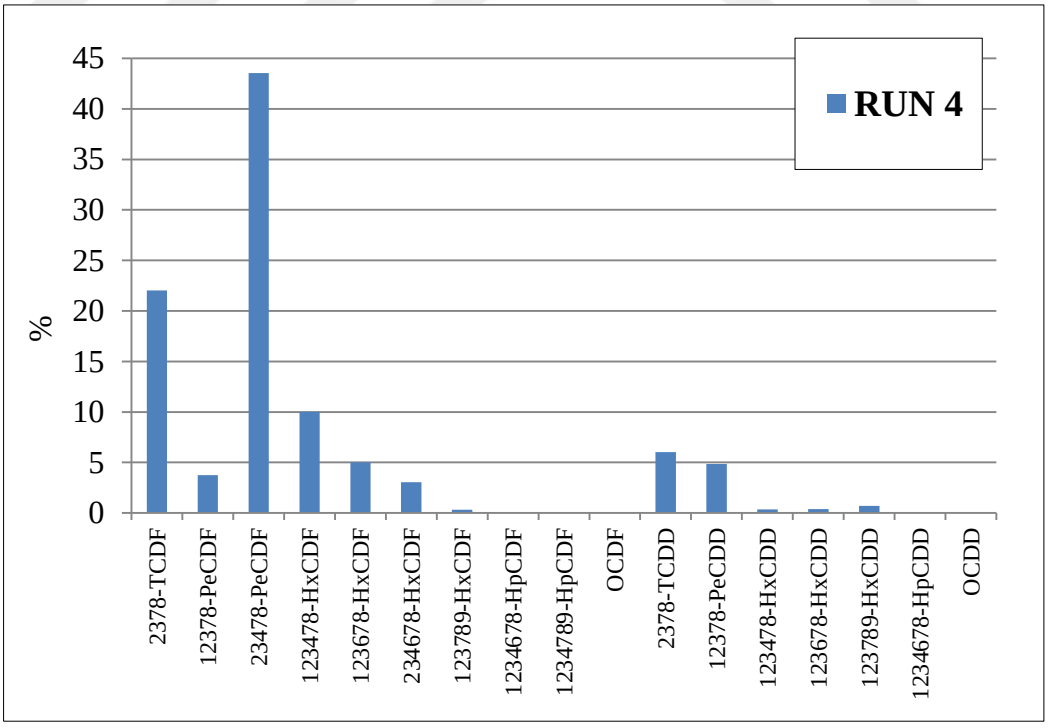


Figure 6.24. Congener Percentage Distribution in Run4.

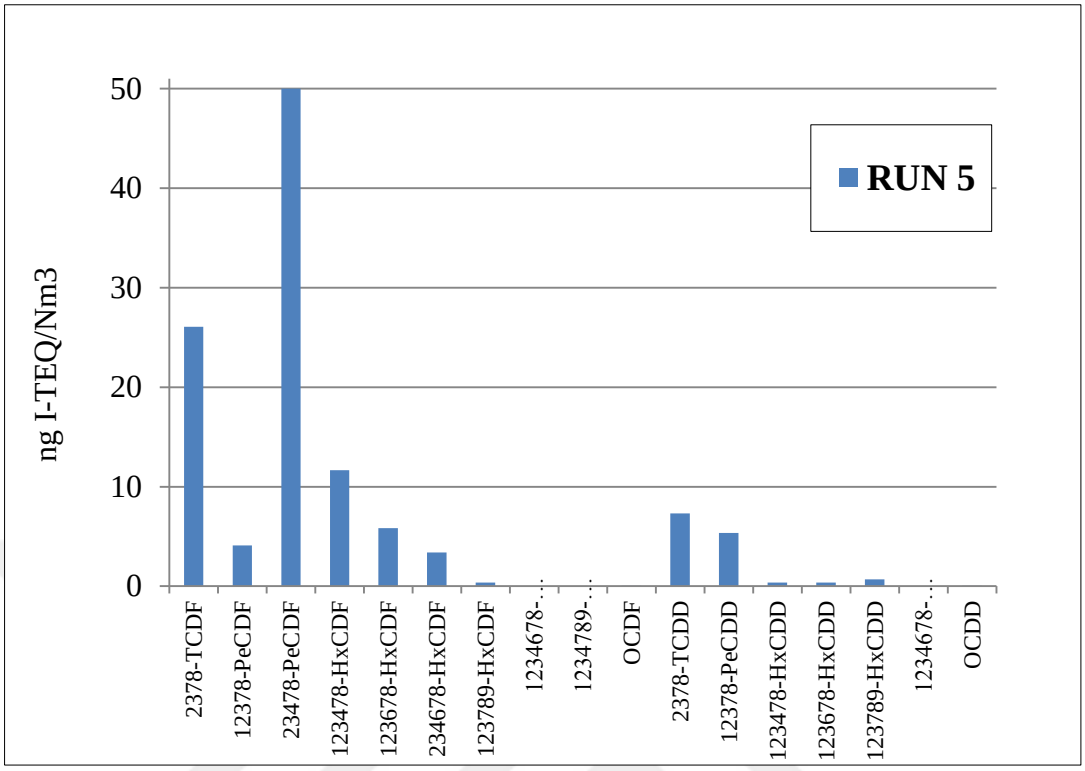


Figure 6.25. Congener distribution in Run5.

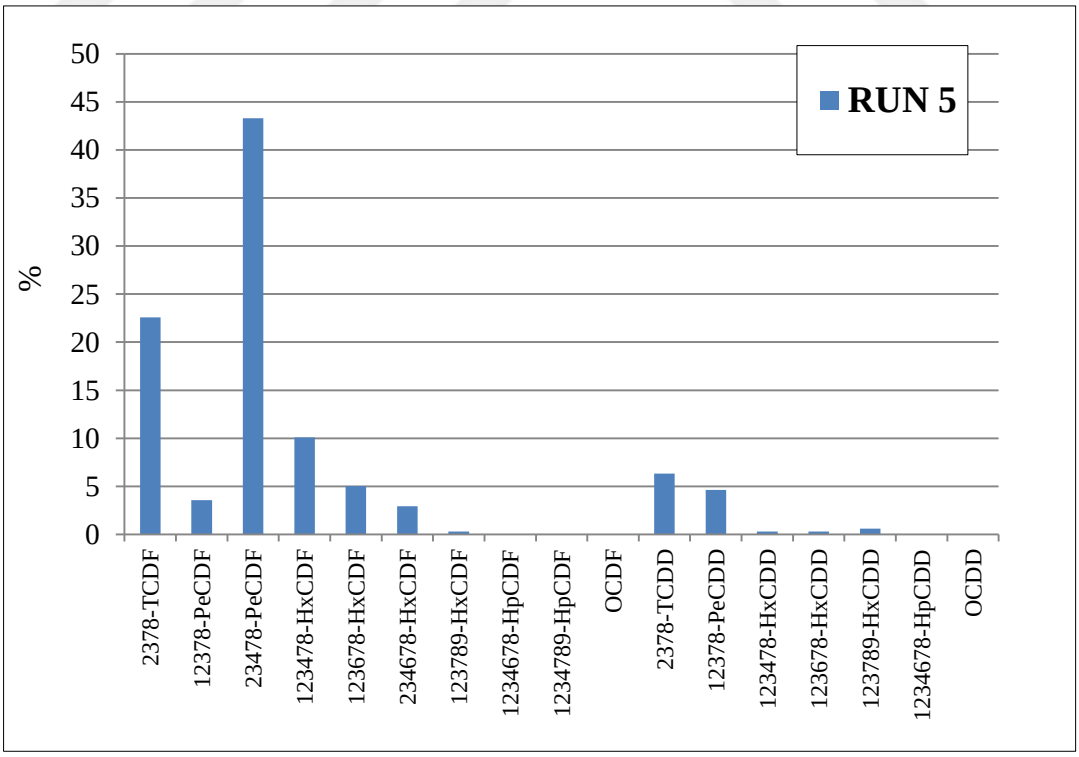


Figure 6.26. Congener Percentage Distribution in Run5.

Overeall congeners concentrations and percentage distributions were given as bar grapf in Figure 6.27 and Figure 6.28., respectively.

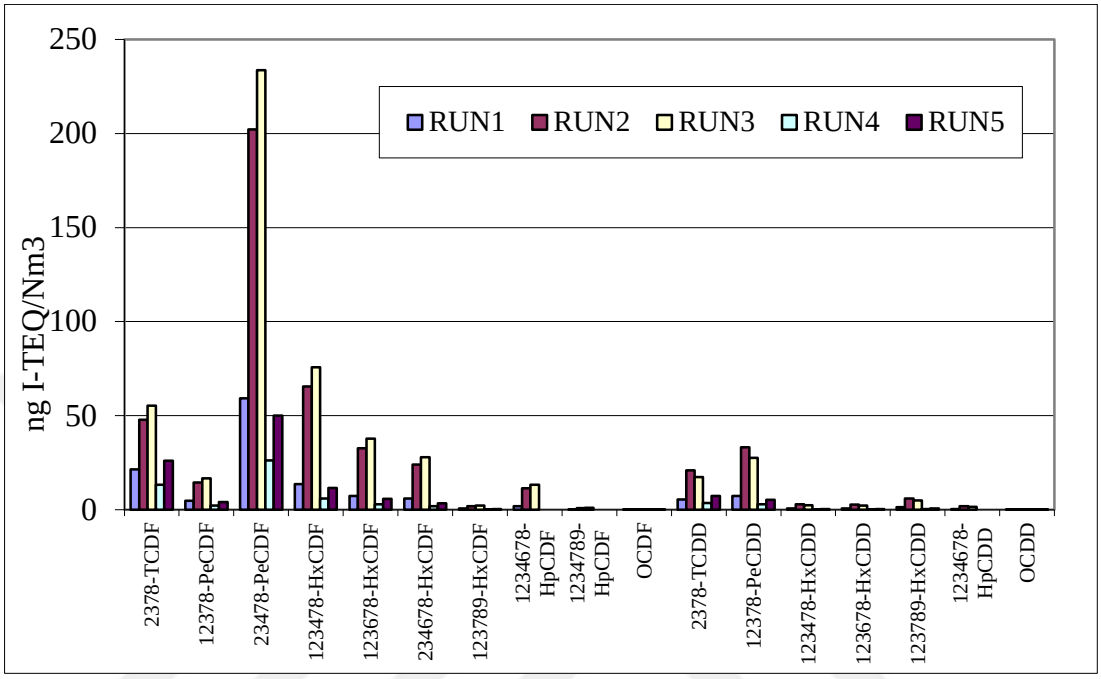


Figure 6.27. Overall congener distribution in syngas.

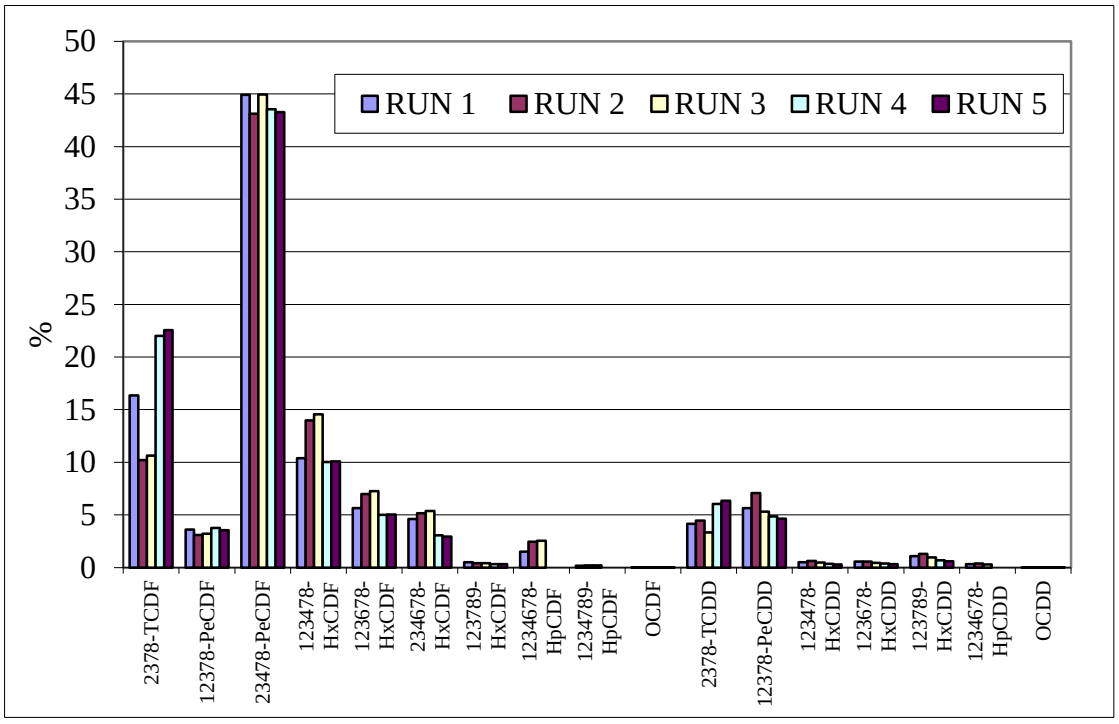


Figure 6.28. Overall PCDD/F congener TEQ percentage distribution in syngas.

The most dominant 5 congeners in syngas are given in Table 6.7. below. 23478-PeCDF is the most dominant congener in all Runs. 2378-TCDF and 123478-HxCDF are the following congeners which shared the second and the third dominant places shiftly. 2378-TCDD, 12378-PeCDD, and 123678-HxCDF shared the fourth and the fifth dominant congener places in syngas.

Table 6.7. Dominant congeners in syngas.

Dominant Congeners	Run 1	Run 2	Run 3	Run 4	Run 5
1. dominant	23478-PeCDF	23478-PeCDF	23478-PeCDF	23478-PeCDF	23478-PeCDF
2. dominant	2378-TCDF	123478-HxCDF	123478-HxCDF	2378-TCDF	2378-TCDF
3. dominant	123478-HxCDF	2378-TCDF	2378-TCDF	123478-HxCDF	123478-HxCDF
4. dominant	123678-HxCDF	12378-PeCDD	123678-HxCDF	2378-TCDD	2378-TCDD
5. dominant	12378-PeCDD	123678-HxCDF	234678-HxCDF	123678-HxCDF	123678-HxCDF

Other than syngas, bottom ash and adsorbant bed materials were also analysed for dioxin concentrations. The furan and dioxin concentrations and the PCDF/PCDD ratios in bottom ash were given in Table 6.8. The dioxin concentrations and percentage profiles were also given as bar graph in Figure 6.29.

Table 6.8. The PCDF/D ratios in bottom ash.

	RUN 1	**RUN2**	**RUN3**	**RUN4**	**RUN5**
PCDF, ng I-TEQ / g (%)	0.0046 (88.5)	0.020 (83)	0.084 (87.5)	0.009 (90)	0.478 (83)
PCDD, ng I-TEQ/ g (%)	0.0006 (11.5)	0.004 (17)	0.012 (12.5)	0.001 (10)	0.095 (17)
PCDF/D	**7.6**	**5.5**	**7**	**9**	**5**
TOTAL, ng I-TEQ/ g (%)	0.0052 (100)	0.024 (100)	0.096 (100)	0.01 (100)	0.573 (100)

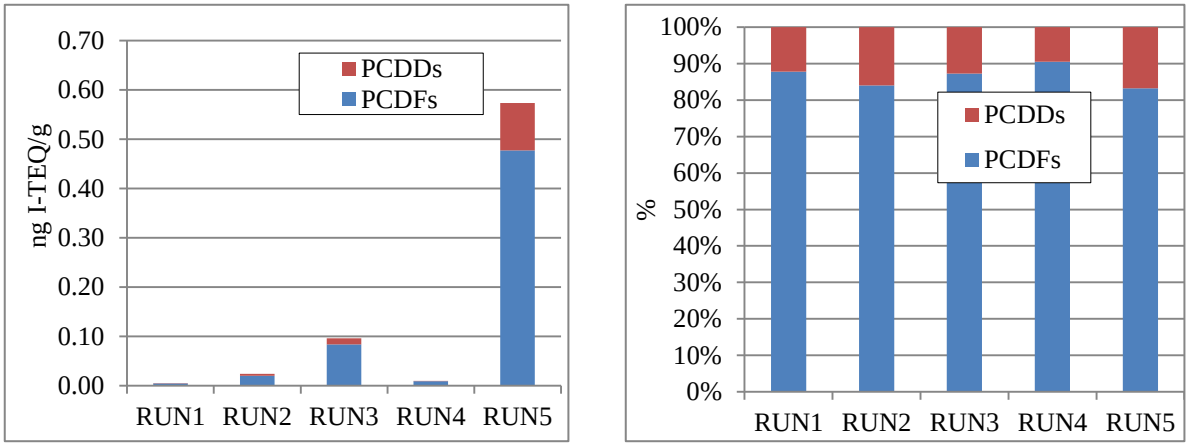


Figure 6.29. PCDD/PCDF concentrations and percentage profile in bottom ash.

The congener distribution in bottom ash was given in Figure 6.30. below. Overall dioxin concentrations in bottom ash were below the limits except Run5.

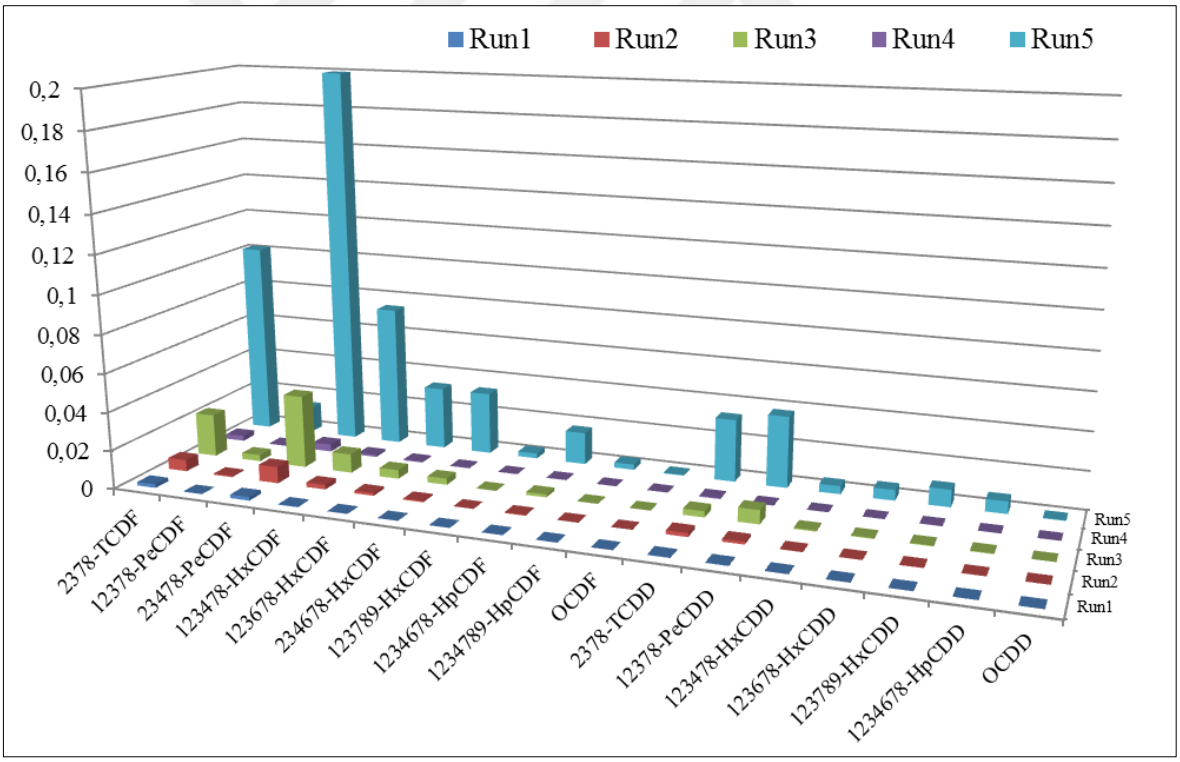


Figure 6.30. The congener distribution in bottom ash.

The most dominant congeners in bottom ash also were given in Table 6.9.

Table 6.9. Dominant congeners in bottom ash.

Bottom ash	Run1	Run2	Run3	Run4	Run5
1. dominant	2378-TCDF	23478-PeCDF	23478-PeCDF	23478-PeCDF	23478-PeCDF
2. dominant	23478-PeCDF	2378-TCDF	2378-TCDF	2378-TCDF	2378-TCDF
3. dominant	123478-HxCDF	123478-HxCDF	123478-HxCDF	123478-HxCDF	123478-HxCDF
4. dominant	2378-TCDD	2378-TCDD	12378-PeCDD	123678-HxCDF	12378-PeCDD
5. dominant	12378-PeCDD	123678-HxCDF	123678-HxCDF	2378-TCDD	2378-TCDD

The furan and dioxin concentrations and the PCDF/PCDD ratios in adsorbant materials were given in Table 6.10. The most dominant congeners of the adsorband materials also were given in Table 6.11.

Table 6.10. PCDF/D ratios in adsorbant materials.

	DOLOMITE	PERLIT COLUMN		AC	
	Total for 5 Runs	Run 1-2-3	Run 4-5	Run 1-2-3	Run 4-5
PCDF, ng I-TEQ / g	0.074	4.523	6.580	0.467	0.493
(%)	(88.1)	(84.3)	(88.7)	(88)	(89)
PCDD, ng I-TEQ/ g	0.010	0.842	0.833	0.063	0.063
(%)	(11.9)	(15.7)	(11.3)	(12)	(11)
PCDF/D	**7.13**	**5.37**	**7.89**	**7.36**	**7.87**
TOTAL, ng I-TEQ/ g	0.084	5.365	7.413	0.531	0.555
(%)	(100)	(100)	(100)	(100)	(100)

Table 6.11. Dominant congeners in adsorbant materials.

	Dolomite Column	Perlite Column		Activated Carbon Filter	
	Run 1,2,3,4,5	Run 1,2,3	Run 4,5	Run 1,2,3	Run 4,5
1 dominant	23478-PeCDF	23478-PeCDF	23478-PeCDF	23478-PeCDF	23478-PeCDF
2 dominant	2378-TCDF	2378-TCDF	2378-TCDF	2378-TCDF	2378-TCDF
3 dominant	123478-HxCDF	2378-TCDD	123478-HxCDF	123478-HxCDF	123478-HxCDF
4 dominant	123678-HxCDF ve 2378-TCDD	123478-HxCDF	2378-TCDD	2378-TCDD	123678-HxCDF
5 dominant	12378-PeCDD	12378-PeCDD	123678-HxCDF	12378-PeCDD	2378-TCDD
6 dominant	12378-PeCDF	123678-HxCDF	12378-PeCDD	123678-HxCDF	234678-HxCDF

The overall dioxin concentrations in bottom ash and the adsorbent materials were given in Table 6.12.

Table 6.12. Dioxin measurement results in bottom ash and bed materials.

RUNs	**BOTTOM ASH, ng I-TEQ/g**	**DOLOMITE, ng I-TEQ/g**	**PERLITE, ng I-TEQ/g**	**AC, ng I-TEQ/g**
RUN 1	0.0052	0.085	5.365	0.531
RUN2	0.0242			
RUN3	0.0959			
RUN4	0.01		7.413	0.555
RUN5	0.573			

Dioxin concentrations in bottom ash were 0.0052; 0.0242; 0.0959; 0.01; and 0.573 ng I-TEQ for Run1 to Run5, respectively. Total dioxin concentration in dolomite for the sum of all 5 Runs was 0.085 ng I-TEQ. Dioxin results in hazelnut shell used as perlit bed material were 5.365 ng I-TEQ for sum of Run1, Run2, and Run3, and 7.413 ng I-TEQ for the sum of Run 4 and Run5. Activated carbon dioxin results were 0.53 ng I-TEQ for the sum of Run1, Run2, and Run3 and 0.55 ng I-TEQ for the sum of Run 4 and Run5.

6.2.1. Dioxin Formation Mechanism

According to the results, it has been hypothesized that the PCDD/F formation mechanism is “de novo synthesis” in the existing research study. The primary indicative reason for the suggestion of the de novo synthesis for dioxin formation was the PCDF/PCDD ratios which were greater than 1 in all media. Thus, PCDF/PCDD ratios indicate that the reactions were favorable for the formation of PCDFs by de novo synthesis. Everaert and Baeyens (2002) not only suggest that PCDF/PCDD ratio exceeds 1 in de novo synthesis but also the degree of chlorination pointed towards the dominant presence of HpCDD and OCDD for the dioxins, and PeCDF, HxCDF and HpCDF within the furan group.

Secondly, when dioxin measurements are compared with each other with the flowchart sequence, it can be seen that the highest dioxin concentrations were in the perlite column bed material which was approximately 60-90 times higher than dioxin result in the dolomite column. Moreover, the bottom ash results, except Run 5, have the lowest dioxin concentrations in comparison with the dolomite and perlite column dioxin concentrations. It is believed that the dioxin concentration in bottom ash during Run 5 caused by a malfunction on sampling or measurement. The dioxin concentrations were observed on the right side of the process in other words at the post-combustion zone of the system which reflects the zone after the reactor. Concludingly, the PCDF/PCDD ratios and the post combustion zone accumulation of dioxin concentrations are the supporting ideas for the suggestion of dioxin formation mechanism as de novo synthesis. However, the preconditions for de novo synthesis must be met in order to form dioxins. Thus, the requirements for de novo synthesis such as oxygen, fly ash, chlorine source, metal catalyst, suitable temperature range for the formation and macromolecular residual carbon are examined step by step.

The relationship between ER and dioxin concentrations in syngas revealed that oxygen has a direct effect on dioxin formation. This effect occurred as expected that the dioxin concentrations increased with the increasing air feeding. It is a known fact that the O_2 is one of the pre-requisites for dioxin formation. On the other hand, the gasification

process has a reducing atmosphere which prevents the formation of dioxins. Thus, it is suggested that the oxygen participated in dioxin formation not in the gasifier part of the system but in the post-combustion zone of the set-up. After the gasification period was completed in each Run, the system was purged with excessive air in order to cool down the reactor and make the set-up ready for the following Run.

Another crucial pre-requisite for dioxin formation via de novo mechanism is chlorine. Chlorine is produced from HCl and the HCl was released as the result of PVC thermal decomposition at about 200-400°C temperature range. This degradation occurred probably in the pyrolysis zone before gasification began. Afterwards, the released hydrochloric acid which is in the gas-phase at that moment was oxidized by oxygen in the presence of copper (II) chlorides as a catalyst in the Deacon Process. It can be assumed that the Deacon Process occurred between 350-450^{o}C from the literature knowledge. The molecular chlorine which is the product of the Deacon Process, participated to the dioxin formation mechanism as chlorine source.

If the HCl would be measured in the gasifier, the concentration would be higher than the measured amount in syngas. Due to the chlorine production from HCl via Deacon; there should be more HCl at the gasifier part of the set-up. The measured HCl is the remaining, unreacted HCl. At that moment both HCl and Cl_2 existed in the gas phase. According to the literature, the chlorine may accumulate in different sized fly ash particles (Cobo et al. 2009) and retained in tar, char, ash and slag after gasification (Takeda et al. 2006). Thus, the accumulated chlorine reacted with the embedded carbon to form chlorinated aromatic compounds. Accordingly, gasphase chlorine was transfered/turned to chlorine before inclusion in PCDD/F.

Raghunathan & Gullett (1996) injected unextracted incinerator ash into the post-combustion zone of an experimental furnace reactor. This means that the embedded carbon material in the fly ash was not destroyed in the hot zone. Raghunathan & Gullett introduced HCl into the apparatus to simulate operation of MWI plants. HCl reacted with oxygen via the Deacon process to form chlorine, which then enhanced the production of PCDD/F by the novo route, chlorinating aromatic carbon structures of the carbon

embedded in fly ash. An increase in HCl concentration correlated with an increase in PCDD/F emissions.

Another important pre-requisite is fly ash. Fly ash particles carried into the post-combustion zone of the set-up and served as the necessary surface for PCDD/F formation at lower temperatures. It is suggested that the fly ash released from the gasifier played a leading role in dioxin formation via de novo synthesis. Also it is suggested that the high air flow, which was used during purging, drag large amounts of particulate matter and fly ash embedded with carbon containing gasification products towards to the post-combustion zone of the system. The dioxin samplings were performed during only gasification periods; however, the carried fly ash retained within the system as additional particulate matter which contributed to the dioxin formation in the following runs.

One of the solution options of eliminating the movement of the ash particles and prevent to form dioxin like compounds is gasification and melting processes. Due to the high temperature in gasification and melting processes, Yamamoto et al. (2000) maintained dioxin concentrations lower than 0.01 ng-TEQ/Nm^3 at higher than 1000^oC with rapid cooling. Also Yamawaki in 2003 pointed up that the fast cooling after the gasification reactor has crucial importance to avoid the formation of dioxin in gasification process. Kikuchi (2005) has also maintained high fuel gas temperatures as 1070^oC, 1194^oC, and 1200^oC at gasification-melting furnace outlet during municipal waste, plastic waste and PVC waste gasification, respectively. Even the PVC waste had the high chlorine content among other wastes, the dioxin concentrations for all waste gasification experiments were below 0.01 ng-TEQ/Nm^3 in gas phase due to the high temperature operation. Gand et al. (2007) decomposed dioxins in fly ash at over 1100^oC. Kwak et al. (2006) measured 0.03 ng-TEQ/Nm^3 dioxin concentration in another gasification-melting process due to the high temperature operation. Rapid cooling advantage can also be seen in Mendoza et al.'s study in 2006.

The main focus points of the gasification and melting processes is melting the fly ash in order to stabilize the fly ash by melting and limit the movement of ash particles within the systems. This control mechanism prevents the formation of dioxins by eliminating the

ash participation on dioxin formation mechanism. More sophisticated systems, combining pyrolysers or gasifiers and combustors with the primary aim of melting part of the ashes and of reducing dioxin formation, were proposed in Germany and further developed and built in Japan (Leckner 2015).

Besides chemical properties of gasification fly ash such as containing unburned carbon, PAH compounds, and chlorine, the particle size of the hazelnut shell fly ash has to be considered for dioxin formation. The size distribution analyses of hazelnut shell were obtained from the previous studies in Tubitak-MRC which used the same feedstock before. According to the results, hazelnut shell fly ash size ranges from 0.724 μm to 1905.5 μm. Sheng-yong et al. (2007) found that the formation of PCDDs was mainly facilitated by the two size fractions, 104–125 μm and <37 μm, while the formation of PCDFs was favored by the two other size fractions, >177 μm and 53–104 μm. Badreddine and François in 2008, have investigated municipal solid waste incinerator (MSWI) solid residue which consists of MSWI bottom ash and fly ash mixture for dioxin load in different particle size fractions. The good relation between the PCDD/F content and the particle size demonstrates that the fine fraction is enriched with PCDD/F compounds. The sub-sample with the finest fraction (<0.1 mm) showed by far a higher PCDD/F content, as 6590 ng I-TEQ/ kg, seven times above the other particle fractions. Moreover, Chen et al., 2006, found that the major peaks in particle size distribution for the PCDD/F content for 2 different samples were in a particle size <0.21 mm, that is, 16.1 and 4.37 pg I-TEQ/g, respectively. Thus, it is assumed /obvious that the particle size distribution of hazelnut shell fly ash represents a suitable physical property for dioxins formation via de novo synthesis.

Another pre-requisite is metal compounds which are used in Deacon Process as catalyst to form molecular chlorine. Metal compounds came with the hazelnut shell into the system. Fly ash from thermal waste treatment processes which has a catalytic role for de novo synthesis contains macromolecular carbon or residual carbon, various organic compounds, chloride, and metal ions. According to its constituents a variety of chloroaromatic compounds forms, through a heterogeneous mechanism taking place on the fly ash (Stieglitz and Vogg, 1987; Addink and Olie, 1995; Kakuta et al., 2007). The

elemental analyses of the fly ash of hazelnut shell were given in Table 6.13. It can be seen from the data that necessary metal catalysts were present in the ash matrix.

Table 6.13. Hazenut shell ash analyses.

	23.02.2009	01.12.2011	01.12.2011
Element	Concentration, %		
Al	1.019	2.799	0.426
Ba	0.149	-	0.092
Br	-	0.006	-
Ca	25.258	14.254	21.809
Cl	0.188	1.396	0.138
Cr	0.061	0.058	0.024
Cu	0.061	0.178	0.038
Fe	1.248	2.817	0.787
K	27.802	30.13	13.961
Mg	5.719	2.927	7.714
Mn	0.801	0.067	7.068
Mo	0.011	0.019	0.026
Na	0.902	1.071	1.1
Ni	0.029	0.016	0.022
O	30.159	32.419	36.325
P	2.089	2.438	2.969
Pb	-	0.017	0.009
Rb	0.029	0.046	0.014
S	1.919	2.456	6.333
Si	2.352	6.539	0.905
Sr	0.055	0.037	0.095
Ti	0.069	0.192	0.7038
Y	0.005	0.007	0.003
Zn	0.078	0.111	0.103

Joung et al., 2006, besides oxygen effect, revealed the catalyst effect on dioxin formation during gasification. Total dioxins concentration increased 15 times after catalyst addition.

Gullett et al. (1992) determined that the formation of PCDD is enhanced up to three orders of magnitude in the presence of metal catalysts, such as Cu (II), reaching a maximum around 400°C. Gullett et al. in 1990a examined the catalytic effect of copper and iron compounds for their behavior in promoting formation of chlorine, Cl_2, which is the major chlorinating agent of PCDDs and PCDFs (Gullett et al. 1990b). Formation of Cl_2 occurred as a result of a metal-catalyzed reaction of HCl with O_2. Catalytic activity was greatest at a temperature of approximately 400 °C, supporting a theory of de novo synthesis of PCDDs and PCDFs on fly ash particles in post-combustion zone. Similar to the existing research study, it is suggested that the Deacon Process took place to form Cl_2 after HCL generation following the PVC decomposition with temperature. Hinton and Lane in 1991b suggest that chlorine, copper, sodium, potassium, and zinc have a positive correlation with PCDD/F concentration, with copper being the most effective. Kobylecki indicated that dioxin/furan formation during any natural or human activity requires three basic ingredients: an organic starting material, a chlorine source, and, in processes with relatively low temperatures, a metallic catalyst. In Stieglitz et al.'s study (1989) only trace amounts of PCDD/Fs were found, without metal chlorides. Any metals present within the gas stream or in the materials of construction may act as a catalyst to dioxin formation (Unilabs Environmental, 1999).

Another prerequisite which is the suitable temperature range, 200-450^{o}C, was occurred between gasifier exit and heat exchanger inlet during the experiments. This pathway is approximately 2.5 meters long and according to the mean 1.62 m/s gas velocity, a gas particulate would pass this pathway in 1.5 sn. It is assumed that the dioxins formed via de novo synthesis within this pathway at the post-combustion zone of the set-up. However, the dolomite column is in that pathway and the dioxins concentrations were measured as 0.085 ng I-TEQ/ g in the column. This can be explained with the tar cracking and dioxin depressant effect of dolomite. The formation zone can be seen in Figure 6.31.

Steady-state temperature profiles of each Run were given between Figure 6.32 and Figure 6.36. It can be seen from the Figures that the assumed dioxin formation zone temperatures almost have same characteristics.

Figure 6.31. Dioxin formation zone of the set-up.

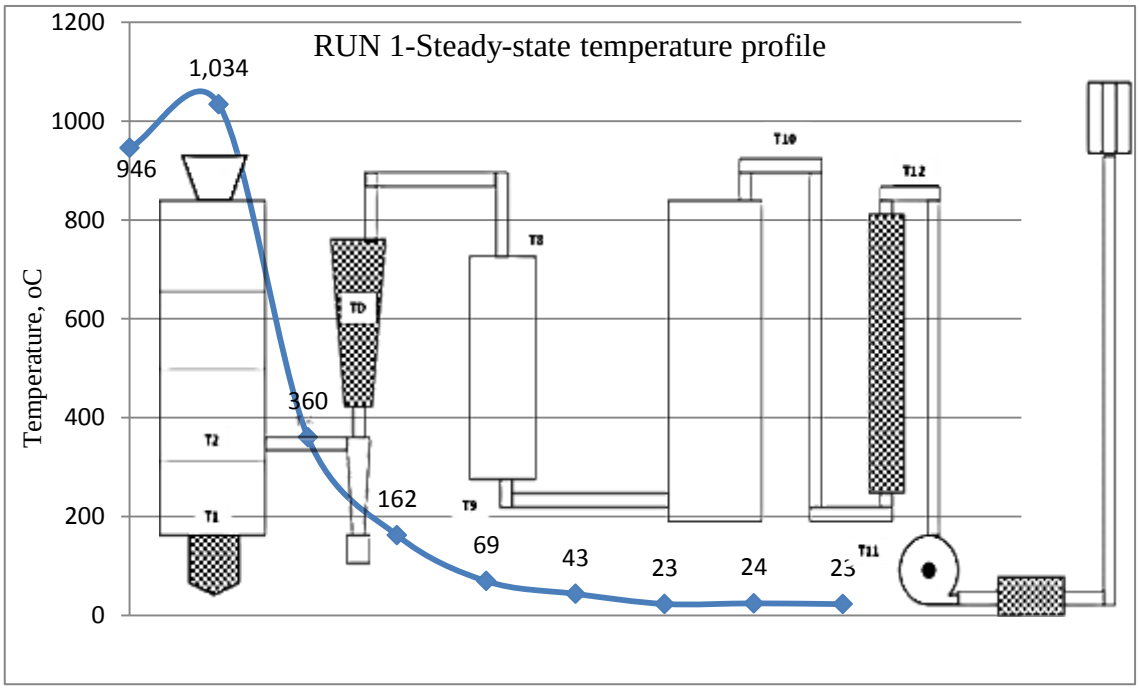


Figure 6.32. Average temperature profile of Run 1.

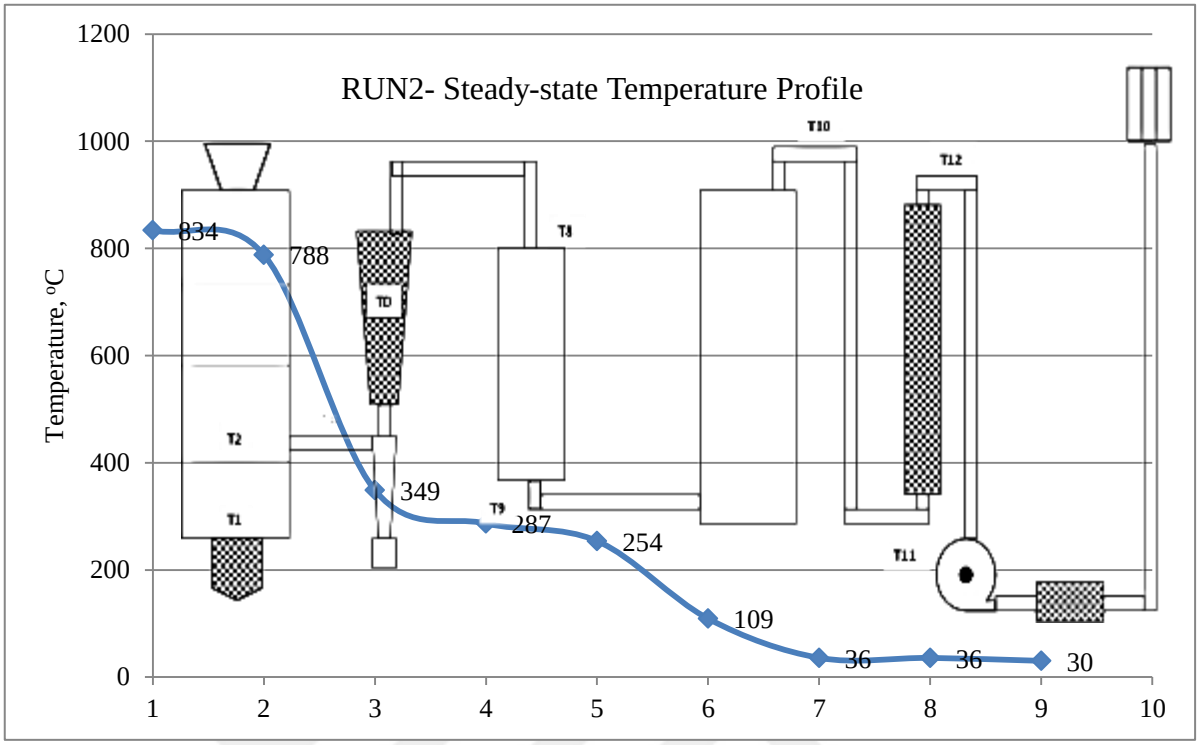


Figure 6.33. Average temperature profile of Run 2.

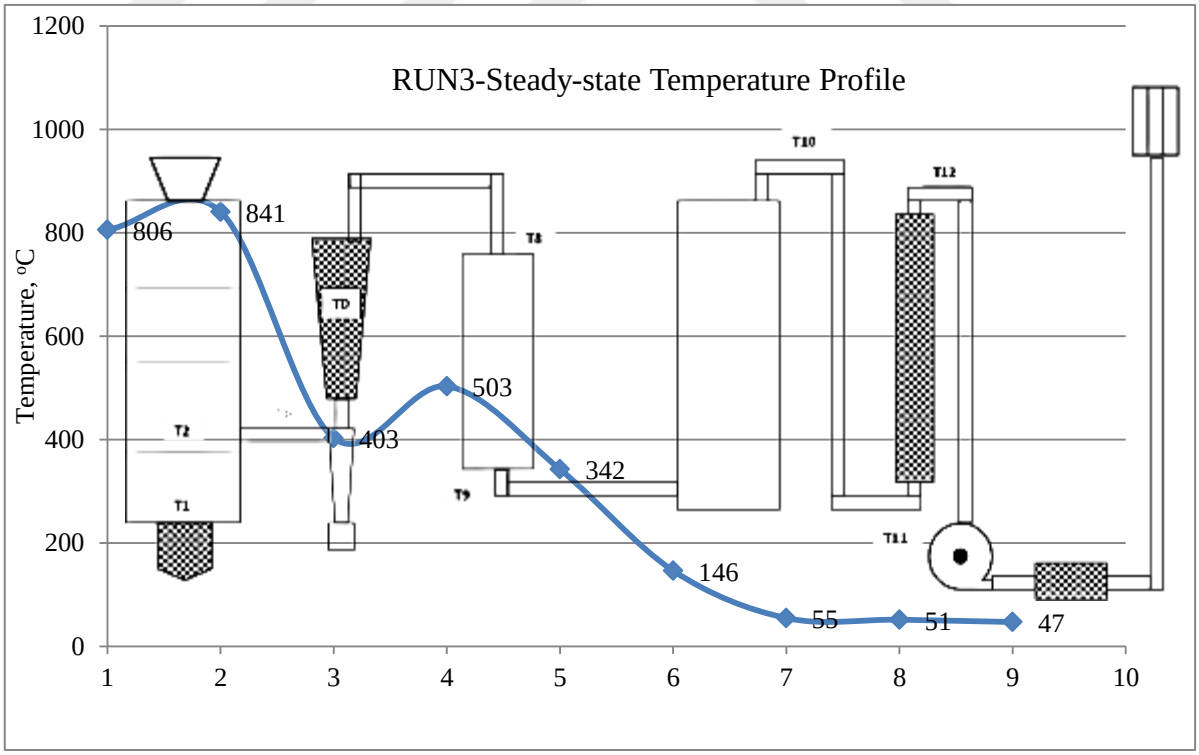


Figure 6.34. Average temperature profile of Run 3.

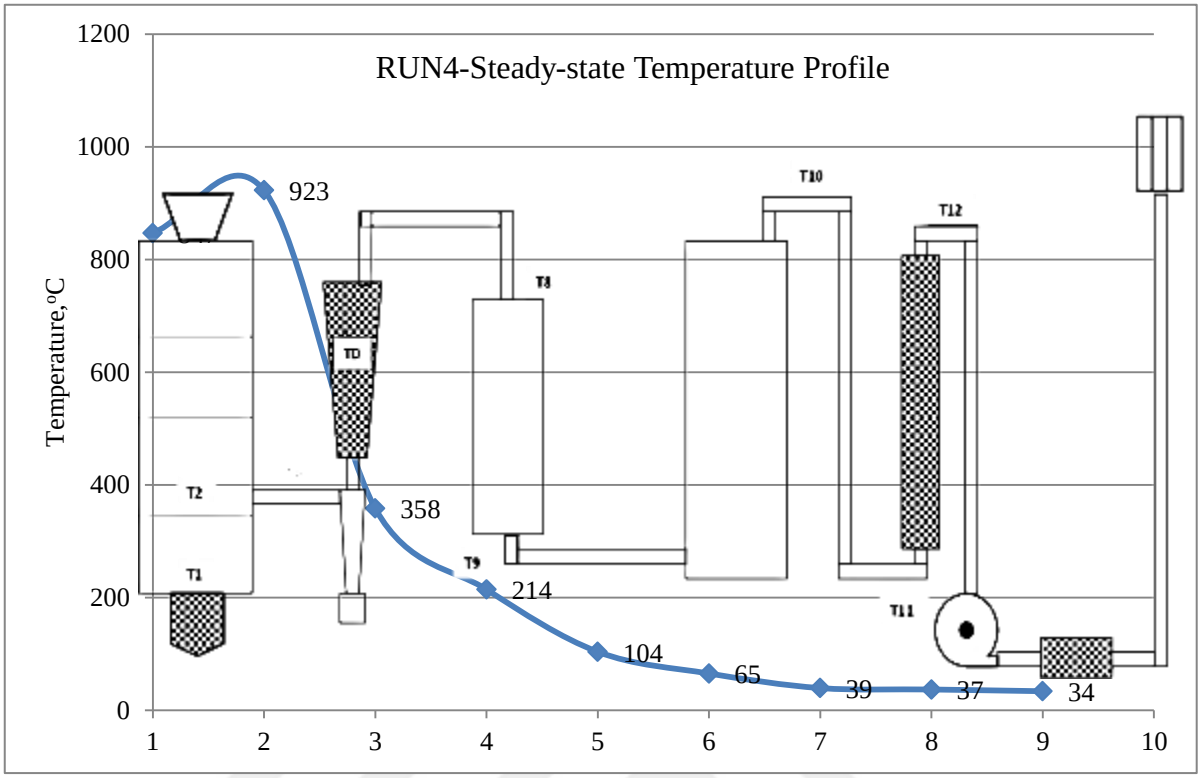


Figure 6.35. Average temperature profile of Run 4.

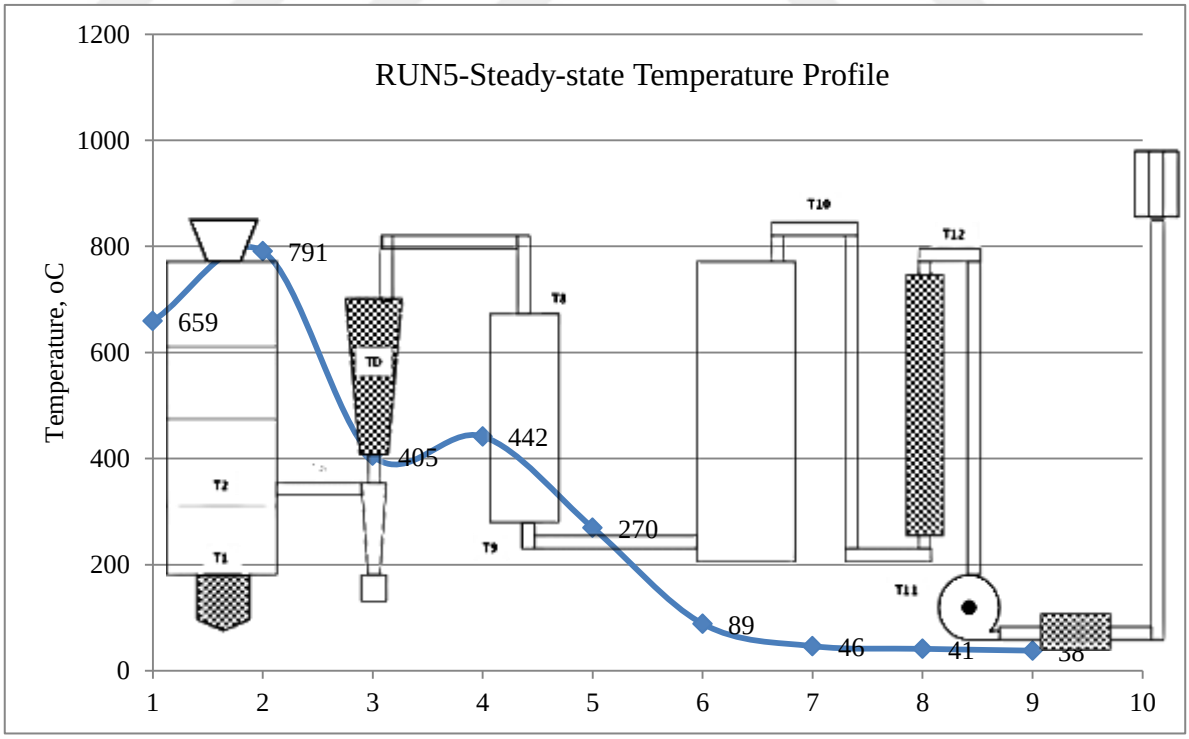


Figure 6.36. Average temperature profile of Run 5.

The macromolecular carbon for de novo synthesis maintained from tar compounds which produced as a result of the nature of the gasification process. Tar was carried with syngas to the cooler parts of the system; thus, it served as the macromolecular residual carbon for de novo synthesis and enhanced the carbon content of fly ash. Kawamoto and Mabuchi, 2001, also agree with the effect of carbon on dioxin formation. They have presented the ultimate effect of carbon on dioxin formation with fly ash catalyst mechanism. The scientists assumed that carbon macromolecules existing in fly ash functioned as an important carbon source for dioxin formation.

It can be remembered that the process acted as "Flaming Pyrolitic Gasification" which uses smaller amounts of air/oxygen and has ER <0,25. The maximum ER value used in the experiments was 0.19 that this corresponds to Flaming Pyrolitic Gasification conditions which produces more tar; thus, significant amount of tar produced as a result of the operating conditions. The excessive tar production was tried to get under control with system preparation experiments. Most of tar was captured in the adsorption beds. However, due to the nature of gasification process and the down-draft set-up configuration, excessive tar production was occurred in any cases. Tar also caused condensate production and clogged the system as mentioned before. Gang et al. (2007) agree with this result according to their findings that when ER is lower than 0.15, gasification can hardly be completed in time and the gasifier will be jammed by reactants.

Other than ER, low temperature affected the tar production excessively. Tar production in gasification is enhanced at lower temperature runs. Especially run 2 and run3 have lower operation temperatures according to the lesser amount of feedstock used in the experiments. Relationships between tar compounds with ER and temperature are given in Figure 6.37 and Figure 6.38., respectively.

The measured tar compounds in the research study are listed below and the produced tar within the system can be seen in Figure 6.39.

- Benzene C_6H_6
- Toluene C_7H_8
- Ethylbenzene C_8H_{10}

- m-Xylene C_8H_{10}
- o-Xylene C_8H_{10}
- p-Xylene C_8H_{10}
- Acetic acid $C_2H_4O_2$

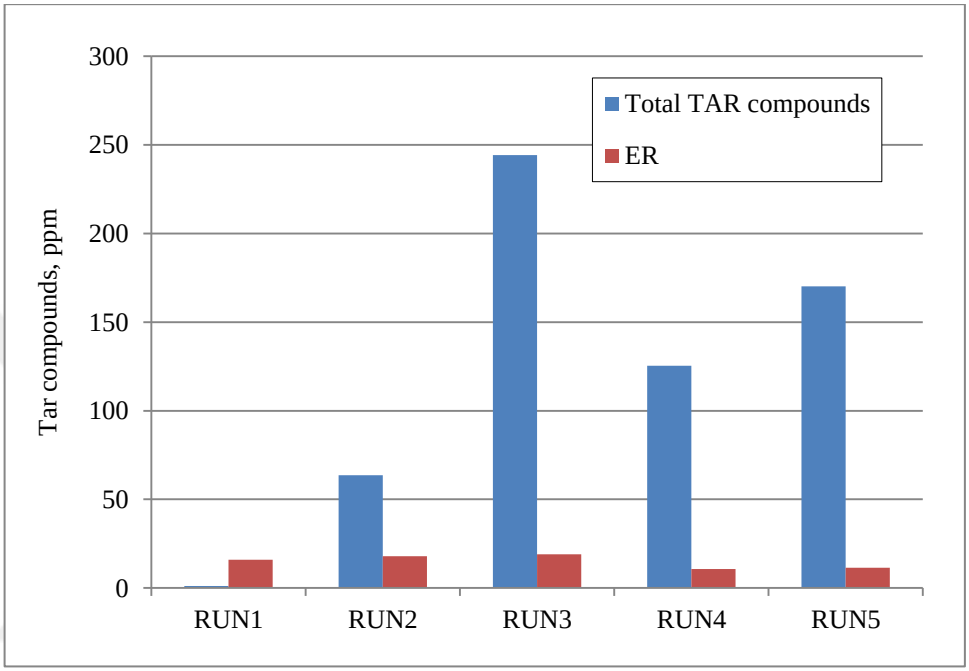


Figure 6.37. Relationship between tar compounds and ER.

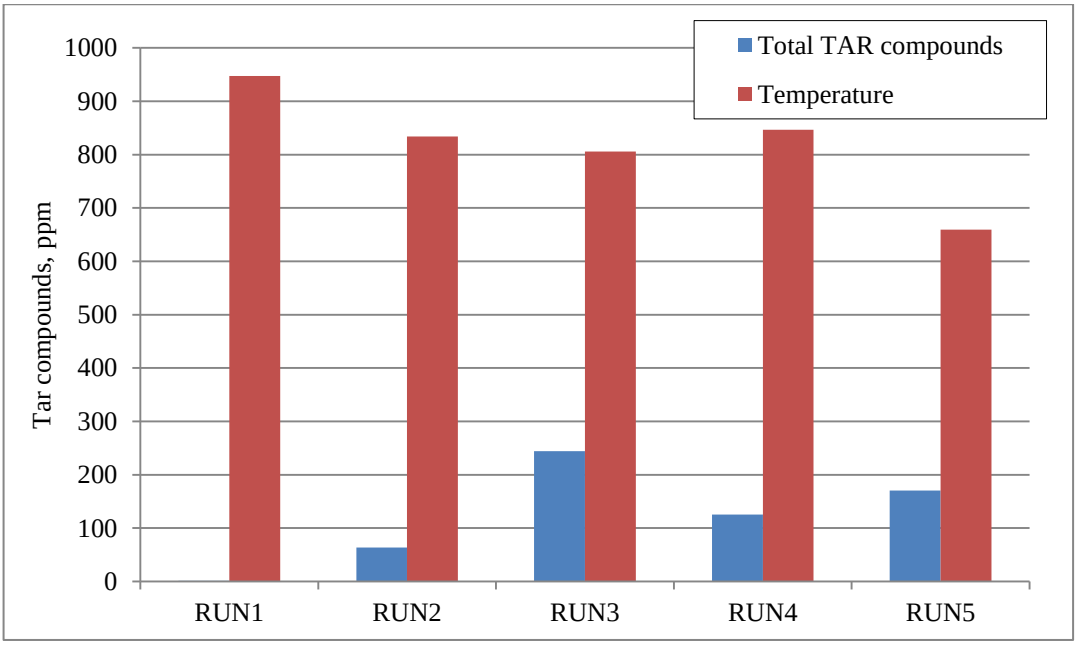


Figure 6.38. Relationship between tar compounds and temperature.

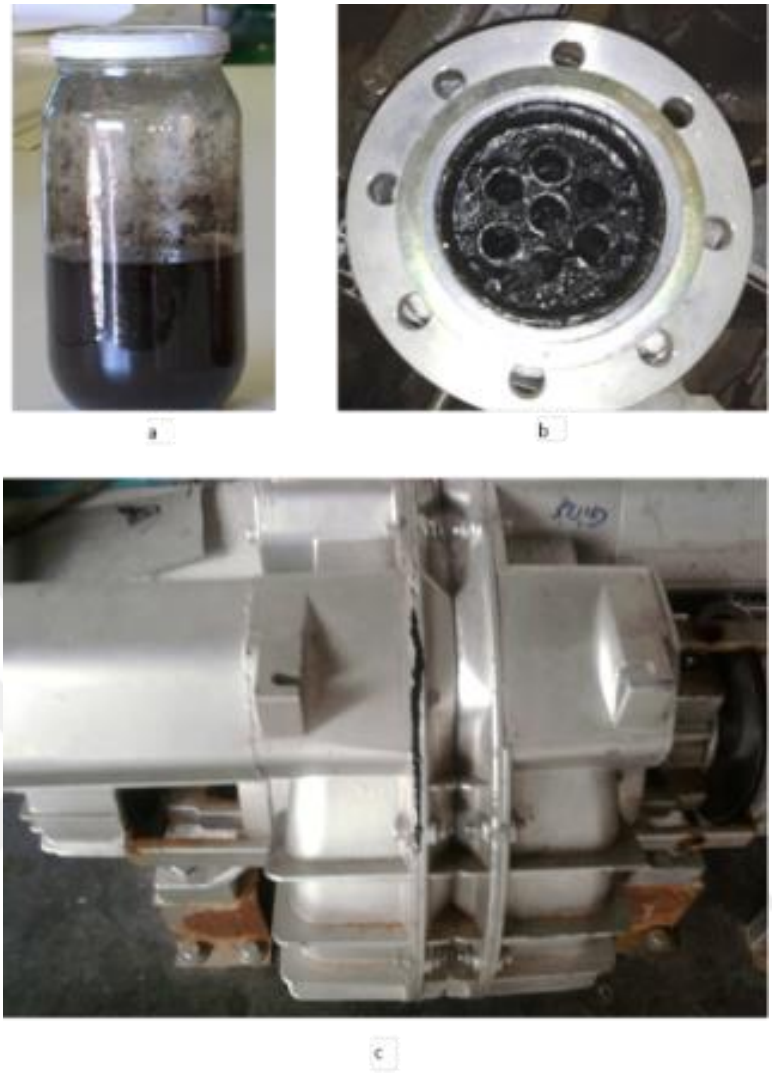


Figure 6.39. Tar formation within the experimental set-up components a) Condensate water from heat exchanger, b) Heat exchanger inside, c) Tar leakage from the ID Fan.

It is also believed that other than process conditions, the organic constituents of hazelnut shell strongly affected the tar production. Hazelnut shell is a lignocellulosic biomass which consists of mainly cellulose, hemicellulose, and lignin. It has 41-43% lignin and 24-26% cellulose. According to Egsgaard and Larsen, 2001, pyrolysis of lignin produces phenolic compounds which are dominant primary tar constituents. The tar formation which is a nature step of gasification occurred excessively with the effects of all leading factors discussed above. Organic constituents of hazelnut shell which obtained from the literature were shown in Table 6.14.

Table.6.14. Hazelnut shell constituents from literature.

Constituent, %	Yesim Arslan, Nurdan Eken-Saracoğlu	Buçin Aslan Çöteli	Hanzade Haykiri-Acma, Serdar Yaman	Demirbas, A.
Lignin	43.1	42.5	41.6	42.5
Hemicellulose	27.5	29.9	-	29.9
Cellulose	24.7	25.9	-	25.9

The concentrations of measured tar compounds with dioxin results in syngas were given in Table 6.15. below. It can be seen from the results that the dioxin concentrations increased with the increased tar concentarations.

Table 6.15. Tar compounds and dioxin concentrations.

	Run 1	Run 2	Run 3	Run 4	Run 5
Total TAR compounds, ppm	1.14	63.56	244.19	125.34	170.09
Dioxins, ng I-TEQ/Nm^3	131.7	468.7	519.7	60.3	115.5

Due to the excessive tar formation, it is assumed that the primary tars were produced during the experiments from biomass components and most probably converted to the secondary and tertiary tar compounds such as PAH. This PAH compounds had a significant effect on dioxin formation as carbon source. PAHs are possibly involved as precursors in the de novo synthesis for dioxins (Leclerc et al., 2006). PCDD/Fs can be considered as chlorinated PAHs (Zevenhoven and Kilpinen, 2001). PAHs can react catalytically with fly ash present in the postcombustion zone to produce compounds like dioxins.

In conclusion, it is suggested that the polychlorinated dibenzo paradioxins and furans formed between gasifier exit and heat exchanger inlet via de novo mechanism with the contribution of tar compounds and fly ash.

6.2.2. Operating Conditions Effect on Dioxins and Congeners

The effect of operating parameters such as ER, temperature, feedstock chlorine rate and HCl concentrations in syngas on dioxin formation was evaluated in order to better understand the dioxin formation mechanism during the conventional gasification process with down-draft gasifier.

6.2.2.1. Oxygen Effect on Dioxin Formation in Syngas. The results showed that ER and dioxin concentrations are directly proportional with each other. It should be remembered that ER is the rate of the actual air-fuel ratio used in the experiment to the stoichiometric air-fuel ratio; thus, ER increases with air feeding. In other words, dioxin concentrations increased with increased air feeding (oxygen). Joung et al., 2009, also agree with the oxygen effect on dioxin formation during gasification process. The amount of PCDD/Fs at 0.5 air/fuel ratio was 75 times higher than PCDDs/PCDFs at 0 air/fuel ratio. PCDFs were domina”nt both in pyrolysis and gasification conditions as occurred in the existing research study. Joung et al., 2006, also showed the oxygen effect on dioxin formation one more time.

In the literature, scientists have found similar results between oxygen feeding and formed dioxins in gas stream. Addink and Olie (1995) and Ryan and Altwicker (2000) showed that the rate of PCDD/Fs formation increase when the oxygen concentration was varied from 1% to 10%. Pek´arek et al. (2001) found the concentration of PCDD/Fs was distinctly decreasing during transition from oxygen rich atmosphere to pure nitrogen. Zhang et al. (2008) investigated the effect of O_2 level on PCDD/Fs formation in a municipal solid waste (MSWI); increasing O_2 concentration from 6.0% to 10.5% led to a higher yield of PCDD/Fs (16.9 to 34.3 ng/Nm^3). Although oxygen’s effect on dioxin formation has been investigated commonly for incineration and the literature about the dioxin formation has been mostly created by dioxin formation studies about incineration, there is consensus in the literature among the laboratory-, pilot-, and field-scale researchers that formation of PCDDs and PCDFs is dependent upon O_2 concentration (Gullett and Lemleux, 1994). The effect of the O_2 level in the flue gas on PCDD/Fs formation was of particular interest (Jeong-Eun, 1999) and has been the subject of numerous studies.

The parallel behavior between ER values and total dioxin concentrations in syngas can be seen in Figure 6.40. Also, the correlation between ER and dioxins can be seen in Figure 6.41. The coefficient of determination was found R^2=0.79 that the parameters are almost dependent on each other.

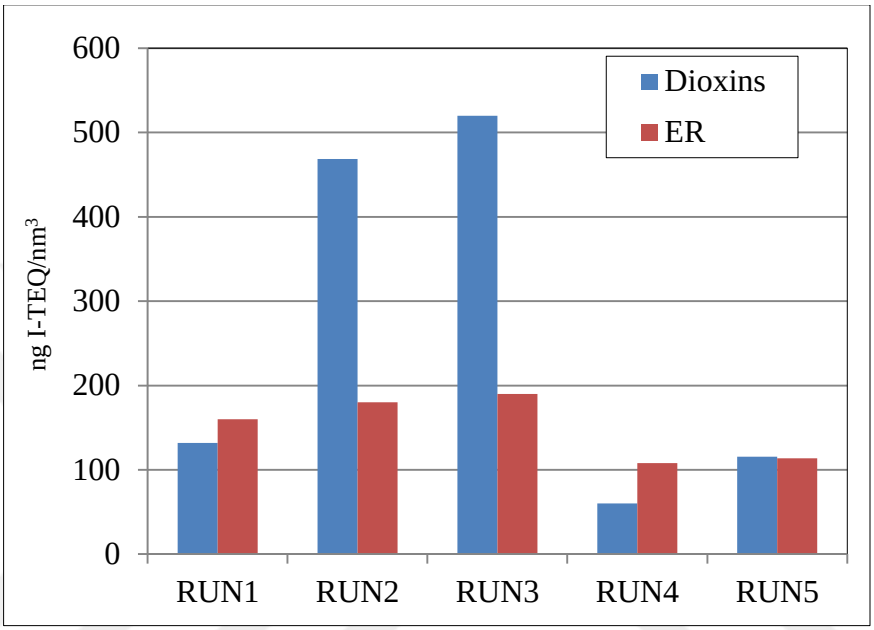


Figure 6.40. Relationship between ER and syngas dioxin concentrations.

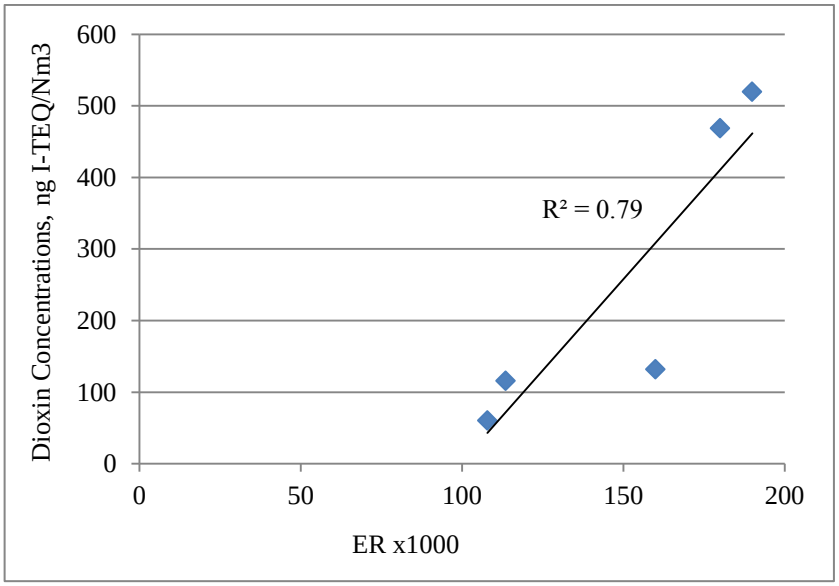


Figure 6.41. Correlation between ER and syngas dioxin concentrations.

In spite of the slight increases on ER values, dioxin concentrations increased prominently in the first 3 runs. The ER effect on formation of each congener can be examined more clearly with the coefficient of determination values given in Table 6.16. The most oxygen dependent congener was 123789-HxCDF following by 1234789-HpCDF, 1234678-HpCDD, 1234678-HpCDF, and 234678-HxCDF, respectively. However the oxygen dependency sequence of the congeners is not similar with the overall dominant congener sequence which was given in Table 6.7. before. Different congener yields may be occurred with the changing operating conditions and different formation characteristics of each congener.

Table 6.16. Congeners vs ER – R^2.

Congeners	R^2
2378-TCDF	0.7258
12378-PeCDF	0.7996
23478-PeCDF	0.7925
123478-HxCDF	0.7681
123678-HxCDF	0.7808
234678-HxCDF	0.8129
123789-HxCDF	0.8563
1234678-HpCDF	0.8173
1234789-HpCDF	0.8519
OCDF	0.7554
2378-TCDD	0.6545
12378-PeCDD	0.7503
123478-HxCDD	0.7739
123678-HxCDD	0.8005
123789-HxCDD	0.7802
1234678-HpCDD	0.8312
OCDD	0.7530
Total-TEQ	**0.79**

Jiao et al. agree with the ER effect on dioxin formation that the increased ER values contribute the dioxin formation.

Also, congeners distribution in Joung et al.'s 2009 study has similarities with the existing research study. It can be seen that the congener distribution in char has stronger similarity than the distribution in syngas.

6.2.2.2. Temperature Effect on Dioxin Formation in Syngas. Secondly, the relationship between temperature and dioxin concentrations in syngas was evaluated. Temperature and dioxin concentrations are inversely proportional with each other that dioxin formation stayed lower at higher reactor temperatures. The oxidation and reduction zone temperatures and dioxin concentrations in syngas were given together in Figure 6.42.

Temperature effected dioxin concentration with its effect on tar craking. The high temperatures decompose the large tar molecules that pass through the combustion zone (All Power Labs). In the oxidation zone, the molecular carbon containing compounds is converted to CO_2 and H_2O. This conversion mechanism has occurred in the higher temperatured runs more effectively than the lower ones. Accordingly, tar compounds are destroyed more effectively at higher temperature runs. The remaining carbon containing compounds pass throught to the post-combustion zone within the fly ash particles and participated to the dioxin formation. Lower temperature may be the indicator in gasification that the tar compounds from pyrolysis step could not be cracked effectively in oxidation zone.

6.2.2.3. Chlorine Content / Hyrogen Chloride Effect on Dioxin Formation in Syngas. As mentioned previously, the chlorine content of the feedstock was different in first 3 runs and the last 2 runs. However, the results indicated that the chlorine rates didn't directly affect the dioxin concentrations. The results showed that chlorine was not proportional with the dioxins in syngas. Even though the feedstock was prepared obtaining %1 and %2 chlorine rates in order to observe the chlorine effect on dioxin formation, no direct relationship was observed between the chlorine rate of feedstock and the dioxin concentrations. Also, chlorine has no relationship with HCl in syngas. However, there is a strong correlation

between HCl and dioxins in syngas. Feedstock chlorine content with HCl and dioxin concentrations in syngas were given in Table 6.17.

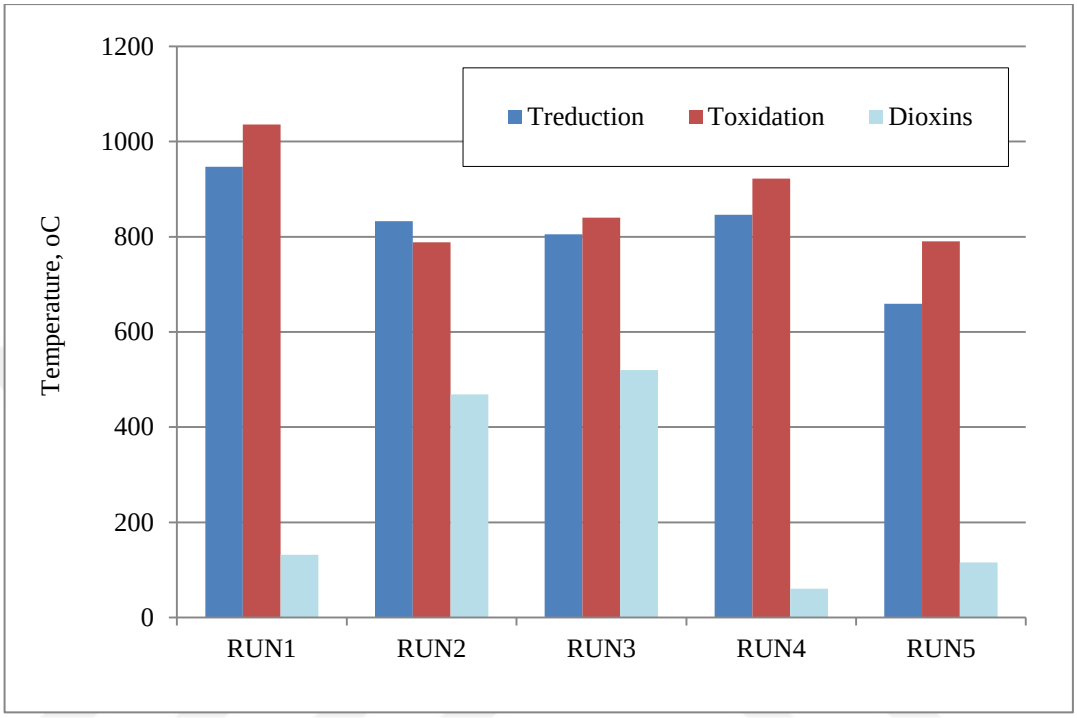


Figure 6.42. Relationship between reactor temperatures and dioxin concentrations.

Table 6.17. Feedstock chlorine content and syngas dioxin concentrations.

	Unit	RUN1	RUN2	RUN3	RUN4	RUN5
Chlorine (input)	% w/w	1	1	1	2	2
Chlorine (input)	gr	100	75	75	200	200
Dioxins (produced/output)	ng I-TEQ/Nm^3	131.7	468.7	519.7	60.3	115.5
HCl (produced/output)	ppmv	7.87	32.54	40.21	2.04	5.39

HCl and dioxin concentrations and the coefficient of determination, R^2 which was found 0.994, were given in Table 6.18. and Figure 6.43, respectively.

Table 6.18. HCl concentrations and dioxin concentrations.

	Unit	RUN1	RUN2	RUN3	RUN4	RUN5
HCl	ppmv	7.87	32.54	40.21	2.04	5.39
Dioxins	ng I-TEQ/Nm^3	131.7	468.7	519.7	60.3	115.5

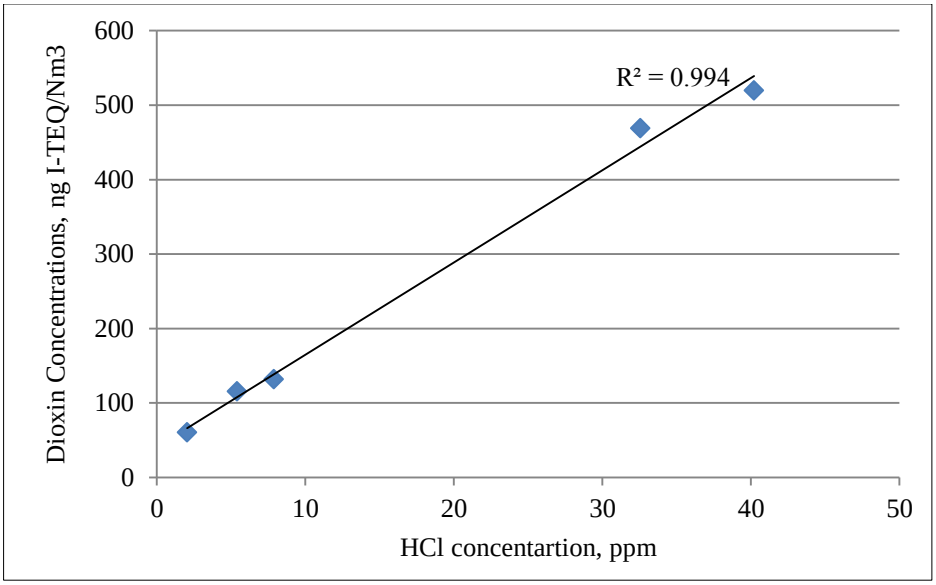


Figure 6.43. Correlation between HCl and dioxin concentrations.

The differences between HCl concentrations in the Runs, in spite of the same chlorine rate usage at first 3 Runs and the rest 2 Runs are same, can be explained with the operating parameters effect on HCl formation. Therefore, the relationships between HCl with ER and temperature were examined. It was found that the relationship between HCl and operating parameters is similar with the relation between dioxin concentrations and the operating parameters. HCl concentrations in the syngas and ER values for each Run were given in Table 6.19. Also, the parameters were correlated and the coefficient of determination was found R^2=0.7976. Results showed that HCl was positively and directly proportional with ER. The produced HCl increased with the increasing oxygen within the system. Correlation between HCl and ER values can be seen in Figure 6.44. Wei et al. found similar relationship that the increasing air enhanced the release of HCl in biomass gasification in 2005. The increased HCl might be caused to form more molecular chlorine which involved in dioxin formation in the existing study.

Table 6.19. HCl and ER relationship.

	Unit	RUN1	RUN2	RUN3	RUN4	RUN5
HCl	ppmv	7.87	32.54	40.21	2.04	5.39
ER	-	16	18	19	10.79	11.36

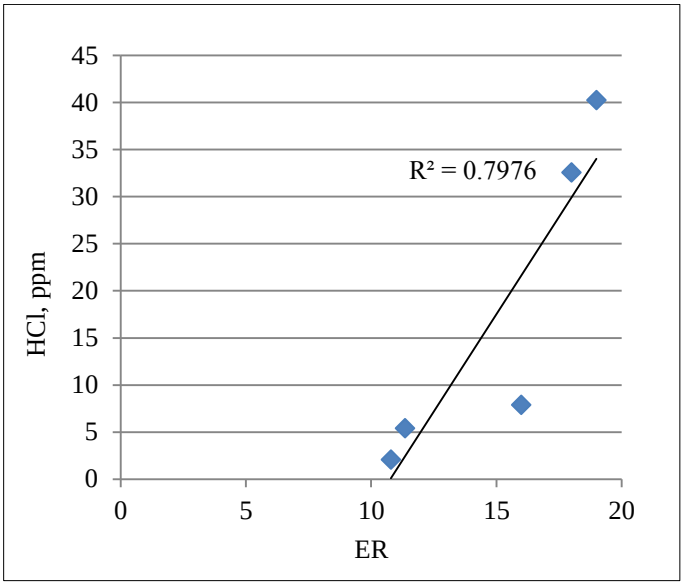


Figure 6.44. HCl and ER correlation.

In addition to the ER, temperature has an effect on HCl production during the experiments. The HCl concentrations increased with the decreasing temperature in all Runs. Blasing et al. in 2011 reached the similar relationship between HCl and temperature, which is that the release of HCl is decreasing with increasing temperature. HCl and the reduction zone temperature values were given in Table 6.20.

Table 6.20. HCl and reduction zone temperatures.

	Unit	RUN1	RUN2	RUN3	RUN4	RUN5
T	^{o}C	947	833	805	846	659
HCl	ppmv	7.87	32.54	40.21	2.04	5.39

Consequently, HCl increased with increasing ER and decreased with the increasing temperature, which is the same relationship between dioxin concentrations with ER and

temperature. Porbatzki et al. (2011) found a similar relationship between HCl and temperature during the gasification process that the amount of HCl decreased with higher temperature.

Kuramochi et al. (2005) could not find linear relationship between HCl and chlorine although the chlorine contents of three biomass fuels (bio-dried wood, railroad ties and cacao shells) are at the same level at that study. This can be due to the chlorine speciation in gas-phase, like HCl, varies with operating conditions such as equivalence ratio and temperature Wikström et al. (2003) or can be due to the effect of other elements such as heavy metals or alkali and alkaline earth metals (Kuramochi et al., 2005).

Additionally, the relationship between dioxin congeners and HCl concentrations were presented with correlation. The coefficients of determinations, R^2, which have high numbers, were given in Table 6.21. It can be seen from the table that 23478-PeCDF has the strongest correlation with HCl.

The results indicated that ER and temperature directly effected the overall dioxin concentrations; however, operating parameters did not play a leading role on congeners profile. Effects of the operating parameters on congener distribution differed from one congener to another one. Some congeners were affected mainly from ER values, others from temperature or HCl concentration. This can be explained with the combination of overall effect of all operating parameters with macromolecular carbon structure and formation characterisrics of each congener. Although there were slight differences, the congener distribution in all mediums showed strong similarity. It is believed that the ash particles contained the same macromolecular carbon compounds that may cause to form almost similar congeners in all mediums.

The strongest R^2 values were obtained from the correlation with HCl and dioxin concentrations. This means that the congener formation was affected mostly from HCl concentration. Thus, the interaction between carbon structure and chlorine molecules is getting more definable reason for congener distribution / speciation. HCl is an important parameter and the effect on dioxin formation is clear from the correlation. Furthermore,

work on combustion of waste has shown that HCl together with different carbon sources are the precursors for dioxin formation and that the formation in the postcombustion zone is a significant contributor (Bjorkman and Stromberg, 1997).

Table 6.21. Congeners and HCl corelation.

Congeners	R^2
2378-TCDF	0.9627
12378-PeCDF	0.9978
23478-PeCDF	0.998
123478-HxCDF	0.9962
123678-HxCDF	0.9972
234678-HxCDF	0.9969
123789-HxCDF	0.9926
1234678-HpCDF	0.9913
1234789-HpCDF	0.9869
OCDF	0.9942
2378-TCDD	0.8823
12378-PeCDD	0.9133
123478-HxCDD	0.9139
123678-HxCDD	0.9084
123789-HxCDD	0.9132
1234678-HpCDD	0.9062
OCDD	0.9146
Total-TEQ	**0.9940**

Results showed that the dominant congeners in all dioxin measurement mediums such as syngas, bottom ash, and adsorbant materials are almost similar. 23478-PeCDF is the most dominant congener in all mediums and runs. 2378-TCDF is the second dominant congener while 123478-HxCDF and 2378-TCDF are the third ones. 2378-TCDD, 12378-PeCDD, and 123678-HxCDF shared the fourth and the fifth dominant congener places in all mediums. The similarity of congener sequencing both in syngas, bottom ash, and

adsorbant materials led the idea that the congener formation originated from the similar/same formulated macromolecular carbon compounds.

7. CONCLUSIONS

A conventional down-draft gasifier with gas cleaning unit were used to perform the research experiments in order to better understand the dioxin formation during gasification of hazardous waste. It is intented to reveal the dioxin formation mechanisms and leading effecting factors to the formation during conventional gasification process.

One of the main findings of the study is that the dioxins formation mechanism is de novo synthesis**.** Gasification itself shouldn't produce dioxins; however, the conditions at the post-combustion zone of the set-up significantly contributed the dioxin formation. The combination of the fly ash and tar compounds enhanced the dioxin formation in the post combustion zone of the set-up.

Another significant finding from the investigation of congeners distribution is that all dioxin congeners formed from the similar carbonaceous compounds. It is suggested that the same carbon structure played role in dioxin formation not only in syngas but also in bottom ash and adsorbent materials within the set-up.

According to the examination of the operating parameters, it was found that the dioxin concentrations increased with the increasing ER and the decreasing temperature. HCl has direct effect on dioxin concentrations while the feedstock chlorine content rate didn't play role in dioxin concentrations. The measured HCl concentration is the remaining HCl in syngas at the exit point of the set-up. The main HCl was produced via PVC thermal decomposition. Chlorine which was used on dioxin formation produced from that HCl via Deacon Process. It is assumed that the remaining / measured HCl is proportional with the first HCl concentration which was released at the end of the PVC decomposition. The relationships between HCl with ER and temperture have parallel behavior with the relationship between dioxin concentrations. HCl was the most effecting parameter to the dioxin formation according to the congener distribution examination.

The experimental set-up configuration was designed previously for basic gasification efficiency evaluation experiments. However in the existing study, it is used to evaluate dioxin formation during gasification with modelled hazardous waste feedstock. The difficulties, the technical limitations and shortcomings which were encountered during the experiments were syngas flow reading, secondary air feeding without heating, bottom ash handling, and dioxin sampling. It is intended to take syngas samples after gasifier before cyclone in order to determine the dioxin concentration in the reactor; however, the sampling equipment was not appropriate to take samples at that high temperature.

The gasification temperature was the most result effecting shortcoming of the experiments. Excessive tar production and insufficient tar conversion occurred according to that low temperature and enhanced dioxin formation at post-combustion zone. However, due to this operating conditions, examination of the dioxin concentrations provided better understanding for further studies.

Gasification of hazardous waste is relatively new subject among the gasification research studies. According to the findings, the fly ash and tar generation are the most important issues and key factors for dioxin formation during gasification. The fly ash must be removed from the system to prevent its serving as a dioxin formation media. According to the gasification process nature, tar formation, conversion and accumulation should be taken under control with optimum operating conditions such as 1100-1200^{o}C oxidation zone temperature and approximately 900^{o}C reduction zone temperature as well as addition of tar treatment units.

Although it is possible to avoid dioxin formation in the reactor due to the nature of the gasification process reductive medium, the post-combustion zone formation mechanism should be considered and taken under control.

Gasification process can be used as an alternative way to dispose hazardous wastes if appropriate process configuration is designed to control fly ash and tar generation in order to avoid and eliminate the dioxin formation. Also the operating parameters should be well controlled to provide an efficient gasification.

8. FUTURE WORK

For the future steps of the research study, the following suggestions are made:

- It should be added ash melting unit into the pilot plant in order to stabilize the fly ash to prevent dioxin formation.

- Further research experiments may be conducted with a different biomass feedstock which may has lesser amount of lignin content in order to contribute to reduce the tar production.

- Dioxin sampling should be made available at the gasifier exit in order to monitor the dioxins formation during gasification.

- Set-up equipment and materials which will be used in the set-up should be high temperature resistant up to1200^{o}C.

- Precursor compounds such as benzene, chlorobenzene, phenol, chlorophenol should be measured in gas-phase in order to better understand the contribution of those compounds to dioxin formation.

- Investigation of the morphology and chemical properties of the carbonaceous materials such as tar compounds which produced during gasification should be done. For this purpose, tar sampling points should be maintained within the system.

- Fly ash within the set-up should be analyzed for dioxin concentrations on it.

- HCl may be recovered from the system in oder to prevent the contribution of HCl to the dioxin formation.

- Set-up design should be modified to allow fast cooling of the syngas after gasifier.

- The gasifier should be designed to maintain higher operating temperatures above a certain level. Higher operating temperatures allow getting more efficient gasification process conditions.

- Tar treatment steps should be sdded to the system in order to prevent tar contriution to dioxins formation.

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