COMBUSTION CHARACTERISTICS AND THERMAL UTILIZATION OF SEWAGE SLUDGE AND COAL MIXTURES

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ABSTRACT

COMBUSTION CHARACTERISTICS AND THERMAL UTILIZATION OF SEWAGE SLUDGE AND COAL MIXTURES

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Management of sewage sludge is generally one of the greatest problems that municipalities face due to its large quantities and different characteristics. Since dry sludge has a heating value close to a lignite coal, this energy can be recovered and used. The aim of this thesis is to investigate the beneficial use of sewage sludge by exploring its energy content. In this context, six Wastewater Treatment Plants (WWTPs) are chosen with different characteristics. Proximate and ultimate analysis, calorific value determination and thermogravimetric analysis (TGA) are carried out on the samples to determine the characteristics of sludges of these WWTPs. Then, co-combustion of these sludges with coal is investigated in a laboratory scale batch combustor. Sludge samples are added to coal at 3, 5, 10, 20, and 30% by wt. and combusted to see the effect of sludge addition on combustion efficiency and emissions. Elemental composition of ashes is also determined by X-Ray Fluorescence (XRF). In ash analysis of sludges alkali content was found in the range of 0.5-1.5% by wt. showing high slagging and fouling tendencies in the combustor if burned alone.

Results of the experiments have shown that thermal characteristics of sludges depend on types and operating conditions of wastewater and sludge treatment processes. In combustion experiments as the sludge addition to fuel mixtures increased, carbon monoxide formation also increased and the efficiency of combustion is reduced. Lastly, kinetic analysis with TGA experiments show that sewage sludge decomposes according to multiple reaction models, however, the most dominant models are based on nucleation processes.

Keywords: sewage sludge, thermal analysis, combustion

ÖZ

ARITMA ÇAMURLARI VE KÖMÜR KARIŞIMLARININ ISIL DAVRANIMI VE YANMA KARAKTERİSTİKLERİ

ATAK, Onur
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Atık su arıtma tesislerinde oluşan arıtma çamurunun yönetimi, çamur miktarının çok fazla olmasından ve çamurun değişken özelliklerinden dolayı bu tesisleri işleten Belediyelerin karşılaştıkları en büyük problemlerden biridir. Diğer taraftan kurutulmuş arıtma çamurunun ısıl değerinin linyit kömürlerine yakın olması, bu enerjinin geri kazanımını önemli kılmaktadır. Bu tezin amacı, arıtma çamurlarının enerji içeriğini belirleyerek bu çamurların yararlı kullanımını araştırmaktır. Bu kapsamda, değişik özellikler gösteren altı adet atık su arıtma tesisi seçilmiştir. Alınan arıtma çamuru örneklerinin yaklaşık ve elemental analizleri yapılmış, kalorifik değerleri belirlenmiş ve termogravimetrik analiz ile arıtma çamurlarının yanma kinetikleriincelenmiştir. Daha sonra, laboratuvar ölçekli bir kesikli yakma reaktöründe arıtma çamuru-kömür karışımlarının yakılması araştırılmıştır. Arıtma çamurları kömüre kütlece %3, 5, 10, 20, 30 oranında karıştırılarak, arıtma çamuru eklenmesinin yanma verimine ve emisyonlara etkisi incelenmiştir. Ayrıca arıtma çamuru külünün elemental komposizyonu X-Ray Fluorescence (XRF) analizi ile belirlenmiştir. Arıtma çamuru örneklerinden elde edilen küllerin elemental kompozisyon çalışmasında alkali içeriğinin %0.5-1.5 arasında olduğu ve bu kompozisyonun da çamur tek başına yakıldığında cüruf oluşumunu artırabileceği belirlenmiştir.

Deney sonuçları, arıtma çamurunun termal karakterizasyon parametrelerinin atık su ve çamur arıtma prosesi tiplerine ve bu proseslerin çalışma koşullarına göre değiştiğini göstermiştir. Ayrıca, arıtma çamuru ile kömürün yakılması deneylerinde karışımdaki arıtma çamuru oranının artması, karbon monoksit emisyonlarını artırarak yanma veriminin azalmasına yol açmıştır. Son olarak, TGA deneyleri ile yapılan kinetik analiz sonucunda, arıtma çamuru yanmasının birbirinden farklı birçok reaksiyon modeline göre gerçekleştiği açığa çıkarılmıştır. Çalışılan deneysel koşullarda baskın olan modelin nükleasyon (nucleation) proseslerine dayandığı bulunmuştur.

Anahtar sözcükler: arıtma çamuru, termal analiz, yakma

To my family, to the one who I believe will be somewhere beyond here.

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My brother, life is easier when we stand shoulder to shoulder and when we support each other.

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CHAPTER 1

INTRODUCTION

Sewage sludge is a byproduct of wastewater treatment. It is mainly constituted of excess microorganisms that are produced during wastewater treatment as well as the pollutants in wastewater. As a semi solid mixture, water constitutes remaining fraction of sewage sludge. Water content of sewage sludge depends on treatment processes. For instance, dewatering is commonly used last step in sludge treatment process line. Therefore, sewage sludge leaves the system with typical moisture content of about 75%. Remaining is a mixture of organic and inorganic solids. Organic fraction of sewage sludge contains mostly carbon. Also, it contains nutrients like nitrogen and phosphorus in varying amounts. Other important feature of organic fraction of sewage sludge is that microorganisms, pathogens and trace organic pollutants such as PCBs (polychlorinated biphenyls), NPEs (nonylphenol ethoxylates) are present in sewage sludge. Inorganic fraction of sewage sludge includes constituents which are beneficial such as calcium, magnesium, iron, potassium and sodium as well as heavy metals such as cadmium, arsenic, chromium, copper, lead, mercury and so on.(Surampalli et al. 2009) Therefore, it can be said that uncontrolled disposal of sewage sludge to the environment causes risk on both nature and public health.

Traditionally, landfilling is the common method to dispose sewage sludge. However, due to limitations on available land and increasing quantities of sewage sludge production, this option is about to be abandoned. For instance, in Turkey, a person generates 40 gram sewage sludge on dry basis which yields approximately 3600 tons of sewage sludge per day. This makes a substantial amount of waste which should be handled.

Starting on 1980's landfilling of sewage sludge was started to be replaced by some beneficial use. Nutrient characteristics of sewage sludge is determined to be similar with industrial nutrients. As a result, use of sewage sludge as a fertilizer accepted as a potential replacement for landfilling. However, toxic characteristics of sewage sludge limits this option. Today, more stringent regulations are being applied as these toxic characteristics become clearer. Therefore, agricultural use of sewage sludge is determined to be an alternative for handling of sewage sludge while still a more sustainable solution is needed.

In 1990's use of sewage sludge in thermal processes became a topic of investigation since it offers a way of using the organic constituents (calorific value) of sludge by combustion processes. With this alternative, coal fired thermal power plants, cement production facilities, municipal solid waste incinerators became available for sewage sludge. In this option, heating content of sewage sludge is utilized to replace fuels in thermal processes (Werther and Ogada 1999).With these studies, it is determined that sewage sludge can substitute coal in such processes which results in both finding an alternative for management of sewage sludge and reduced use of primary fuel. However, the studies are limited since this is a recent approach in sludge management. Therefore, more information is needed especially in linking the wastewater and sludge treatment processes with the combustion characteristics of sludge.

In this context, this study aims to define thermal characteristics sewage sludge from different wastewater treatment plants and to investigate the combustion efficiency of sludge as an alternative fuel. Samples are obtained from six different wastewater treatment plants three times in a year to observe the effects of wastewater and sludge treatment processes on thermal characteristics of sewage sludge. On these samples, proximate and ultimate analysis are conducted in order to define thermal characteristics of sewage sludge. Thermogravimetric analysis (TGA) is studied to reveal processes on combustion of sewage sludge by means of kinetic analysis. Also, elemental composition of sewage sludge ash is determined by XRF analysis. These samples are combusted in a lab-scale batch combustion reactor and the combustion efficiencies are investigated.

The structure of the thesis is as follows. Chapter 2 in the following section provides a brief literature review. Then the materials and methods used to reach the aim of the study are described in Chapter 3. Chapter 4 summarizes and discusses the results obtained and a brief conclusion is given in Chapter 5. Finally in Chapter 6 suggestions for future work are provided.

CHAPTER 2

LITERATURE REVIEW

This chapter consists of three major topics. First, general information regarding treatment, disposal and thermal processing of sewage sludge are reviewed. Then, use of sewage sludge in thermal processes are discussed. Brief information about historical development of chemical reaction kinetics and its application to thermal decomposition of materials are stated. Finally, studies in literature regarding thermal decomposition of sewage sludge are also discussed.

2.1. Sources and Treatment of Sewage Sludge

Sewage sludge is a by-product of wastewater treatment processes. While wastewater is subjected to physical, chemical and biological operations to achieve removal of constituents in wastewater such as settle able solids, organic forms of carbon, nitrogen, phosphorus, treated wastewater and sludge are formed. According to process which is applied to wastewater, formed sludge has different characteristics (Sanin, Clarkson, and Vesilind 2011).

2.1.1. Sources of Sewage Sludge

Physical operations which are applied in wastewater treatment includes sedimentation and filtration processes. In primary sedimentation process, settle able solid content of wastewater is concentrated by gravity. Therefore, a semi-solid by product, called primary sludge, is formed (Metcalf 2002).

Chemical operations mainly consists of series of process which are called as coagulation, flocculation and sedimentation. Chemical processes are applied to wastewater to achieve flocculants of various constituents such as heavy metals or phosphorus. Sludge which is produced during chemical treatment of wastewater includes coagulants and flocculants which are introduced, also the constituent which is aimed to be removed from wastewater (Metcalf 2002).

Biological operations are applied in order to treat organic carbon, nitrogen and phosphorus content of wastewater. The idea of biological wastewater treatment process is to achieve removal of constituents in wastewater by forming an activated sludge which is concentrated in a tank where wastewater is introduced. In this process, biomass of activated sludge is fed with wastewater; while microorganisms use carbon and nutrients in wastewater as source of energy for reproductive activities, treatment of wastewater is achieved. However, excessive biomass is produced in this process and it is removed from the system (Anthony and Howard 2004). This portion of biomass is called as secondary (biological, excess) sludge (Henze 2002).

2.1.2. Treatment of Sewage Sludge

The main purpose of sewage sludge treatment is to increase dry matter content and achieve biologically stabilized residue. In order to increase dry matter content of sewage sludge, thickening, dewatering and drying are applied. Sludge stabilization is achieved by anaerobic, aerobic or chemical processes (Hartenstein 1981).

Sludge thickening is a preliminary process of sewage sludge treatment which is either used for increasing the concentration of biological sludge removed from activated sludge process (Mixon 1981), or obtaining a denser primary sludge. Sludge thickening process benefits from the effect of gravity as well as flotation. As the volume of water in sludge is reduced by %50, up to 5% solids content sludge can be obtained (Katz and Geinopolos 1967).

Sludge stabilization is the following sludge treatment process which is applied to thickened sludge. Stabilization can be achieved by either biological or chemical process. Biological sludge stabilization is operated under anaerobic or aerobic conditions. Activity of microorganisms in stabilization unit is enhanced in biological sludge stabilization process, therefore microorganisms are allowed to use organic fraction of sludge as source of energy. As a result, used organic fraction is converted into gas and stabilized residue (Werther and Ogada 1999).

Anaerobic sewage sludge stabilization is a biological sludge stabilization process which is conducted in the absence of oxygen. Typically, there are four steps in biochemical conversion of organic matter which is occurred in anaerobic digestion. Hydrolysis, acidogenesis, acetogenesis and methanogenesis are steps which are aimed to be achieved in anaerobic sludge stabilization process. Organic portion of sewage sludge is converted into methane, carbon dioxide and hydrogen sulphide; as well as solid residue which is removed from the system as effluent of the process. Remaining sludge residue is called as anaerobically stabilized sludge which has low pathogen content and relatively low biological activity (Appels et al. 2008).

Aerobic sewage sludge stabilization is another biological sludge stabilization process in which speeding up the endogenous respiration of microorganisms under the presence of oxygen is achieved. Organic fraction of sludge is oxidized to carbon dioxide and water and nitrification can also occur. Complex forms of organic matter contained in sewage sludge is oxidized to biologically stable products, therefore, structure of sludge after aerobic stabilization is shifted into simpler, more stable form (Turovskiy and Mathai 2006).

Cannibal sludge stabilization is a patented process that uses specialized microorganisms which have enormous biological activity. Excess biological activated sludge is directed into cannibal process tank. Therefore, similar to biological wastewater treatment process, cannibal microorganisms are actually fed with excess sludge. With minimal oxygen supply, this process achieves high solids removal efficiency. It is operated in a continuously mixed tank and effluent is discharged into biological wastewater treatment process, therefore, a solid separation unit is used to eliminate solids build-up in wastewater treatment unit (Siemens 2008).

Lime stabilization is a chemical stabilization process which involves the addition of quick lime (CaO) to sludge until pH reaches 12. Lime stabilization process can be applied to thickened and dewatered sludge in different processes (Christensen 1987). Increasing pH to 12 reduces pathogenic activity, prevents odor formation by enhancing reactions between calcium and sulfur and forms precipitates of heavy metals. Therefore, stabilized residue is formed ("Uses of Lime Biosolids and Sludge" 2013).

Sludge dewatering is applied after one of the sludge stabilization processes. The aim of dewatering is to reduce water content of sludge which yields lower transportation cost and reduces produced sludge mass. It is also applied to increase the mass loadings to sludge drying process, since it is easier to dry sludge which has lower moisture content. Stabilized sewage sludge which has %1-4 dry solids is transformed into a material which is called as 'cake' having %20-30 dry solids by dewatering. Pressure, vacuum or centrifugal forces are used in sludge dewatering process (Porteous). Decanters (High 1988), belt filters and vacuum filters are used as mechanical devices for dewatering process (Werther and Ogada 1999).

Sludge drying is the last step in sewage sludge treatment. It is used to achieve further volume reduction of sewage sludge, to obtain biologically stable material which allows for easier transportation or handling and to make sewage sludge usable in thermal process (Werther and Ogada 1999) which requires fully dried material such as thermal power plants or cement kiln (Stasta et al. 2006). Solar energy as well as thermal energy from combustion processes are used for sewage sludge drying. Use of solar energy is carried by spreading dewatered sewage sludge to a controlled land where high solar energy is available. Thermal drying of sewage sludge consists of two different mechanisms; direct drying is a high rate operation where high temperatures are reached. Indirect drying is achieved by countercurrent introduction of low temperature air to sewage sludge which is sprayed in a filter medium to obtain a thin film. Regardless, both methods of thermal drying enables sewage sludge having more than %90 dry solids content (G. Chen, Yue, and Mujumdar 2002).

2.2. Disposal and Beneficial Use of Sewage Sludge

Even though sludge goes through a treatment during which its unpleasant characteristics is amended and its volume is reduced significantly; at the end of treatment there is still a high quantity of material left behind. This part of sludge management is challenging since there are not so many options.

After treatment of sewage sludge, most typical application is to send to landfilling. It is the simplest operation which offers to handle sludge with least amount of cost. On the other hand, huge quantities of sludge could become a limiting factor where land is scarce. Therefore, in order to achieve sustainable sewage sludge management, alternatives to landfilling of sewage sludge have been used. Composting, agricultural usage and thermal treatment of sewage sludge are the most frequently used sewage sludge management alternatives.

Figure 2.1 shows that in 1985 landfilling consists the most widely applied sewage sludge disposal method in Europe. However, it has gradually been replaced by use of sewage sludge in thermal processes when it is realized that landfilling is out of option. It can be seen in Figure

2.2 that in 2004, application of landfilling is reduced significantly in developed countries of Europe.

Although landfilling of sewage sludge is aimed to be limited, it still constitutes the dominant management method in developing countries due to its low cost. However, trend is to apply more strict regulations to reduce the application of landfilling (H. Wang et al. 2008).

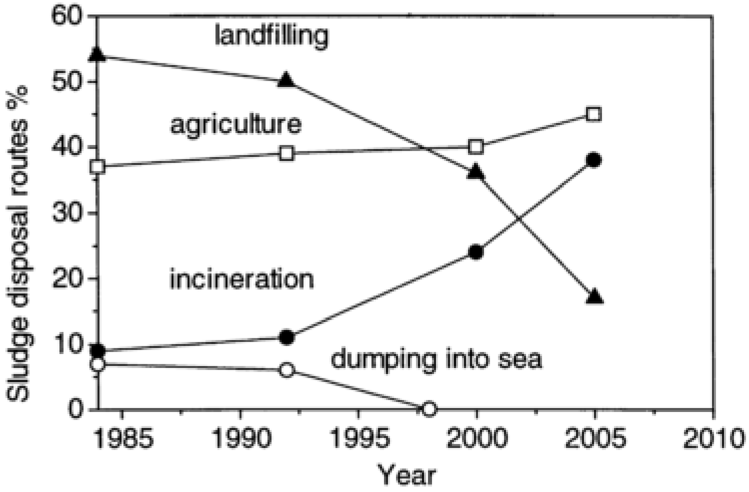


Figure 2.1 Projections for sewage sludge management in Europe (Werther and Ogada 1999)

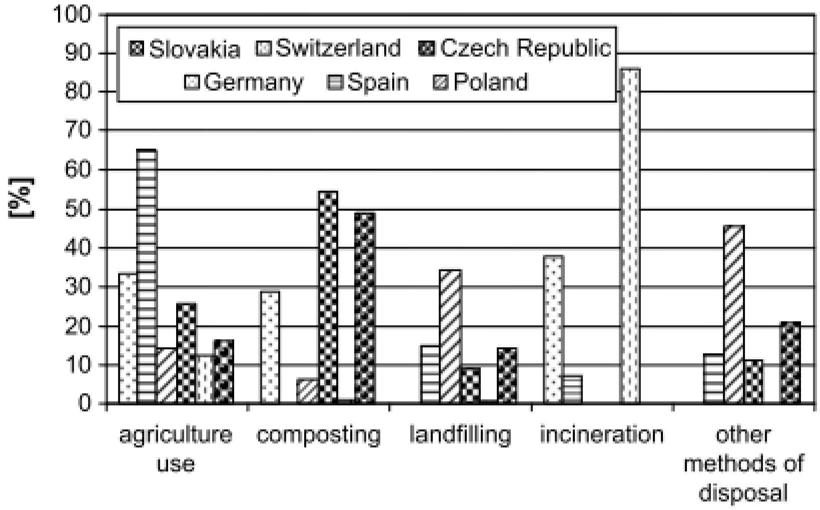


Figure 2.2 Sewage sludge disposal and beneficial use in Europe in 2004 (Stehlík 2009)

Sewage sludge have been considered as a candidate for replacement of industrial fertilizer due to its nutrient content (Fytili and Zabaniotou 2008). With sewage sludge usage in agriculture, energy need for production of industrial fertilizers could also be saved (Werther and Ogada 1999).

However, agricultural use of sewage sludge has been gradually restricted since it is regarded as risky due to the presence of pathogens, heavy metals and trace organic compounds in sludge (Manara and Zabaniotou 2012). Also, there are some technical difficulties of agricultural use of sewage sludge since sewage sludge is being produced continuously, while fertilizers are applied in certain periods of a year in agriculture. In addition, public opinion regarding sewage sludge is generally negative, therefore it brings a negative impact on agricultural use of sewage sludge (Fytili and Zabaniotou 2008). Summation of these factors yields that agricultural use may not be a sustainable solution for handling of sewage sludge.

Use of sewage sludge in thermal processes becomes an attractive solution since it enables both handling of sludge and substitution of primary fuels. Sewage sludge is an organic substance, in fact it has a calorific value close to brown coal in dry basis. Therefore, when it is dried, it is considered as a biomass, an alternative to primary fuels, to be used in thermal processes. Table 2.1 and 2.2 shows the calorific values of sewage sludge at different stages of treatment as well as its comparison with other common fuels, respectively.

Table 2.1 Heating value of various types of sewage sludge (Fytili and Zabaniotou 2008)

Type of sludge	Heating value (MJ/Kg of DS)	
	Range	Typical
Raw sludge	23–29	25.5
Activated sludge	16–23	21
Anaerobically digested primary sludge	9–13	11
Raw chemically precipitated primary sludge	14–18	16
Biological filter sludge	16–23	19.5

Table 2.2 Comparison of heating value of sewage sludge with other fuels/alternative fuels (Manara and Zabaniotou 2012)

Fuels	Heating value
Coal	14,600–26,700 kJ kg^{-1}
Plastics, wood, paper, rags, garbage	17,600–20,000 kJ kg^{-1}
Wood	16,000–20,000 kJ kg^{-1}
Dry sewage sludge	12,000–20,000 kJ kg^{-1}
Wet sewage sludge	1000–3000 kJ kg^{-1}
Gas-oil	45,500 kJ kg^{-1}
Black liquor	12,500–15,500 kJ kg^{-1}
Natural gas	38,000 kJ kg^{-3}
Coke-oven gas	19,000–22,000 kJ kg^{-3}
Synthetic coal gas	10,800 kJ kg^{-3}
Blast-furnace gas	4400–5300 kJ kg^{-3}

Thermal processes in which sewage sludge could be used involves numerous applications. Mainly, it can be divided into three categories, mono combustion, co-combustion and alternative process. Availability of various types of thermal processes also enhances the applicability of this option. Figure 2.3 lists thermal processes in which sewage sludge could be used. Sewage sludge could be introduced to mono-incineration systems and co-combustion systems. Mono incineration systems that is suitable for sewage sludge includes multiple hearth furnaces, smelting furnaces. Co-combustion systems refer sewage sludge addition in thermal power plants which operates fluidized bed or pulverized coal combustion. Cement factories can use sewage sludge as an alternative fuel as well. Also, there are other thermal processes where sewage sludge is suitable such as, wet oxidation, pyrolysis, and gasification and so on.

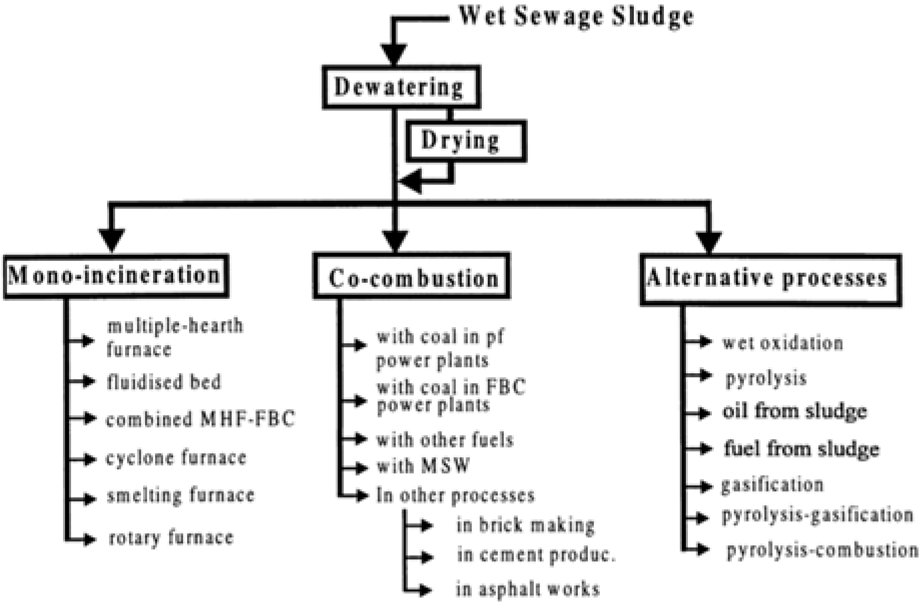


Figure 2.3 Processes which are available for thermal treatment of sewage sludge (Werther and Ogada 1999)

The fact that many thermal processes which can be used for sewage sludge management attracts attention to investigate the applicability of these processes on sewage sludge. Therefore, case studies regarding the use of sewage sludge in thermal processes are discussed in the following section.

2.3. Studies on Thermal Processing of Sewage Sludge

Literature regarding analysis of sewage sludge in combustion reactors involves investigation of partitioning of heavy metals, fate of PCDD/F's or monitoring of combustion gases, i.e. sulfur and nitrogen oxides. Studies on laboratory scale or pilot scale reactors, as well as industrial applications are reported for investigation of pyrolysis, gasification and combustion of sewage sludge. Laboratory and pilot scale combustion reactors are mainly consists of various types of fluidized bed reactors and drop tube furnaces. Cement factories, coal-fired power plants, municipal solid waste incinerators are common examples which are selected in investigation of use of sewage sludge in thermal processes.

2.3.1. Pyrolysis/Gasification of Sewage Sludge

Pyrolysis is the phenomena which defines solid substances' decomposition at temperatures around 300-350ºC. Presence of heat affects molecular bonds of materials which are forced to break and generate smaller molecules which may then form even bigger molecules. Nevertheless, the effect of heat alone causes materials undergo a thermal decomposition which is called as the phenomena of pyrolysis (Moldoveanu 2009).

Gasification is the process of obtaining gaseous fuel from a solid fuel. Application of this process can benefit from the phenomena of pyrolysis, as well as partial oxidation. In order to achieve gaseous substances out of a solid carbonaceous type of material (coal, biomass, sewage sludge etc.) hot steam, steam/air or even oxygen could be introduced. The material is converted to H_2, CO and CH_4 (Higman and Burgt 2008).

Investigation of sewage sludge pyrolysis mainly involves characterization of gaseous products. In the study which is conducted by Ishica et al. (2011), end products of co-pyrolysis of sewage sludge and clay mixtures. Effect of clay presence, mainly composed of a silica and aluminum oxide, is investigated by a lab scale, electrically heated furnace. Batches of dried sewage sludge and clay mixtures are subjected into furnace under the presence of nitrogen. CO, H_2 and CH_4 gases are continuously monitored by gas chromatography. As a result, it is reported that presence of clay reduces occurrence of CH_4 and CO while enhances H_2 formation (Ischia et al. 2011).

Characteristics of char which is obtained from gasification/pyrolysis process is studied in literature. A study conducted by Chun et al. (2011) investigates surface area, average pore diameter and average pore volume of char which is produced by pyrolysis of sewage sludge in a process called as combined screw/rotary kiln gasifier which is shown in Figure 2.4. In this complex process, produced hot steam is counter currently subjected to dried sewage sludge. End products of the process, gaseous products and char is sampled through gas outlet and char outlet, respectively. Analysis of gases which consists of H_2, CH_4, CO, CO_2 are conducted by a gas chromatograph. Tests on char consists of specific surface area determination, scanning electron microscopy (SEM) analysis of pores, energy dispersive X-Ray spectroscopy for chemical composition.

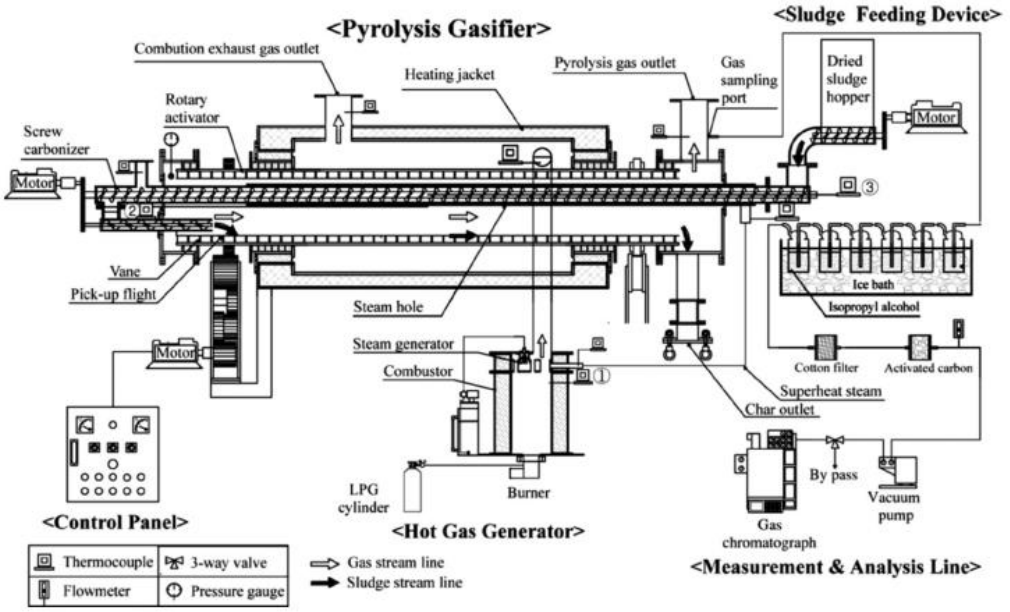
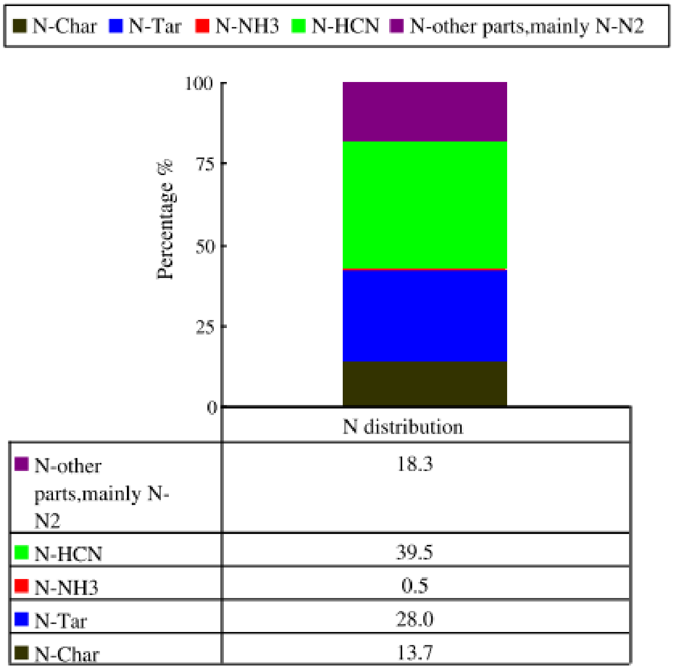


Figure 2.4 Schematic drawing of the process which is used for pyrolysis of sewage sludge sample (Chun, Kim, and Yoshikawa 2011)

Chemical composition analysis reveals that char consists large amount of carbon and oxygen, which contribute 95% of total mass. Remaining is inert alkalis and earth alkalines. Due to its carbon content, produced char shows adsorbent behavior with specific surface area and pore characteristics close to industrial activated carbon. It is also reported that composition of produced gases is associated with process variables, steam flow rate, operating temperature, moisture content of dried sewage sludge. However, under steady state conditions pyrolysis gas which has calorific value approximately 10000 kj/Nm^3 is produced.

While pyrolysis/gasification of sewage sludge is a promising technology which provides both valuable gaseous fuel and activated char, it involves some problems. Formation of NO_x precursors is a topic of investigation.

Since pyrolysis/gasification are typically carried in an inert atmosphere, nitrogen content of sewage sludge is not oxidized; it is converted to gaseous form as HCN and NH_3 which can be further oxidized to NO_x when they are emitted to atmosphere. Also, some portion of nitrogen could be gasified as N_2. Remaining nitrogen is contained in tar and char. Figure 2.5 shows forms of nitrogen contained in sludge as a result of sewage sludge pyrolysis (H. Chen, Namioka, and Yoshikawa 2011).



	N distribution
🟪 N-other parts,mainly N-N2	18.3
🟩 N-HCN	39.5
🟥 N-NH3	0.5
🟦 N-Tar	28.0
⬛ N-Char	13.7

Figure 2.5 Partitioning of nitrogen in sewage sludge pyrolysis(H. Chen, Namioka, and Yoshikawa 2011)

It is presented by Tian et al. (2002) that ratio of HCN and NH_3 formation is depended on temperature, at lower temperatures (around 400-500 ^oC), NH_3 is favored, on the other hand temperatures more than 700^oC is enough is to break bonds of amino acids in sewage sludge which increases HCN formation (F.-J. Tian et al. 2002).

Since organic part of sewage sludge is mainly consisted of volatile matter (Thipkhunthod et al. 2006), HCN represents 80% of gaseous forms of nitrogen which is contained in sewage sludge. Another important gaseous forms of nitrogen is NH_3. The process of formation of NH_3 is reported to be reactions between nitrogen and hydrogen at elevated temperatures and release of amino acids in lower temperatures.

However, gasification of sewage sludge is reported to be carried at high temperatures to promote the production of H_2. Operating temperature should be higher than 800C^o to increase reactivity of sewage sludge, which is lower than that of other alternative fuels such as paper, food wastes and plastics (Nipattummakul et al. 2010). One option could be co-gasification of sewage sludge with biomasses. It is reported that co-gasification of sewage sludge with wood chips, where ratio of sewage sludge in mixture is less than 50%, does not have a negative impact on syngas yield (Seggiani et al. 2012).

Another negative impact of sewage sludge pyrolysis is formation of tars. Tars, which are defined as organic compounds in evolved gases which have higher molecular weight than benzene (Mun, Kang, and Kim 2009). These organic materials cause severe impact on process equipment once they condenses. Therefore, minimization of tar formation is essential (Milne, Abatzoglou, and Evans 1998). Studies on minimization of tars by adjustment of operating conditions reveals that changing air supply on gasification process does have little impact on amount of tar produced (Phuphuakrat et al. 2010). Therefore, applicability of various adsorbents which can be installed as flue gas cleaners are studied. It is reported that venturi scrubbers and adsorbents made by sawdust efficiently remove tars made of light PAHs and phenols (Phuphuakrat et al. 2010). Also, waste oil is reported to be a good candidate for the removal of tar compounds which contains nitrogen (H. Chen, Namioka, and Yoshikawa 2011). Activated carbon is used for tar removal in which 90% tar removal could be achieved (Mun, Kang, and Kim 2009).

2.3.2. Combustion of Sewage Sludge

Basically, combustion is accepted as the oxidation process between a fuel and an oxidant in a controlled medium which results in heat release (Borghi and Destriau 1998). Fuels are defined as materials which produce heat when they react with an oxidant. Traditionally, non-renewable carbon based fossil materials are accepted as primary fuels and biomass other renewable materials are classified as alternative fuels (McAllister, Chen, and Fernandez-Pello 2011). Therefore, due to its organic content, sewage sludge could be classified as an alternative fuel and it could be used in combustion processes (Werther and Ogada 1999). Studies regarding sewage sludge combustion are published to investigate the effects of sewage sludge on combustion efficiency, ash characteristics, heavy metal partitioning and some other aspects of combustion.

Cement factories offer an option for sewage sludge utilization as an alternative fuel. A review conducted by Uson et al. (2013) states that along with other wastes and biomasses (municipal solid waste, meat and bone animal meal, end-of-life tires) sewage sludge could be used to replace primary fuels in cement production process. Especially, using alternative fuels, as well as sewage sludge in pre-calciner does not affect the quality of cement and performance of the combustion process. It is also reported that using alternative fuels at the main burner (in the rotary kiln) may bring some disturbances in flame characteristics due to high volatile content of such fuels. In case of sewage sludge, limitations occur when potassium and chlorine content is high. On the other hand, adsorbent capacity of cement raw material have an impact that heavy metal emission and PCDD/F emissions which result in sewage sludge combustion is low. Therefore, these advantages also favors sewage sludge use in cement factories, for both replacement of primary fuels and to sustain a clean, environmental friendly sludge management option (Aranda Usón et al. 2013).

Besides cement factories, there are full scale applications in coal fired thermal power plants. In Poland, such an application is investigated (Stelmach and Wasielewski 2008). As sewage sludge is substituted to coal as 1% by weight for 18 hours of operation, process variables are measured. Temperature distribution of combustion chamber, power output, heat losses and gaseous emissions are controlled. It is determined that substitution of coal with sewage sludge reduces boiler efficiency, temperature of combustion chamber and the thermal power output only by a slight amount. Heat losses are reported as a minor increase. While CO, NO_x, SO_2 HCl and HF are determined be relatively stable, sharp increase in TOC emission is observed. Therefore, it is concluded that use of sewage sludge in a coal fired thermal power as alternative fuel by an amount of 1% by weight does not upset the efficiency of combustion process and the efficiency of boiler during 18 hours of operation. Emissions apart from TOC are not harmfully affected either.

Emission profile of sewage sludge combustion is further investigated by Deng et al. N_2O, HCN, HCl, NO_x, SO_2 and some hydrocarbons such as methane, hexane, propane, benzene, and cyclohexane are measured as sewage sludge, coal and various sewage sludge coal mixtures are combusted. A lab scale, electrically heated fluidized bed reactor is used. It is observed that gaseous emissions; N_2O, HCN, HCl, SO_2 are increased sharply when sewage sludge is mixed with coal with a ratio of 1:1 by weight on dry basis. NO, CO, NO_2, NH_3 and HF are not affected. On the other hand, when sewage sludge is used alone, nearly all of concentration of gaseous products are doubled, including organic compounds. It is also reported that addition of CaO has a retarding effect on formation of these pollutants (Deng et al. 2009).

Sewage sludge combustion is investigated in lab scale drop tube furnace by Kim & Lee. Sewage sludge samples and a coal sample which is used in a full scale thermal power plant are studied. Continuous feeding is operated to achieve residence time as 1 second. For temperatures ranging from 1100ºC to 1400ºC combustion efficiency is measured. It is reported that at 1400ºC, both sewage sludge and coal yield the same efficiency. However, as temperature decreases yield of sewage sludge combustion decreases significantly when compared to coal sample (J. Kim and Lee 2010). Same trend is observed when temperatures kept constant but residence time is changed. While yields obtained in sewage sludge combustion are sensitive to change in residence time, yields with coal are not. Residence time lower than 0.8 second lowers yields dramatically. The reason for this observation is stated as higher temperature range of sewage sludge devolatilization.

An alternative approach could be the combustion of sewage sludge in a pressurized medium, so that energy which is stored in gaseous products of combustion could be used in a turbine. This kind of turbine is already available in automobile industry called turbocharger, which uses hot exhaust gases to produce power. Therefore, Murakami et al. (2009) proposes a process for an alternative to a conventional incineration plant in Japan which uses this technology. A pilot scale pressurized fluidized bed combustion reactor is built and a turbocharger with various supplementary units are installed. Results of sewage sludge combustion in a pressurized medium are better combustion efficiency and obtaining energy carrying exhaust gases which is converted to electricity in turbocharger. It is reported that steady state operations of sewage sludge combustion for electricity production in turbocharger is achieved. It is proposed that converting existed version of incinerator to new technology could save 25% of supplementary fuel need. Also, extra 50% energy which older incinerator required could be saved since these units are not used in proposed process. In addition, it is reported that average CO, NO_x and N_2O emissions of proposed technology are lower than older incinerator (Murakami et al. 2009). However, corrosive nature of fly ash which is produced in sewage sludge combustion is not mentioned.

In fact, formation of chlorine compounds becomes a subject of study which simulates combustion and gasification of sewage sludge in a pressurized medium. Potential forms of chlorine are calculated using *FactSage* chemical equilibrium software. Composition of sewage sludge and process conditions which represent combustion and gasification are determined. It is reported that HCl is the form of chlorine when sewage sludge is combusted at temperatures 800-1400^{o}K. Increasing oxygen concentration by applying more excess air results conversion of HCl to KCl. For gasification process, pressure and air excess (gasification gas i.e. H_2O) decreases formation of HCl (Wei, Schnell, and Hein 2005). It is a fact that chlorine and alkali compounds can promote corrosion which occurs in high temperature surfaces such as heat exchangers (Spliethoff 2010).

2.3.3. Characteristics of Ash Produced in Combustion of Sewage Sludge

It is known that alkali and earth alkaline compounds in biomass such as sewage sludge affects behavior of ash which is derived. Formation of deposits on surfaces like heat exchangers can occur when biomass is used extensively. Low fusion and melting temperatures of biomass ash is the reason of formation of deposits on various surfaces of a combustion unit, a phenomena called as *slagging* and *fouling* (Spliethoff 2010).

To quantify the relationship between ash composition of materials and their slagging/fouling tendency, such indices are used (Table 2.3). Basically, these indices depend on the ratio of alkalis and sulfur in ash composition.

Table 2.3 Empirical relations for slagging and fouling tendency of ash composition (S.-W. Park and Jang 2011a)

Classification	Index	Formula
Slagging	Base-to-Acid Ratio (B/A)	$\frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3}$
	Iron to Calcium Ratio (I/C)	$\frac{Fe_2O_3}{CaO}$
	Sulfur Ratio (Rs)	$\left(\frac{B}{A}\right) xS(in\ dry\ fuel)$
Fouling	Total Alkalis (TA)	$Na_2O + K_2O$
	Na2O Ratio (Rf)	$\left(\frac{B}{A}\right) xNa_2O$
	Fouling Ratio (Fu)	$\left(\frac{B}{A}\right) xNa_2O + K_2O$

Classification	Index	Tendency		
		Low	Medium	High
Slagging	Base-to-Acid Ratio (B/A)	<0.5	0.5<B/A<1	>1
	Iron to Calcium Ratio (I/C)	<0.31 or >3	<10.3 <I/C<3	≠1
	Sulfur Ratio (Rs)	<0.6	0.6<Rs<2	>2
Fouling	Total Alkalis (TA)	<0.3	0.3<TA<0.4	>0.4
	Na2O Ratio (Rf)	<0.2	0.2<Rf<0.5	<0.5
	Fouling Ratio (Fu)	≤0.6	-	0.6<Fu≤40

There are also equations which account for phosphorus. Since phosphorus is not involved in coal or any carbon based primary fuel, it is not inserted in original equations. However, to be able to quantify ash characteristics of biomass, it is added. Therefore, above equations have the following form;

Base-to-Acid Ratio: $B/A = \frac{Fe_2O_3+CaO+MgO+K_2O+Na_2O+P_2O_5}{Al_2O_3+SiO_2+TiO_2}$

Na_2O ratio (Rf), Fouling index (Fu), Sulfur ratio (Rs) are all dependent on B/A ratio. Therefore, calculation of these indexed are corrected according to new B/A.

A modelling study which uses chemical equilibrium tool for determining effects of sewage sludge-coal co combustion on slagging/fouling indices of generated ash reveals that addition of sewage sludge to coal at %15 results in severe slagging. High ash ratio of sewage sludge and composition of sewage sludge ash are stated as reasons (Plaza et al. 2009).

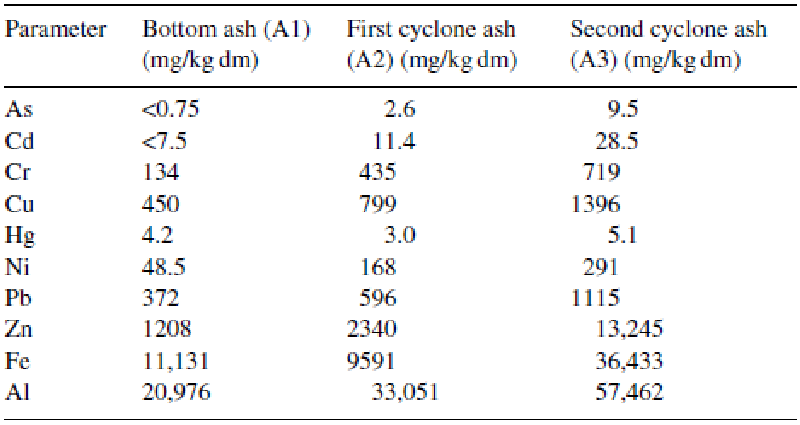
Experimental studies which are conducted on the composition of sewage sludge ash reveals that wastewater treatment and sludge treatment process have a high impact. A study which is conducted on two different sewage sludge sample which are originated from different plants where chemical phosphorus removal reports that chemical agent for phosphorus precipitation plays significant role in slagging/fouling index of sewage sludge ash. Use of $(Al(SO_4))_3$ or $(Fe_2(SO_4))_3$ differentiates the content of Al and Fe in ash composition (L. Wang et al. 2012).

Another aspects of sewage sludge ash is its ecotoxicological properties that is, the presence of heavy metals, PAHs, PCDD/Fs in ash, partitioning of such pollutants between bottom and fly ash.

Deng et al. (2009) studies the effect of sewage sludge addition to coal combustion by means of change in exotoxicological characteristics of ash. It is observed that in case where sewage sludge and coal mixed prior to combustion, concentration of PAHs and PCDD/Fs are increased. Both on flue gas and fly ash, PAH concentration which is originated from sewage sludge combustion is 4 to 10 times higher than the ones originating from coal combustion. PAH’s from mixture of sewage sludge – coal combustion lies somewhere between those values. However, it is concluded that sewage sludge addition to coal combustion up to 1:1 ratio increases the formation of PAHs, PCDD/Fs (Deng et al. 2009).

Heavy metal distribution between bottom and fly ash are reported to be in favor of fly ash. In a study conducted by Lapa et al. (2007) sewage sludge is mono-combusted in a pilot scale fluidized bed reactor where bottom ash and fly ashes from two cyclones are collected. As it is shown in Table 2.4, it is observed that heavy metal concentrations in latter cyclone ash is much higher than that of first cyclone and bottom.

Table 2.4 Partitioning of heavy metals during sewage sludge combustion(Lapa et al. 2007)



Parameter	Bottom ash (A1) (mg/kg dm)	First cyclone ash (A2) (mg/kg dm)	Second cyclone ash (A3) (mg/kg dm)
As	<0.75	2.6	9.5
Cd	<7.5	11.4	28.5
Cr	134	435	719
Cu	450	799	1396
Hg	4.2	3.0	5.1
Ni	48.5	168	291
Pb	372	596	1115
Zn	1208	2340	13,245
Fe	11,131	9591	36,433
Al	20,976	33,051	57,462

On the other hand, eluates of these ashes show that heavy metals contained in sewage sludge ash are trapped in the matrix. Similarly, lower toxic effects of ash eluates on selected indicator organisms are observed (Lapa et al. 2007). Same research group published another paper using same sewage sludge sample, same reactor but with a different rank of coal. Consequently, same results are obtained (Barbosa et al. 2009).

Mercury emissions are investigated in detail by Duan et al. (2010). In a pilot scale circulating fluidized bed reactor, formation, partitioning and control of mercury emissions are studied. Sample of investigation are selected as sewage sludge - coal mixture which are mixed by a ratio of 1:9. Partitioning of Hg between bottom ash, fly ash and flue gas as well as effect of calcium sorbents, excess air coefficient, SO_2 and NO_x on Hg concentrations are investigated. It is concluded that, due to high vaporization rate of Hg, more than 95% of total Hg is released to flue gas. Also, amount of Hg retains in fly ash is much higher than that of bottom ash. Form of Hg in flue gas is mainly Hg^0, because Cl content of both sewage sludge and coal is very low. Therefore, oxidation of Hg^0 to Hg^{+2} are not enhanced. Addition of calcium based adsorbents, CaO and $CaCO_3$ show some adsorption effect while CaO performs better. Increase in excess air also affects Hg adsorption in fly ash by changing combustion efficiency. Lowered combustion efficiency yields more unburnt carbon in fly ash. Consequently more unburnt carbon adsorbs Hg. SO_2 and NO_x increases formation of Hg^{+2} in flue gas by reacting with Hg^0. However, they do not have an effect on the concentration Hg in fly ash (Duan et al. 2010).

Studies on sewage sludge ash chemistry are expanded to recover phosphorus. Pettersson et al. (2008) published series of papers regarding leaching of heavy metal during phosphorus extraction from sewage sludge ash. Co-combustion of wood and sewage sludge in a 12MW circulating fluidized bed combustion is operated. Two sewage sludge samples are studied which originate from two different wastewater treatment plants. Both treatment plants use chemical precipitation for phosphorus removal. However, ferric sulphate and aluminum sulphate are used in these treatment plant separately. In operation three cases are applied; in first one limestone is subjected into combustion chamber in addition to sewage sludge – wood mixtures, in second case, hydrated lime is applied to bag filter to change ash composition and reduce HCl and SO_2. No lime is used in third case. As a result of operation, bottom ash, bag filter ash and secondary cyclone ash are obtained. Phosphorus extraction operation consists of reducing pH of collected ash samples to 0.5 – 2.5 by adding aluminum/ferric sulphate. It is observed that major part of phosphorus is concentrated on fly ash. Extraction process is applied efficiently where aluminum sulfate is used for both extraction agent and phosphorus removal in wastewater treatment plant. It is reported that 75-95% extraction of phosphorus from fly ash is achieved. In addition, it is concluded that application of limestone or hydrated lime for SO_2 capture does not positively or negatively affect phosphorus yield (Pettersson, Åmand, and Steenari 2008b).

Release of heavy metals during phosphorus extraction is investigated as the second part of the previous study (Pettersson, Åmand, and Steenari 2008a). It is reported that heavy metals apart from aluminum and cadmium are contained in the ash matrix, thus release of heavy metals to leachate is not observed. On the other hand, cadmium levels found in extracts are comparable to raw phosphorus rocks in various parts of the world. Aluminum levels are high since aluminum sulfate is used as extraction agent, however it is proposed that pH would be increased to form insoluble aluminum hydroxide. Therefore, it is concluded that phosphorus in ash which occurs by combustion of sewage sludge could be extracted in a leachate which shows similar characteristics with phosphorus mineral found in nature. The efficiency of extraction could be increased by using aluminum sulfate both as chemical precipitation agent of phosphorus in wastewater treatment plants and extraction agent of ash.

2.4. Kinetics of Sewage Sludge Combustion

2.4.1. Temperature Dependence of Chemical Reactions

Studies to define the behavior of solids under elevated temperatures are based on an application of transition state theory. Although transition state theory was developed for basic reactions which occurs in gaseous state (A. K. Galwey 2008), at the beginning of the second half of twentieth century, it started to be used for explaining the rate of decomposition of solids in thermal analysis. General expression which is used to define the temperature dependence of rate of decomposition of solids was stated as follows;

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad \text{Eq. 2.1.}$$

k(T): temperature dependence of rate of reaction (s^{-1}) ;
f(α): reaction model;

With these statement, rate of thermal decomposition of solids are assumed to be a function of temperature and progress of decomposition.

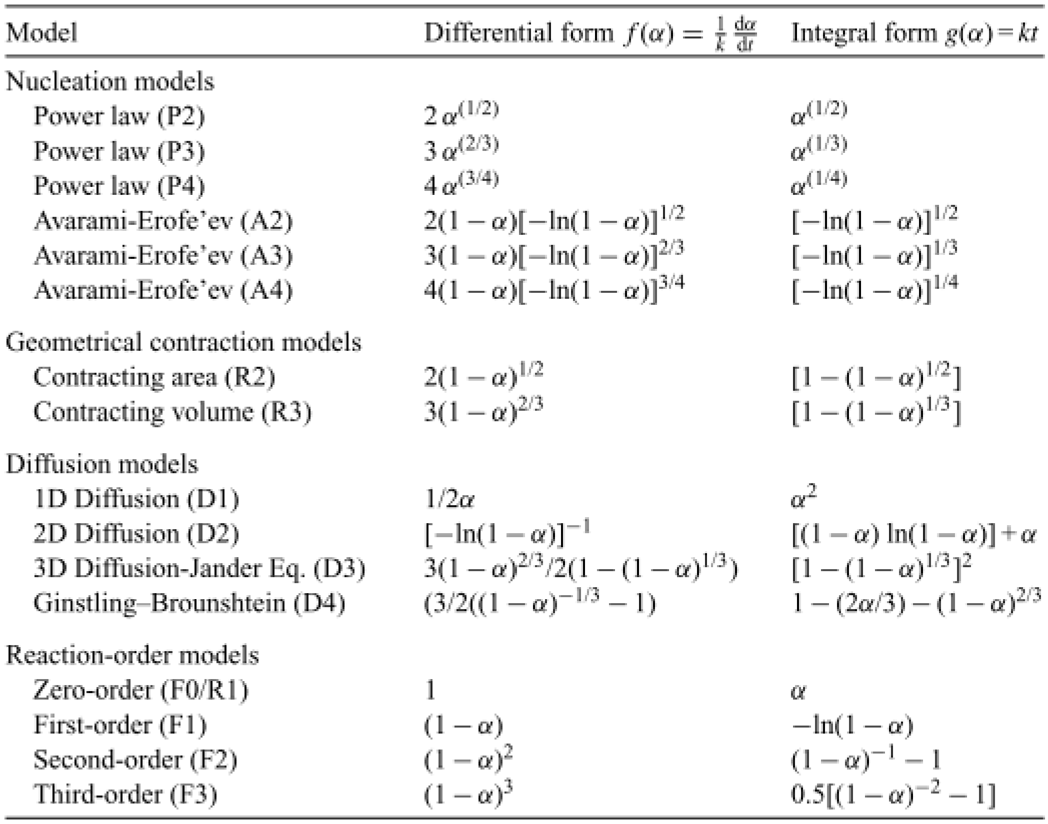
Temperature dependence of any chemical reaction is a subject where first studies were published 150 years ago. Amongst series of empirical approaches, Arrhenius Equation is accepted as the most widely used statement due to its simplicity and accuracy (Laidler 1984).

$$k(T) = Ae^{-E/RT} \qquad \text{Eq.2.2.}$$

A: Frequency factor (s^{-1});
E: Activation energy (j/mole);
R: Ideal Gas Constant (j/mole/K);
T: Temperature (K);

f(α) is used to define the kinetic model of thermal decomposition. Apart from other branches of chemistry, in the field of thermal analysis, reaction models represent the effect of progression of reactions to rate of reaction. Progress of reaction can either accelerate or decelerate the rate of reaction. Therefore, reaction models represent only this effect, rather than pathways or intermediate steps which occurs (Andrew K. Galwey 2004). Table 2.5 shows a number of different reaction models that are commonly used in the field of thermal analysis.

Table 2.5 Some forms of reaction models used in thermal analysis (Khawam and Flanagan 2005b)



Model	Differential form $f(\alpha)=\frac{1}{k}\frac{d\alpha}{dt}$	Integral form $g(\alpha)=kt$
Nucleation models		
Power law (P2)	$2\,\alpha^{(1/2)}$	$\alpha^{(1/2)}$
Power law (P3)	$3\,\alpha^{(2/3)}$	$\alpha^{(1/3)}$
Power law (P4)	$4\,\alpha^{(3/4)}$	$\alpha^{(1/4)}$
Avarami-Erofe'ev (A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Avarami-Erofe'ev (A3)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Avarami-Erofe'ev (A4)	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Geometrical contraction models		
Contracting area (R2)	$2(1-\alpha)^{1/2}$	$[1-(1-\alpha)^{1/2}]$
Contracting volume (R3)	$3(1-\alpha)^{2/3}$	$[1-(1-\alpha)^{1/3}]$
Diffusion models		
1D Diffusion (D1)	$1/2\alpha$	α^2
2D Diffusion (D2)	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
3D Diffusion-Jander Eq. (D3)	$3(1-\alpha)^{2/3}/2(1-(1-\alpha)^{1/3})$	$[1-(1-\alpha)^{1/3}]^2$
Ginstling–Brounshtein (D4)	$(3/2((1-\alpha)^{-1/3}-1)$	$1-(2\alpha/3)-(1-\alpha)^{2/3}$
Reaction-order models		
Zero-order (F0/R1)	1	α
First-order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
Second-order (F2)	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third-order (F3)	$(1-\alpha)^3$	$0.5[(1-\alpha)^{-2}-1]$

2.4.2. Kinetic Analysis of Thermal Decomposition of Solids

Earlier studies which uses the concept temperature dependence of chemical reaction for explaining rate of thermal decompositions of solids roots back from 1950's. In this earliest method, Kissinger uses the second derivative of Eq.2.1 to get relationship below (Kissinger 1956);

$$\frac{d(ln\frac{\beta}{T_{max}^2})}{d(\frac{1}{T_{max}})}=-\frac{E}{R} \qquad \text{Eq. 2.3.}$$

β = heating rate, dT/dt (K/s);

In this method, it is possible to calculate the activation energy which corresponds to the maximum value of mass loss rate. However, this method is limited to the maximum mass loss rate point, therefore activation energy value is calculated for a single point in whole conversion range.

However, there are numerous studies in literature which proposes a method to define rate of thermal decomposition, mainly by calculating Activation energy and frequency factor to obtain rate constant. These methods utilizes an approximation of the integral which is shown as below;

$$\int_0^a \frac{da}{f(a)} = A \int_o^t e^{-E/RT} dt \qquad \text{Eq. 2.4.}$$

$$\int_0^a \frac{da}{f(a)} = \frac{A}{B} \int_o^T e^{-E/RT} dT \qquad \text{Eq. 2.5.}$$

Since in 1960's softwares which is aided by powerful computers were not available, above integral which has not an exact solution is approximated by Doyle (1961) as below;

$$\int_0^a \frac{da}{f(a)} = g(a) = \frac{ART^2}{EB} e^{-\frac{E}{RT}} \qquad \text{Eq. 2.6.}$$

After the derivation of approximation of temperature integral, many methods to define kinetic triplet (reaction model, activation energy and frequency factor) is presented. These methods can be divided into two groups according to their approach to Eq. 2.1 and 2.2 as "isoconversional" methods and "model fitting" methods (Brown, Maciejewski, and Vyazovkin 2000).

Model Fitting Methods

Claiming that it is possible to derive kinetic triplet, the method often referred to as "Coats and Redfern" arouse an attention in the field of thermal analysis in 1960's. This method utilizes Doyle's approximation in order to derive such a relationship;

$$ln \frac{g(a)}{T^2} = ln \left[\frac{AR}{BE}\left(1 - \frac{2R\bar{T}}{E}\right)\right] - \frac{E}{RT} \text{ (Coats and Redfern 1965)} \qquad \text{Eq. 2.7.}$$

As it can be seen in Eq. 2.7, from a thermogravimetric data, kinetic triplet can be calculated. First, Integral form of reaction model is assumed, then using temperature data from experiment, a linear relationship can be constructed, yielding activation energy and frequency factor. Most satisfying relation is held for accepted assumption, and reaction model is determined (Coats and Redfern 1964).

However, studies have shown that (Ebrahimi-Kahrizsangi and Abbasi 2008) model fitting methods are incapable of distinguishing different assumptions on reaction models (Vyazovkin et al. 2011). They give unrealistic results for activation energy and frequency factor with coefficient of linearization close to unity (Khawam and Flanagan 2005a). Therefore model fitting methods should not be used for determining kinetic interpretation of thermal analysis data (Vyazovkin and Wight 1999).

Model Free Methods

In general, model free methods uses series of non-isothermal thermogravimetric data to utilize a linear relationship which is derived by an approximation of Eq. 2.5. According to the numerical approximation used, form of linear relationship is changed. However, a general form could be stated such as (Vyazovkin et al. 2011);

$$\ln\left(\frac{B}{T^x}\right) = Cons - y(\frac{E}{RT}) \qquad \text{Eq. 2.8.}$$

All of model free methods end up with different values for x and y according to approximation used for numerical integration of temperature integral (Eq. 2.5).

One of the most commonly applied model free method is called as "Ozawa-Flynn-Wall" method. It uses Doyle's approximation of integral equation in Eq. 2.5 for obtaining such a relationship that;

$$\ln(B) = -0{,}457\frac{E}{RT} + Constant \qquad \text{Eq. 2.9.}$$

Values taken from 3 or more experiment with different heating rates which corresponds to same conversion point should give a straight line which is used to calculate activation energy (Standardization 2005).

Another method which is named by its founders, "Kissinger-Akahira-Sunrose" uses linear relationship between heating rate and temperature for selected values of conversion.

$$\ln(B/T^2) = \ln(\frac{AR}{E}) - \frac{E}{RT} \qquad \text{Eq. 2.10.}$$

It can be seen that the approximation used in Kissinger-Akahira-Sunrose is actually Doyle's approximation which is carried one step further from Ozawa-Flynn-Wall method.

Burnham, converts the relationship which is used in Coats-Redfern model fitting to obtain an isoconversional method resulting (Burnham and Braun 1999);

$$\ln\left(\frac{B}{T^2\left(1-2R\frac{T}{E}\right)}\right) = -\frac{E}{RT} + \ln(-\frac{AR}{Eln(1-a)}) \qquad \text{Eq. 2.11.}$$

In order to calculate activation energy, first an initial value is assumed to derive the left hand side of the equation. Activation energy could be found after initiating iterative procedure.

Friedman method proposes an isoconversional method which requires no approximation of the integral equation. Natural logarithm of the differential form of the rate equation

$$\ln\left(\frac{da}{dt}\right) = lnA + lnf(a) - E/RT \qquad \text{Eq. 2.12.}$$

implies that series of T vs. ln(da/dt) should give a straight line which can be used to calculate activation energy (Friedman 1964).

Freeman and Carroll defined a method which is also called as Arrhenius method. Unlike isoconversional methods, one heating rate is sufficient to determine activation energy. General expression is converted to;

$$\frac{-E/R\Delta(\frac{1}{T})}{\Delta\ln(1-a)} = \frac{\Delta\ln(-\frac{d(1-a)}{dt})}{\Delta\ln(1-a)} - (1-a) \qquad \text{Eq. 2.13.}$$

And it is derived that $\frac{\Delta(\frac{1}{T})}{\Delta\log(1-a)}\ vs\ \frac{\Delta\log(-\frac{d(1-a)}{dt})}{\Delta\log(1-a)}$ should give a straight line with the slope of –E/2.3R (Freeman and Carroll 1958).

Advanced Methods in Kinetic Analysis

Distributed Activation Energy Model (DAEM) is an alternative approach which is used to define thermal decomposition kinetics (Primak 1955). Unlike model fitting or isoconversional methods, in this model, number of candidate reactions are found according to peaks observed in DTG profile. Then, activation energies which correspond to peaks are determined. Distribution of activation energy from peak value is assumed to have a certain statistical profile; Gaussian distribution is the most commonly used type. Then, using distribution of activation energies, frequency factor and form of reaction mechanism can be determined. The strength of this method is that it is possible to determine the amount and sequence of reactions which occur in an experiment.

Non-parametric kinetics (NPK) method uses a simple technique from Applied Mathematics field. *Singular Value Decomposition* is used to divide a vector into its components. Since it is accepted in thermal analysis that reaction rate profile is a vector which is a multiplication of functions of conversion and temperature, it can be used to differentiate reaction rate needless to do any predictions (Sempere et al. 2002). Non-isothermal experiments having different heating rates is proposed to be sufficient for determining kinetic triplet over a region of conversion (Ruiz-Femenia and Caballero 2011).

2.5. Studies on Thermal Analysis of Sewage Sludge

Earliest studies on thermal analysis of sewage sludge began in 1980’s. With differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) is used as main tool in thermal analysis of sewage sludge. As more sophisticated instruments become available, TGA were used in conjunction with mass spectroscopy (MS) and/or Fourier transform infrared spectroscopy (FTIR). The fundamental aim of thermal analysis which has been conducted for sewage sludge is generally limited to calculation of activation energy since the field of thermal analysis is not fully established for explaining rate of complex reactions which occurs in unknown mixtures, like sewage sludge. However, some studies tries to give insights regarding reaction kinetics of thermal decomposition of sewage sludge.

Urban and Antal published one of the earliest studies which considers sewage sludge as a candidate alternative energy source. In this perspective, thermal characteristics of sewage sludge is tried to be defined by using thermogravimetry and differential scanning calorimetry.

Using Friedman method, two zones were defined in which activation energy differs significantly. It is found that, as thermal conversion reaction continues, activation energy of unstabilized sewage sludge is raised from 120 kj/mole to 240 kj/mole (David L. Urban, Michael J. Antal 1982).

Another study which uses a differential method similar to Friedman as the method of calculation of activation energy determines a profile of activation energy throughout thermal conversion of sewage sludge. Pyrolysis is simulated in TGA by selecting carrier gas as nitrogen. According to the method of kinetic analysis, four experiments having different heating rates, 5, 10, 15, 20 ºC/min are conducted. Although it is concluded that activation energy of sewage sludge sample has a characteristic profile which is initially around 300kj/mole then a reduction to 200 kj/mole and goes up to 500 kj/mole, no other study regarding remaining kinetic triplet is presented. However, it is reported that CO_2, CO and CH_4 are main products of sewage sludge pyrolysis which consists of 70% of total gas produced (Othman et al. 2010).

Differential method of Friedman is used by Wu et al. (2006) with some derivations. An additional relation to Friedman method is presented to obtain frequency factor and order of reaction. It is assumed that if reaction follows reaction order mechanism, the relationship;

$$ln\left[\frac{{da}/{dt}}{e^{(-E(a)/RT)}}\right] = lnA(a) + n(a)\ln(1-a) \qquad \text{Eq. 2.14.}$$

Should give a straight line for correct n. However, since it is assumed that form of reaction model follows reaction order mechanism, it is failed to determine realistic results of frequency factor and order of reaction. Therefore, it is concluded that the material of the study, oil sludge has a complex behavior and it cannot be explained by simple reaction mechanisms.

Zhai et al. (2011) uses Arrhenius method to conduct kinetic analysis. Assuming reaction order mechanism, activation energy, frequency factor and order of reactions are calculated for volatile decomposition range of sewage sludge samples. Non-realistic reaction order values are accompanied by changing activation energy and frequency factor values which all contradicts with fundamental assumption of thermal analysis, kinetic triplet should not deviate with heating rate of samples. It has been reported that with the help of FTIR addition to TGA module, identification of various functional groups which corresponds to different phases of thermal decomposition of sewage sludge sample is achieved. However, it is stated that no additional interpretation of FTIR spectra is conducted, therefore, presented functional group is observed only visually by FTIR spectra.(Zhai et al. 2011) However, it is reported in literature that identification of functional groups from an unknown mixture (such as sewage sludge) requires some procedures (Windig and Guilment 1991). Ferrase et al. (2003) uses an approach known as SIMPLISMA to detect some of the components of evolved gas of TGA-FTIR analysis of sewage sludge. As a result, it is reported that detection and differentiation of constituents in evolved gas which is produced by thermal decomposition of sewage sludge requires statistical treatment of FTIR spectra.

“Ozawa-Flynn-Wall” is another popular method which is used in thermal analysis. Otero et al., use this method to obtain activation energy of samples which consists of sewage sludge - coal mixtures. Having supported with DSC, it is concluded that 10% sewage sludge addition to coal alters heat release and DTG profiles of coal significantly. Any addition lower that 10% does not cause dramatic change. It is reported that due to high volatile matter content of sewage sludge which tends to undergo rapid thermal decomposition reaction, addition of sewage sludge causes a shift in temperature – weight profile. Activation energy of coal, sludge and coal sludge samples were determined that highest one belongs to sewage sludge while coal has lowest activation energy. There is no additional interpretation to these results, also remaining kinetic triplet is not mentioned (M Otero et al. 2007).

Same research group, published series of papers (M Otero et al. 2008; M Otero, DÃ±ez, et al. 2002; M. Otero et al. 2006; Sanchez et al. 2009; M Otero et al. 2010; M Otero, Sánchez, and Gómez 2011; Marta Otero et al. 2008; M Otero, Calvo, et al. 2002; L.F. Calvo et al. 2004; M Otero et al. 2007) regarding thermogravimetric analysis of sewage sludge. In all these papers, combination of sewage sludge, coal and different biomass are selected as material of study. Ozawa-Flynn-Wall and/or Kissinger-Akahira-Sunrose are used as method of kinetic analysis. In kinetic analysis point of view, all papers are limited to calculation of activation energy. Although it is tried to compare activation energy values, practical results of activation energy comparison is not reported.

Xiao et al. (2010) uses a non-linear curve fitting method to determine kinetic triplet. In addition, experimental setup is conducted to observe the effect of air composition, therefore, 5 different gas composition from 30% Nitrogen - 70% Oxygen to 70% Nitrogen - 30% Oxygen is used for TGA experiments of sewage sludge, coal and sewage sludge – coal mixtures. In addition to basic conclusions of thermal analysis, like heating rate increases the maximum weight loss rate, it is reported that averaged activation energy over an interval of temperature differs as composition of air changes. This paper also assumes reaction model follows reaction order mechanism, however, calculated values of reaction orders have not a physicochemical meaning (Hanmin Xiao, Ma, and Liu 2010).

Non-linear curve fitting of DTG profiles is studied by Varhegyi et al. (2012) in conjunction with distributed activation energy (DAEM) model. In DAEM, peaks observed in DTG profiles are selected as candidates of reaction to be defined. Successive or parallel reactions could be assumed in this method, and a Gaussian distribution of reactions are assumed. As a result, it is reported that parallel reactions with reaction order mechanisms could adequately fit actual data. Activation energy of sewage sludge sample is calculated as 143 kj/mole for first reaction and 120 kj/mole for second reaction.(Várhegyi, Sebestyén, and Czégény 2012)

Distributed activation energy model has other uses in thermal analysis of sewage sludge. Having initial assumptions as parallel, many first order reactions which occurs in thermal conversion of sewage sludge. It is also assumed that activation energies which belong to corresponding reactions have Gaussian like distribution. Therefore, by using an algorithm which is derived by Scott et al. (2006) it is determined that rate of mass loss which belongs to different heating rates of corresponding TG experiments on sewage sludge is fitted with a good accuracy. Also, it is reported that activation energy of sewage sludge sample has a distribution between 100 kj/mole and 300 kj/mole.

It is reported that results of TGA experiments can be interpreted without kinetic analysis. Although it is not widely accepted, an ignition index and a combustion index are proposed. These values are determined by interpretation of TGA profiles and it is stated that it defines ignition, combustion and burnout time of samples. Vamvuka and Sfakiotakis (2011) use this approach on mixtures of coal and various types of biomass including sewage sludge. It is concluded that additive of biomass to coal increases its reactivity by reducing ignition temperature. In addition, it is reported that sewage sludge has a broader temperature range of thermal conversion than other biomass types (Vamvuka and Sfakiotakis 2011) Devolatilization of volatile compounds in sewage sludge starts at very low temperatures, around 130^{o}C, however temperatures where devolatilization ends reaches up to 580^{o}C, higher/equal than that of coal.

CHAPTER 3

MATERIALS AND METHODS

Sewage sludge samples from different wastewater treatment plants are taken to investigate the thermal properties of wastewater sludge. Dewatered/dried sewage sludge samples were taken from 6 different wastewater treatment plants. Dried, crushed and sieved sewage sludge samples are subjected to proximate, ultimate, thermogravimetric and X-Ray fluorescence analyses. Also, in a lab scale combustion reactor, mixtures of sewage sludge and a primary fuel are combusted at different proportions.

3.1. Wastewater Treatment Plants Investigated

Six wastewater treatment plants, having different wastewater and sludge treatment processes are included in this study. Treatment processes of wastewater treatment plants are listed in Table 3.1

Table 3.1 Wastewater treatment plants

Treatment Plants	Treatment Processes			
	Primary Clarifier?	Wastewater Treatment Process	Sludge Treatment Process	Sludge Dewatering/Drying
A	Yes	A2O	Anaerobic Stabilization	Dewatering + Drying
B	Yes	UCT	Anaerobic Stabilization	Dewatering
C	No	A2O	Cannibal Stabilization	Dewatering + Drying
D	No	A2O	Aerobic Stabilization	Dewatering + Drying
E	No	A2O	Lime Stabilization	Dewatering
F	Yes	A2O	Anaerobic Stabilization	Dewatering + Drying

A2O: Anaerobic-Anoxic-Oxic Biological Wastewater Treatment Process with Nutrient Removal
UCT: University of Cape Town Biological Wastewater Treatment Process with Nutrient Removal

From these wastewater treatment plants, sewage sludge samples were taken from the last line of sludge treatment process. In other words, they were taken at the effluent of either dewatering or drying process. The exception is for wastewater treatment plant E. In this treatment plant, lime stabilization is applied after dewatering process. Therefore, there are two kinds of sewage sludge which is produced in this treatment plant, one is dewatered and the other one is dewatered and lime stabilized sewage sludge. Sludge samples were collected three times throughout a year. List of sewage sludge samples which are taken from wastewater treatment plants are given in Table 3.2.

Table 3.2 Sewage sludge samples

	Date when sewage sludge sample was collected		
Wastewater Treatment Plants	October 2012	February 2013	May 2013
A	A-1	-	A-3
B	B-1	B-2	B-3
C	C-1	C-2	C-3
D	D-1	-	D-3
E	E1-1	-	-
	E2-1	E2-2	E2-3
F	F-1	-	F-3

Sewage sludge samples were collected 3 times at each treatment plant. However, due to logistic reasons, samples were taken from WWTP A-D&F twice. Also, lime stabilized sludge sample was collected once.

Collected sewage sludge samples were brought to Middle East Technical University, Department of Environmental Engineering laboratories for analysis and preparation.

3.2. Characterization of Sewage Sludge Samples

As a first stage of sample preparation, all samples were brought to similar degrees of moisture content. In order to achieve similar moisture content, dewatered samples were air dried at 40°C in an oven for 3-4 days. This pretreatment allows to obtain more than %90 dry matter for a sample, which is the same dry matter content of sewage sludge sample dried at wastewater treatment plant.

After drying, all samples are sieved to 60 mesh sieve size in order to minimize the effect of different particle sizes.

3.2.1. Proximate Analysis

Proximate analysis constitutes determination of moisture, volatile matter, fixed carbon and ash. In order to carry the analysis, first moisture of samples were determined. Moisture is determined by measuring weight loss of samples at 105^{o}C at 2 hours. On the other hand, volatile matter and ash is determined by weight loss at 550 ^{o}C and 750 ^{o}C at 2 hours, respectively. After determination of weight loss at given temperatures, fixed carbon is calculated by the difference of volatile matter and ash from unity at dry basis.

3.2.2. Ultimate Analysis

First set of parameters which are determined in ultimate analysis are carbon, hydrogen, nitrogen, sulfur and oxygen. This analysis is conducted by Truspec Leco CHN-S analyzer at Middle East Technical University, Department of Environmental Engineering. Dried sewage sludge samples are introduced to auto sampler of the device, then content of carbon, nitrogen and hydrogen could be determined simultaneously. There is an add-on for this device to analyze sulfur content which has similar configuration with the main device. Oxygen is calculated by the difference of carbon, nitrogen, hydrogen and ash from unity. Figure 3.1 shows a picture of Truspec Leco CHN-S analyzer.

Figure 3.1 Truspec Leco CHN-S elemental analyzer

Determination of calorific value of samples is also carried in ultimate analysis. A Leco AC 500 Bomb Calorimeter device in Middle East Technical University, Department of Environmental Engineering is used in this experiment. Samples were placed to the holding of the vessel of device and a complete combustion is achieved in medium which is pressurized using pure oxygen. Amount of heat generated in combustion process yields calorific value of samples. A picture of Leco AC 500 Bomb Calorimeter is given in Figure 3.2.

Figure 3.2 Leco AC 500 calorimeter

3.2.3. Micro X-Ray Fluorescence (XRF) Analysis

Determination of inorganic content in sewage sludge ash is carried as the last set of analysis which is conducted in this study. XRF is used as the experimental procedure for this purpose. In XRF anaylsis, sample is fluxed with sodium tetraborate at 1100°C to achieve loss of organics on ignition. Remaining inorganic content of sample pelletized prior to analysis(“Mikro-X Ray Fluoresans (μXRF)” 2013). Major inorganic contents of sample, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn and Fe are determined by this analysis. XRF Analysis is done by Institute of Earth Science, Ankara University.

Data obtained from XRF analysis are used to determine slagging/fouling indices of sewage sludge samples. Then, these values are compared with the limit values that are set in literature. Detailed discussion about slagging/fouling and determination of slagging/fouling indices are reviewed in Section 2.3.3.

3.3. Thermogravimetric Analysis (TGA) of Sewage Sludge Samples

The idea of TG Analysis is measuring the weight and temperature of sample at a constant frequency, i.e. 8 measurement per second in a controlled temperature program. Sample could be either heated at a particular heating rate or exposed to a fixed temperature. At the end of experiment, vector of weight loss and temperature rise both with respect to time are obtained.

In this study, TG Analyses of sewage sludge samples were conducted by Middle East Technical University, Central Laboratory. The instrument, whose picture is given in Figure 3.3, used in this study is Perkin Elmer Pyris STA 6000.

Figure 3.3 Perkin Elmer Pyris STA 6000 TG analyzer

3.3.1. Experimental Procedure

In this study, sewage sludge samples were subjected to TG Analysis. 20 mg dried and sieved sludge samples were introduced to the analyzer. Temperature program is selected as a constant non-isothermal run. That is, sewage sludge samples are heated at a constant heating rate. Each sludge sample is subjected to four non-isothermal run with 4°C/min, 8°C/min, 16°C/min, 32°C/min as heating rate. However, prior to each non-isothermal run, first an isothermal run was conducted at 105°C for 20 minutes to ensure complete moisture loss. Air is selected as medium which is fluxed through the sample with the flow rate of 40 mL/min. Experimental setup of this study is listed in Table 3.3.

Table 3.3 Experimental setup of TGA

Sample Name	Gaseous Medium	Temperature of Isothermal Run (°C)	Duration of Isothermal Run (min)	Heating rate of Isothermal Run (°C/min)	Temperature Range of Non-Isothermal Run (°C)
A-1, B-1, C-1, D-1, E1-1, E2-1, F-1	Synthetic Air (21% Oxygen - 79% Nitrogen	105	20	4, 8, 16, 32	105-950

As it can be seen on Table 3.3 only the first group of samples (October 2012) were involved in TGA. Each sample was analyzed four times with the heating rate of 4, 8, 16, 32°C/min from 105°C to 950°C. Again each sample was first exposed to an isothermal mass loss at 105°C before every experiment. Therefore, 28 TGA curves which belongs to 7 different samples were obtained in this study.

At the end of each experiment, weight loss curve and temperature rise curve is obtained as sample is heated. Due to reactions which takes place during experiments, heating program of sample i.e. 4ºC/min, 8ºC/min etc. does not match with sample's actual heating. Since a constant heating program is applied in experiments, derivative of weight loss and temperature rise with respect to time can be derived. Therefore, 4 curves, weight loss, sample temperature rise, derivative of weight loss with respect to time and derivative of sample temperature rise with respect to time are obtained.

3.3.2. Data Treatment

Data treatment of TG experiments consists of two operations. First operation is *smoothing the derivative curve* and second operation is normalization of parameters to mass loss curve.

3.3.2.1. Derivation and Treatment of Reaction Rate and Heating Rate Curves

First step in data treatment of experiments is defining a basis for weight loss curves which allows to compare different experiments. Although mass of sample which is analyzed was tried to be kept as constant, there are small differences. Weight of samples which are used in TG experiments are listed in Table 3.4.

Table 3.4 Samples subjected to TGA

	4 (ºC/min)	8 (ºC/min)	16 (ºC/min)	32 (ºC/min)
A1-1 (mg)	20.487	19.903	20.189	20.063
B1-1 (mg)	19.971	20.953	21.763	19.751
C1-1 (mg)	14.796	15.039	16.062	15.039
D1-1 (mg)	20.394	19.906	20.714	20.769
E1-1 (mg)	14.876	15.232	14.876	15.232
E2-1 (mg)	15.581	15.568	14.788	15.826
F1-1 (mg)	20.869	19.776	21.159	20.944

In addition to initial weight of samples, their final weight also varies extensively. In order to prevent the systematic error which could be caused by this difference, weight loss is defined as the **extent of conversion** which is referred as **α** with such relationship;

$$\alpha = \frac{w - w_f}{w_i - w_f} \qquad \text{Eq. 3.1.}$$

where;
α: extent of conversion,
w: weight of sample at time t;
w_i: initial weight of the sample;

w_f: final weight of the sample.

Using the relationship above, it is possible to define weight loss curves where values of "α" changes from 0 to 1, meaning 0 as the beginning of experiment while 1 as the end of the experiment. Therefore, variation of initial and final weights of the samples are brought to the same basis.

After defining extent of conversion of samples, derivative of weight loss with respect to time and derivative of sample temperature rise with respect to time curves are obtained through simple differentiation operation as given in Eq. 3.2 and Eq. 3.3.

$$\left({}^{d\alpha}/_{dt}\right)_i = \frac{a_i - a_{i+1}}{t_i - t_{i+1}} \qquad \text{Eq.3.2.}$$

$$\left({}^{dT}/_{dt}\right)_i = \frac{T_i - T_{i+1}}{t_i - t_{i+1}} \qquad \text{Eq.3.3.}$$

where;

$\left({}^{d\alpha}/_{dt}\right)_i$: derivative of extent of conversion with respect to time, rate of reaction,

$\left({}^{dT}/_{dt}\right)_i$: derivative of temperature rise with respect to time, heating rate, β

However, due to the nature of the differentiation operation, resultant derivatives contains too much noise. In order to overcome this problem, Savitzky-Golay filtering(Caballero and Conesa 2005) is used through a MATLAB 2012a© code and one sample illustration is given in Figure 3.4. Sample codes are given in Appendix C.

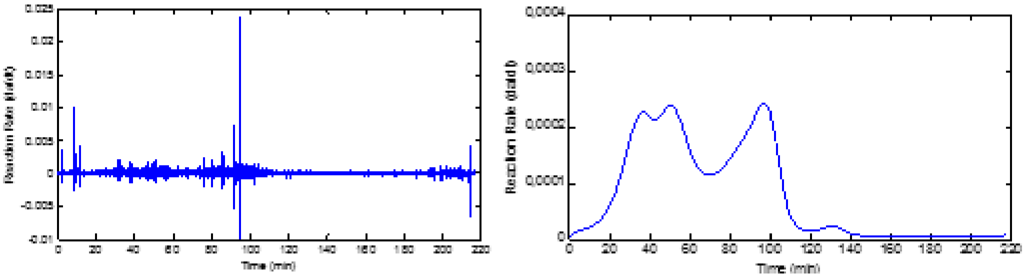


Figure 3.4 The effect of Savitzky-Golay filtering

3.3.2.2. Normalization of Data

Next step of data treatment involves interpolating resultant curves for certain extent of conversion values. It is a fact that application of four different heating program yields above mentioned curves having different size. That is, since temperature interval in all experiments is constant, from 105°C to 950°C, amount of measurement which takes place differs from one heating program to another. For instance, in 4ºC/min heating rate program, there are 105,000 measurements while in 32ºC/min, measurements are reduced to 13,125. Table 3.5 shows the amount of measurement which is done at each experimental setup.

Table 3.5 Measurements done in TG experiments

Heating Rate	4 (ºC/min)	8 (ºC/min)	16 (ºC/min)	32 (ºC/min)
Number of Measurements	105000	52500	25250	13125

In order to obtain reaction rate, heating rate and temperature rise profile throughout extent of conversion, an interpolation operation is done. In this operation, values of these curves for certain values of extent of conversion is determined. The range of extent of conversion selected is 0,010 to 0,980. Therefore, for each extent of conversion point, values of reaction rate, heating rate and sample temperature is calculated using a MATLAB 2012a© operators, *polytool*, *polyfit* and *polyval.* Sample codes are given in Appendix C. Resultant vectors have the following form which is shown in Table 3.6.

Table 3.6 Final form of experimental data

Extent of conversion, α	Sample Temperature, ºC	Sample Heating Rate, ºC/min	Reaction Rate, α/min
0,010	T_1	β_1	δ_1
0,011	T_2	β_2	δ_2
.	.	.	.
.	.	.	.
.	.	.	.
0,980	T_{971}	B_{971}	δ_{971}

The application of interpolation of temperature, heating rate and reaction rate over extent of conversion allows for obtaining same sized vectors whose original size is different. Also, it is possible to derive the change of temperature, heating rate and reaction rate as extent of conversion increased, that is, as the experiment continues.

3.3.3. Kinetic Analysis

Kinetic analysis of samples contains three subtopics; determination of activation energy, calculation of reaction rate and its comparison with actual data and specifying the appropriate reaction model.

3.3.3.1. Determination of Activation Energy

In this study, the method which is derived by Friedman (1964) is used for calculation of activation energy. Rate of reaction for thermal decomposition of solid generally described by the relationship is turned into;

$$\left({}^{da}\!/_{dt}\right) = Ae^{-Ea/RT}f(a) \qquad \text{Eq. 3.4.}$$

where;

$\left({}^{da}\!/_{dt}\right)$: Reaction rate,
A: Frequency factor,
E_a: Activation energy,
T: Temperature,
R: Ideal gas constant,
f(α): Reaction model,

It should be kept in mind that reaction rate, frequency factor, activation energy, temperature and reaction model are functions of extent of conversion. Section 3.3.2.2 explains the procedure for data treatment and Table 3.6 shows that the only independent variable is the extent of conversion “α”.

Taking natural logarithm of both side;

$$\ln\left(\frac{da}{dt}\right)_{\alpha} = lnA_{\alpha} + lnf(a) - E_{\alpha}/RT_{\alpha} \qquad \text{Eq. 3.5.}$$

Using data of parallel experiments of a sample with four different heating rates, series of T_α and $\left(\frac{da}{dt}\right)_{\alpha}$ which correspond to extent of conversion values are obtained. For each point of extent of conversion, linear correlation of parameters could be derived.

$$slope = -E_a/R \qquad \text{Eq. 3.6.}$$

$$intercept = lnA_a + lnf(a) \qquad \text{Eq. 3.7.}$$

Activation energy of sample is calculated by using slope of linear relationship. Also, coefficient of correlation for each correlation is determined. High correlation coefficient ensures the reliability of activation energy.

In this study, the method of activation energy calculation is limited to Friedman Method only. Integral model free methods and model fitting methods, which are explained before, are omitted due to their assumptions and limitations.

3.3.3.2. Calculation of Reaction Rate

Quality of data obtained in TG experiments can be checked by fitting calculated reaction rate with actual reaction rate data. In order to calculate the reaction rate;

$$\left({da}/{dt}\right)_{calculated} = Ae^{-Ea/RT}f(a) \qquad \text{Eq. 3.8.}$$

the above expression is used. On the other hand, actual reaction rate is determined by using experimental data in Eq. 3.9;

$$\left({da}/{dt}\right)_{actual} = \frac{a_i - a_{i+1}}{t_i - t_{i+1}} \qquad \text{Eq. 3.9.}$$

Therefore, it is possible to compare these two profiles to check whether Friedman Method successfully defines the activation energy and the reaction rate.

3.3.3.3. Identification of Reaction Model and Frequency Factor

Determination of remaining kinetic triplet, frequency factor and reaction model, is the next step once it is proven that Friedman Method works properly. First of all, the relationship;

$$intercept = lnA + lnf(a) \qquad \text{Eq. 3.10.}$$

is taken as the starting point. It is a fact that reaction model has particular forms which are stated throughout the history of thermal analysis. Table 3.7 summarizes these reaction models (Vyazovkin et al. 2011).

Table 3.7 Reaction models used in kinetic analysis (Vyazovkin et al. 2011)

Reaction Model	Code	f(α)	g(α)
Nucleation Models			
Power Law	P2	$2\alpha^{(1/2)}$	$\alpha^{(1/2)}$
Power Law	P3	$3\alpha^{(2/3)}$	$\alpha^{(1/3)}$
Power Law	P4	$4\alpha^{(3/4)}$	$\alpha^{(1/4)}$
Avarami-Eforeev	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{(1/2)}$	$[-\ln(1-\alpha)]^{(1/2)}$
Avarami-Eforeev	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{(1/3)}$	$[-\ln(1-\alpha)]^{(1/3)}$
Avarami-Eforeev	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{(1/4)}$	$[-\ln(1-\alpha)]^{(1/4)}$
Geometrical Contraction Models			
Contracting Area	R2	$2(1-\alpha)^{(1/2)}$	$1-[(1-\alpha)^{(1/2)}]$
Contracting Sphere	R3	$3(1-\alpha)^{(2/3)}$	$1-[(1-\alpha)^{(1/3)}]$
Diffusion Models			
1D Diffusion	D1	$1/(2\alpha)$	α^2
2D diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	$[(1-\alpha)\ln(1-\alpha)]+\alpha$
3D Diffusion-Jander Eq	D3	$[3(1-\alpha)^{(2/3)}]/2(1-(1-\alpha)^{(1/3)})$	[1-(1-α)^1/3]^2
Ginstling-Brounshtein	D4	$3/2((1-\alpha)^{(-1/3)}-1)$	$1-2\alpha/3-(1-\alpha)^{(2/3)}$

Reaction Order Models			
Zero Order	FO-R1	1	α
First Order	F1	1-α	-In(1-α)
Second Order	F2	$(1-\alpha)^2$	$(1-\alpha)^{-1}$ -1
Third Order	F3	$(1-\alpha)^3$	$0.5[(1-\alpha)^{-2}-1]$

The idea is to assume a reaction model and to generate frequency factor which corresponds to the model. Since reaction models stated above has particular values over extent of conversion, frequency factor, which is valid for assumed reaction model, could be derived using intercept relationship mentioned above. As a result, 16 pair of reaction model and frequency factor is generated for a sample.

After construction of frequency factor – reaction model pairs, next step involves finding which pair actually explains thermal decomposition of sample. In order to do this, **time vector** is defined with the following statement (Vyazovkin et al. 2011);

$$t(a) = g(a)/Ae^{-Ea/RT} \qquad \text{Eq. 3.11.}$$

where,
t(α): time vector,
g(α): integral form of reaction model,
A: frequency factor,
Ea: activation energy,
R: ideal gas constant,
T: sample temperature.

There is also an ASTM standard (ASTM E1641-07, Standard Test Method for Decomposition Kinetics by Thermogravimetry) which utilizes Eq. 4.6 by defining g(α) as a first order reaction (ASTM E 1641-07).

Since frequency factor, activation energy, reaction model are vectors where extent of conversion is independent variable, result is also a vector which represents time expired for unit change in extent of conversion.

Therefore, if actual sample temperature profiles are used in this equation, one should be able to calculate how much time has passed to achieve certain degree of conversion during an experiment. Also, above equation can be used to compare reaction model assumptions, which lead different time requirement predictions.

It is also possible to compare derivatives of time predictions and actual data. From a TG result, derivative of time passed with respect to unit change in extent of conversion can be calculated. Moreover, results obtained from time vector is suitable to be differentiated with respect to unit change in extent of conversion. Therefore, comparison of predictions and actual data can be done in differentiated form.

Regardless of the form of the comparison, either integral of differentiated form, this method can successfully separate reaction model forms and create such predictions which are comparable with experimental data. Best fit over a particular region of extent of conversion is considered as descriptive reaction model. Going backwards, once a reaction model holds true over a region, frequency factor which corresponds to reaction model becomes correct. Therefore, kinetic parameters of sample over a particular region could be defined.

3.4. Laboratory Scale Combustion Experiments of Sewage Sludge Coal Blends

In order to assess the quality of sewage sludge as an additive fuel in thermal processes, a laboratory scale combustion setup was used. In combustion experiments, pelletized sewage sludge-coal mixture samples are burned in an electrically heated furnace at a fixed temperature. Approximately 0.17 gr of pellets with 5 mm diameter and several millimeters height are used as detailed information could be found in Section 3.4.2. Experimental setup used in this study is a batch reactor, therefore, only one pellet is burned at a time. Cylindrical quartz reactor has dimensions of 50 mm diameter and 1200 mm height.

The effect of sludge addition to coal is observed by analyzing the gaseous products of combustion process. Experimental setup is shown in Figure 3.5.

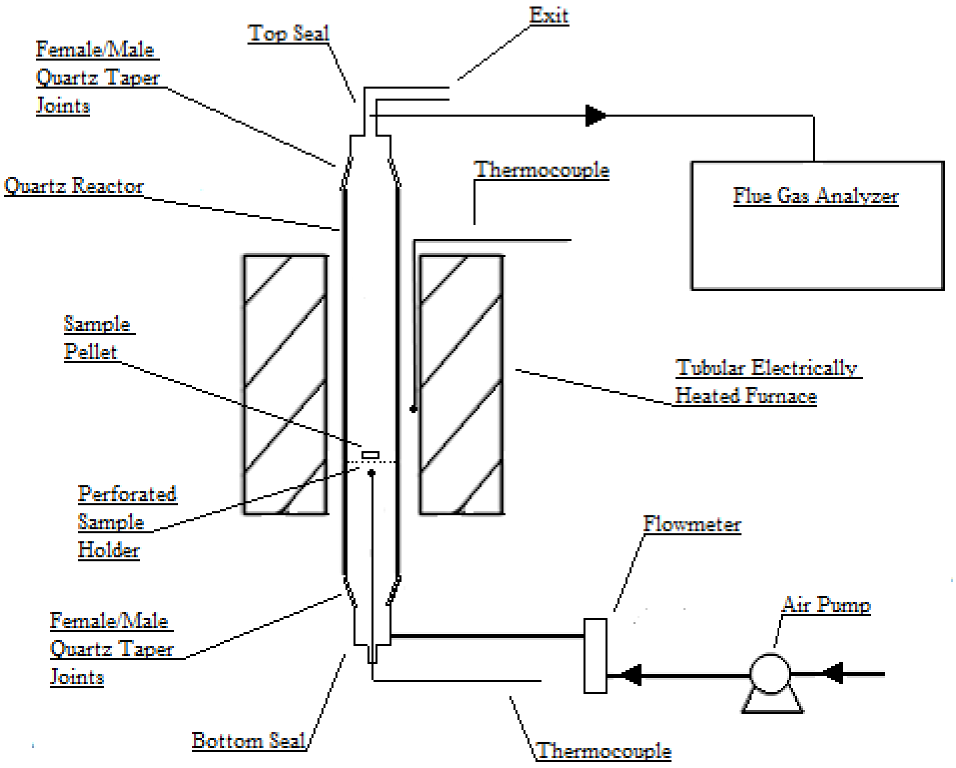


Figure 3.5 Diagram of lab scale combustion setup

At the beginning of combustion experiments, cylindrical quartz reactor is heated by the tubular electrically heated furnace. Temperature of the furnace can be set up to 1100°C, however, combustion temperature is set to 900°C to ensure the protection of quartz reactor from extreme temperatures. Thermocouples located close to furnace wall in the combustion zone allow adjusting the temperature of the furnace, so that temperature of the combustion zone is 900°C.

When the temperature of the combustion zone reaches to 900°C, air is introduced from the bottom of the reactor. Flow meter is used to adjust the flow rate of air given to the reactor. After that, top seal of the reactor is opened to drop the sample pellet into the reactor and is closed quickly. Pellet instantly reaches to the combustion zone of the reactor and combustion starts instantaneously. After the seal at the top of the reactor is closed, the gas analyzer starts sampling the flue gas. Combustion is finished when oxygen concentration of the flue gas reaches back to the atmospheric concentration, which is 20.9%.

3.4.1. Flue Gas Analyzer

O_2, CO_2, CO, NO, NO_2 and SO_2 in the combustion gas are continuously monitored by Madur Photon flue gas analyzer. The analyzer consists of two units; first unit, which is called as PDG-100, is used for conditioning of flue gas. Moisture in the flue gas is trapped in this unit. Therefore, results of analysis are reported on dry basis. Also, filtration of solid particles in the flue gas is done in this unit.

Figure 3.6 Madur photon flue gas analyzer

Conditioned flue gas is analyzed in Photon unit. O_2 and CO_2 is measured in % by volume, other gases are measured in ppm. Unit conversion of gases which are measured in ppm is also available in the Photon unit; therefore it is possible to convert results to “mg/Nm^3” or “mg/Nm^3 relative into %10 O_2”.

3.4.2. Sample Preparation for Combustion Experiments

First set of sewage sludge and a coal samples are selected to investigate sewage sludge – coal combustion. Temperature of combustion can be predetermined by using temperature control program of the electrically heated furnace and it is selected as 900°C, which is the highest available temperature for the furnace. In order to observe the effects of sewage sludge addition to coal during combustion, sewage sludge – coal mixtures are prepared with varying percentages of sludge added to coal in order to create batches of sewage sludge – coal mixtures. Also, the capacity of the reactor used in this study is determined as 1000 cal, therefore mass of each batch is calculated so that each batch will have a calorific value of 1000 calories. Experimental conditions are listed in Table 3.8.

Table 3.8 Experimental conditions of combustion experiments

Sewage Sludge Sample	Percentage of Sewage Sludge in Mixtures on Energy Basis (β)	Temperature (°C)
A-1, B-1, C-1, D-1, E1-1, E2-1, F-1	%0,%3,%5,%10,%15,%30	900°C

Sewage sludge to coal ratios in mixtures is determined using the following formula;

$$1000\ calories = M_1(gr).LHV_{sewage\ sludge}(cal/g) + M_2(gr).LHV_{coal}(cal/g) \quad \text{Eq. 3.12.}$$

where;
M_1 = Mass of sewage sludge added to mixtures shown in Table 3.10 (g)
M_2 = Mass of coal added to mixtures shown in Table 3.10 (g)
LHV = Lower Heating Value on dry basis (cal/g)

M_1 and M_2 values used in preparing mixtures are determined to give the percentages shown in Table 3.8. It can also be stated by the relationship given below;

$$Percentage\ of\ SS\ (\%) = \frac{M_1(gr).LHV_{sewage\ sludge}(cal/g)}{M_1(gr).LHV_{sewage\ sludge}(cal/g)+M_2(gr).LHV_{coal}(cal/g)}100 = \frac{M_1(gr).LHV_{sewage\ sludge}(cal/g)}{1000\ calories}100 \quad \text{Eq. 3.13.}$$

Calorific value and moisture content of sewage sludge samples and mass of each sample used for combustion experiments (total calories = 1000 cal) are given in Table 3.9 and 3.10, respectively.

Table 3.9 Calorific value of sewage sludge samples and coal

Sample Name	LHV (cal/g)	Moisture (%)
A-1	2389,3	3,26
B-1	3341,5	5,88
C-1	3290,8	3,53
D-1	2961,7	1,63
E1-1	1958,3	6,04
E2-1	3395,5	12,67
F-1	2411,5	1,51
Coal	6128,4	4,3

Table 3.10 Sample mass used to create different fuel mixtures for combustion experiments (calorific value = 1000 cal)

	Sample Name	%0 sludge addition	%3 sludge addition	%5 sludge addition	%10 sludge addition	%20 sludge addition	%30 sludge addition
M_1	A-1 (gr)	0	0,0130	0,0216	0,0433	0,0865	0,1298
	B-1 (gr)	0	0,0095	0,0159	0,0318	0,0636	0,0954
	C-1 (gr)	0	0,0095	0,0158	0,0315	0,0630	0,0945
	D-1 (gr)	0	0,0103	0,0172	0,0343	0,0686	0,1030
	E1-1 (gr)	0	0,0163	0,0272	0,0543	0,1087	0,1630
	E2-1 (gr)	0	0,0101	0,0169	0,0337	0,0674	0,1012
	F-1 (gr)	0	0,0126	0,0211	0,0421	0,0842	0,1263
M_2	Coal (gr)	0,1706	0,1655	0,1621	0,1535	0,1365	0,1194

Last step of sample preparation is to pelletize sewage sludge and coal mixtures prior to combustion experiments. For this purpose, a hand sized pellet press is used. In order to obtain sewage sludge – coal mixtures whose percentages are given in Table 3.8, first corresponding amounts of sewage sludge and coal samples whose masses are listed in Table 3.10 are mixed in separate holders. Then, mixtures are poured into the mold of the pellet press and pressure is applied. Since pelletizer used in this study is a hand sized, manually operated tool, it is not possible to adjust the pressure by a controller. Nevertheless, pressure applied in each palletizing operation is tried to be kept same. As a result, batches of sewage sludge – coal mixtures in the form of cylindrical pellets with 0.5 mm diameter and several millimeters height are made.

3.4.3. Combustion Experiments and Interpretation of Results

Concentrations of O_2, CO_2, CO, NO, NO_2 and SO_2 measured in a batch combustion experiment is given in Fig.3.7. Based on results of each experiment, material balance on carbon, nitrogen and sulfur for each experiment is performed. Carbon, nitrogen and sulfur content of mixtures are already known by ultimate analysis. Using gaseous emission profiles obtained from Madur analyzer, amount of carbon, nitrogen and sulfur released through combustion experiment is calculated.

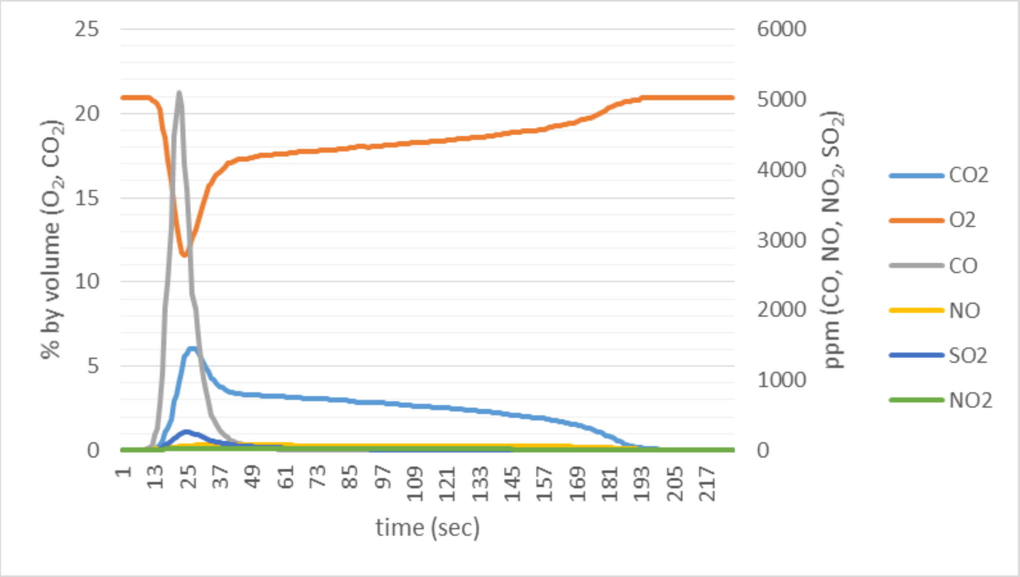


Figure 3.7 Emissions measured in a combustion experiment

Start and end of each experiment can be observed by the change of profiles; i.e. oxygen concentration returns to its original value of %20.95 when experiment ends. Time passed in experiments can also be followed and flow rate of gases is known, therefore, an integration to calculate mass of carbon, nitrogen and sulfur can be done using the following relationships;

Mass of sulfur;

$$M_S = 2{,}86 Q_{analyzer} 32/64 \int_{t_{start}}^{t_{end}} Conc.of\ SO_2(ppm)\,dt \qquad \text{Eq. 3.13.}$$

Mass of nitrogen;

$$M_S = 2{,}056 Q_{analyzer} 14/46 \int_{t_{start}}^{t_{end}} Conc.of\ NO_2(ppm)\,dt + 1{,}34 Q_{analyzer} 14/30 \int_{t_{start}}^{t_{end}} Conc.of\ NO(ppm)\,dt \qquad \text{Eq. 3.14.}$$

Mass of carbon;

$$M_S = 1{,}25 Q_{analyzer} 12/28 \int_{t_{start}}^{t_{end}} Conc.of\ CO(ppm)\,dt + Q_{analyzer} P_{analyzer} 12/T/R/100 \int_{t_{start}}^{t_{end}} Conc.of\ CO_2(\%)\,dt \qquad \text{Eq. 3.15.}$$

where;

$Q_{analyzer}$: Volumetric flow rate of gas sampling by analyzer
$P_{analyzer}$: Pressure of gas sampling by analyzer
t_{start}: Time when experiment starts
t_{end}: Time when experiment ends
R: Ideal gas constant
T: Temperature

The coefficients of 2.86; 2,056; 1.34; 1.25 are the conversion factors of gases from ppm to mg/Nm^3 for SO_2, NO_2, NO and CO, respectively. On the other hand, 32/64; 14/46; 14/30; 12/28 are the ratios of molecular weights of S, N and C to SO_2, NO_2, NO and CO, respectively.

CHAPTER 4

RESULTS AND DISCUSSION

In this section, results of thermal characterization of sludge samples including proximate/ultimate analysis, micro XRF analysis, TG analysis as well as the combustion experiments which are explained in experimental setup in Section 3.4 are given.

4.1. Thermal Characterization of Sewage Sludge Samples and Coal

In the scope of thermal characterization, proximate and ultimate analyses were conducted on sewage sludge samples. Also, elemental composition of sewage sludge ashes is determined.

4.1.1. Proximate/Ultimate Analysis of Sewage Sludge Samples and Coal

Proximate analysis of sewage sludge samples on dry basis are given in Table 4.1. Moisture content of air dried samples is also determined. Proximate and ultimate analysis was conducted on triplicate samples. Therefore, the results presented in Table 4.1 are the averages of these triplicate analysis. Standard errors are also presented with the averaged results.

Table 4.1 Proximate analysis of sewage sludge and coal

Sample	Moisture (%)*	Volatile Matter (%)**	Fixed Carbon (%)**	Ash (%)**
A-1	3.3±0.09	47±0.07	5.0±0.24	48±0.57
A-3	4.7±0.06	47±0.26	5.1±0.19	47.9±0.26
B-1	5.9±0.12	65.8±0.07	3.6±0.13	30.6±0.19
B-2	9±0.43	69.1±0.52	4.7±0.37	26.2±0.16
B-3	6.2±0.1	68.9±0.09	5.0±0.15	26.1±0.25
C-1	3.5±0.05	63.1±0.09	2.2±0.06	34.7±0.04
C-2	4.9±0.08	61.6±0.16	2.9±0.34	35.6±0.77
C-3	4.2±0.03	62.5±0.02	2.8±0.29	34.6±0.82
D-1	1.6±0.03	59.6±0.04	1.6±0.03	38.9±0.02
D-3	4.1±0.04	57.2±0.07	2.4±0.29	40.4±0.76
E1-1	6±0.06	34.2±0.02	7.4±0.3	58.4±0.83
E2-1	12.7±0.17	64.3±0.24	4.2±0.23	31.5±0.27
E2-2	5.7±0.19	78.1±0.14	3.6±0.13	18.4±0.06
E2-3	4.1±0.15	74.4±0.23	4.2±0.16	21.3±0.11
F-1	1.5±0.05	45.8±0.13	3.2±0.09	51±0.09

F-3	2.3±0.05	40±0.04	4.5±0.06	55.5±0.08
Coal	4.3±0.03	29.3±0.11	53.5±0.12	17.2±0.22

[*] % by weight

[**] % by weight on dry basis

-Numbers after dash indicates seasons when samples are taken.

-E1 and E2 are taken from same wastewater treatment plant; E1 is taken after lime stabilization, E2 is taken before lime stabilization.

It can be seen in Table 4.1 that E1-1 has the highest ash content and lowest volatile matter content of all samples. Treatment plant E has A2O process for wastewater treatment and lime stabilization for sludge treatment. Therefore the plant does not use any biological treatment process for sludge stabilization. E1-1 is sampled from the plant after lime addition, whereas E2 samples were collected before lime addition. When results of E1-1 and E2 samples are compared, it can be seen that lime stabilization directly reduces volatile matter and increases ash content. Also the lack of additional processes for sludge stabilization could be the reason for high volatile matter content of E2 samples. In addition, B and C samples have high volatile matter and low ash content. Sample F and A has the lowest volatile matter and highest ash content. Lastly, sample C lies in the middle considering volatile matter and ash content.

Calorific value and elemental composition of combustible portion of sewage sludge samples are determined in the scope of ultimate analysis and the results are given in Table 4.2.

Table 4.2 Ultimate analysis of sewage sludge and coal

	Carbon (%)*	Hydrogen (%)*	Nitrogen (%)*	Sulfur (%)*	Oxygen (%)*	Calorific Value (cal/g)**
A-1	27.19±0.08	3.9±0.03	5.06±0.06	0.86±0.01	15±0.05	2389.34±1.63
A-3	23.14±0.07	3.29±0.01	3.79±0.01	0.75±0.01	21.2±0.03	2174.57±41.62
B-1	35.85±0.18	5.19±0.02	7.69±0.1	1.56±0.03	19.1±0.08	3341.54±17.58
B-2	35±0.04	4.81±0.01	5.27±0.01	1.74±0.03	27±0.02	3581.46±140.34
B-3	32.69±0.03	4.52±0.01	5.22±0.06	1.62±0.02	29.9±0.03	3110.45±14.61
C-1	35.14±0.01	4.59±0.03	6.21±0.03	1.29±0.02	18±0.02	3290.77±29.39
C-2	31.55±0.01	4.03±0.01	5.01±0.01	1.46±0.01	22.4±0.01	3092.58±20.51
C-3	31.88±0.02	3.95±0.01	5.01±0.04	1.63±0.02	22.9±0.02	3076.97±11.59
D-1	31.53±0.11	4.55±0.02	7.11±0.11	0.67±0.00	17.2±0.06	2961.7±10.96
D-3	27.3±0.03	3.94±0.01	5.1±0.04	0.67±0.00	22.6±0.02	2708.22±8.19
E1-1	24.19±0.09	3.75±0.04	4.53±0.02	0.63±0.01	8.5±0.04	1958.33±82.38
E2-1	35.42±0.28	5.04±0.02	6.6±0.04	0.78±0.02	20.7±0.09	3395.48±22.91
E2-2	37.79±0.32	5.34±0.05	6.72±0.04	0.81±0.01	31±0.11	3852.22±18.63
E2-3	36.26±0.09	5.1±0.02	6.45±0.12	0.77±0.01	30.1±0.06	3566.63±21.74
F-1	26.76±0.02	3.85±0	3.84±0.03	1.79±0.07	12.8±0.03	2411.48±9.66

F-3	21.21±0.01	3.11±0.01	2.78±0.00	1.62±0.02	15.7±0.01	1931±2.96
Coal	63.80±0.15	3.65±0.02	1.88±0.04	0.55±0.02	12.94±0.06	6128.43±66.75

[*] % by weight on dry basis

[**] Lower heating value on dry basis (cal/g)

First of all, it should be stated that results obtained in proximate/ultimate analysis are in conformity with the literature data. A summary which includes the average values and the ranges obtained in this study and from the literature is given in Table 4.3.

Table 4.3 Comparison of proximate/ultimate analysis with data from literature

	Volatile Matter (%)**	Carbon (%)**	Ash (%)**	Calorific Value (cal/g)***
Literature[*]	24-52-71	10-31-46	15-39-73	1000-2982-4500
This Study	34-58-78	24-31-37	18-37-58	1900-2927-3800

Values in the middle correspond to average values

[**] % by weight on dry basis

[***] Lower heating value on dry basis (cal/g)

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[*] According to the values which are taken from following papers:(Azuara et al. 2013; Biagini et al. 2002; Boran et al. 2008; L F Calvo et al. 2004; Cao et al. 2013; Casajus et al. 2009; H. Chen, Namioka, and Yoshikawa 2011; Chun, Kim, and Yoshikawa 2011; Conesa et al. 2009; Deng et al. 2009; Domínguez et al. 2008; Domínguez et al. 2006; Duan et al. 2010; Elled, Davidsson, and Åmand 2010; M. Belén Folgueras, Díaz, and Xiberta 2005; M.B. Folgueras and Díaz 2010; M.Belén Folgueras et al. 2003; M.Belén Folgueras, María Díaz, and Xiberta 2004; Font, Fullana, and Conesa 2005; Font et al. 2001; Francisca Gómez-Rico et al. 2005; J. Han et al. 2012; X. Han et al. 2012; Helena Lopes et al. 2003; Hernandez et al. 2011; Horttanainen et al. 2010; Hossain, Strezov, and Nelson 2009; Inguanzo et al. 2002; Ischia et al. 2011; Ji et al. 2010; Jiang, Du, and Yang 2010; Judex, Gaiffi, and Burgbacher 2012; J.-K. Kim and Lee 2011; J. Kim and Lee 2010; H.-S. Lee and Bae 2009; Li et al. 2009; Lin and Ma 2012; Ma et al. 2011; J. a Menéndez, Inguanzo, and Pis 2002; J. a. Menéndez et al. 2005; J. a. Menéndez et al. 2004; Mun, Kang, and Kim 2009; Murakami et al. 2009; Muthuraman, Namioka, and Yoshikawa 2010; Nadziakiewicz and Kozioł 2003; Nielsen et al. 2011; Nilsson, Gómez-Barea, and Cano 2012; Nowicki et al. 2010; M Otero, DÃ±ez, et al. 2002; M Otero et al. 2010; Marta Otero et al. 2008; Othman et al. 2010; S.-W. Park and Jang 2011b; S.-W. Park and Jang 2011a; S.-J. Park et al. 2011; Plaza et al. 2009; Pokorna et al. 2009; Rodriguez et al. 2008; S. a. Scott et al. 2007; S. Scott et al. 2006; Sebestyén et al. 2011; Seggiani et al. 2012; Solimene et al. 2010; Soria-Verdugo et al. 2013; Thipkhunthod et al. 2006; F.-J. Tian et al. 2002; Y. Tian et al. 2011; Toraman et al. 2004; Urciuolo et al. 2012; Vamvuka and Sfakiotakis 2011; Várhegyi, Sebestyén, and Czégény 2011; L. Wang et al. 2012; L. Wang et al. 2011; R. Wang et al. 2011; Wei, Schnell, and Hein 2005; Werther and Ogada 1999; Z. Wu et al. 2012; Wzorek 2012; Han-min Xiao, Ma, and Lai 2009; Hanmin Xiao, Ma, and Liu 2010; Yang et al. 2008; Zhai et al. 2011; J. Zhang et al. 2013; Q. Zhang et al. 2012)

Sewage sludge is mainly composed of volatile matter and ash. Volatile matter content of sewage sludge samples used in this study ranges between 34.2% and 78.1%. Similarly, ash content of sewage sludge samples changes between 18.4% and 58.4%. Fixed carbon does not have such a particular range because it is always significantly lower than the volatile matter. Maximum fixed carbon determined in samples is 7.4%.

Ultimate analysis of samples reveals that organic fraction of sewage sludge samples contain predominantly carbon and oxygen. Nitrogen and hydrogen generally have similar values and their percentage in samples is not higher than 8%. Sulfur has the lowest percentage among all elements, varying from 0.6% to 1.8%. Calorific value of samples varies between 1900 and 3800 cal/g on dry basis.

It can be understood from proximate and ultimate analysis that thermal characterization does not have constant and predictable values. It should be noted that sludge stabilization process certainly has an impact on proximate and ultimate analysis. Sewage sludge E2, which is not stabilized at all, has the highest calorific value in all cases. However, even though sewage sludge B undergoes an anaerobic stabilization, it comes the second in calorific value. Sample C is taken from a plant that has a special sludge stabilization process, cannibal stabilization, has approximately same calorific values with sample B, which is anaerobically stabilized. This all means that sludge stabilization process does have a certain impact on calorific value of sewage sludge, however, there are other factors that affect the calorific value as well.

Variation in thermal characteristics is observed even for sludge samples taken from the same wastewater treatment plant. Figure 4.1 demonstrates the changes in calorific values of sewage sludge samples taken in different periods of a year.

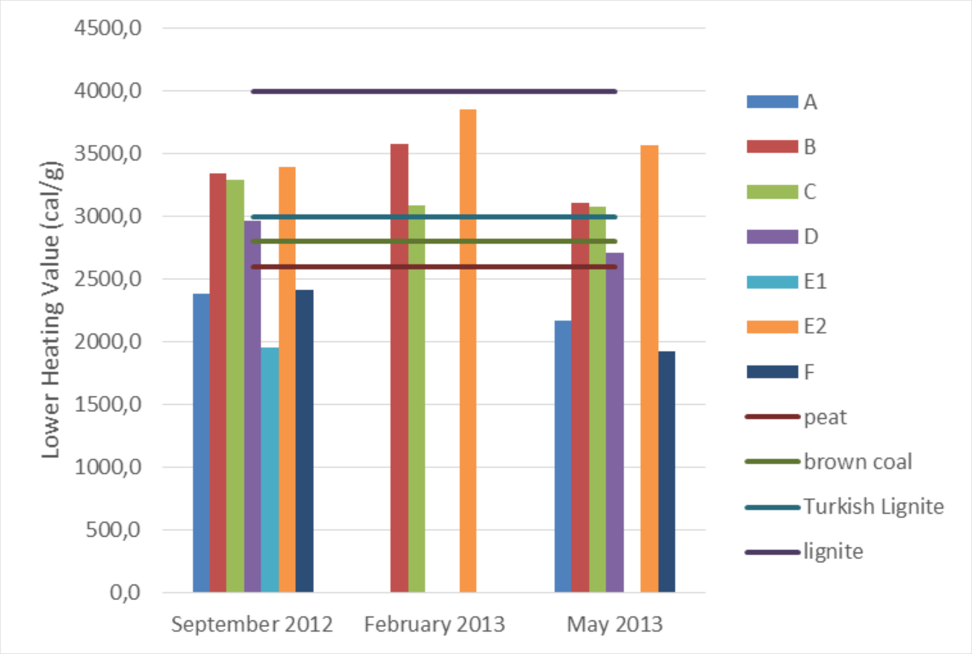

Figure 4.1 Change in calorific values of sewage sludge samples

It can be seen in Figure 4.1 that differences of calorific value with sampling within the same plant at different times can go up to 500 cal/g in some cases. This kind of variation can lead to erroneous conclusions if a prediction is made according to only one measurement. For instance, sewage sludge E2 can be considered as a candidate as an additive fuel if such a conclusion is based on a measurement which is done in February, 2013, where calorific value of the sludge is close to that of lignite. However, calorific value of the sludge from the same treatment plant is measured in another time lower than 3400 cal/g, approximately 500 cal/g lower than the first case. This kind of variation indicates that operating parameters of wastewater treatment plant and characteristics of wastewater could affect calorific value of sewage sludge. Therefore, in order to indicate such a variation in a particular sewage sludge from a wastewater treatment plant, calorific value of sewage sludge should be measured periodically in a year.

To determine the calorific values of sludge one has to have a bomb calorimeter which may not be available in every laboratory. So it would be good if calorific value of sludge can be correlated with a frequently and easily measured parameter. One candidate parameter for this is the volatile matter content of sludge. Figure 4.2 shows that for the sludge samples, the VM and calorific values of sludges correlates well. Therefore, one way of estimating calorific value of a sewage sludge can be to use such a relationship between the volatile matter and the heating value of the sludge, as shown in Figure 4.2.

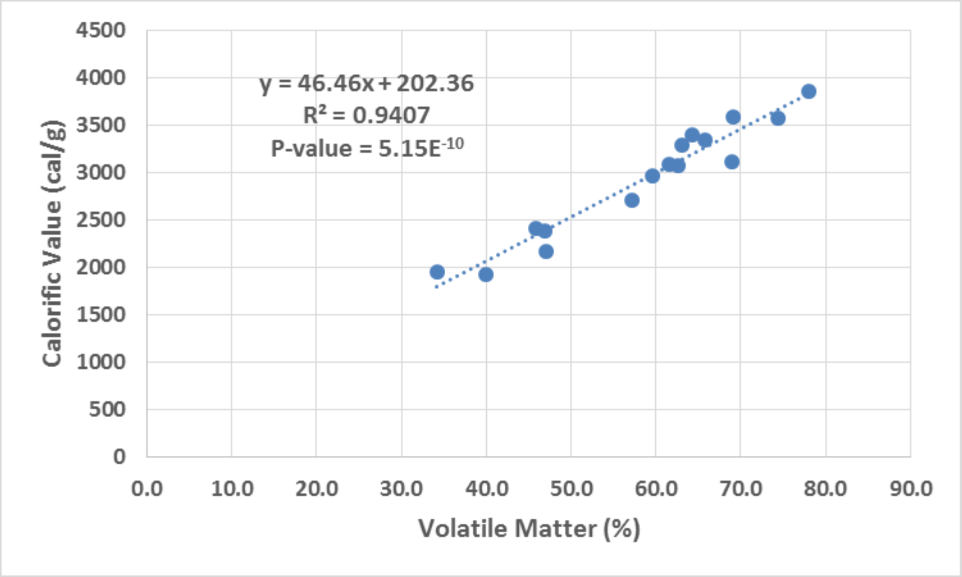

Figure 4.2 Correlation between calorific value and volatile matter of samples

It can be seen from Figure 4.2 that there is a good correlation between the calorific value and the volatile matter content of sewage sludge samples used in this study. The correlation coefficient has been found to be 0.94 with the P-value of $5.87E^{-8}$. P-value tests the probability whether the hypothesis holds or not. Hypothesis in the case given in Figure 4.2 is that when a new data point enters the sample space, whether it falls in the correlation of 0.94 or not. P-value of $5.87E^{-8}$ indicates that a new data will be in the range of correlation with the probability of (1- $5.87E^{-8}$)100%. Therefore, it can be said that coefficient of correlation found in Figure 4.2 is statistically accurate since 0.05 is generally considered as the upper limit for P-value (Moyé 2006). Such an empirical relationship can be used to estimate calorific value of an unknown sewage sludge sample which is generated in a wastewater treatment plant since the volatile matter content is a continuously measured parameter in a treatment plant.

To check if volatile matter correlates well with calorific value for a larger set of sludge samples, volatile matter contents and calorific values of as many sewage sludges as possible were obtained from literature. A correlation between volatile matter contents and calorific values of these sludges was tried to be found. Correlation obtained between volatile matter contents and calorific values of many sewage sludges is given in Fig. 4.3. Coefficient of this correlation which is found to be 0.770 with the P-value of $1.23E^{-24}$ indicates that there is a relation between these two parameters. However, correlation coefficient cannot be used to perform predictions. Additionally, it was a point of interest to see if a correlation exists between carbon contents and calorific values of these sludges. Therefore, carbon contents and calorific values of different sludges obtained from the literature were plotted in Figure 4.4. As can be seen from the figure, there is a good relationship between these parameters although there is a scattering of data to a certain extent. The correlation coefficient has been found to be 0.817 with the P-value of $1.78E^{-33}$. This is quite normal because the data was generated by different researchers from different parts of the world which have used sewage sludge samples originated from various treatment plants.

Also a correlation was sought between the carbon and volatile matter contents of the sludges of the literature are given in Figure 4.3. As can be seen from the figure, a strong correlation between these parameters could not be found. The correlation coefficient was 0.769 with the P-value of 4.49E^{-29}. Therefore, it was understood that this correlation cannot be used to estimate the calorific value of a sludge from its carbon content.

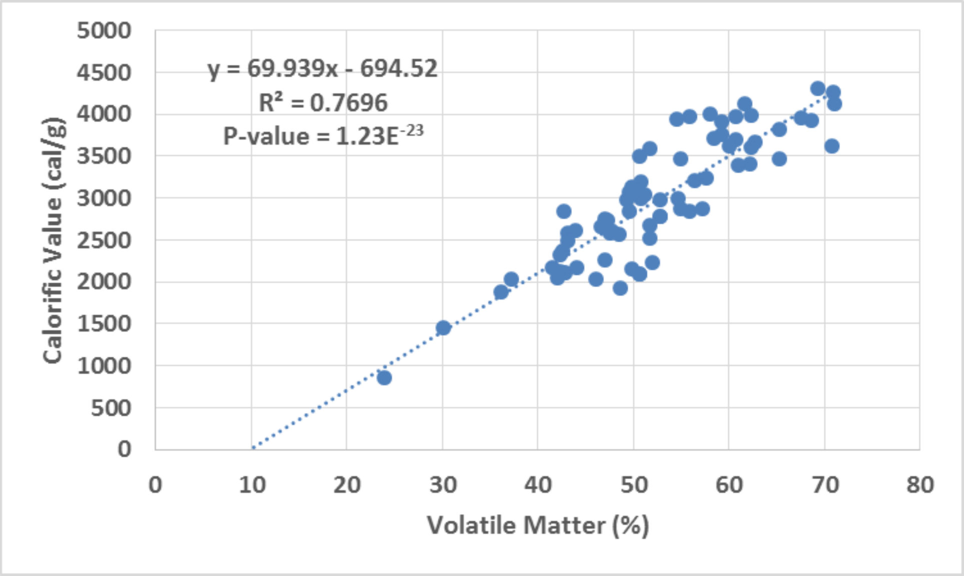

Figure 4.3 Correlation between volatile matter contents and calorific values of sludges obtained from literature data[†]

[†] According to the values which are taken from following papers: (Azuara et al. 2013; Biagini et al. 2002; Boran et al. 2008; L F Calvo et al. 2004; Cao et al. 2013; Casajus et al. 2009; H. Chen, Namioka, and Yoshikawa 2011; Chun, Kim, and Yoshikawa 2011; Conesa et al. 2009; Deng et al. 2009; Domínguez et al. 2008; Domínguez et al. 2006; Duan et al. 2010; Elled, Davidsson, and Åmand 2010; M. Belén Folgueras, Díaz, and Xiberta 2005; M.B. Folgueras and Díaz 2010; M.Belén Folgueras et al. 2003; M.Belén Folgueras, María Díaz, and Xiberta 2004; Font, Fullana, and Conesa 2005; Font et al. 2001; Francisca Gómez-Rico et al. 2005; J. Han et al. 2012; X. Han et al. 2012; Helena Lopes et al. 2003; Hernandez et al. 2011; Horttanainen et al. 2010; Hossain, Strezov, and Nelson 2009; Inguanzo et al. 2002; Ischia et al. 2011; Ji et al. 2010; Jiang, Du, and Yang 2010; Judex, Gaiffi, and Burgbacher 2012; J.-K. Kim and Lee 2011; J. Kim and Lee 2010; H.-S. Lee and Bae 2009; Li et al. 2009; Lin and Ma 2012; Ma et al. 2011; J. a Menéndez, Inguanzo, and Pis 2002; J. a. Menéndez et al. 2005; J. a. Menéndez et al. 2004; Mun, Kang, and Kim 2009; Murakami et al. 2009; Muthuraman, Namioka, and Yoshikawa 2010; Nadziakiewicz and Kozioł 2003; Nielsen et al. 2011; Nilsson, Gómez-Barea, and Cano 2012; Nowicki et al. 2010; M Otero, DÄ±ez, et al. 2002; M Otero et al. 2010; Marta Otero et al. 2008; Othman et al. 2010; S.-W. Park and Jang 2011a; S.-W. Park and Jang 2011b; S.-J. Park et al. 2011; Plaza et al. 2009; Pokorna et al. 2009; Rodriguez et al. 2008; S. a. Scott et al. 2007; S. Scott et al. 2006; Sebestyén et al. 2011; Seggiani et al. 2012; Solimene et al. 2010; Soria-Verdugo et al. 2013; Thipkhunthod et al. 2006; F.-J. Tian et al. 2002; Y. Tian et al. 2011; Toraman et al. 2004; Urciuolo et al. 2012; Vamvuka and Sfakiotakis 2011; Várhegyi, Sebestyén, and Czégény 2011; L. Wang et al. 2012; L. Wang et al. 2011; R. Wang et al. 2011; Wei, Schnell, and Hein 2005; Werther and Ogada 1999; Z. Wu et al. 2012; Wzorek 2012; Han-min Xiao, Ma, and Lai 2009; Hanmin Xiao, Ma, and Liu 2010; Yang et al. 2008; Zhai et al. 2011; J. Zhang et al. 2013; Q. Zhang et al. 2012)

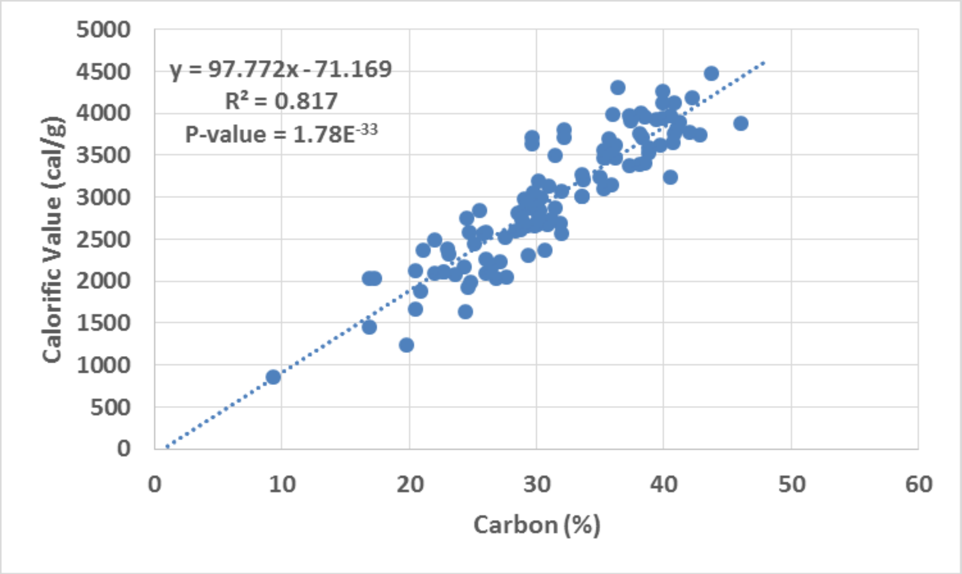

Figure 4.4 Correlation between carbon contents and calorific values of sludges obtained from literature data‡

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‡ According to the values which are taken from following papers: (Azuara et al. 2013; Biagini et al. 2002; Boran et al. 2008; L F Calvo et al. 2004; Cao et al. 2013; Casajus et al. 2009; H. Chen, Namioka, and Yoshikawa 2011; Chun, Kim, and Yoshikawa 2011; Conesa et al. 2009; Deng et al. 2009; Domínguez et al. 2008; Domínguez et al. 2006; Duan et al. 2010; Elled, Davidsson, and Åmand 2010; M. Belén Folgueras, Díaz, and Xiberta 2005; M.B. Folgueras and Díaz 2010; M.Belén Folgueras et al. 2003; M.Belén Folgueras, María Díaz, and Xiberta 2004; Font, Fullana, and Conesa 2005; Font et al. 2001; Francisca Gómez-Rico et al. 2005; J. Han et al. 2012; X. Han et al. 2012; Helena Lopes et al. 2003; Hernandez et al. 2011; Horttanainen et al. 2010; Hossain, Strezov, and Nelson 2009; Inguanzo et al. 2002; Ischia et al. 2011; Ji et al. 2010; Jiang, Du, and Yang 2010; Judex, Gaiffi, and Burgbacher 2012; J.-K. Kim and Lee 2011; J. Kim and Lee 2010; H.-S. Lee and Bae 2009; Li et al. 2009; Lin and Ma 2012; Ma et al. 2011; J. a Menéndez, Inguanzo, and Pis 2002; J. a. Menéndez et al. 2005; J. a. Menéndez et al. 2004; Mun, Kang, and Kim 2009; Murakami et al. 2009; Muthuraman, Namioka, and Yoshikawa 2010; Nadziakiewicz and Kozioł 2003; Nielsen et al. 2011; Nilsson, Gómez-Barea, and Cano 2012; Nowicki et al. 2010; M Otero, DÃ±ez, et al. 2002; M Otero et al. 2010; Marta Otero et al. 2008; Othman et al. 2010; S.-W. Park and Jang 2011a; S.-W. Park and Jang 2011b; S.-J. Park et al. 2011; Plaza et al. 2009; Pokorna et al. 2009; Rodriguez et al. 2008; S. a. Scott et al. 2007; S. Scott et al. 2006; Sebestyén et al. 2011; Seggiani et al. 2012; Solimene et al. 2010; Soria-Verdugo et al. 2013; Thipkhunthod et al. 2006; F.-J. Tian et al. 2002; Y. Tian et al. 2011; Toraman et al. 2004; Urciuolo et al. 2012; Vamvuka and Sfakiotakis 2011; Várhegyi, Sebestyén, and Czégény 2011; L. Wang et al. 2012; L. Wang et al. 2011; R. Wang et al. 2011; Wei, Schnell, and Hein 2005; Werther and Ogada 1999; Z. Wu et al. 2012; Wzorek 2012; Han-min Xiao, Ma, and Lai 2009; Hanmin Xiao, Ma, and Liu 2010; Yang et al. 2008; Zhai et al. 2011; J. Zhang et al. 2013; Q. Zhang et al. 2012)

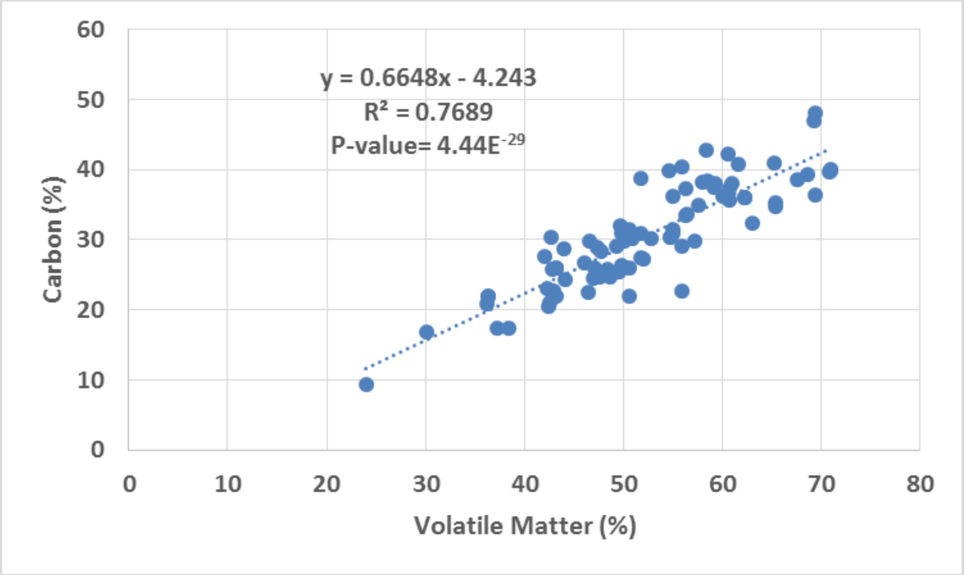


Figure 4.5 Correlation between volatile matter and carbon contents of sludges obtained from literature data[§]

4.1.2. Determination of Ash Composition of Sewage Sludge Samples by XRF Analysis

Inorganic elements which constitute the ash of sewage sludge samples were determined by using XRF analysis in this study. Results of XRF analysis are reported on dry basis in Table 4.4.

[§] According to the values which are taken from following papers: (Azuara et al. 2013; Biagini et al. 2002; Boran et al. 2008; L F Calvo et al. 2004; Cao et al. 2013; Casajus et al. 2009; H. Chen, Namioka, and Yoshikawa 2011; Chun, Kim, and Yoshikawa 2011; Conesa et al. 2009; Deng et al. 2009; Domínguez et al. 2008; Domínguez et al. 2006; Duan et al. 2010; Elled, Davidsson, and Åmand 2010; M. Belén Folgueras, Díaz, and Xiberta 2005; M.B. Folgueras and Díaz 2010; M.Belén Folgueras et al. 2003; M.Belén Folgueras, María Díaz, and Xiberta 2004; Font, Fullana, and Conesa 2005; Font et al. 2001; Francisca Gómez-Rico et al. 2005; J. Han et al. 2012; X. Han et al. 2012; Helena Lopes et al. 2003; Hernandez et al. 2011; Horttanainen et al. 2010; Hossain, Strezov, and Nelson 2009; Inguanzo et al. 2002; Ischia et al. 2011; Ji et al. 2010; Jiang, Du, and Yang 2010; Judex, Gaiffi, and Burgbacher 2012; J.-K. Kim and Lee 2011; J. Kim and Lee 2010; H.-S. Lee and Bae 2009; Li et al. 2009; Lin and Ma 2012; Ma et al. 2011; J. a Menéndez, Inguanzo, and Pis 2002; J. a. Menéndez et al. 2005; J. a. Menéndez et al. 2004; Mun, Kang, and Kim 2009; Murakami et al. 2009; Muthuraman, Namioka, and Yoshikawa 2010; Nadziakiewicz and Kozioł 2003; Nielsen et al. 2011; Nilsson, Gómez-Barea, and Cano 2012; Nowicki et al. 2010; M Otero, DÃ±ez, et al. 2002; M Otero et al. 2010; Marta Otero et al. 2008; Othman et al. 2010; S.-W. Park and Jang 2011a; S.-W. Park and Jang 2011b; S.-J. Park et al. 2011; Plaza et al. 2009; Pokorna et al. 2009; Rodriguez et al. 2008; S. a. Scott et al. 2007; S. Scott et al. 2006; Sebestyén et al. 2011; Seggiani et al. 2012; Solimene et al. 2010; Soria-Verdugo et al. 2013; Thipkhunthod et al. 2006; F.-J. Tian et al. 2002; Y. Tian et al. 2011; Toraman et al. 2004; Urciuolo et al. 2012; Vamvuka and Sfakiotakis 2011; Várhegyi, Sebestyén, and Czégény 2011; L. Wang et al. 2012; L. Wang et al. 2011; R. Wang et al. 2011; Wei, Schnell, and Hein 2005; Werther and Ogada 1999; Z. Wu et al. 2012; Wzorek 2012; Han-min Xiao, Ma, and Lai 2009; Hanmin Xiao, Ma, and Liu 2010; Yang et al. 2008; Zhai et al. 2011; J. Zhang et al. 2013; Q. Zhang et al. 2012)

Table 4.4 Inorganic element contents of sewage sludges used in this study (% by wt.)

	A-1	B-1	C-1	D-1	E1-1	E2-1	F-1
Na_2O	0.07	0.07	0.19	0.05	0.06	0.05	0.27
MgO	0.87	0.94	0.75	0.61	0.40	0.49	0.71
Al_2O_3	3.23	0.84	2.54	2.80	0.40	0.58	3.77
SiO_2	10.31	3.13	6.86	7.76	1.56	2.33	8.38
P_2O_5	1.79	2.74	1.12	1.87	0.91	1.57	1.44
SO_3	1.23	1.77	1.53	0.72	0.56	0.60	2.15
Cl	0.17	0.14	0.17	0.09	0.07	0.11	0.65
K_2O	1.06	0.45	1.04	1.43	0.64	1.04	0.89
CaO	8.51	6.39	4.35	1.92	21.24	4.21	6.84
TiO_2	0.32	0.17	0.29	0.27	0.07	0.12	0.41
V_2O_5	0.01	0.00	0.01	0.01	0.01	0.00	0.01
Cr_2O_3	0.04	0.02	0.02	0.06	0.01	0.02	0.44
MnO	0.05	0.04	0.03	0.04	0.01	0.02	0.04
Fe_2O_3	2.34	3.06	2.57	2.14	0.58	1.01	2.77

It can be seen in Table 4.4 that Si and Ca are the most abundant inorganic elements in sewage sludges tested in this study. Moreover, Fe, K, S, P and Al are other inorganic elements that are found in high concentrations.

Inorganic elements found in ash are the precursor of the phenomena called "slagging and fouling". Slagging and fouling occur in combustion processes; therefore, potential of occurrence of these events in co-combustion of sewage sludge with another fuel is determined. Slagging is the deposit of bottom ash in the walls of reactor's combustion zone. It is mainly caused by melting of bottom ash and alkali metals which reduces the melting point of ash. On the other hand, fouling occurs due to the deposit of fly ash particles on heat exchanger surfaces in upper parts of the reactor where temperature is relatively colder (Teixeira et al. 2012).

Slagging and Fouling indices in this study are calculated by using compositions given in Table 4.5. Slagging indices which are used in this study are "base to acid ratio" (B/A), "iron calcium ratio" (I/C) and "sulfur ratio" (Rs). Total Alkalis (TA), Na_2O ratio (Rf) and Fouling index (Fu) are indices which represent fouling tendency of samples (Park and Jang, 2011a). The slagging and fouling indices are calculated for sludge samples taken from different wastewater treatment plants.

An example calculation of slagging and fouling indices for sludge sample A-1 is illustrated below:

$$Base\ to\ Acid\ Ratio\ (B/A) = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O + P_2O_5}{Al_2O_3 + SiO_2 + TiO_2}$$
$$= \frac{2.34 + 8.51 + 0.87 + 1.06 + 0.07 + 1.79}{3.23 + 10.31 + 0.32} = 1.1$$
$$Iron - Calcium\ Ratio\ (I/C) = \frac{Fe_2O_3}{CaO} = \frac{2.34}{8.51} = 0.3$$
$$Sulfur\ Ratio\ (S) = (B/A)xS = 1.1x1.23 = 1.3$$
$$Total\ Alkalis\ (TA) = Na_2O + K_2O = 0.07 + 1.06 = 1.1$$
$$Na_2O\ Ratio\ (Rf) = (B/A)xNa_2O = 1.1x0.07 = 0.1$$
$$Fu = (B/A)x(Na_2O + K_2O) = 1.1x1.1 = 1.2$$

Illustration above shows the use of relevant formula for the determination of slagging-fouling indices of Sample A-1. This procedure was applied for all samples whose elemental compositions are given in Table 4.4. Results of such calculations along with the reference levels for low, medium and high slagging and fouling indices are listed in Table 4.5.

Table 4.5 Slagging and fouling indices of sewage sludge samples

Slagging Fouling Indices of Sewage Sludge Samples								Limit Values(Park and Jang, 2011a)		
	A-1	B-1	C-1	D-1	E1-1	E2-1	F-1	Low	Medium	High
B/A	1.1	3.3	1.0	0.7	11.7	2.8	1.0	<0.5	0.5<B/A<1	>1
I/C	0.3	0.5	0.6	1.1	0.0	0.2	0.4	<0.31 or >3	<10.3 <I/C<3	≠1
S	1.3	5.8	1.6	0.5	6.6	1.7	2.2	<0.6	0.6<Rs<2	>2
TA	1.1	0.5	1.2	1.5	0.7	1.1	1.2	<0.3	0.3<TA<0.4	>0.4
Rf	0.1	0.2	0.2	0.0	0.7	0.1	0.3	<0.2	0.2<Rf<0.5	<0.5
Fu	1.2	1.7	1.3	1.1	8.2	3.0	1.2	≤0.6	-	0.6<Fu≤40

Table 4.5 shows that all sewage sludge samples have moderate to high slagging and fouling tendency when compared to limit values. Base to acid ratio (B/A) of all samples are higher than "high" class, except from sample D-1. In terms of iron to calcium ratio (I/C), three samples have low grade and remaining samples have moderate grade. Sulfur ratio of D-1 sample have low propensity, A-1, C-1 and E2-1 have moderate and B-1, E1-1 and F-1 have high grade. Amount of total alkalis in all samples have higher than "high" limit value. Also, fouling index of all samples are higher than "high class" limit value. Therefore, it can be summarized that indices presented in this study imply that use of sewage sludge in combustion processes can have negative impact. This result actually supports conclusions which are summarized in literature review, Section 2.3.3. Therefore, it can be concluded that composition of sewage sludge ash is a limiting factor on its use in combustion processes. In co-combustion process of sewage sludge and coal, ash composition of sewage sludge could

prevent its use in excess amounts. This issue has to be critically considered when determining the quantity of sludge to be used as additive fuel.

4.2. Co-combustion of Sewage Sludge and Coal

In this set of experiments, the effect of sewage sludge addition on the efficiency of coal combustion is determined. In order to reveal the effect of sludge addition, first only coal samples were combusted in the reactor. Then, sewage sludge and coal mixtures with varying degrees of sludge addition were used in the combustion reactor. All different types of sludge samples were added at 3%, 5%, 10%, 20% and 30% fractions to coal, based on calorific values that make 1000 calories in total. As a result, change in combustion efficiency was calculated.

In order to determine the efficiency of combustion process, mass balance on carbon is conducted. The success of each combustion experiment is determined by calculating the amount of carbon which transforms into carbon dioxide.

First step of creating a mass balance is to determine how much carbon is introduced into the reactor in each set of experiment. The calculated values are given in Table 4.6.

Table 4.6 Amount of carbon introduced into reactor by different fuel mixtures

	0%*	3%*	5%*	10%*	20%*	30%*
A-1 (gr)	0.1041	0.1044	0.1046	0.1051	0.1060	0.1070
B-1 (gr)	0.1041	0.1042	0.1043	0.1044	0.1047	0.1051
C-1 (gr)	0.1041	0.1042	0.1042	0.1044	0.1046	0.1049
D-1 (gr)	0.1041	0.1042	0.1042	0.1043	0.1046	0.1048
E1-1 (gr)	0.1041	0.1047	0.1051	0.1060	0.1080	0.1099
E2-1 (gr)	0.1041	0.1041	0.1041	0.1041	0.1041	0.1042
F-1 (gr)	0.1041	0.1043	0.1044	0.1048	0.1055	0.1062

* Ratio of sewage sludge in fuel mixtures; 0% represents batches which contain no sewage sludge; 30% indicates mixtures prepared by 30% sludge and 70% of coal.

Amount of coal and sewage sludge used in the experiments were listed in Table 3.10. By using the data in this table, carbon contents in each sample was calculated and are given in Table 4.6. Then, if the fraction of carbon which transforms into carbon dioxide (CO_2) and carbon monoxide (CO) is calculated, then the efficiency of carbon combustion in the experiments can be determined.

The procedure to calculate the amount of carbon which has been transformed into carbon monoxide and carbon dioxide is given in Section 3.4.3. An example figure showing the results of triplicate batch combustion experiments can be seen in Figure 4.6. Graphical representations of triplicate experiments which are conducted in each set of experiments are given in Appendix A. An example calculation is performed to illustrate the procedure is given in Figure 4.6.

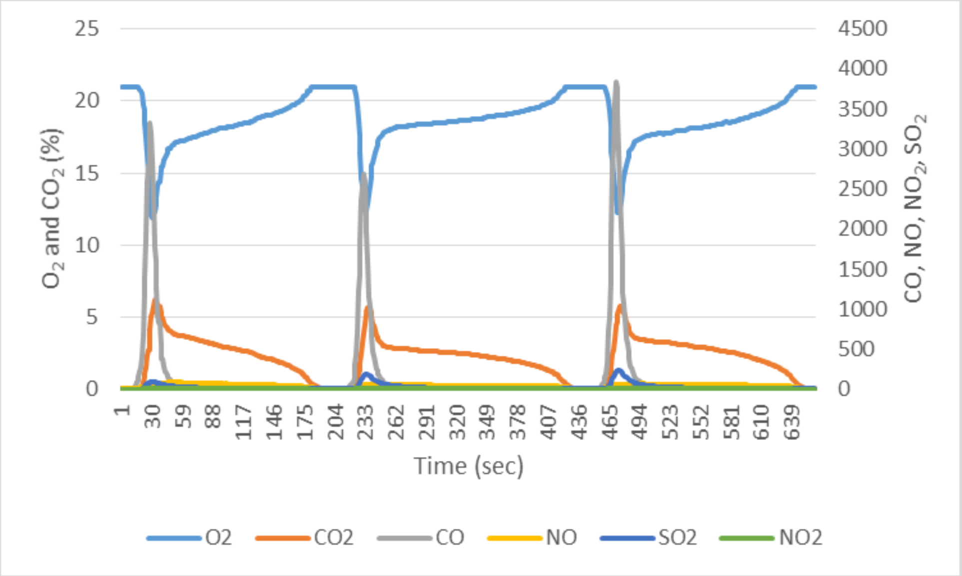


Figure 4.6 Result of co-combustion of coal with 3% A-1 sludge

In this graphical representation, change in O_2 and CO_2 are shown on the left hand side of the graph. The flue gas analyzer measures these gases as % by volume basis. On the other hand, CO, NO, NO_2 and SO_2 profiles which are measured in ppm unit are shown on the right hand side of the graph. Measurements of flue gas composition are performed in every two seconds; therefore profiles of gaseous products are plotted with respect to time.

It can be seen in Appendix A that as soon as pellets are dropped into the reactor, there is a sharp decrease in oxygen concentration in the reactor and increase in carbon monoxide and carbon dioxide. On the average, oxygen level is dropped immediately to 10%, carbon dioxide rises around 5-10%. Concentration of carbon monoxide depends on the sludge additive in mixtures, it can be around 1000 ppm when sewage sludge percentage is 3-5%. On the other hand, it could go up to 6000 ppm when mixtures with 30% sewage sludge is burned. The first region in combustion experiments last 30-40 seconds, then carbon monoxide formation stops and carbon dioxide and oxygen levels gradually go back to atmospheric values.

One reason behind this two-step combustion could be the nature of sewage sludge and coal. First region where carbon monoxide formation occurs could be the result of rapid devolatilization of volatile matter present in sewage sludge. When devolatilization ends, char in sewage sludge and coal can start to be burned in a more stable medium.

Another possible reason could be the temperature difference between reactor and pellets at the beginning of experiments. As soon as sample is introduced to the reactor, rapid heating of pellet occurs in the reactor. Therefore, as sample is heated, conditions of incomplete combustion could be satisfied. This could be further supported by the fact that time passed during the first step of combustion in each experiments are quite similar. Since mass of pellets are also very similar to each other, as it can be seen in Table 3.10, the time required for heating of pellets should be close to each other.

The first step of determination of combustion efficiency is to determine the mass of carbon transformed into carbon dioxide and carbon monoxide. The following formula is used.

$$M_{carbon} = 1.25 Q_{analyzer} 12/28 \int_{t_{start}}^{t_{end}} Conc. of\ CO(ppm)\, dt + Q_{analyzer} P_{analyzer} 12/T/R/100 \int_{t_{start}}^{t_{end}} Conc. of\ CO_2(\%)\, dt \qquad \text{Eq. 4.1.}$$

where,

M_{carbon}: mass of carbon (g)
$Q_{analyzer}$: Flow rate of analyzer (L/s)
t: time (second)
$P_{analyzer}$: Pressure (atm)
R: Ideal gas constant (L.atm/K/mole)
T: Temperature (Kelvin)

Equation 4.1 allows for calculation of amount of carbon in the form of oxides. The first part of the equation calculates CO and the second part of the equation calculates CO_2. Summation of the two gives total carbon. Since combustion experiments were carried in triplicate tests, the calculations shown above were done three times and results were averaged.

For the sample result given in Figure 4.6 (Sample A-1), detailed calculations for the carbon content detected in the flue gas are shown below:

$$M_{carbon} = \frac{(M_{carbon\ from\ CO_2})_{experiment1} + (M_{carbon\ from\ CO_2})_{experiment2} + (M_{carbon\ from\ CO_2})_{experiment3}}{3} + \frac{(M_{carbon\ from\ CO})_{experiment1} + (M_{carbon\ from\ CO})_{experiment2} + (M_{carbon\ from\ CO})_{experiment3}}{3}$$

$$M_{carbon} = \frac{0.100925 + 0.105844 + 0.109471}{3} + \frac{0.000966 + 0.000759 + 0.001114}{3}$$

$$M_{carbon} = 0.1064\ gr$$

Similar calculations were conducted for other samples/ experiments and the results are given in Table 4.7.

Table 4.7 Percentage of carbon that is captured as carbon monoxide and carbon dioxide in combustion experiments (%)

	0%*	3%*	5%*	10%*	20%*	30%*
A-1 (gr)	87.5	101.9	96.5	96.5	95.1	96.4
B-1 (gr)	87.5	101.9	92.2	93.5	99.2	95.2
C-1 (gr)	87.5	105.6	98.9	99.1	99.9	111.9
D-1 (gr)	87.5	105.1	101.9	100.5	96.1	104.7
E1-1 (gr)	87.5	100.2	105.4	108.8	101.6	98.5
E2-1 (gr)	87.5	95.5	100.7	106.4	98.2	94.8
F-1 (gr)	87.5	92.0	101.1	112.2	102.7	99.3

* Ratio of sewage sludge in fuel mixtures; 0% represents batches which contain no sewage sludge; 30% indicates mixtures prepared with 30% sludge and 70% coal.

When the example procedure is iterated for all experiments, percentage of carbon that is captured as carbon monoxide and carbon dioxide can be calculated by using values in Table 4.7. As it can be seen in Table 4.7, carbon balance holds within ±10% error.

The efficiency of the carbon combustion is defined as the ratio of carbon leaving the system as carbon monoxide to total amount of carbon which is introduced into the system. Carbon monoxide is the indicator of incomplete combustion and it can be inferred that combustion efficiency is reduced when carbon monoxide production increases.

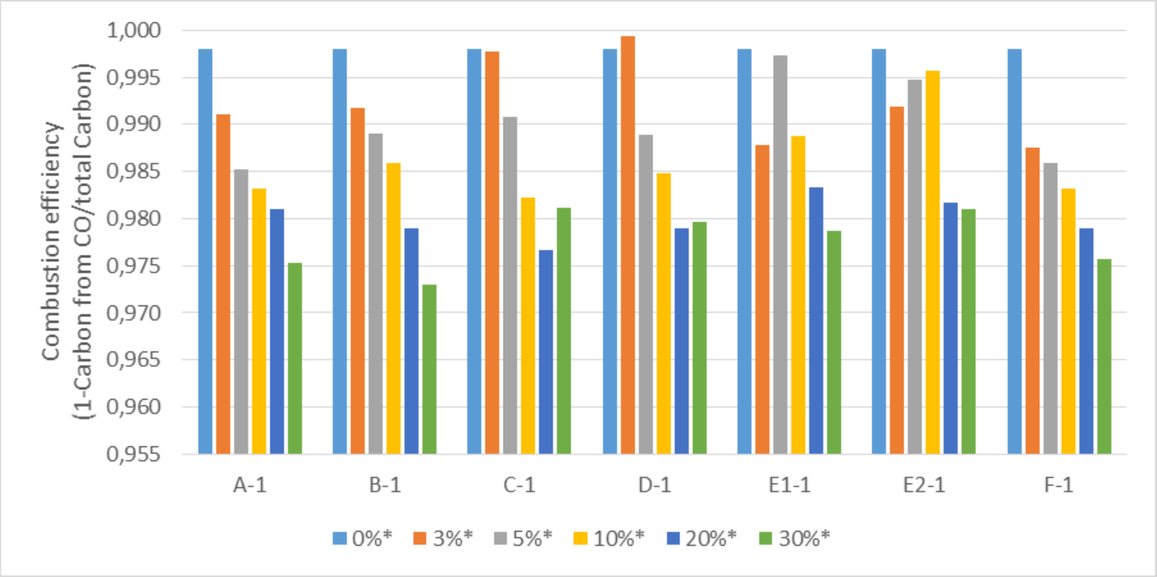
Therefore, combustion efficiency is defined with the following equation;

$$Combustion\ efficiency(\%) = 1 - \frac{Carbon\ showing\ as\ carbon\ monoxide\ in\ the\ flue\ gas}{Carbon\ which\ is\ captured\ as\ carbon\ monoxide + carbon\ dioxide} x100 \qquad \text{Eq. 4.2.}$$

For the example given in Figure 4.6 for the sample A-1, the above calculation will have the following form:

$$Combustion\ efficiency(\%) = 1 - \frac{0.000946}{0.1064} x100 = 99.096$$

Results of calculated combustion efficiencies are shown in Figure 4.7.



* Ratio of sewage sludge in fuel mixtures; 0% represents batches which contain no sewage sludge; 30% indicates mixtures prepared by 30% of sludge and 70% of coal.

Figure 4.7 Combustion efficiencies of samples studied

It can be observed from Figure 4.7 that coal replacement with sewage sludge causes carbon monoxide formation, which is the indication of incomplete combustion. In some cases a critical point is observed, for instance, for sludge samples C-1 and D-1, sludge additions of more than 5% results an increase in carbon monoxide formation. In A-1, B-1 and F-1, no critical point is observed. However, increase of sludge ratio in mixtures gradually decreases combustion efficiency. In some cases there are some results which contradict the expectations. In E1-1 and E2-1, profiles in Figure 4.7 suggest that there is a point where carbon monoxide formation reaches a local minimum, however it cannot be the case. These results indicate there may be an experimental error. Nevertheless, both cases imply that addition of this sludge to coal in amount more than 20% decreases combustion efficiency.

It should be noted that combustion efficiencies obtained in this study is only applicable to this experimental setup. Different experimental setups, lab-scale of pilot scale as well as full scale applications could yield different efficiencies of sewage sludge combustion. For instance, example study summarized in Section 2.3.2 reports that more than 1% sewage sludge addition as additive fuel for coal for a given full scale thermal power plant results in reduced combustion efficiency. On the other hand, Lee et al. (2007) reports that nearly 100% combustion efficiency is achieved in a lab-scale fluidized bed reactor even in mono combustion of sewage sludge, once operating conditions for sewage sludge combustion is optimized (Lee et al. 2007). The experimental set-up and reactor conditions used in this study yields a maximum of 99.7 % combustion efficiency without any sludge addition as can be seen from Figure 4.7.

In summary, it can be concluded that given a combustion system which is optimized for coal, co-combustion of sewage sludge and coal reduces the combustion efficiency when sewage sludge is used in increasing amounts. The point where sewage sludge addition upsets combustion efficiency depends on the type of sludge since it is observed in this study that different flue gas compositions are achieved with different fuel mixtures.

Mass balances on nitrogen and sulfur are also conducted in this study. For the example given in Figure 4.6 for Sample A-1 the calculation procedures for sulfur and nitrogen are demonstrated below:

$$M_{Sulfur} = 2.86 Q_{analyzer} 32/64 \int_{t_{start}}^{t_{end}} Conc.\, of\ SO_2 (ppm)\, dt \qquad \text{Eq. 4.3.}$$

where,
M_{sulfur}: mass of sulfur (g)
$Q_{analyzer}$: Flow rate of analyzer (L/s)
t: time (second)
2.86: constant for changing concentration of SO_2 from ppm to mg/Nm^3
32/64: Ratio of Molecular Weight of Sulfur and SO_2

$$M_{Sulfur} = \frac{(M_{sulfur\ from\ SO_2})_{experiment1} + (M_{sulfur\ from\ SO_2})_{experiment2} + (M_{sulfur\ from\ SO_2})_{experiment3}}{3}$$

$$M_{Sulfur} = \frac{0.000221 + 0.000364 + 0.000418}{3} = 0.000334$$

For nitrogen determination;

$$M_{nitrogen} = 2.056 Q_{analyzer} 14/46 \int_{t_{start}}^{t_{end}} Conc.\, of\ NO_2 (ppm)\, dt + 1.34 Q_{analyzer} 14/30 \int_{t_{start}}^{t_{end}} Conc.\, of\ NO (ppm)\, dt \qquad \text{Eq. 4.4.}$$

where,
$M_{nitrogen}$: mass of nitrogen (g)
$Q_{analyzer}$: Flow rate of analyzer (L/s)
t: time (second)
2.056: constant for changing concentration of NO_2 from ppm to mg/Nm^3
14/46: Ratio of Molecular Weight of Nitrogen and NO_2
1.34: constant for changing concentration of NO from ppm to mg/Nm^3
14/30: Ratio of Molecular Weight of Nitrogen and NO

$$M_{nitrogen} = \frac{0.0000641 + 0.0000660 + 0.0000550}{3} + \frac{0.000408 + 0.000471 + 0.000483}{3} = 0.000516$$

Same as carbon balance, result of mass balances that are conducted on nitrogen and sulfur are listed in Table 4.8 and Table 4.9, respectively.

Table 4.8 Percentage of nitrogen converted to NO_x in combustion experiments (%)

	0%*	3%*	5%*	10%*	20%*	30%*
A-1	11.8	13.7	13.5	10.8	7.4	6.2
B-1	11.8	13.6	13.2	10.3	9.0	4.7
C-1	11.8	14.1	13.7	11.0	7.3	4.7
D-1	11.8	13.9	14.9	11.6	7.1	5.8
E1-1	11.8	15.0	16.4	12.7	7.9	5.6
E2-1	11.8	13.7	12.8	10.0	6.5	4.2
F-1	11.8	13.1	18.2	15.0	14.1	4.6

* Ratio of sewage sludge in fuel mixtures; 0% represents batches which contain no sewage sludge; 30% indicates mixtures prepared with 30% sludge and 70% coal.

Table 4.9 Percentage of sulfur converted to SO_2 in combustion experiments (%)

	0%*	3%*	5%*	10%*	20%*	30%*
A-1	25.3	30.5	30.1	27.9	16.7	13.8
B-1	25.3	36.1	42.1	43.6	35.5	34.7
C-1	25.3	34.6	24.2	39.2	29.0	42.5
D-1	25.3	43.0	46.1	43.0	30.4	34.1
E1-1	25.3	19.1	25.7	39.5	16.9	16.7
E2-1	25.3	7.3	41.1	45.1	40.5	27.7
F-1	25.3	13.9	75.3	88.2	103.9	29.3

* Ratio of sewage sludge in fuel mixtures; 0% represents batches which contain no sewage sludge; 30% indicates mixtures prepared with 30% sludge and 70% coal.

It can be seen in Table 4.8 and 4.9 that amount of nitrogen and sulfur oxidized is fairly low as compared to nitrogen and sulfur content in samples used in experiments. Nitrogen and sulfur balance did not hold for the experiments. In addition, there is no profile which represents the effect of sludge addition on oxides of sulfur and nitrogen formation, i.e. sulfur and nitrogen oxide concentrations appear to be constant almost in all cases.

Possible reasons for this result could be the amount of fuel mixtures used in experiments. In average, 0.15 gr pellets are burned and resultant SO_2 and NO_x are very low considering sulfur and nitrogen content of sewage sludge and coal samples. Attempt of creating a mass balance for very small amounts of sulfur and nitrogen could be one of the possible reasons of failure in mass balance. Gas analyzer may not measure emissions accurately. SO_2 and NO_x may be condensed during moisture trap in gas conditioning section of the flue gas analyzer, PGD-100. Also, there is a possibility of reactions between nitrogen oxides and unburned hydrocarbons. Nevertheless, experimental setup used in this study was not successful to observe the effect of sludge addition on SO_2 and NO_x formation in co-combustion experiments.

4.3. Kinetic Study of Thermogravimetric Analysis of Sewage Sludge Samples

Thermogravimetric analysis is used to understand kinetic characteristics of sewage sludge combustion. In this study, samples are heated in predetermined heating programs in a TGA and change in mass and temperature of sample is observed.

As explained in Section 3.3.2.1., mass losses of samples are normalized with respect to initial weight of samples and result is called as "extent of conversion". Consequently, profiles of mass loss with respect to time are obtained on this basis. Figure 4.8 illustrates an example of mass loss profile. Remaining profiles are given in Appendix B.

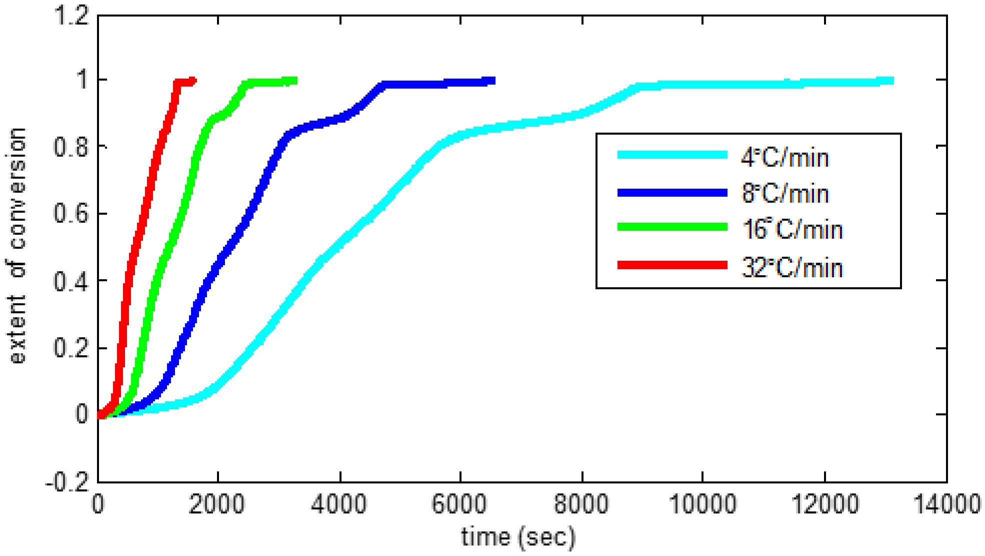


Figure 4.8 Mass loss profiles of sample A-1 in TGA experiments at different heating rates

It can be seen in Figure 4.8 that the extent of conversion is zero at the beginning of experiments. It proceeds and when combustible part of sewage sludge is burned out, extent of conversion reaches unity. The mass loss rate of the sample depends on the heating rate. When the sample is heated at a rate of 32 °C per minute, the complete conversion of the sample occurs in roughly 1500 seconds. However, it takes 9000 seconds for complete conversion of the sample at a heating rate of 4 °C per minute.

Temperature of the sample is another parameter which is constantly monitored by a thermocouple located in close to the sample. Although sample is heated in a constant temperature rise program, the real heating rate observed in the sample generally deviates and makes fluctuations from the heating rate programmed. An example is shown in Figure 4.9 while remaining profiles are given in Appendix B.

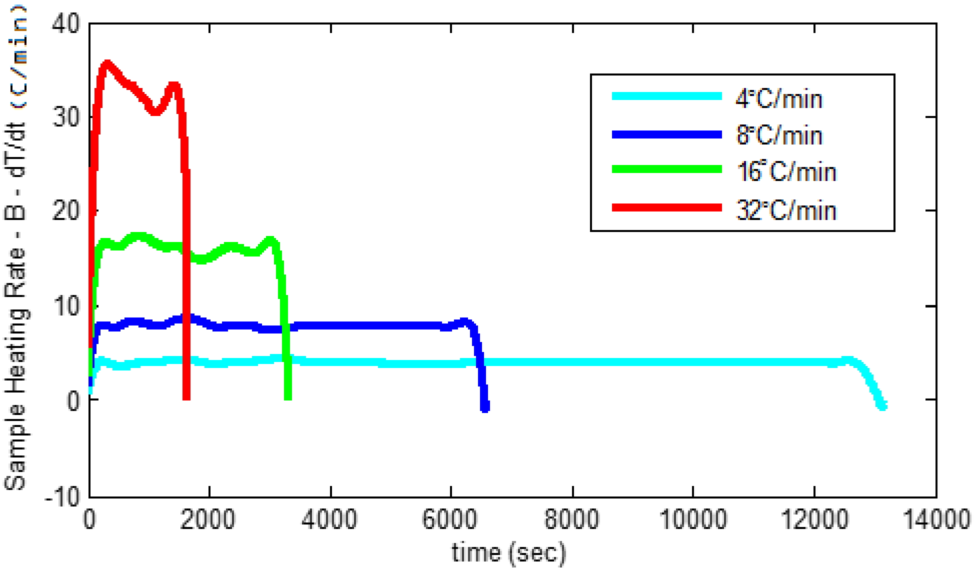


Figure 4.9 Heating rates of sample A-1 in TGA experiments

Figure 4.9 shows that the heating rate of the sample is not constant. It can have higher or lower values from the heating rate programmed indicating that exothermic or endothermic reactions take place in the sample.

Rate of reactions during experiments are determined using the procedure given in Section 3.3.2.1. An example of reaction rate with respect to time in experiments is given in Figure 4.10. Rest of the reaction rate profiles are given in Appendix B.

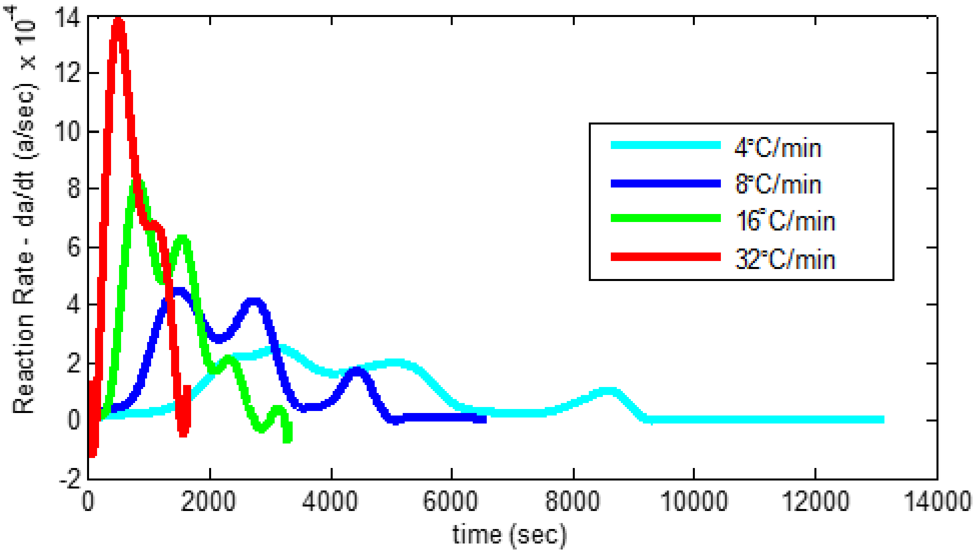


Figure 4.10 Reaction rates of sample A-1 in TGA experiments

Since four heating rates are applied to the sample, 4 different curves are obtained for mass losses with respect to time. In general, comparison of these profiles indicates that the rate of mass loss which has occurred in the sample is not constant. Initial rates are very fast and as time progresses, the rates gradually decrease. When the heating rate is e.g. 32 C/min, the initial reaction rate is the highest. As heating rate decreases, initial reaction rates also decrease and then stops at the end of the reaction. This also means that the particle is burned out. The first peaks in the curves represent the combustion of volatile matter, and later on the other peaks represent the combustion of char, etc.

Results of all TGA analysis where experimental conditions are explained in Section 3.3.3., are given in Appendix B. Mass loss, sample heating rate and reaction rates of each experiment are included in Appendix B.

4.3.1. Activation Energy Calculation

Activation energy of reaction is calculated according to the procedure which is explained in Section 3.3.3.1. Results of activation energy calculations are shown in Figure 4.11. Also, coefficient of correlation regarding activation energy calculation is given in Figure 4.12.7

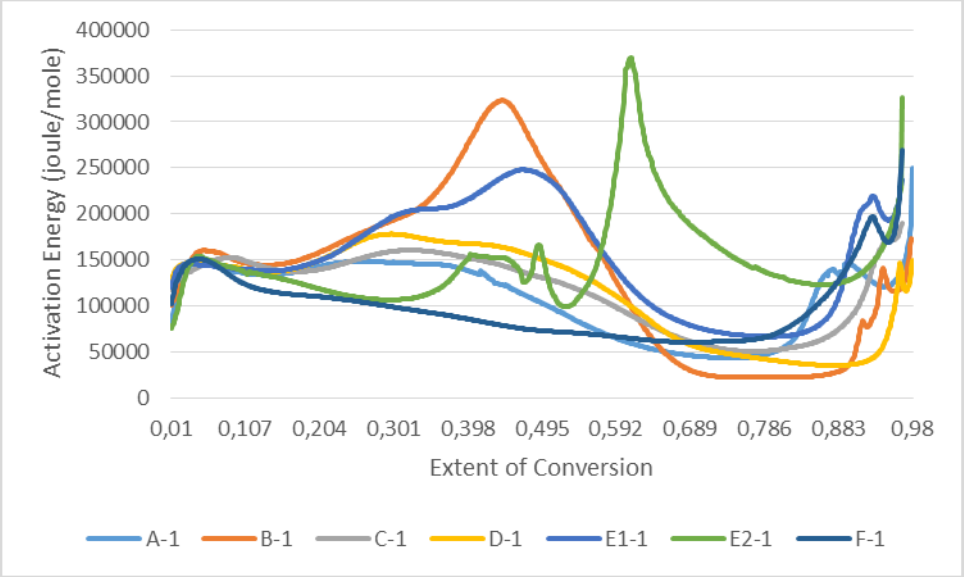


Figure 4.11 Change of activation energy of sewage sludge samples with extent of conversion

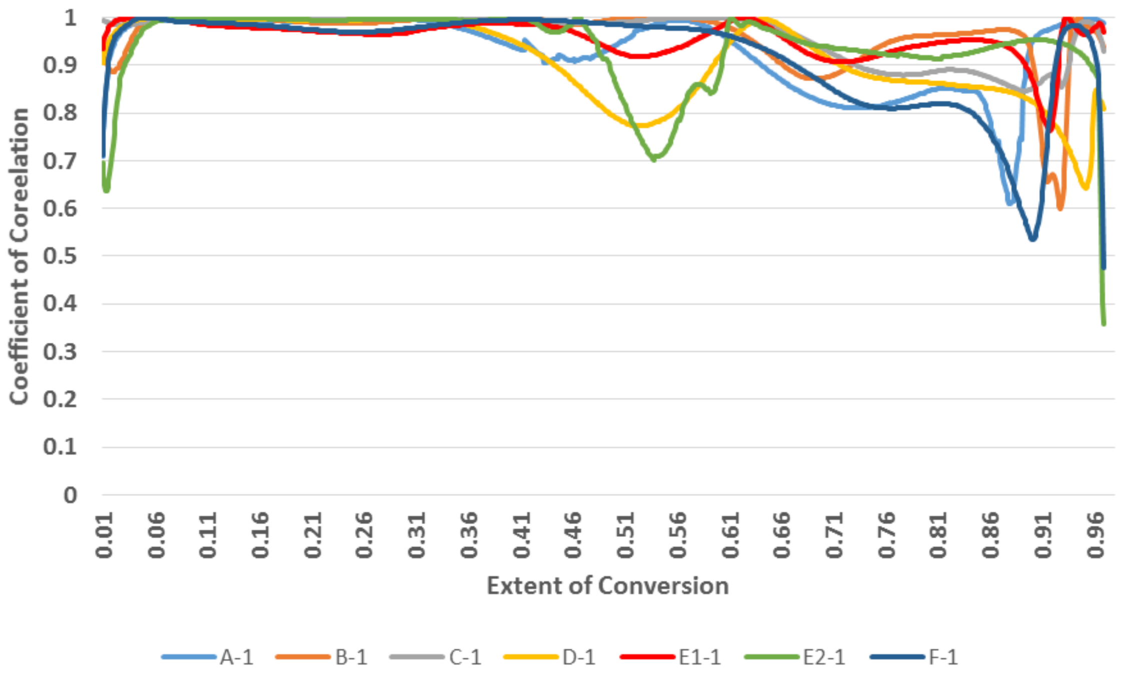


Figure 4.12 Coefficient of correlations obtained in activation energy calculations

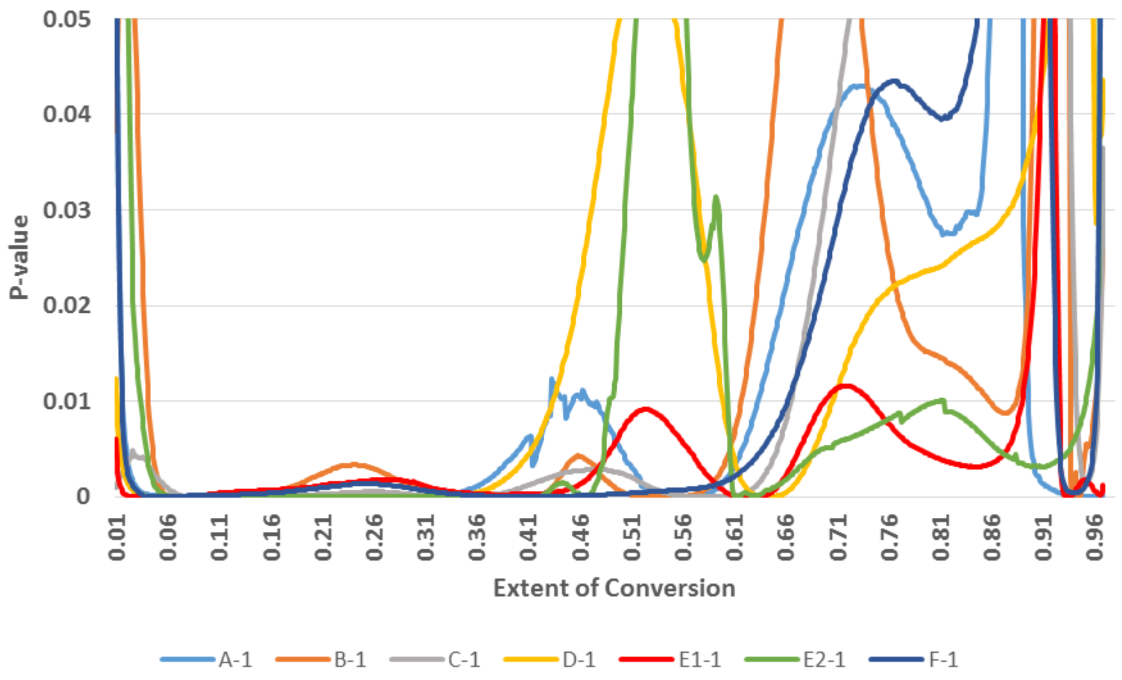


Figure 4.13 P-values which correspond to values of coefficient of correlation obtained in activation energy calculations

Figure 4.11 show that activation energy of sewage sludge samples can have different values. Values vary between 40 kJ/mole and 350 kJ/mole. While A-1, C-1 and D-1 samples have similar trends; E2-1 and F-1 have unique particular profiles. Sample E1-1 and B-1, on the other hand, have similarities over some regions.

Figure 4.12 shows the coefficient of correlation obtained in activation energy calculation. Figure 4.13 shows the accuracy of values of degree of linearization obtained in activation energy calculation. Therefore, Figure 4.12 and Figure 4.13 need to be examined together. It should be kept in mind that any coefficient of correlation which has the P-value higher than 0.05 has no statistical meaning. Therefore, correspondent activation energy value is not statistically useful. Regions where correlation coefficient close to unity also has P-values lower than 0.05 have statistically meaningful activation energy values. Results show that nearly in all experiments, activation energy calculation is correctly determined for the region of 0.010 – 0.400 in terms of extent of conversion. That means, it is correctly calculated for the first half of experiments. An error shows up after this point and reduces degree of linearization to 0.8 and P-values increase more than 0.05 in average. The reason behind this result might be due to change in type of reactions taking place in combustion of samples. Decrease in the rate of mass loss in experiments which occurs in later part of experiments might cause interferences in measuring temperature or weight of sample. Thus, this can result in lower values of coefficient of correlation and subsequently higher P-values.

Activation energies of all samples determined in this study ranges between 30 – 360 kJ/mole, which are comparable with the values reviewed in Section 2.5.

4.3.2. Calculation of Reaction Rate

As it is explained in Section 3.3.3.2, reaction rates measured in TG experiments are tried to be estimated. Results of reaction rate calculation are given in Figure 4.14 - 4.20.

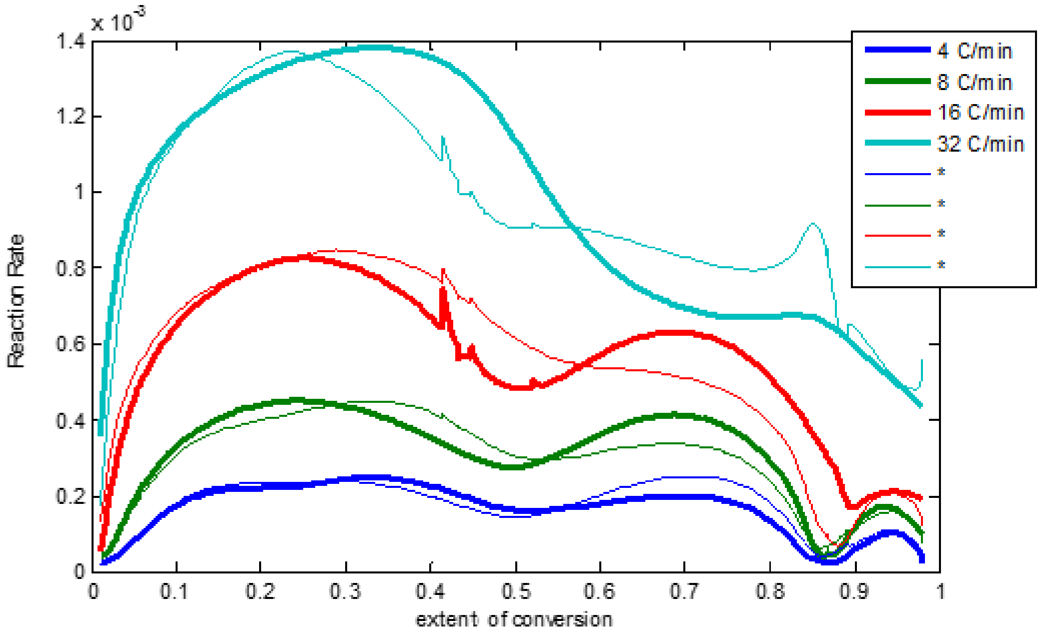


Figure 4.14 Change of reaction rate with extent of conversion- comparison of measured values with calculated values for sample A-1 (* indicates calculated values)

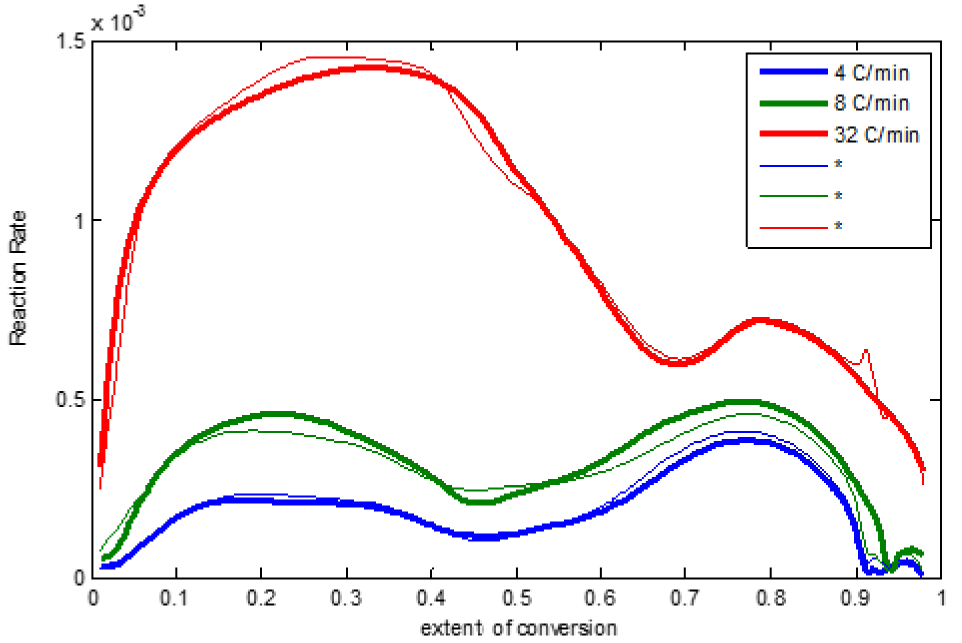


Figure 4.15 Change of reaction rate with extent of conversion- comparison of measured values with calculated values for sample B-1 (* indicates calculated values)

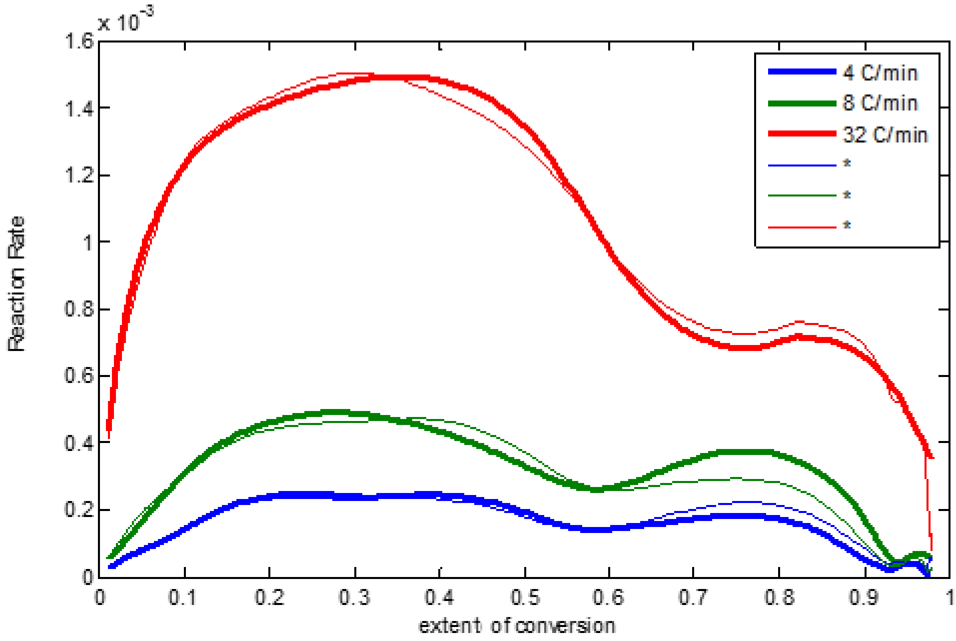


Figure 4.16 Change of reaction rate with extent of conversion- comparison of measured values with calculated values for sample C-1 (* indicates calculated values)

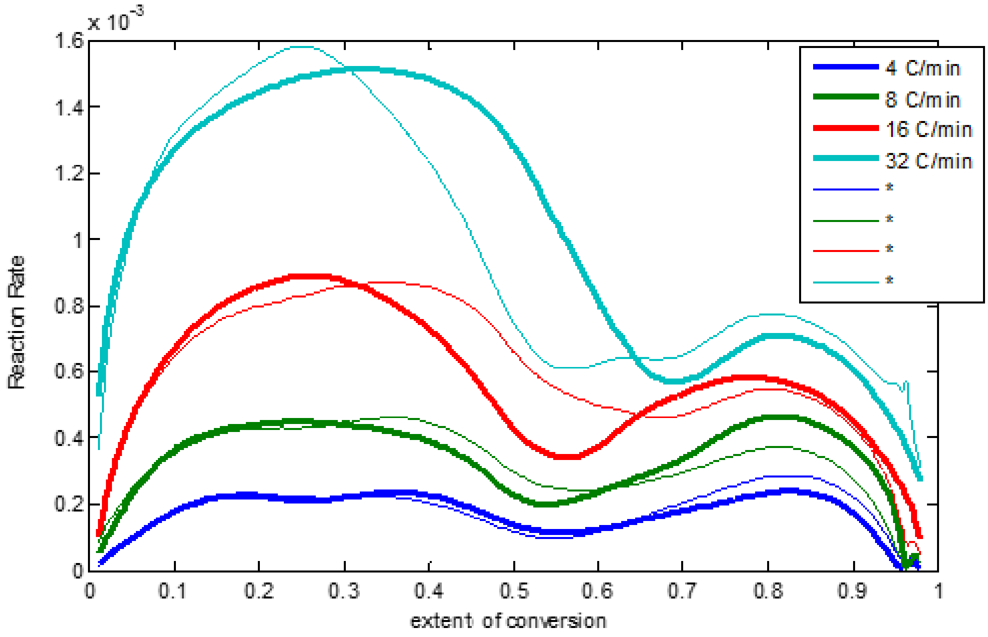


Figure 4.17 Change of reaction rate with extent of conversion- comparison of measured values with calculated values for sample D-1 (* indicates calculated values)

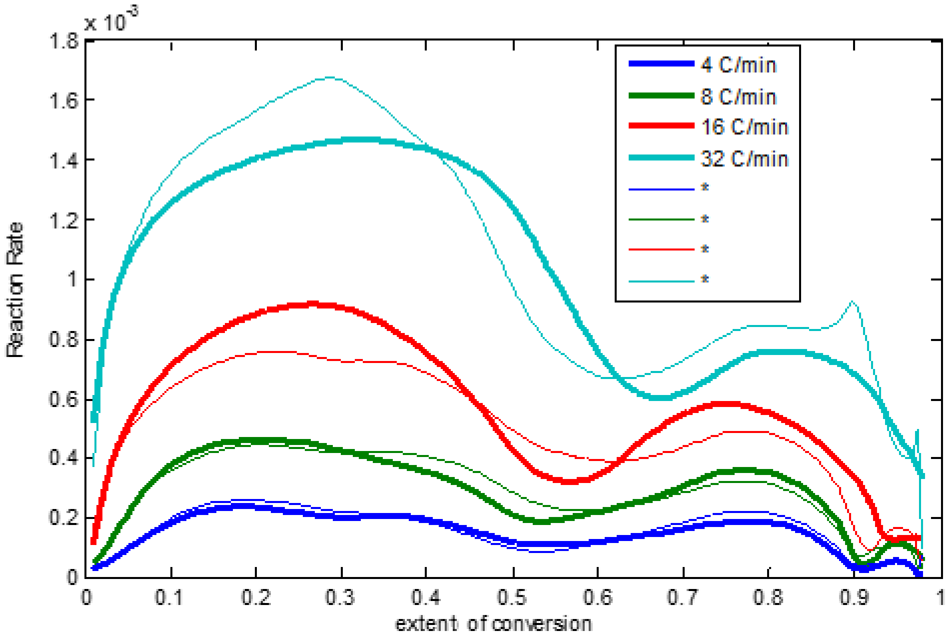


Figure 4.18 Change of reaction rate with extent of conversion- comparison of measured values with calculated values for sample E1-1 (* indicates calculated values)

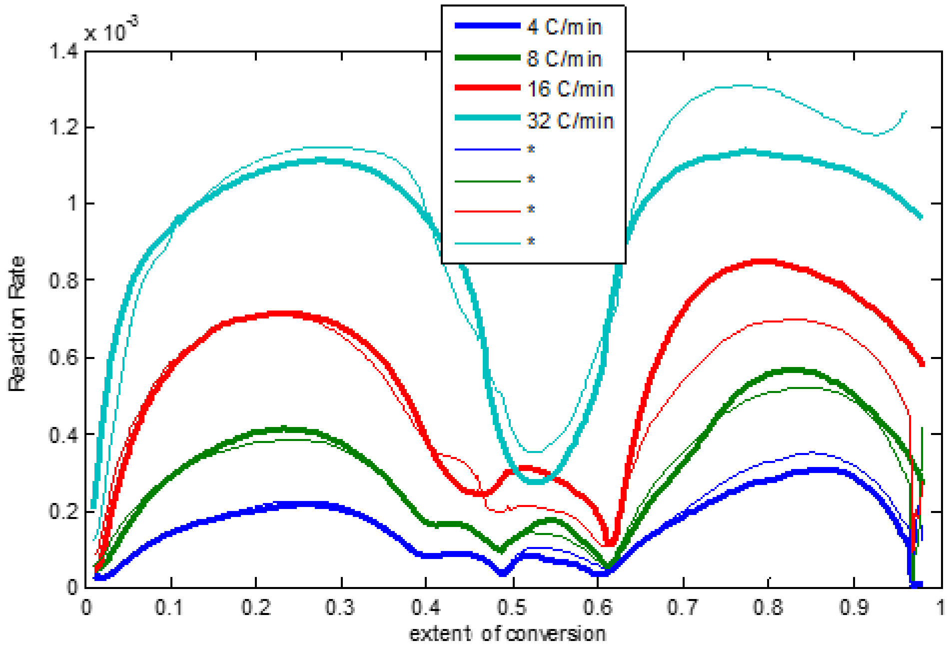


Figure 4.19 Change of reaction rate with extent of conversion- comparison of measured values with calculated values for sample E2-1 (* indicates calculated values)

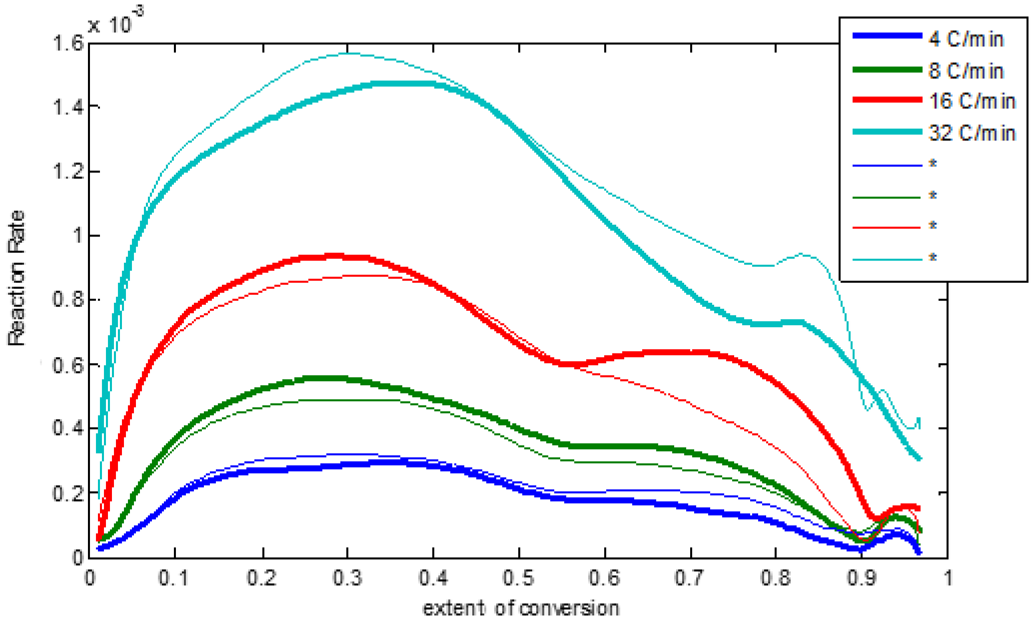


Figure 4.20 Change of reaction rate with extent of conversion- comparison of measured values with calculated values for sample F-1 (* indicates calculated values)

As it is described in Section 3.3.3.2 reaction rate values obtained from experimental data are fitted. However, there are some cases where calculated reaction rates do not fit the experimental data. In general, profiles of reaction rates which belong to heating rates of 4 °C/min and 8 °C/min are successfully fitted. However, errors between the model calculations and the experimental values grow bigger in other heating rates, namely 16 °C/min and 32°C/min. Therefore, it can be inferred that increase in heating rates of the samples definitely have some impact on rates of reactions during experiments. This observation can also be proved by comparing sample heating rates, which are given Appendix B. It can be seen in Appendix B that although temperature program is kept constant, i.e., sample is heated at a constant rate (4, 8, 16, 32 °C), temperature rise in the samples deviates from these values due to endothermic/exothermic reactions taking place in the sample. Moreover, higher temperature deviations are seen in higher heating rates. This was also observed by Vyazvokin et al. (2011) with a recommendation that “temperature deviation should be eliminated by using smaller sample size or lower heating rates, or using kinetic analysis methods which considers deviation of temperature.”

Although the method used in this study is suitable to take account these differences, lower success rate was obtained in fitting of reaction rates to a model at higher heating rates. This brings a question that physical condition of experiment affects the kinetic triplet which is supposed to describe a “chemical” reaction. This is a problem for which an alternative approach is given in the literature. The term “apparent” activation energy is created to be used in the field of thermal analysis. This term refers to an empirical, experiment oriented activation energy, rather than an energy barrier of the rate limiting step.(Andrew K. Galwey 2004) Therefore, results of our study given above can also be used as an example of activation energies representing empirical values which is specific to the experiment. In this case, activation energies given in Figure 4.11 are specific to experiments with heating rates of 4 and 8 °C/min. Activation energies for other two heating rates are close to the first ones but different than previous case with some deviations in reaction rates.

Therefore, it can be concluded that when all experimental conditions are kept similar (with exception of heating rates; it should be kept close to each other) resultant activation energy reflects these set of experimental conditions. Also, different activation energies for the same sample can be obtained by changing the experimental conditions in a controlled program. Effect of change in mass of the sample, gas flow rate, set of heating rates etc. on “apparent” activation energies could be identified with different experimentation.

4.3.3. Determination of Reaction Model and Frequency Factor

The last step of kinetic study is determination of reaction model and corresponding frequency factor. In addition to the Section 3.3.3.3 where procedure is given, an illustration on sample A-1 is given below.

As it is listed in Table 3.8 that there are four kinds of reaction models; **nucleation** models which are represented as A and P, **geometrical contraction** models which are represented as R, **diffusion** models which are represented as D and **reaction order** models which are represented as F. Numbers next to the abbreviation of reaction models indicate the type of such a reaction model. For instance; F1 indicates first order reaction model and R2 indicates contraction area (i.e. 2-dimensional geometrical contraction). Therefore, the aim of this section is to find the best matching reaction model for combustion of sewage sludge samples.

The first step of reaction model and frequency factor determination is to obtain such a relationship for all samples;

$$intercept = lnA + lnf(a) \qquad \text{Eq. 4.5.}$$

Intercept values are obtained during activation energy calculation; in case of sample A-1, intercept values are given in Figure 4.21.

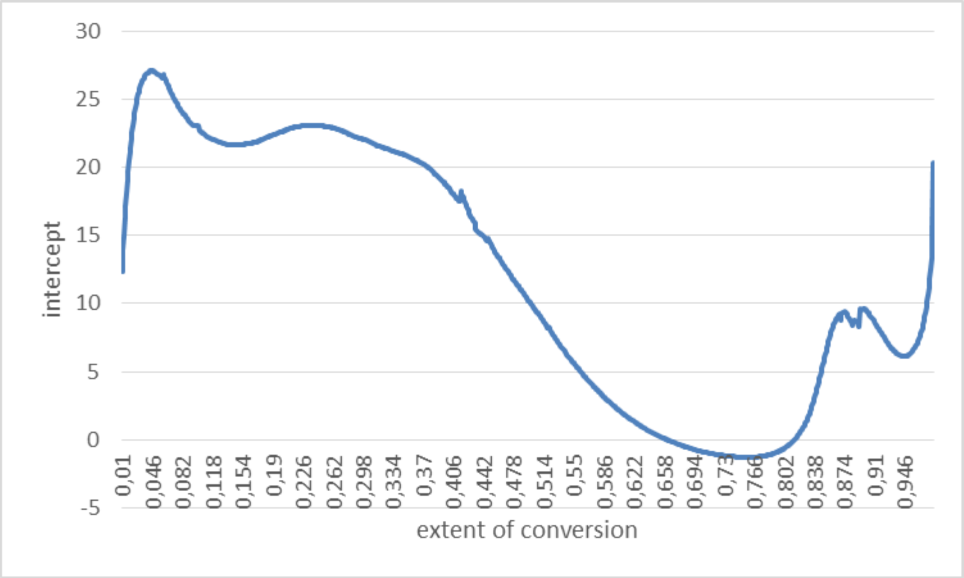


Figure 4.21 Intercept values obtained during activation energy calculation of sample A-1

As it can be seen in Table 3.8, 16 reaction models have different forms, therefore, for each reaction model there will be a different frequency factor. As a result, 16 pairs of reaction models and frequency factors are obtained.

Activation energy and candidate reaction models– frequency factor pairs are determined. Next step is to determine which reaction model – frequency factor is the most suitable pair. In order to test reaction model – frequency factor pairs, following equation is utilized.

$t(a) = g(a)/Ae^{-Ea/RT}$(Vyazovkin et al. 2011) Eq. 4.6.

where,
t(α): time vector,
g(α): integral form of reaction model,
A: frequency factor,
Ea: activation energy,
R: ideal gas constant,
T: sample temperature.

There is also an ASTM standard (E1641-07, Standard Test Method for Decomposition Kinetics by Thermogravimetry) which utilizes Eq. 4.6 by defining g(α) as a first order reaction (ASTM E1641-07).

TGA experiments conducted on A-1 sample generate four different sample temperature profile according to the heating rates (4 °C/min, 8 °C/min, 16 °C/min, 32 °C/min). Also using these profiles, activation energy profile was previously determined. Therefore, according to reaction models – frequency factor pairs that were created, there are 16 different time vectors which are candidates to explain a certain experiment. Result of experimental and calculated values for A-1 sample in 4 °C/min heating experiment is given in Figure 4.22.

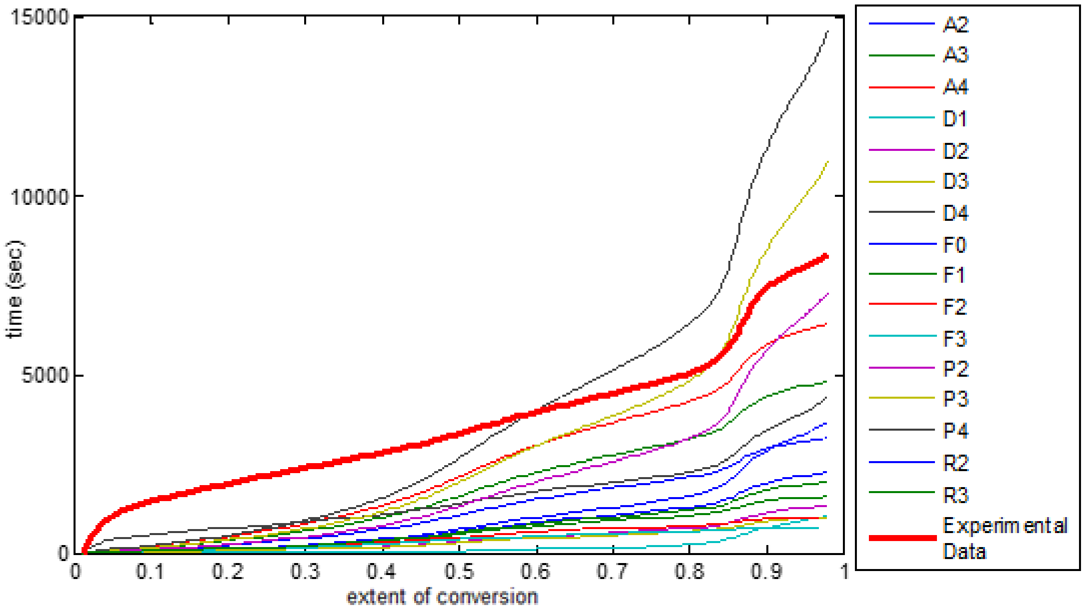


Figure 4.22 Fitting integral time vectors to TGA profile for sample A-1 at 4 °C/min heating rate

In Figure 4.22 thick red line represents experimental data obtained in TGA analysis of Sample A-1 at 4 °C/min heating rate. Other lines are results of time vectors which are created from 16 reaction model – frequency factor pairs. Results of fitting other experimental data to the model are given in Appendix D.1.

As it can be seen in Figure 4.22 none of the reaction models can adequately describe mass loss profile. Same results are obtained for other trials (sludge samples and heating rates) which can be seen in Appendix D.1. Since it is a fact that multiple reactions take place in sewage sludge combustion, this is an expected result. Therefore, differential form of time vector data is fitted to differential form of time profile of the experiments.

Differential fitting is carried out by following a differentiation operation of vectors given in Appendix D.1. In case of example given in Figure 4.22, resultant profiles have the following form as given in Figure 4.23.

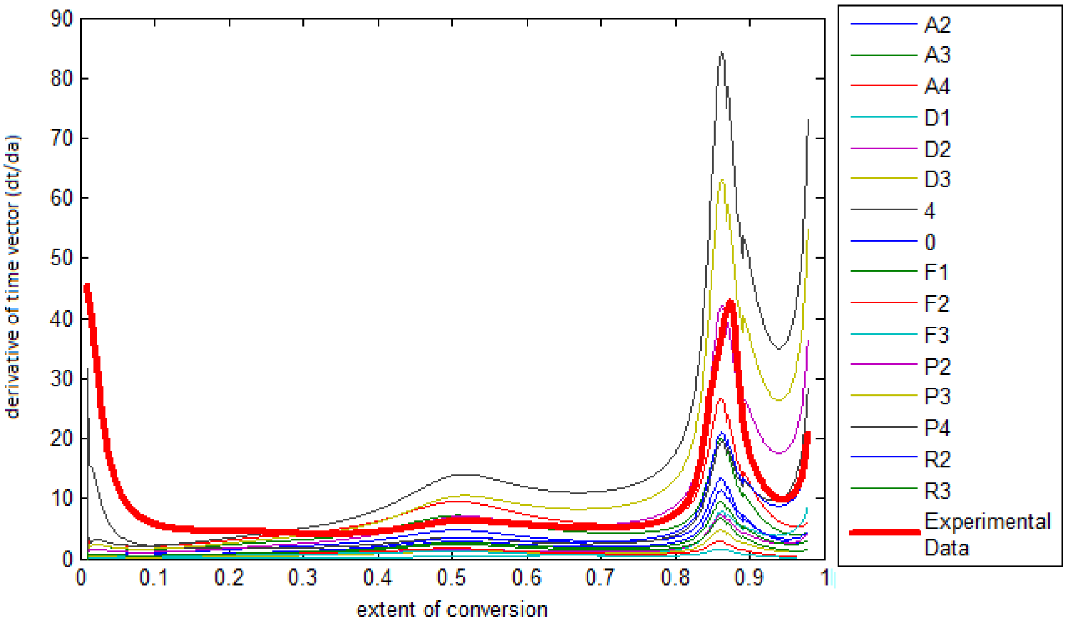


Figure 4.23 Fitting differential time vectors to TGA profile of sample A-1 at 4 °C/min heating rate

Vectors given in Figure 4.23 is the differential form of vectors given in Figure 4.22. These profiles represent the time passed for incremental increase on extent of conversion. Therefore, differential data allow comparing the experimental results with cases in any selected range of conversion.

Closer look at the Figure 4.23 yields the observation that in some regions of extent of conversion, some reaction models can have better fits to the experimental data. <u>This means that during combustion of the sample, different reaction models are applicable.</u> In case of experiment on Sample A-1 at 4 °C/min heating rate, it can be seen that the extent of reaction over the region of 0.3 – 0.9, P2 model provides a satisfactory fit with the experimental data. A similar procedure is followed by Folgueras and Diaz (2013) for two different kinds of sewage sludge samples. However, identification of reaction model is tried to be found using the relationship;

$$\frac{d\alpha}{dT} - lnf(\alpha) = ln\frac{A}{\beta} - \frac{E}{RT} \qquad \text{Eq.4.7.}$$

Problem in this method is that reaction models listed in this study is tried to be inserted into Eq. 4.7 to obtain the best fit which is determined to be the “correct” reaction model. It is proposed that, given the set of reaction models, the one which yields highest coefficient of correlation is the correct form of reaction model; activation energy and frequency factor that correspond to that reaction model also hold. This approach is basically the same with “model fitting methods” which are proved to be inaccurate, as it is explained in Section 2.4.2. Therefore, the reaction order model, which are determined as the correct form are not accurate (M.B. Folgueras, Alonso, and Díaz 2013).

Results of differential fitting for other experiments are given in Appendix D.2. It can be seen in Appendix D.2 that the time required for the combustion in certain regions could be explained by different reaction models. In all cases, reaction order models (F0, F1, F2, and F3), diffusion models (D1, D2, D3, D4) and geometrical contraction models (R2, R3) failed to match with experimental data. On the other hand, nucleation models (P2, P3, P4, A2, A3, and A4) have good fits. There is also an observation that a form of diffusion models, D4, has a trend which has the best approximation to mass loss profiles at the beginning of experiments. Considering the region to 0,100 in the extent of reaction, there is a characteristic profile that all samples have. D4 also fits such a profile but it lies generally below the experimental data.

Results given in Appendix D.2 indicate that representative reaction models are not the same for experimental data of a sample. That is, considering a region of conversion for a sample, when different heating rates are applied, different reactions dominates during the mass loss. This indicates that heating rates change reactions which describe mass loss of the sample. Therefore, it can be concluded that it is not possible to predict behavior of these samples in actual combustion processes using TGA data alone. However, it is proved that type of reaction, activation energy and frequency factor of corresponding reactions which occur in combustion of sewage sludge samples in TGA setup can be determined by using the procedure which is presented in this study. This can be used to identify all factors which affects reactions and rates of such reactions that takes place to fully describe sewage sludge combustion.

Considering different sets of analysis used in this study, it can be concluded that nucleation processes give better fits for mass loss of sewage sludge samples as compared to other reaction rate models.

CHAPTER 5

CONCLUSIONS

Results of this study have shown that calorific values of sewage sludges on dry basis are close to the calorific values of Turkish lignite coals on the average. However, it is observed that calorific value of sewage sludge varies extensively, ranging between 1900 and 3800 cal/g. It is found that calorific value of sludge depends on different factors like treatment method, influent characteristics of wastewater, operating conditions etc. When two sewage sludge samples which come from different wastewater treatment plants having the same treatment process scheme are compared, the calorific values can be quite different. In addition to this, calorific value of sewage sludge samples change throughout an operating year even in the same wastewater treatment plant. Therefore, a comprehensive study which aims to clarify effects of wastewater/sludge treatment processes and their operating conditions on calorific value of produced sludge has been done in this study.

It was also found that volatile matter content can be used in estimating the calorific value of sewage sludge. Volatile matter is a parameter which is measured in wastewater treatment plants in a scheduled routine. As it is presented in this study, the empirical correlation between volatile matter and calorific value of sewage sludge can be used in wastewater treatment plants when a bomb calorimeter is not accessible to measure the calorific value directly.

Although the calorific value of sewage sludge reaches to acceptable levels in some cases, use of sewage sludge in combustion processes is limited due to its combustion and ash characteristics. Slagging and fouling intensity of sewage sludge determined in this study indicates that use of sewage sludge in co-combustion processes needs to be kept in small amounts. Presence of alkaline elements in the sludge gives high base to acid ratio, where base to acid ratio of all sludge samples range between 0.7 and 11.7. It should be noted that values higher than 1 corresponds to high tendency of slagging. Also, sulfur and phosphorus content of sewage sludge ash are high, which makes nearly of all of slagging and fouling indices higher than limit values.

Co-combustion experiments showed that use of sewage sludge in high percentages in the fuel mixture actually lowers the combustion efficiency. Coal combustion efficiency is about 99.7%. However, when mixtures of coal and sewage sludge (3, 5, 10, 20, 30% sewage sludge is added to coal) are combusted, lower combustion efficiencies are obtained as sewage sludge portion is increased in the mixtures. It was found that the efficiency is reduced to nearly 97% in some cases. Therefore, it would be best to consider the combustion process as a final disposal method for the sludge. Using the TGA analysis have shown that the kinetic triplet (activation energy, frequency factor and reaction model) of sludges can be determined to a certain extent using the method presented in this study, depending on the quality of data. This method is an application of Friedman method with some modifications which are explained in Section 3.3. The second conclusion drawn from the TGA results in this study is that physical interferences (mass of sample, heating rate etc.) change the type of reactions that dominates during the loss of mass. This observation leads to the conclusion that kinetic triplet is specific to the set of experiments which are applied and cannot be extrapolated to make some predictions. Given the set of experimental conditions, it is revealed that data obtained in TGA analysis of sewage sludge combustion can be represented by nucleation processes with more accuracy as compared to other reaction models in case high quality data are available.

It should be stated as a limitation of this study that such a reaction model which describes an experiment from beginning to end could not be found. Fits of reaction models to experimental data are applicable to only some regions of conversion. This is due to the heterogeneity of the sludge samples and considered to be a natural finding. To investigate this, studies need to further continue using different experimental setups by changing the variables such as gas flow rate, mass of sample, condition of sample, heating rate, etc.

CHAPTER 6

FUTURE STUDIES AND RECOMMENDATIONS

- Quantitative determination of operating conditions of sludge stabilization process on calorific value of sewage sludge needs to be studied further. This study is limited to identify that there is a certain effect of sludge stabilization process on thermal characteristics of sewage sludge. Further investigations are needed to determine a relationship that describes the change in calorific value of sewage sludge as operating conditions of sludge stabilization process changes.

- This study investigates co-combustion of sewage sludge and coal in a prefixed reactor type and experimental setup. Studies to increase the combustion efficiency coal – sewage sludge mixtures could be conducted. In this regard, different reactor types, experimental conditions can be studied.

- Qualitative comparison of activation energies obtained using different sets of experimental conditions of thermogravimetric analysis need to be done. This study describes a method to perform a kinetic analysis of thermal decomposition of a material. However, the method presented in this study relies on high quality data. Experimental errors are limiting factors on determining kinetic triplet. Therefore, experimental parameters can be changed to obtain data of better quality. Composition and flow rate of air, mass and condition of samples (pellets or loose material), set of heating rates, temperature intervals can be sequentially changed. Using such series of experiments can enable to compare kinetic triplets from different experimental setups. Also, the best experimental conditions which give the data of best quality can be determined.

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APPENDICES

A. Emissions Obtained in Co-Combustion Experiments

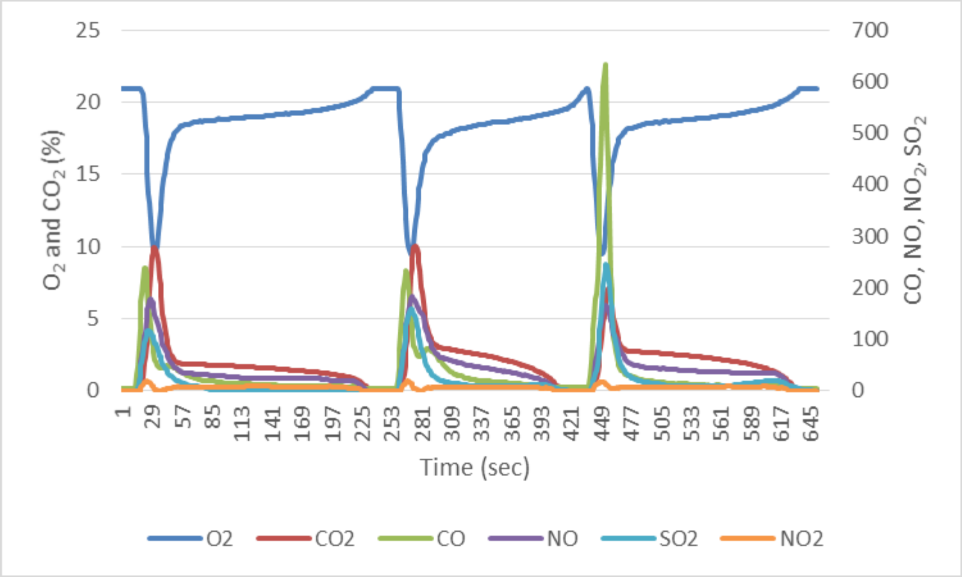

Figure A.1 Results of coal combustion experiment

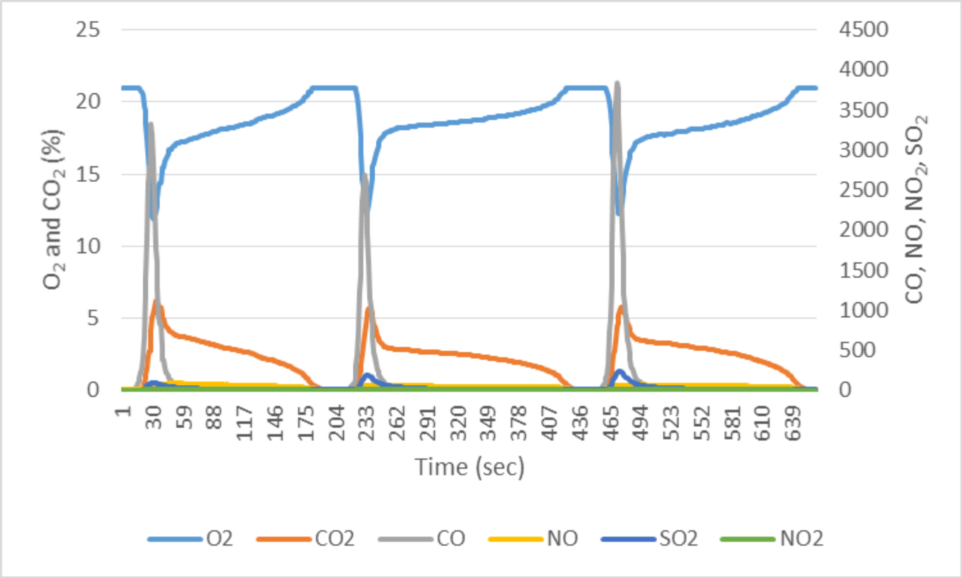

Figure A.2 Result of co-combustion of coal and A-1 sludge with %3 addition

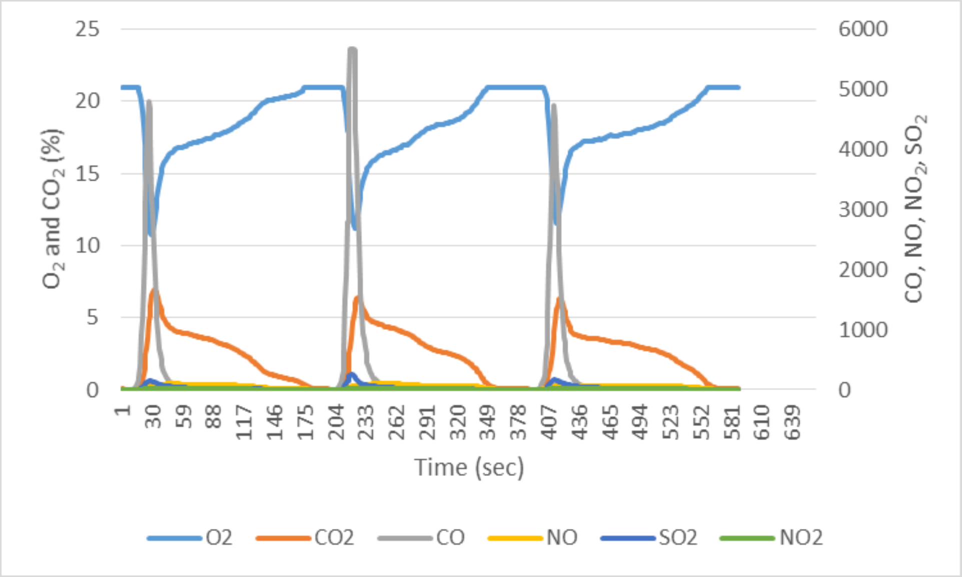

Figure A.3 Result of co-combustion of coal and A-1 sludge with %5 addition

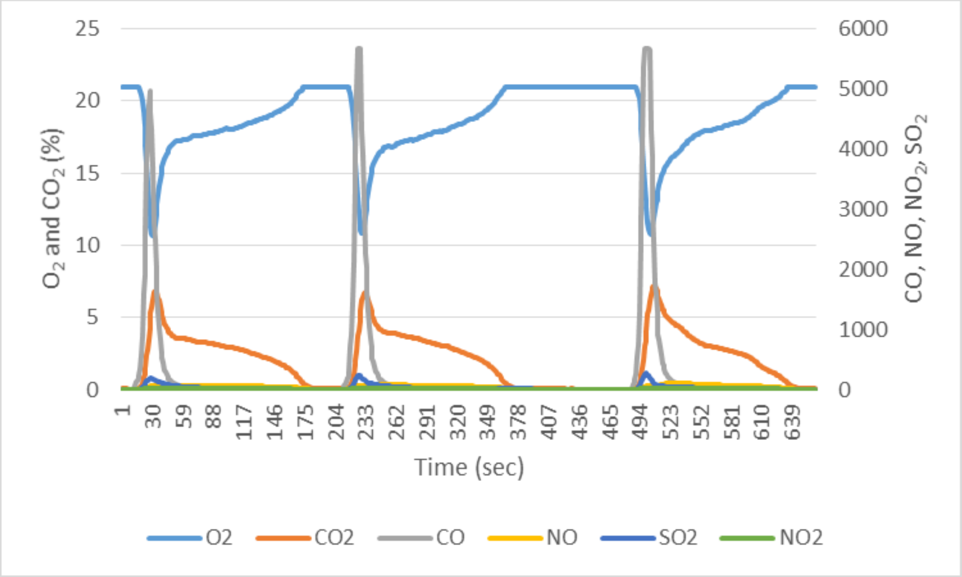

Figure A.4 Result of co-combustion of coal and A-1 sludge with %10 addition

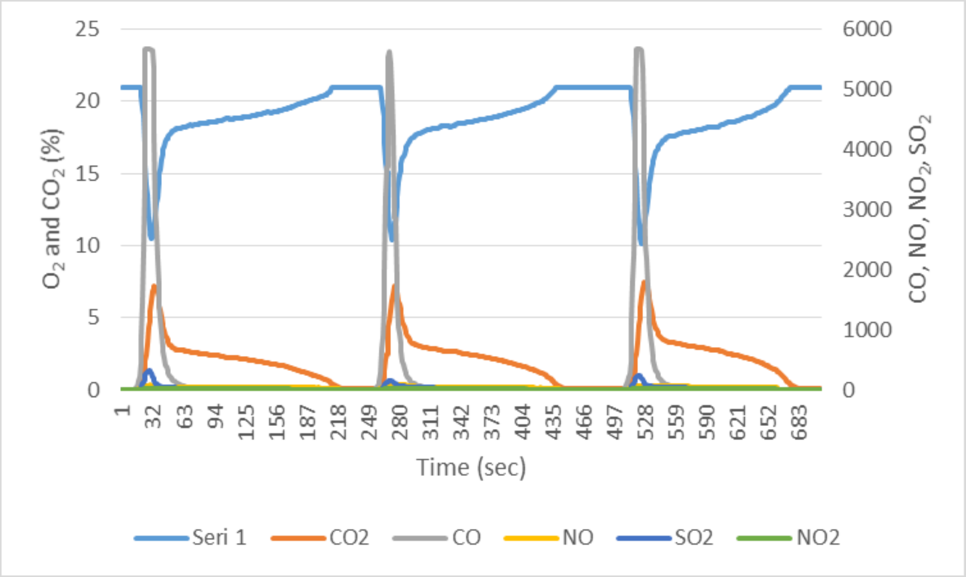

Figure A.5 Result of co-combustion of coal and A-1 sludge with %20 addition

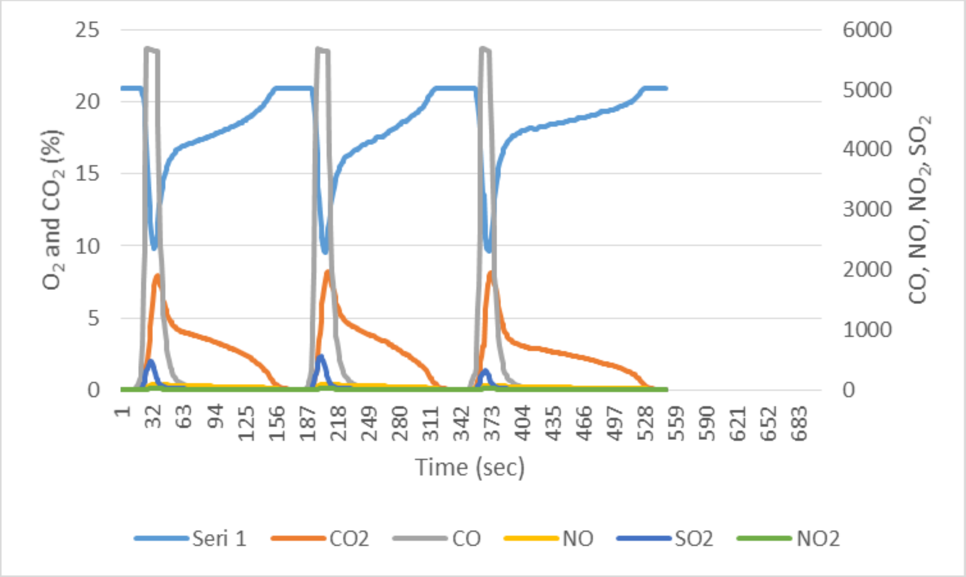

Figure A.6 Result of co-combustion of coal and A-1 sludge with %30 addition

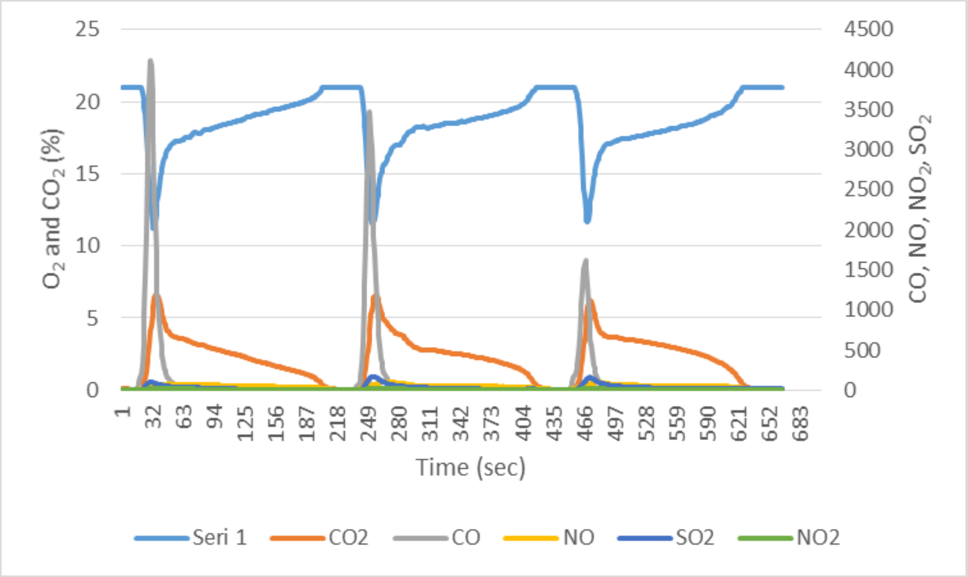

Figure A.7 Result of co-combustion of coal and B-1 sludge with %3 addition

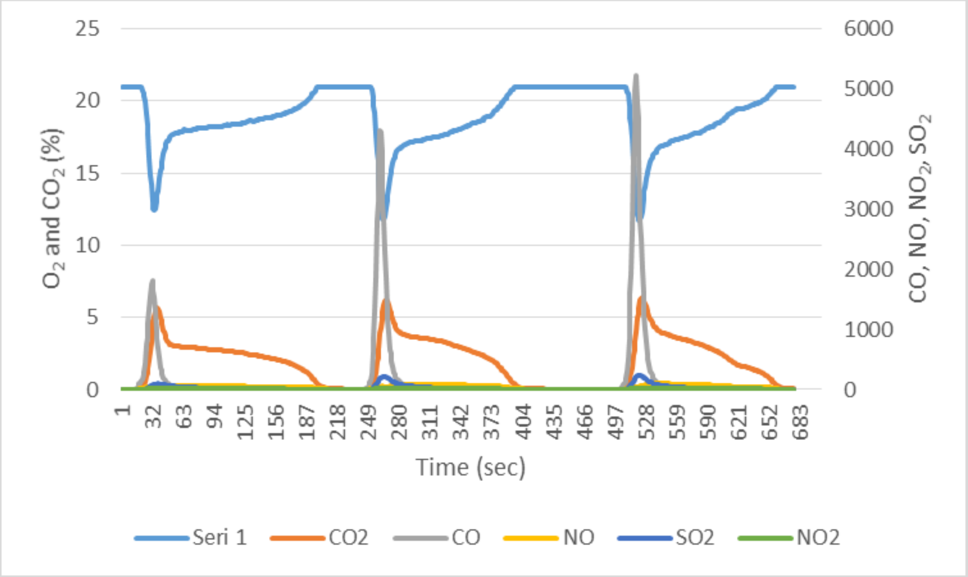

Figure A.8 Result of co-combustion of coal and B-1 sludge with %5 addition

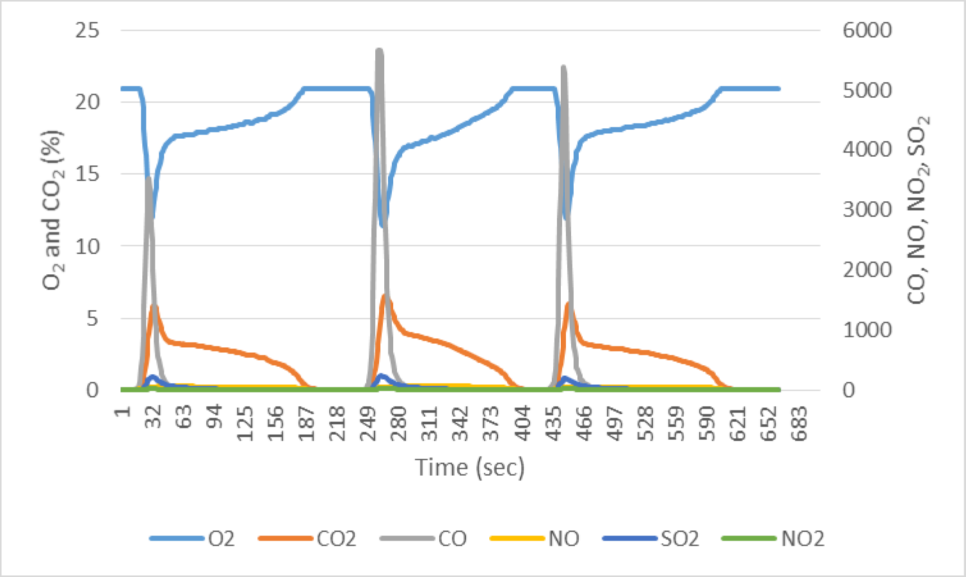

Figure A.9 Result of co-combustion of coal and B-1 sludge with %10 addition

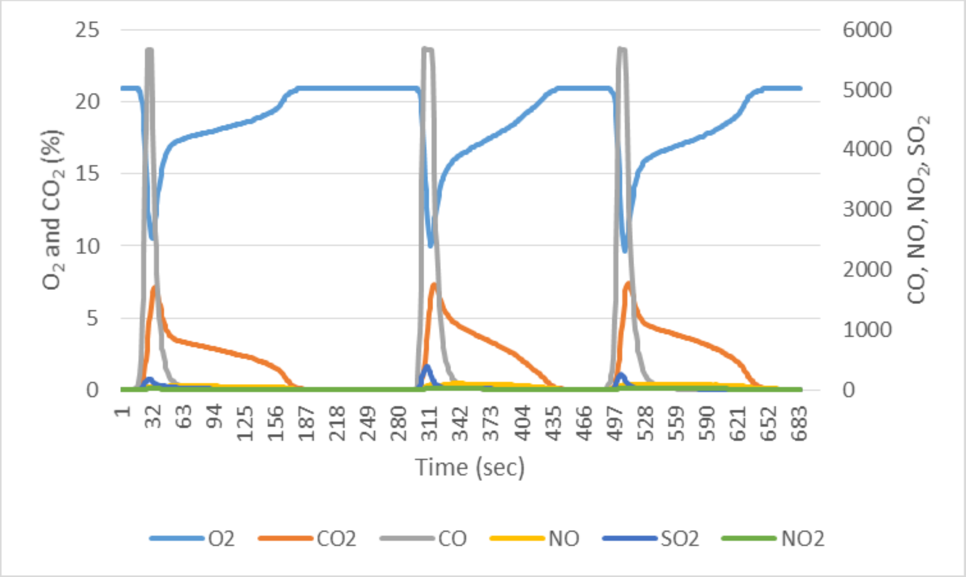

Figure A.10 Result of co-combustion of coal and B-1 sludge with %20 addition

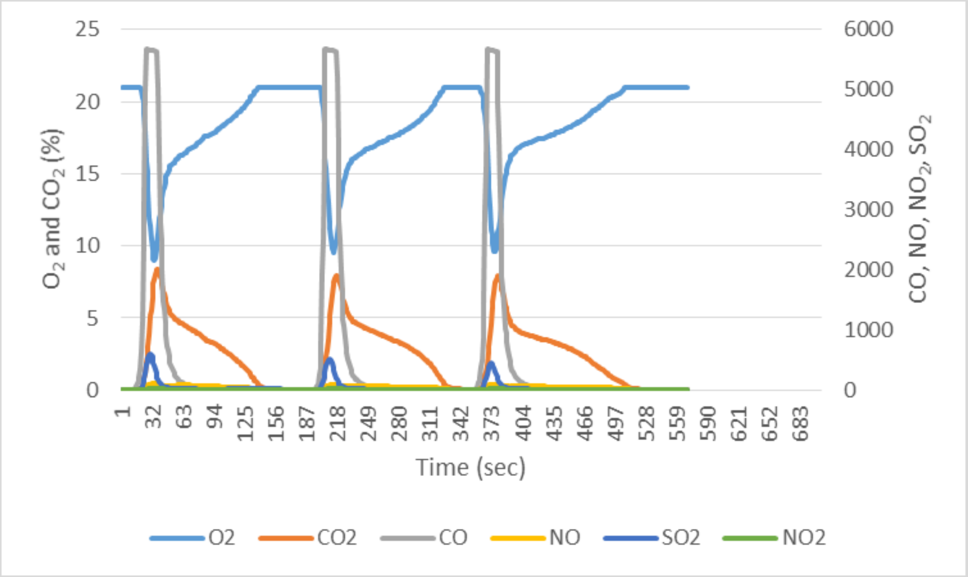

Figure A.11 Result of co-combustion of coal and B-1 sludge with %30 addition

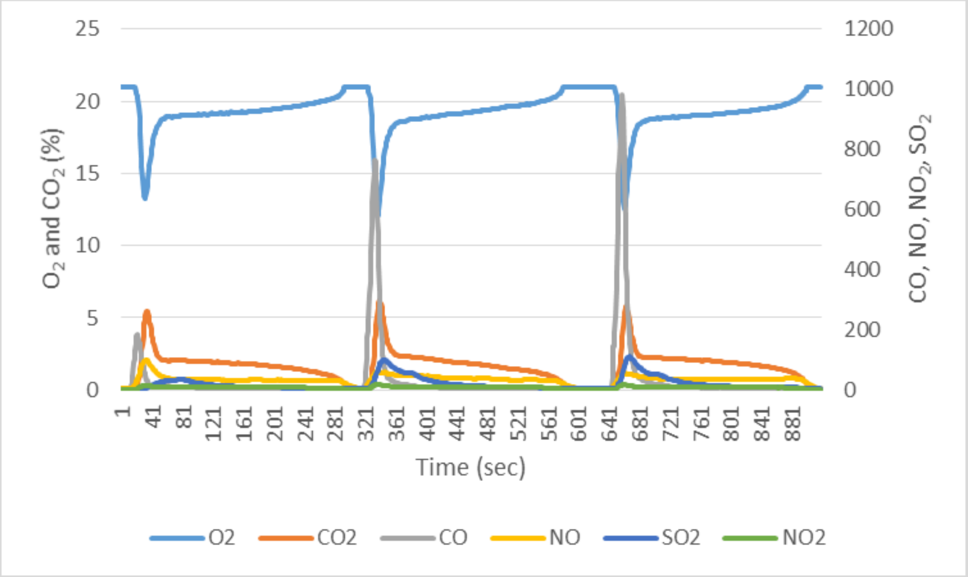

Figure A.12 Result of co-combustion of coal and C-1 sludge with %3 addition

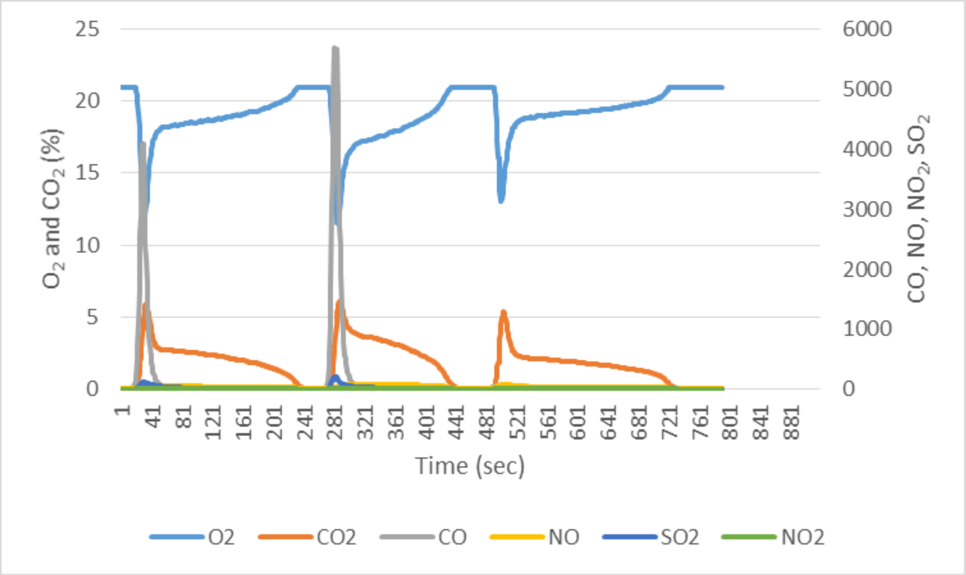

Figure A.13 Result of co-combustion of coal and C-1 sludge with %5 addition

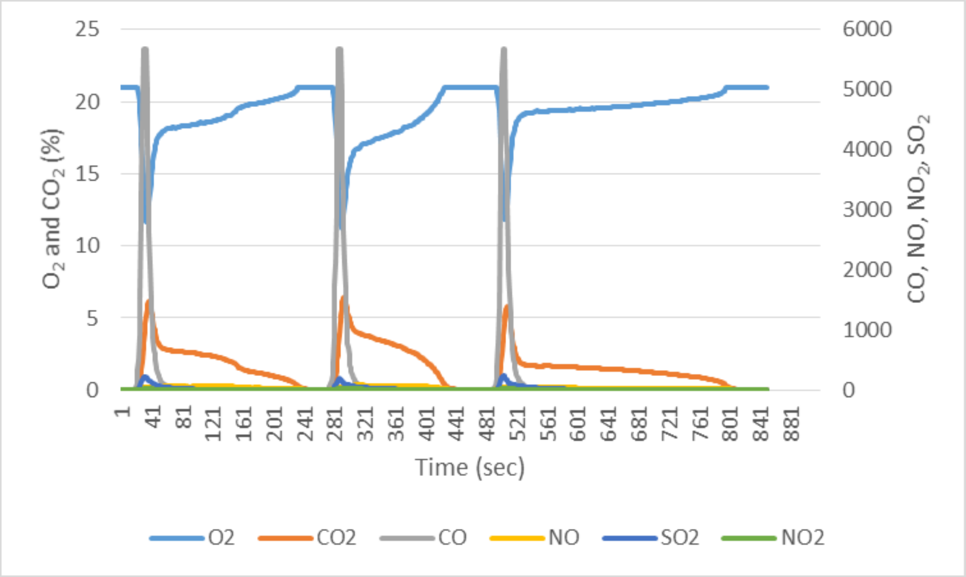

Figure A.14 Result of co-combustion of coal and C-1 sludge with %10 addition

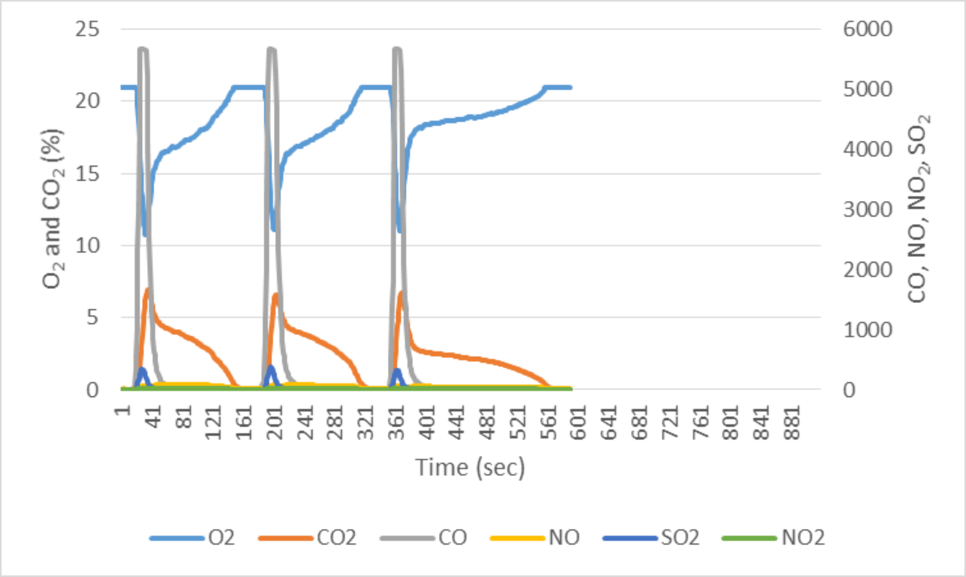

Figure A.15 Result of co-combustion of coal and C-1 sludge with %20 addition

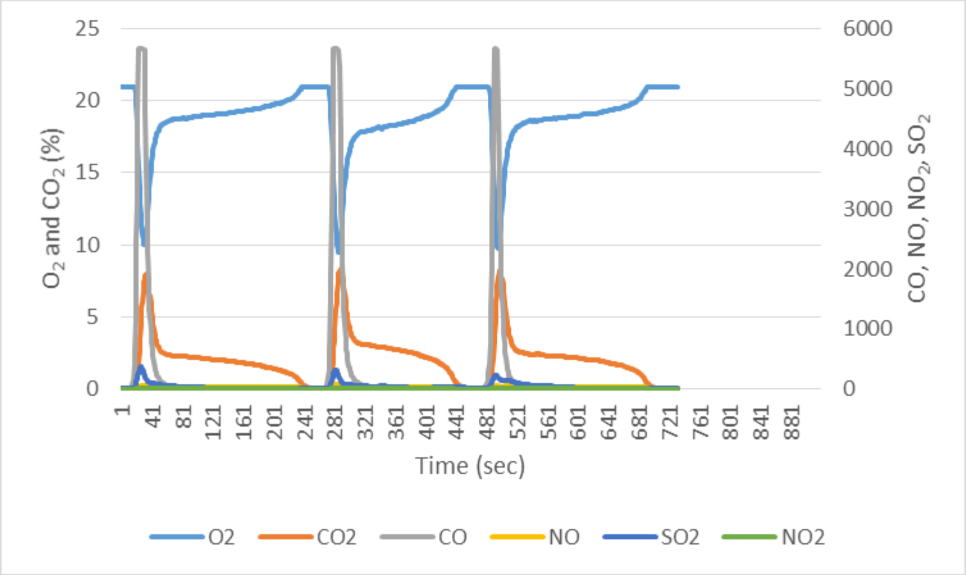

Figure A.16 Result of co-combustion of coal and C-1 sludge with %30 addition

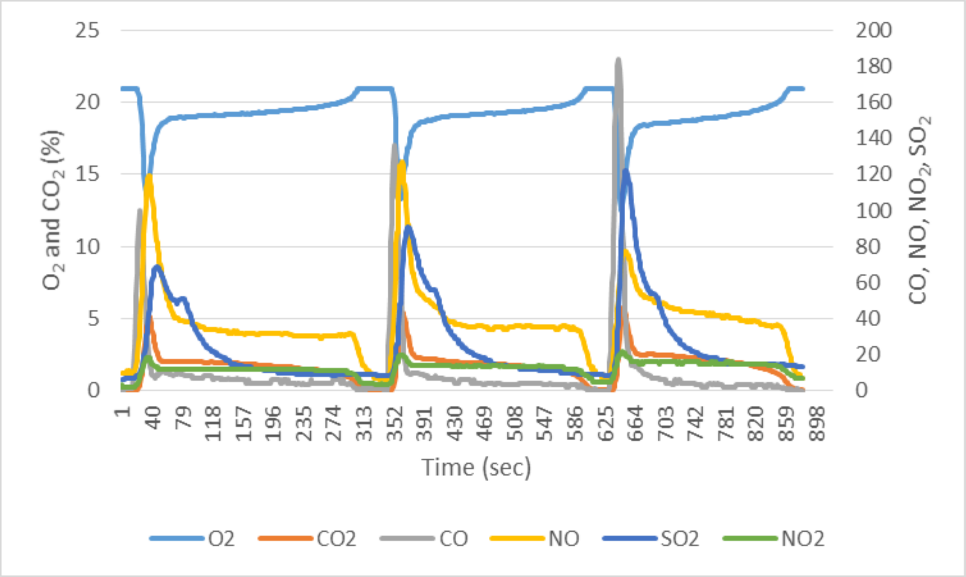

Figure A.17 Result of co-combustion of coal and D-1 sludge with %3 addition

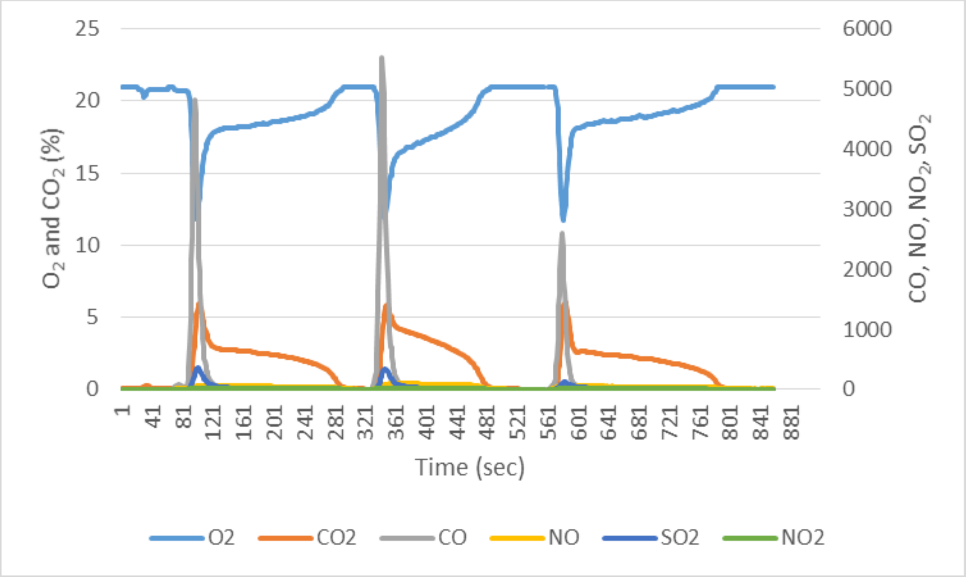

Figure A.18 Result of co-combustion of coal and D-1 sludge with %5 addition

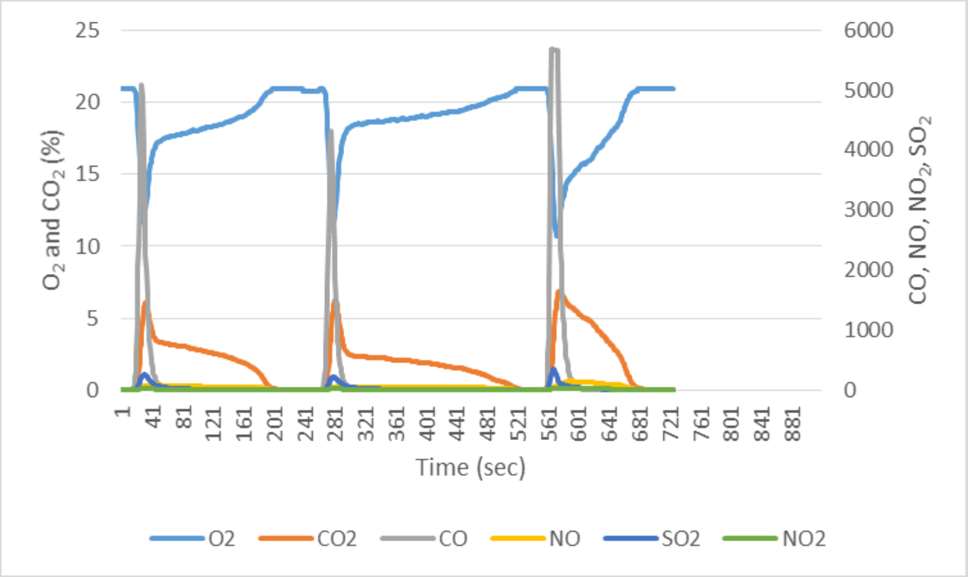

Figure A.19 Result of co-combustion of coal and D-1 sludge with %10 addition

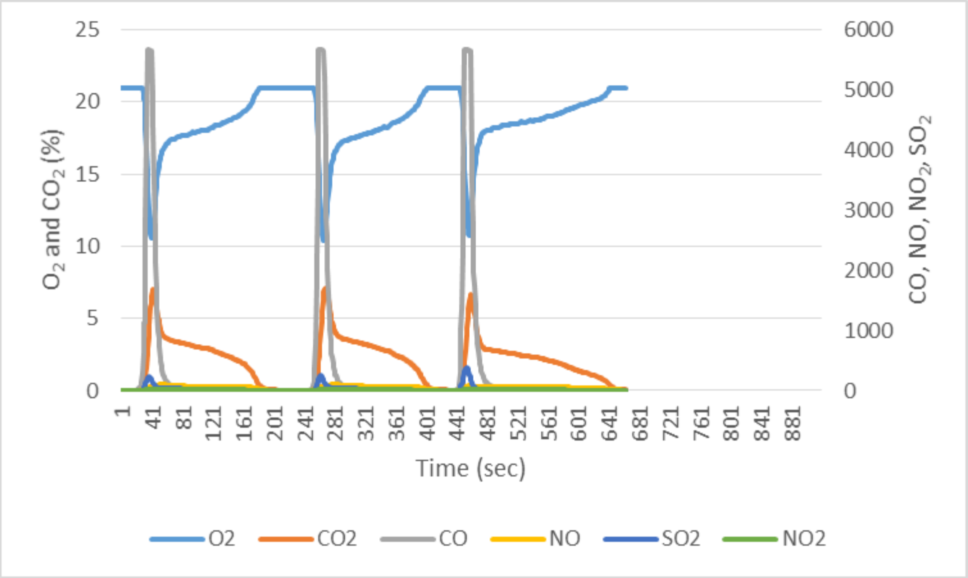

Figure A.20 Result of co-combustion of coal and D-1 sludge with %20 addition

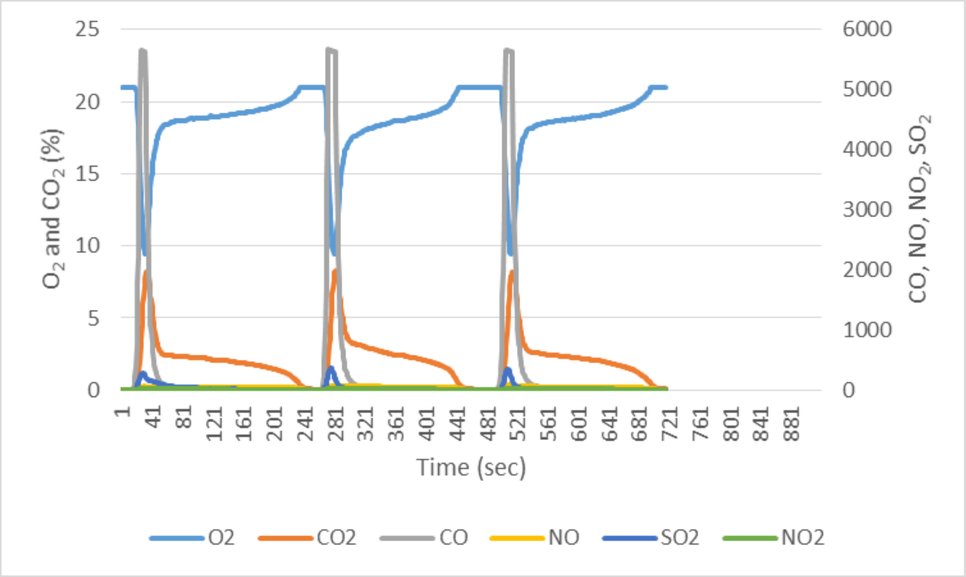

Figure A.21 Result of co-combustion of coal and D-1 sludge with %30 addition

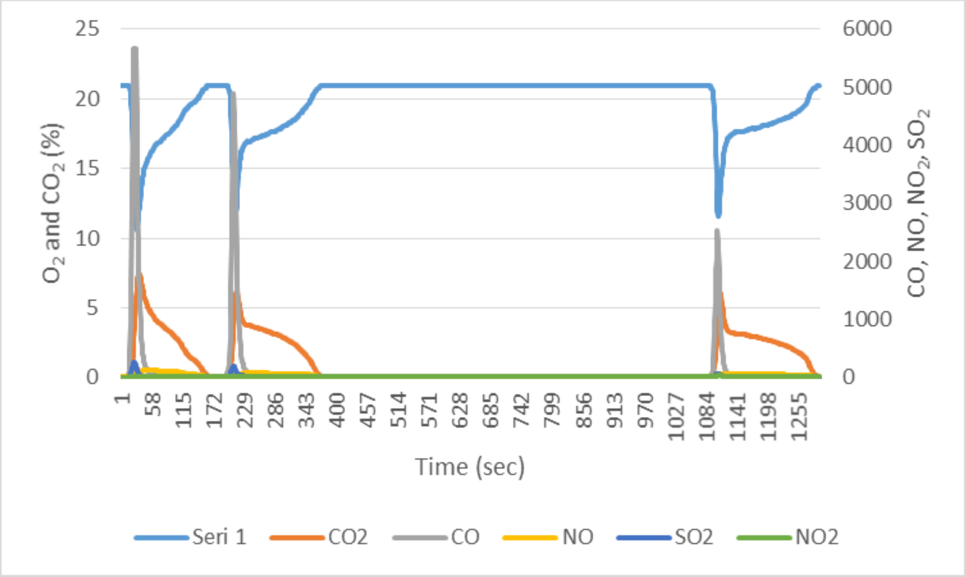

Figure A.22 Result of co-combustion of coal and E1-1 sludge with %3 addition

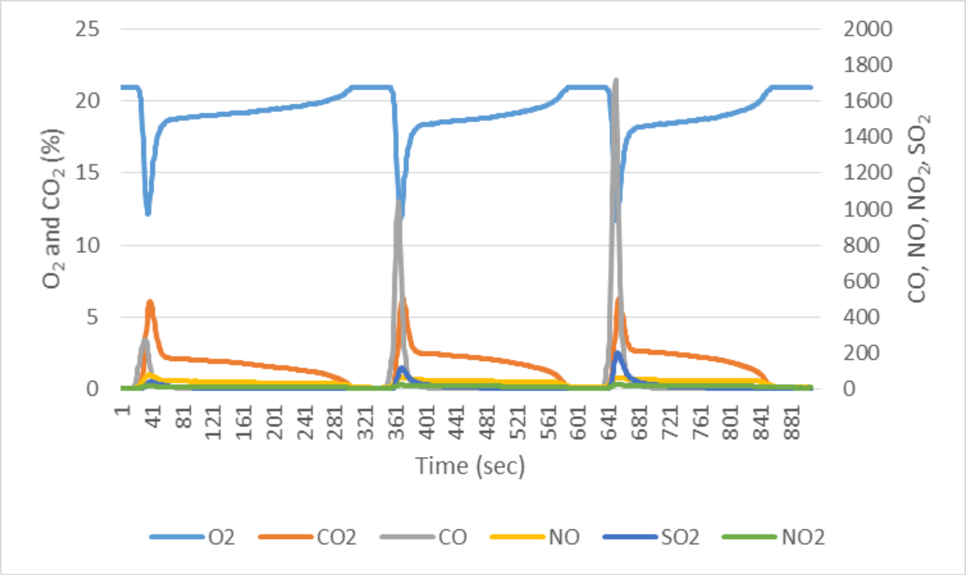

Figure A.23 Result of co-combustion of coal and E1-1 sludge with %5 addition

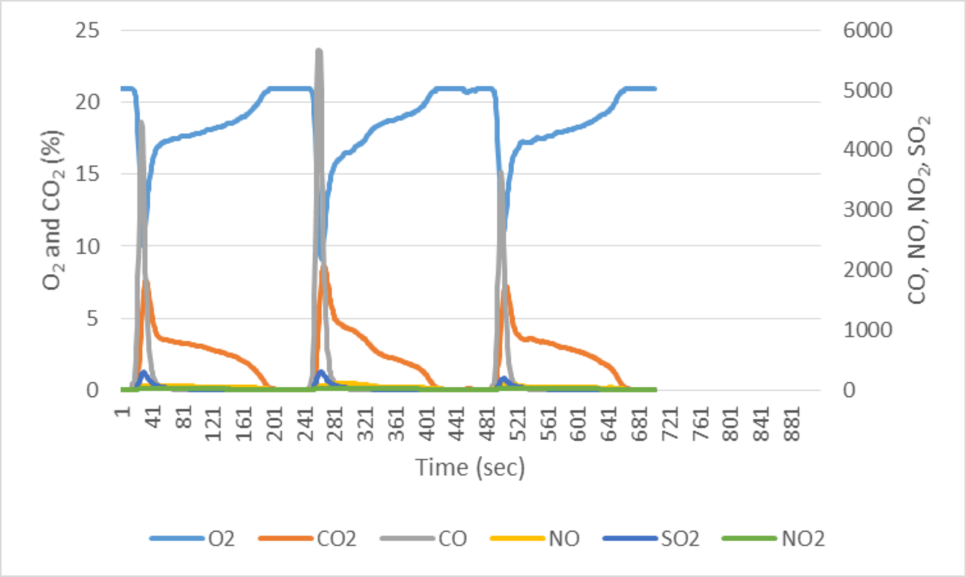

Figure A.24 Result of co-combustion of coal and E1-1 sludge with %10 addition

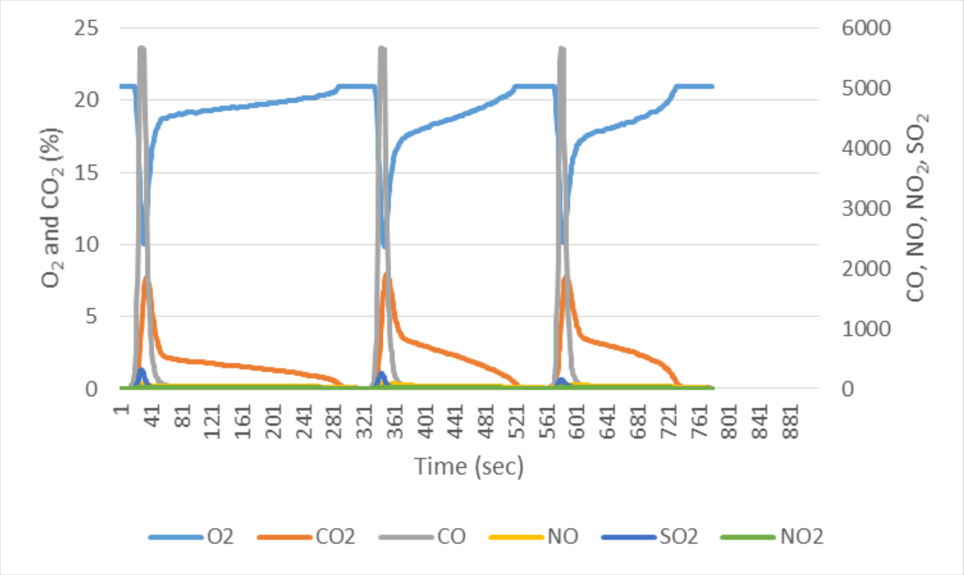

Figure A.25 Result of co-combustion of coal and E1-1 sludge with %20 addition

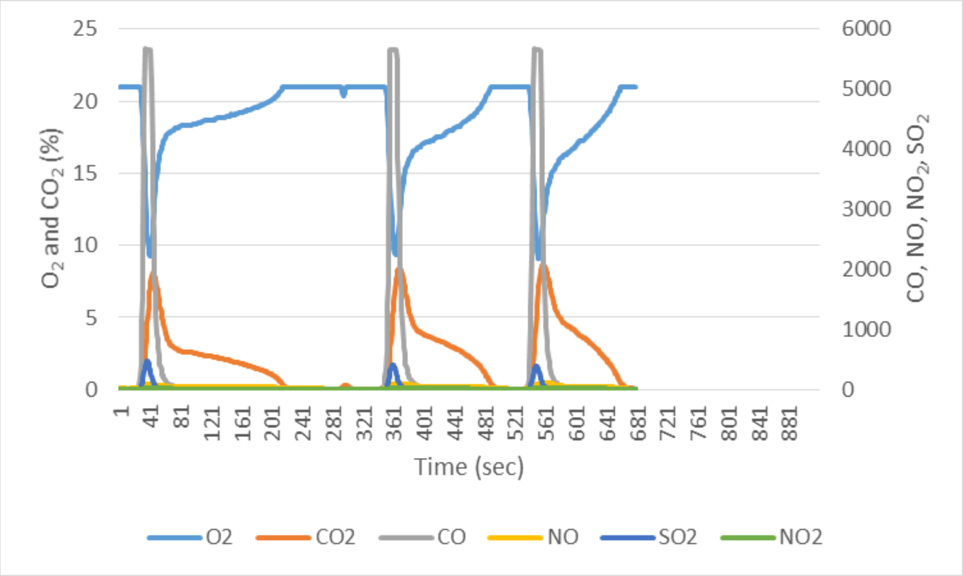

Figure A.26 Result of co-combustion of coal and E1-1 sludge with %30 addition

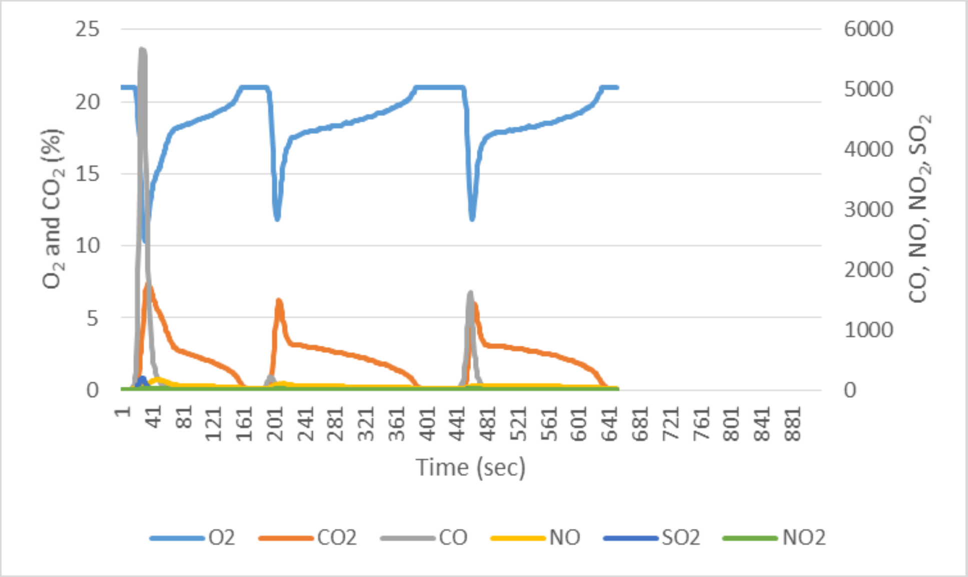

Figure A.27 Result of co-combustion of coal and E2-1 sludge with %3 addition

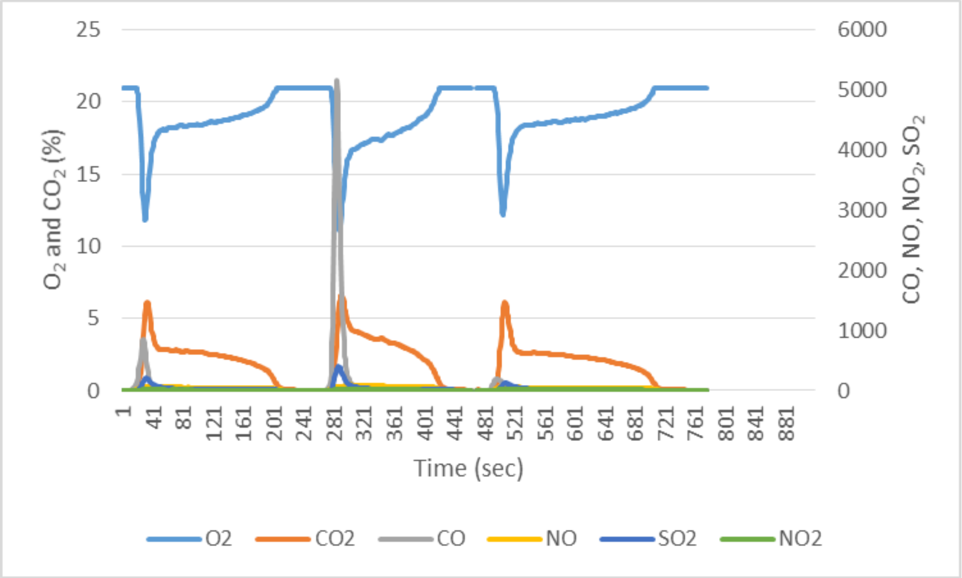

Figure A.28 Result of co-combustion of coal and E2-1 sludge with %5 addition

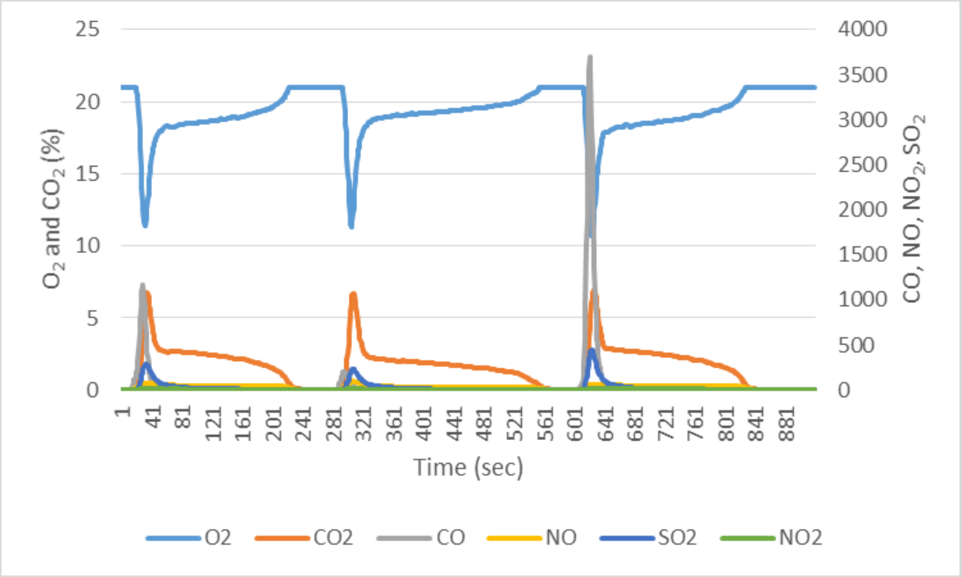

Figure A.29 Result of co-combustion of coal and E2-1 sludge with %10 addition

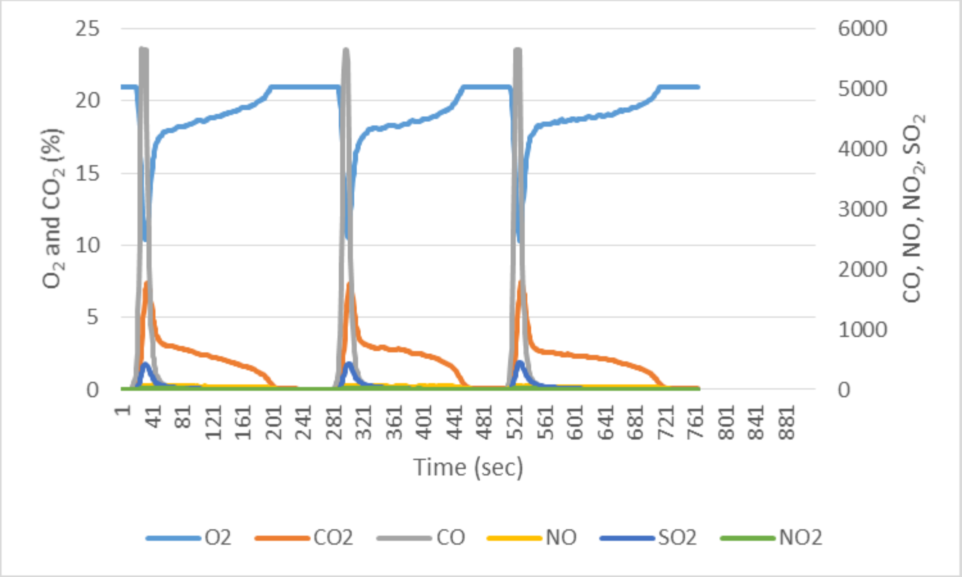

Figure A.30 Result of co-combustion of coal and E2-1 sludge with %20 addition

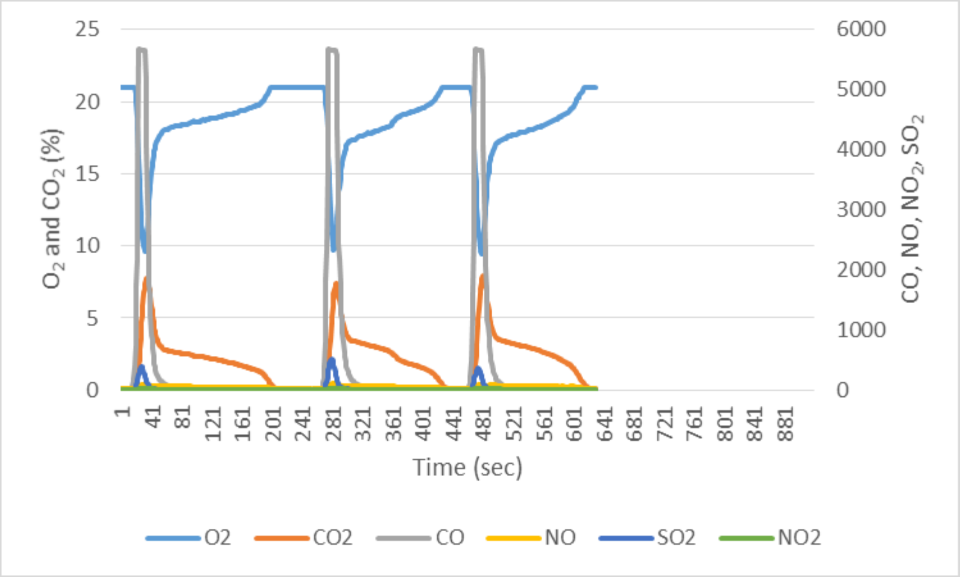

Figure A.31 Result of co-combustion of coal and E2-1 sludge with %30 addition

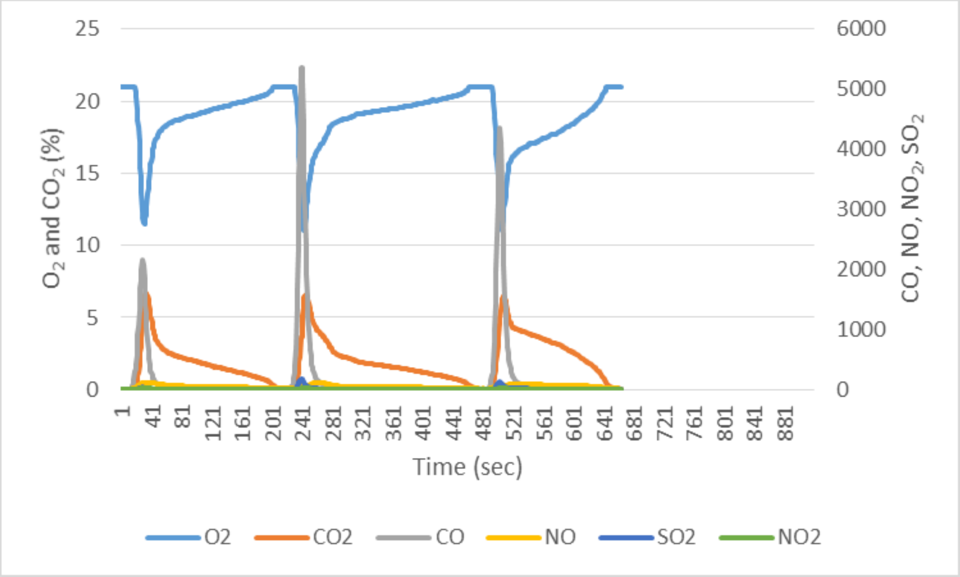

Figure A.32 Result of co-combustion of coal and F-1 sludge with %3 addition

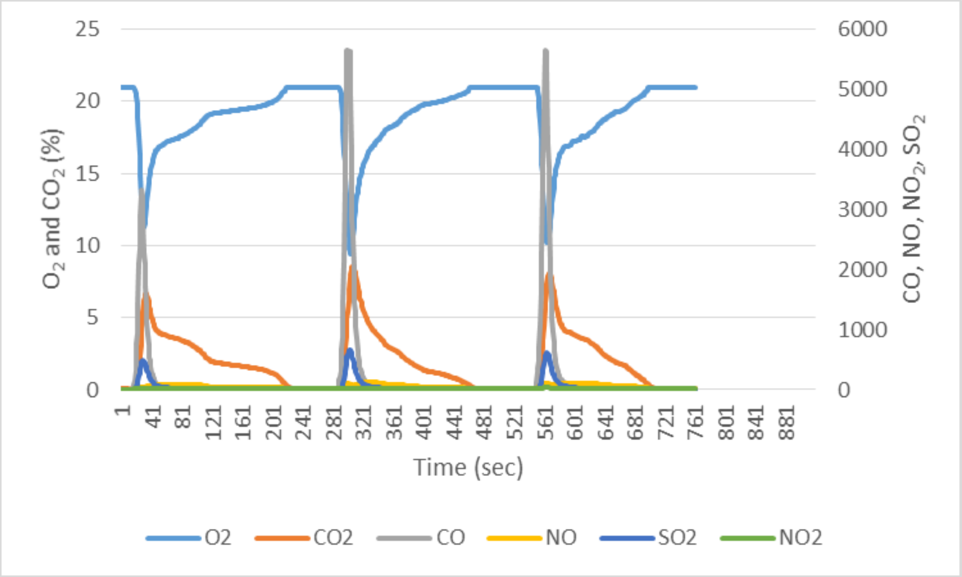

Figure A.33 Result of co-combustion of coal and F-1 sludge with %5 addition

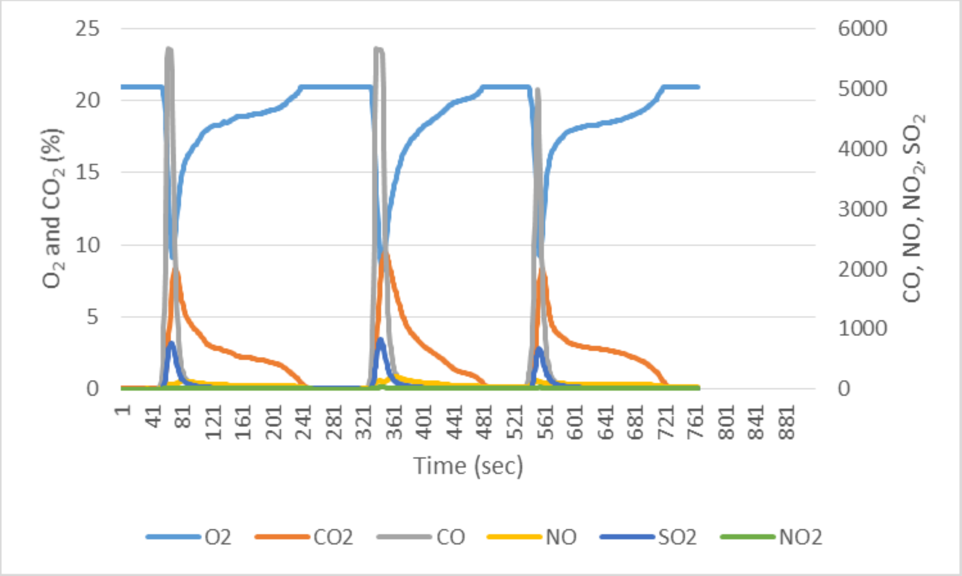

Figure A.34 Result of co-combustion of coal and F-1 sludge with %10 addition

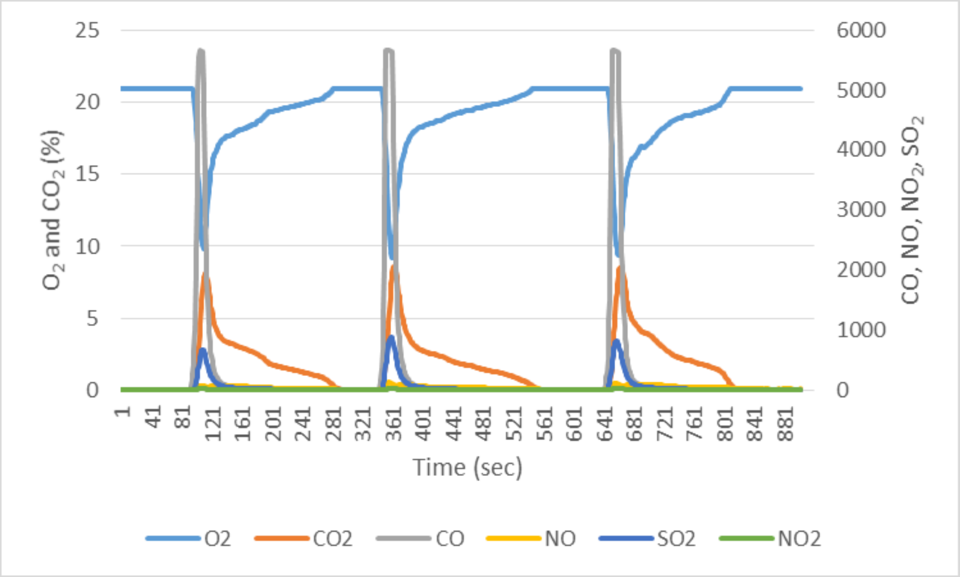

Figure A.35 Result of co-combustion of coal and F-1 sludge with %20 addition

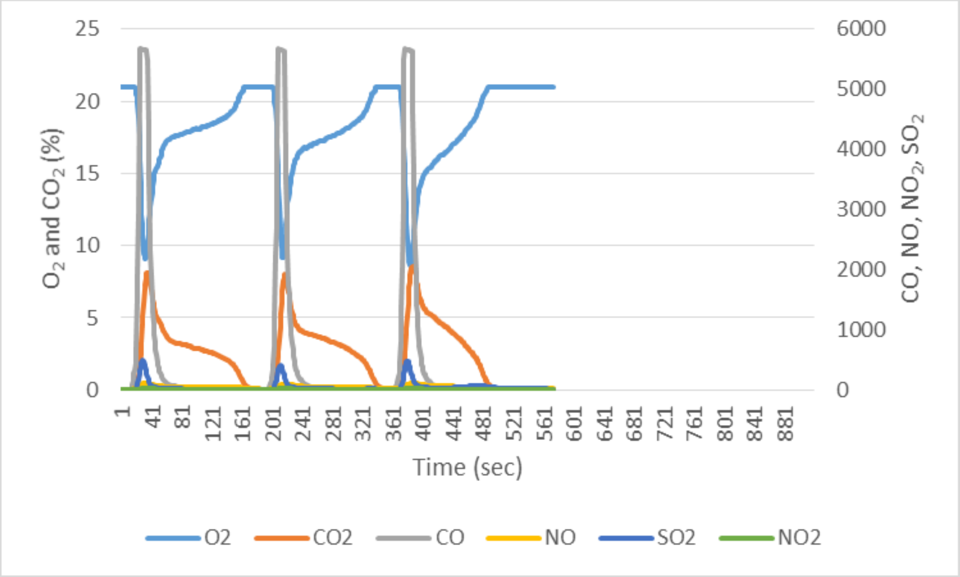

Figure A.36 Result of co-combustion of coal and F-1 sludge with %30 addition

B. TGA Profiles

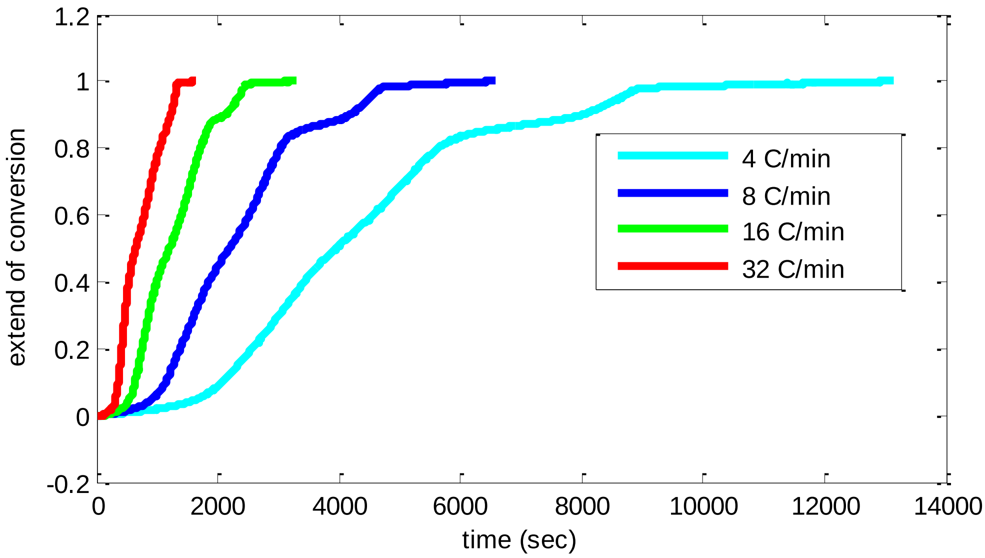

Figure B. 1 Mass Loss Profiles of A-1 Sample in TGA Experiments

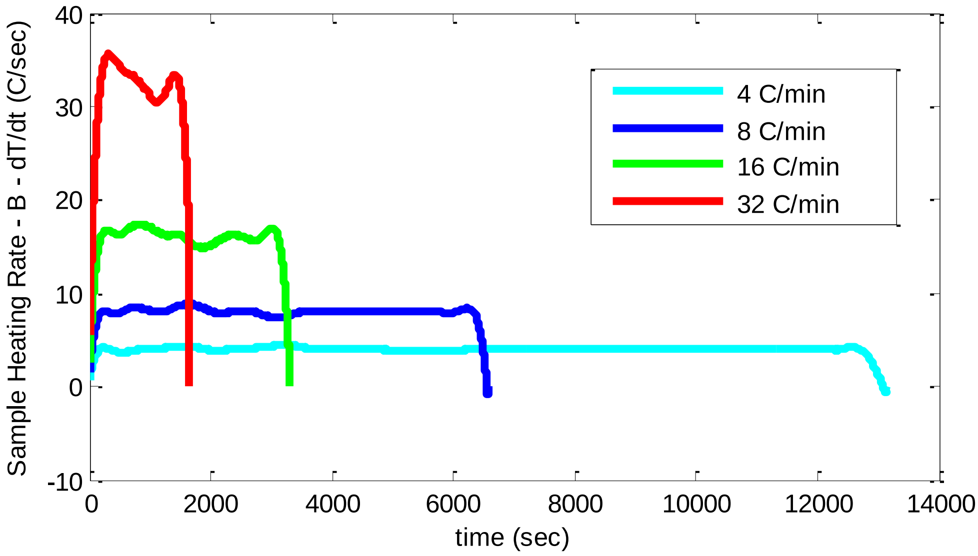

Figure B. 2 Sample Heating Rates of A-1 Sample in TGA Experiments

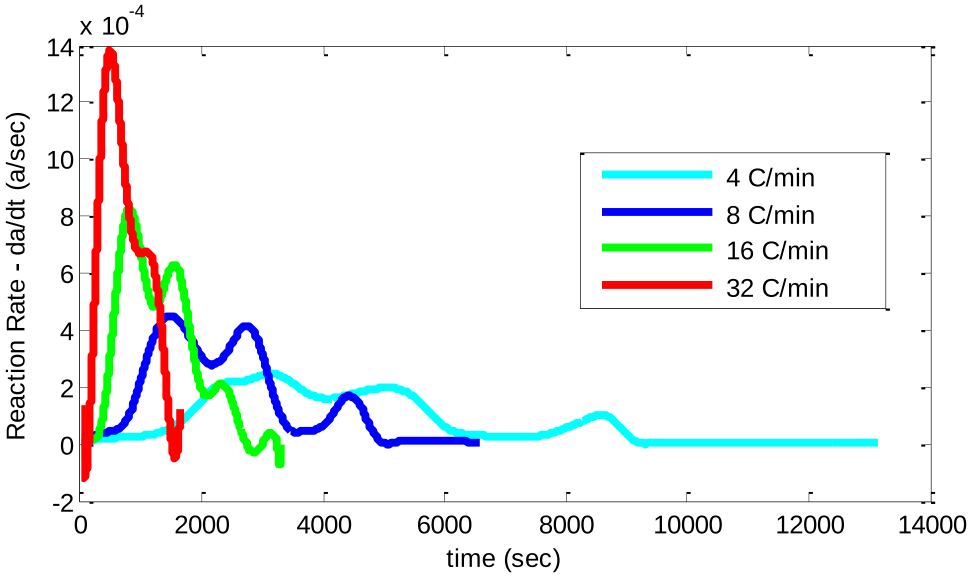

Figure B. 3 Reaction Rates of A-1 Sample in TGA Experiments

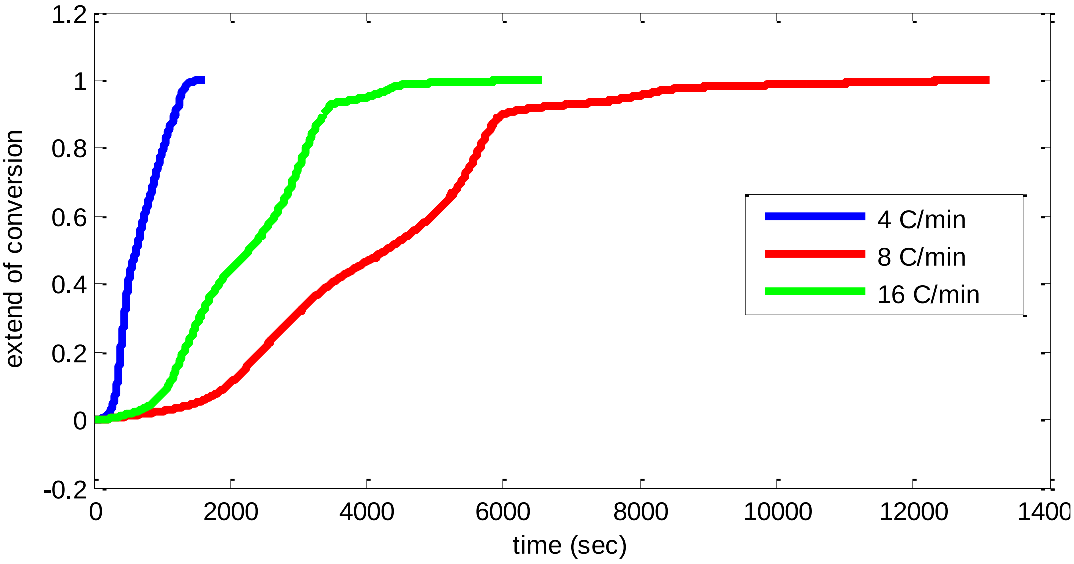

Figure B. 4 Mass Loss Profiles of B-1 Sample in TGA Experiments

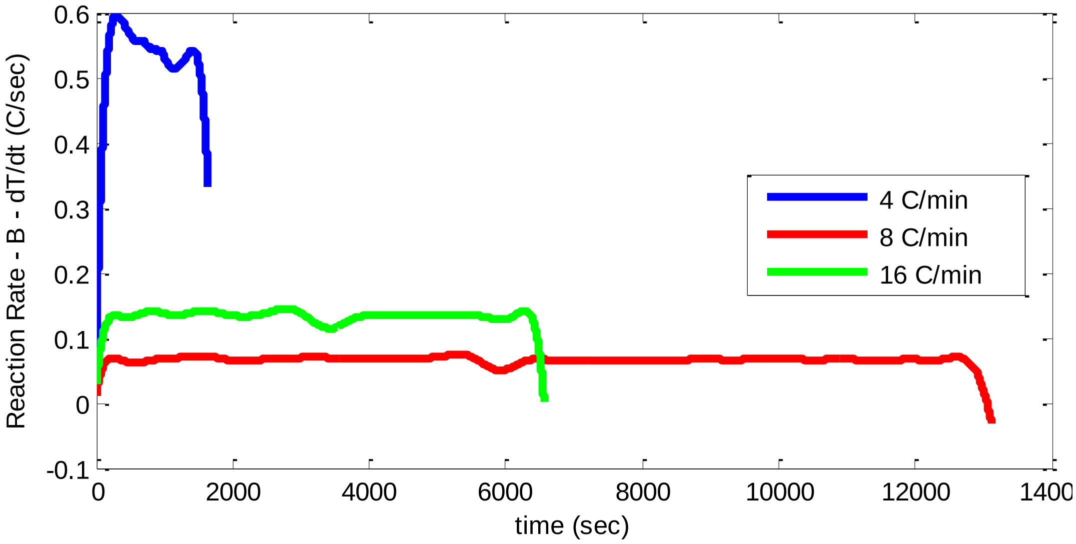

Figure B. 5 Sample Heating Rates of B-1 Sample in TGA Experiments

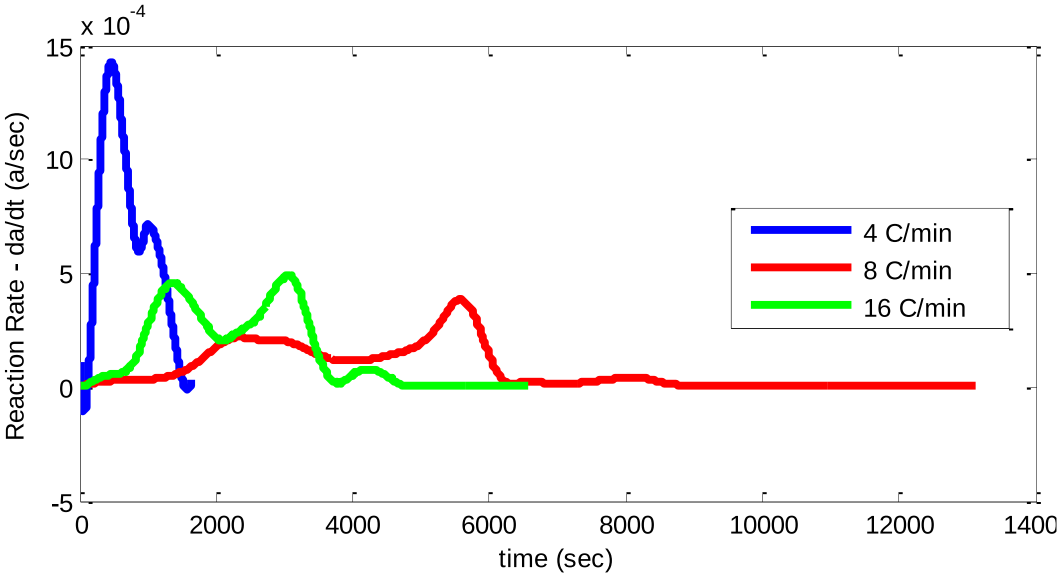

Figure B. 6 Reaction Rates of B-1 Sample in TGA Experiments

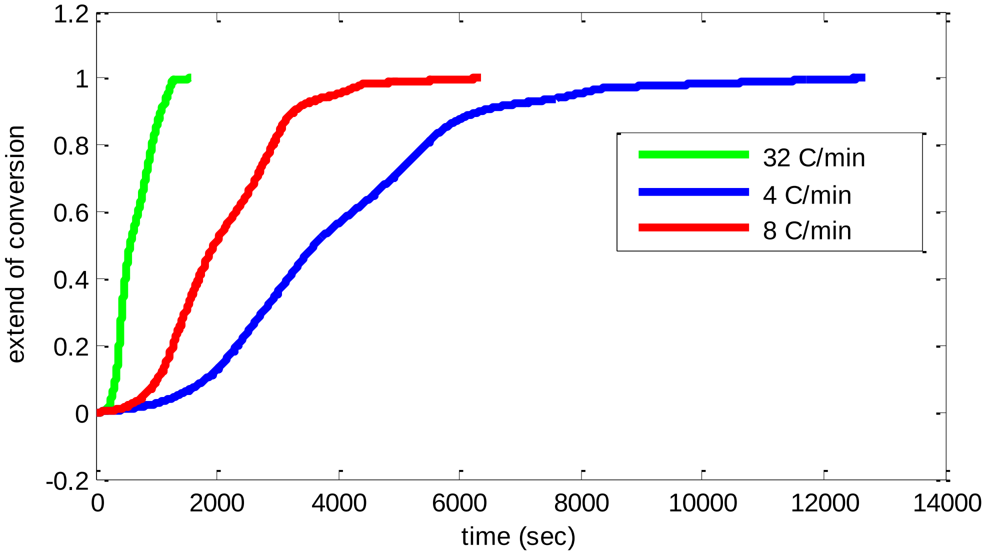

Figure B. 7 Mass Loss Profiles of C-1 Sample in TGA Experiments

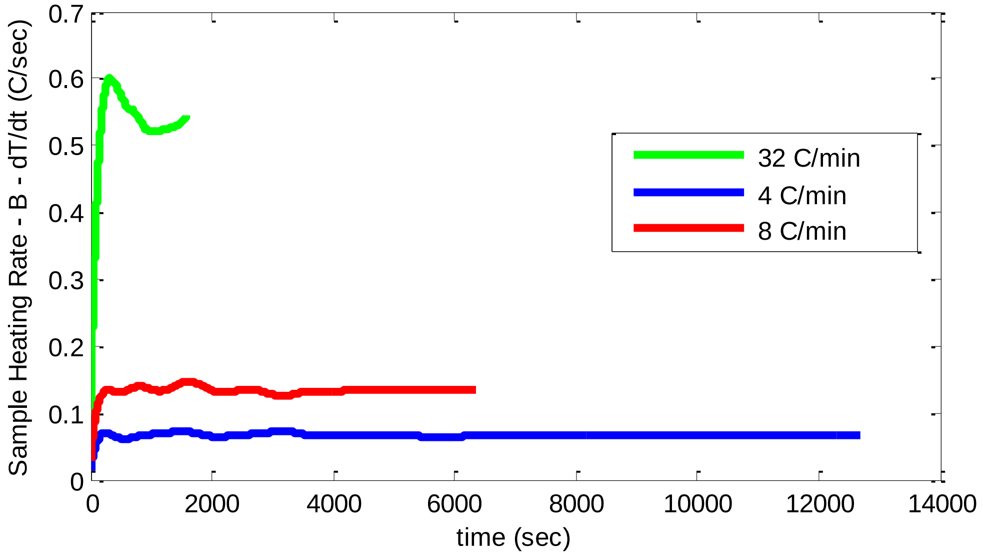

Figure B. 8 Sample Heating Rates of C-1 Sample in TGA Experiments

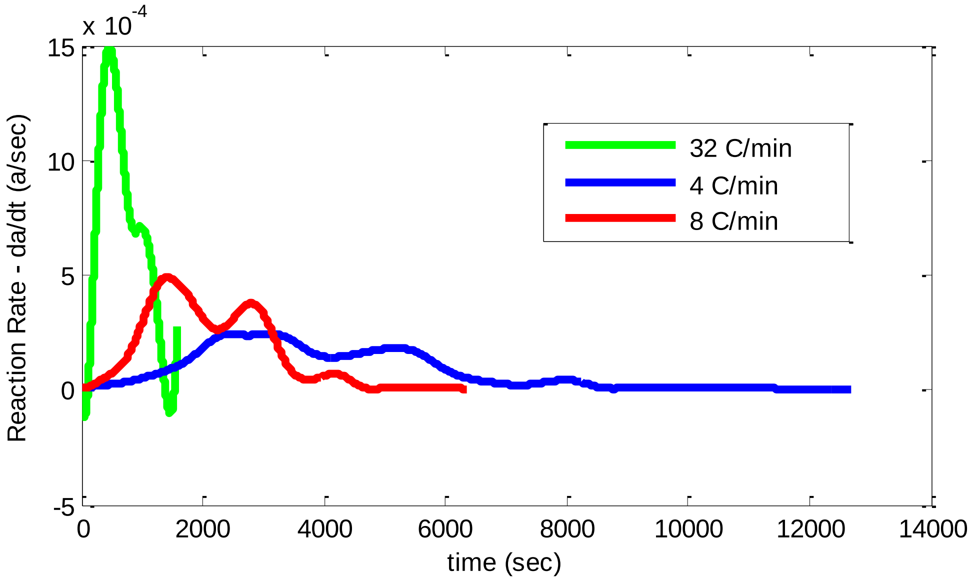

Figure B. 9 Reaction Rates of C-1 Sample in TGA Experiments

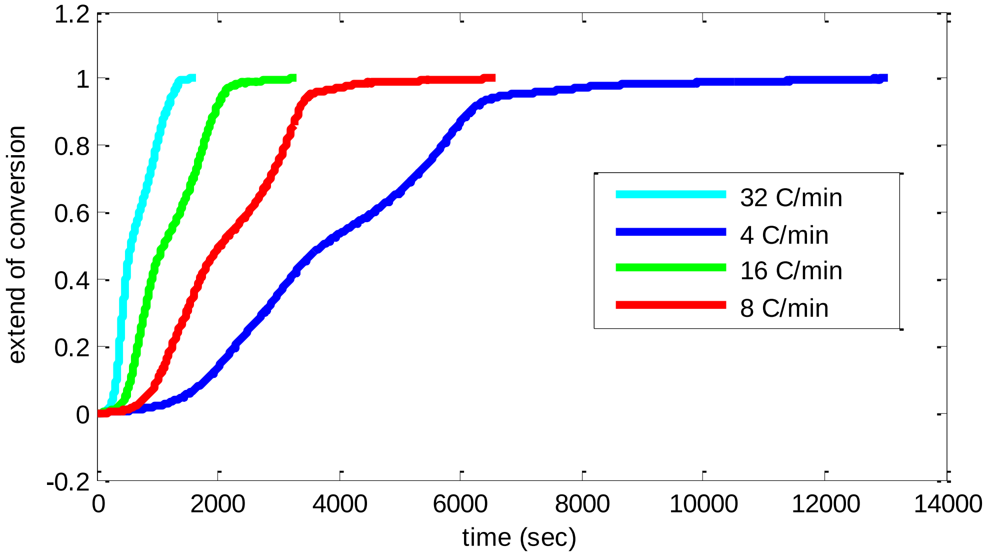

Figure B. 10 Mass Loss Profiles of D-1 Sample in TGA Experiments

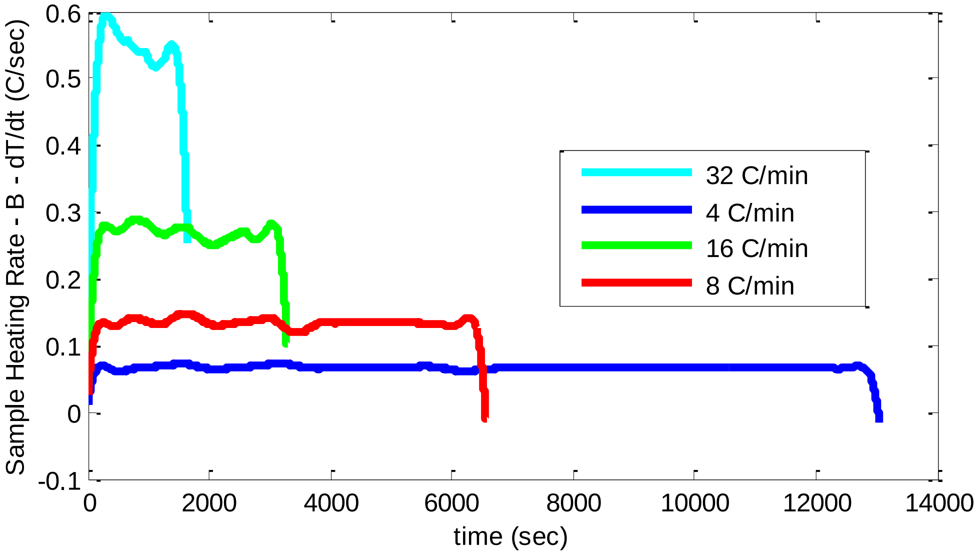

Figure B. 11 Sample Heating Rates of D-1 Sample in TGA Experiments

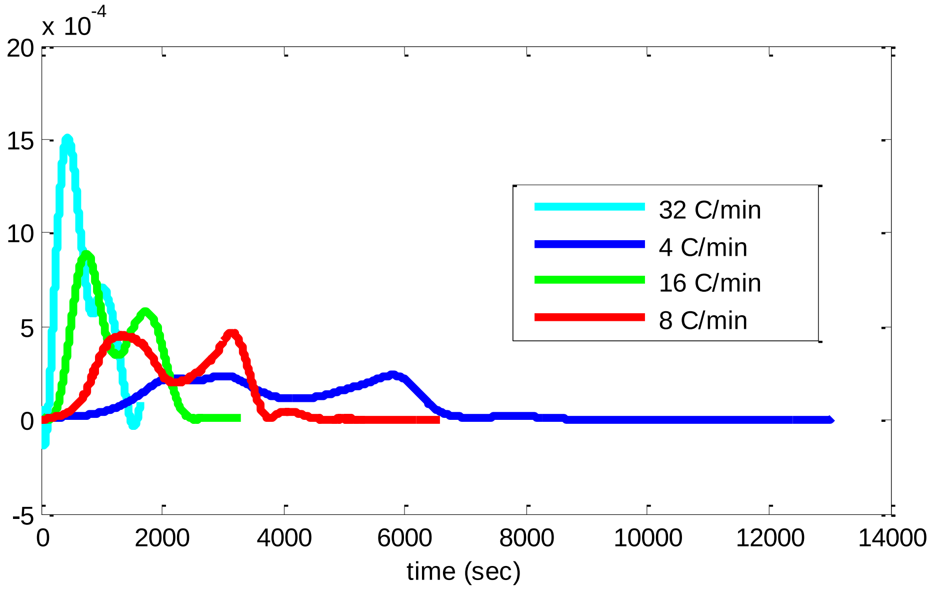

Figure B. 12 Reaction Rates of D-1 Sample in TGA Experiments

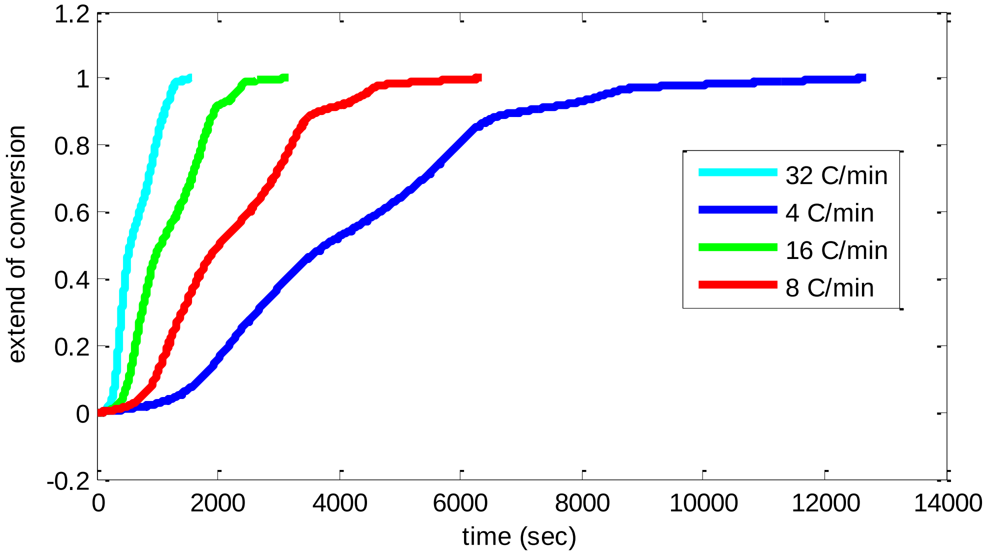

Figure B. 13 Mass Loss Profiles of E1-1 Sample in TGA Experiments

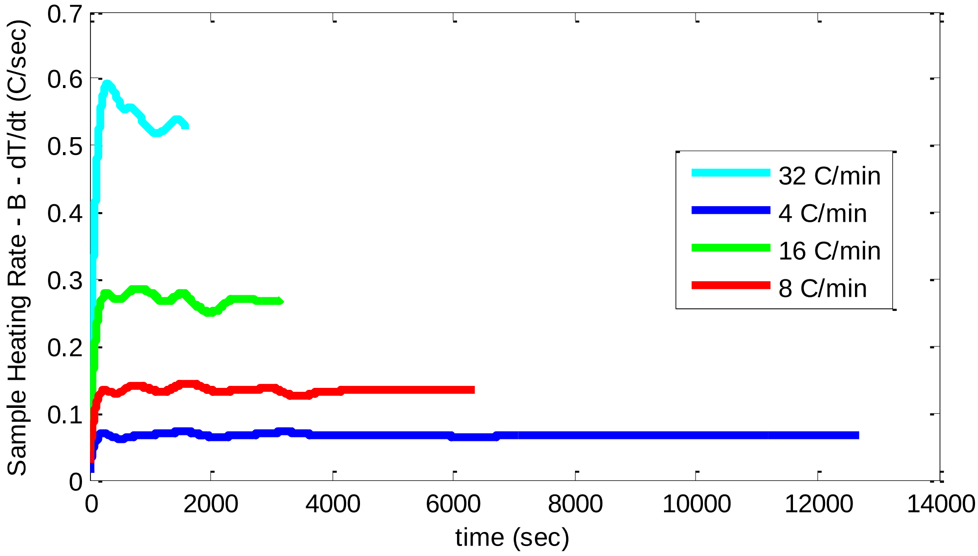

Figure B. 14 Sample Heating Rates of E1-1 Sample in TGA Experiments

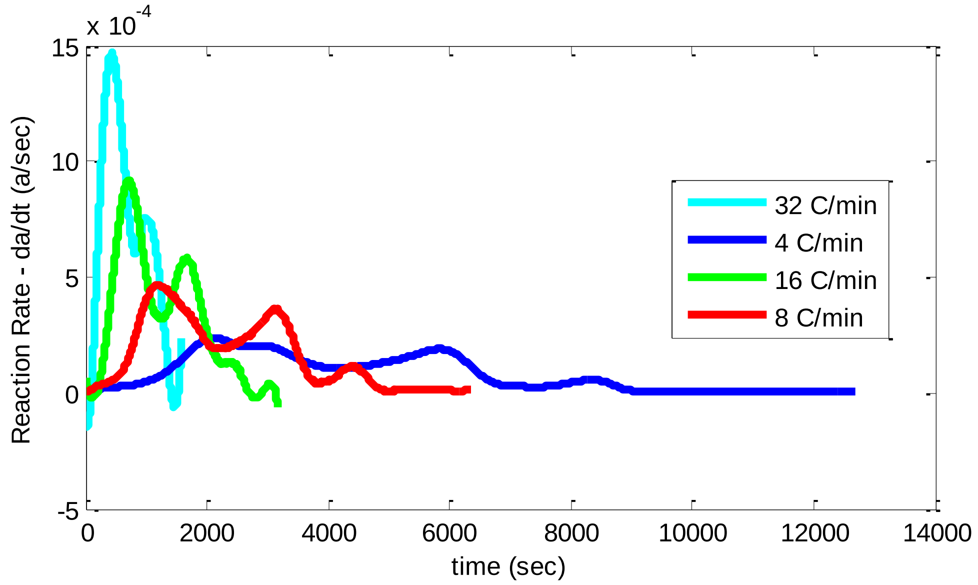

Figure B. 15 Reaction Rates of E1-1 Sample in TGA Experiments

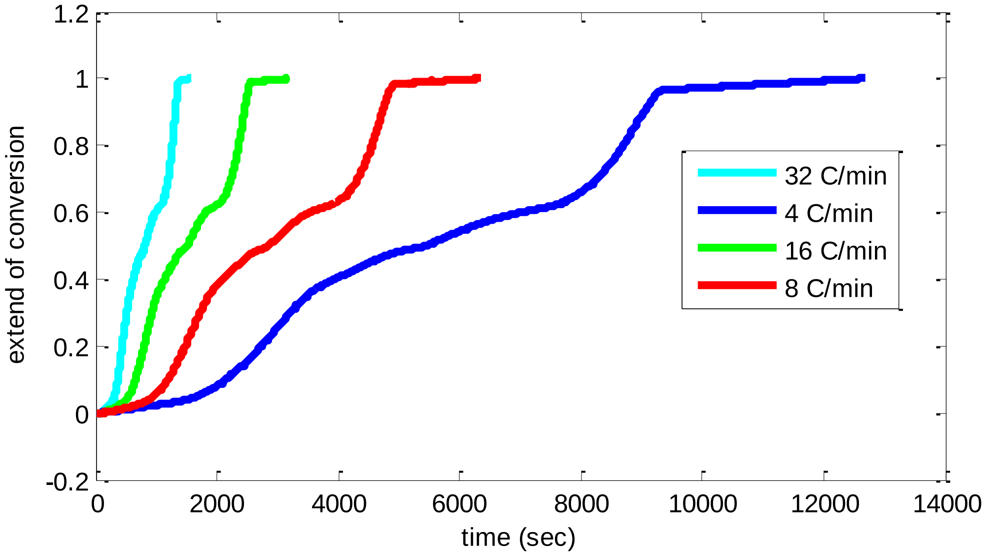

Figure B. 16 Mass Loss Profiles of E2-1 Sample in TGA Experiments

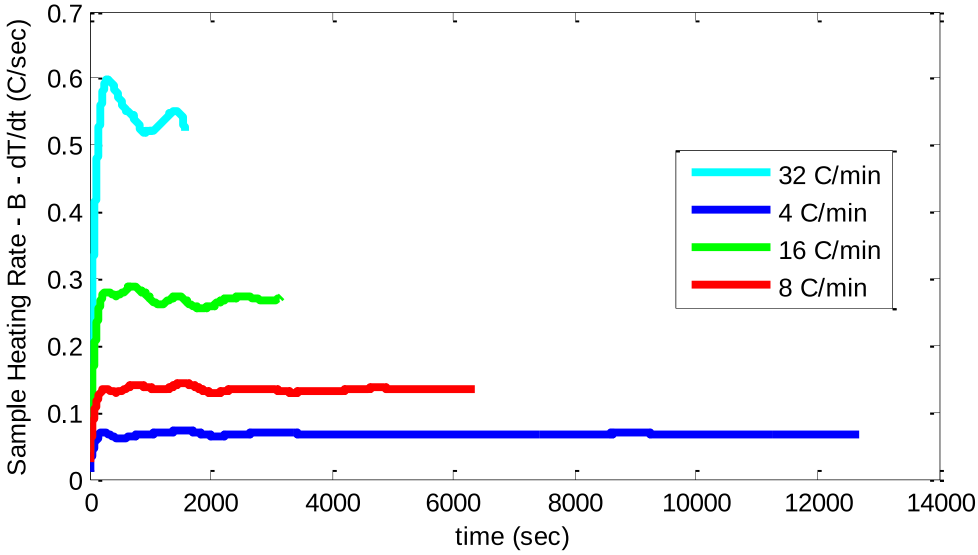

Figure B. 17 Sample Heating Rates of E2-1 Sample in TGA Experiments

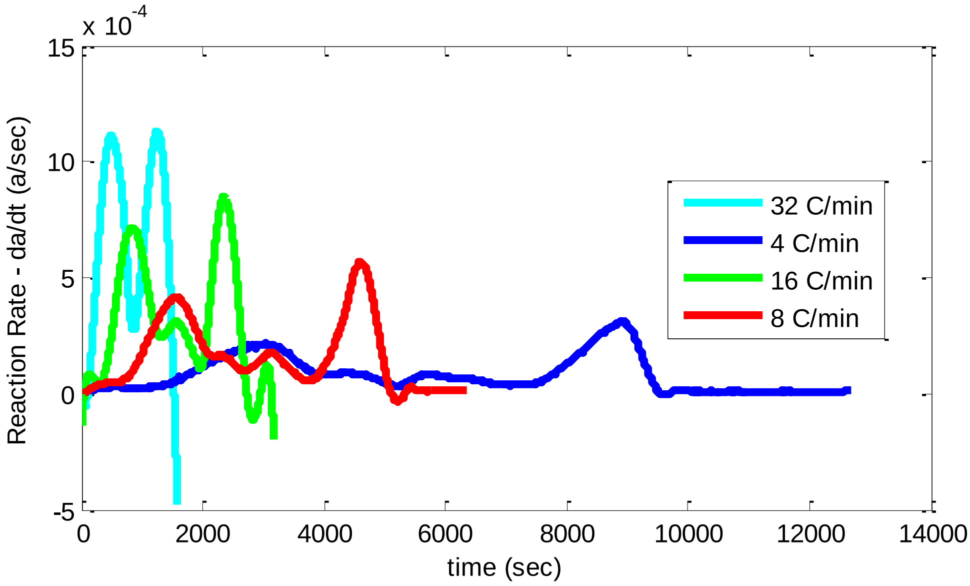

Figure B. 18 Reaction Rates of E2-1 Sample in TGA Experiments

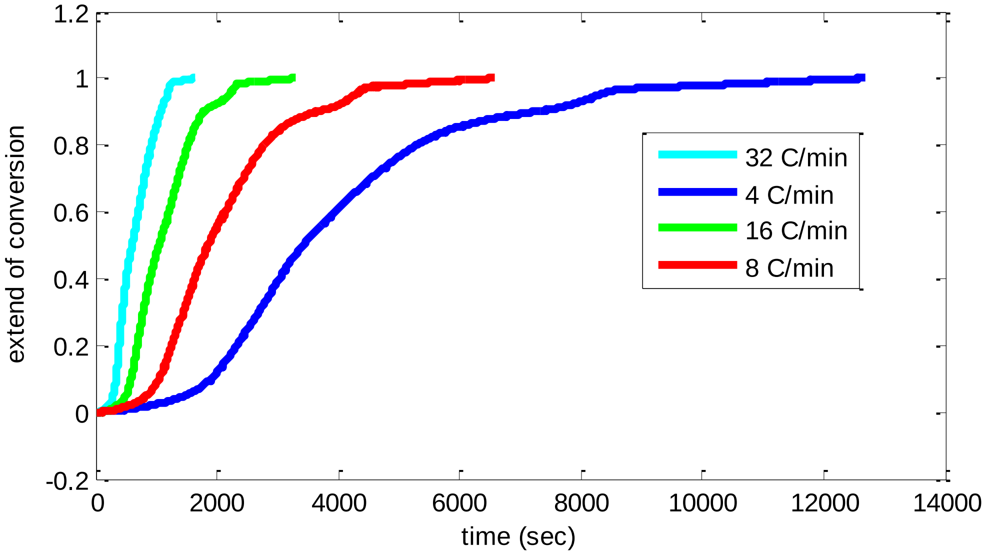

Figure B. 19 Mass Loss Profiles of F-1 Sample in TGA Experiments

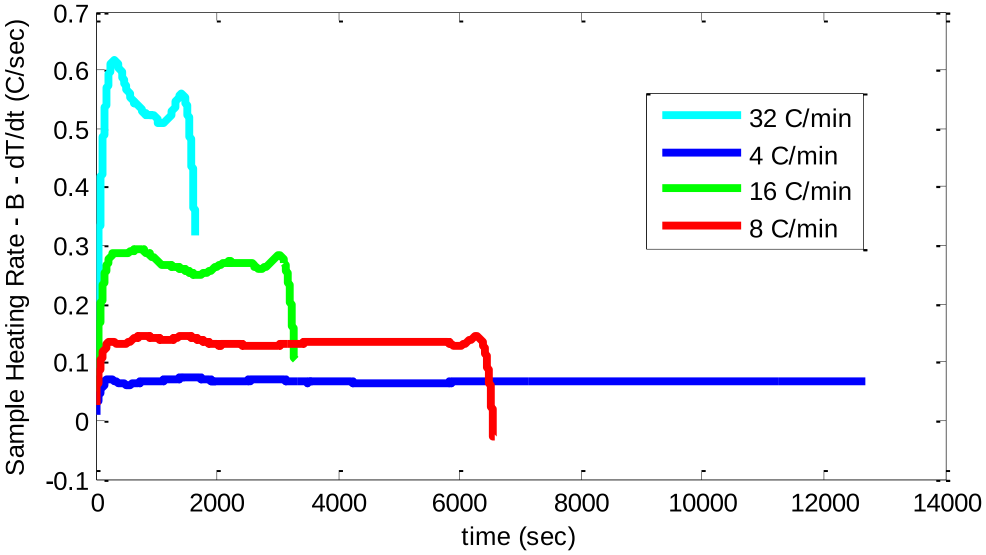

Figure B. 20 Sample Heating Rates of F-1 Sample in TGA Experiments

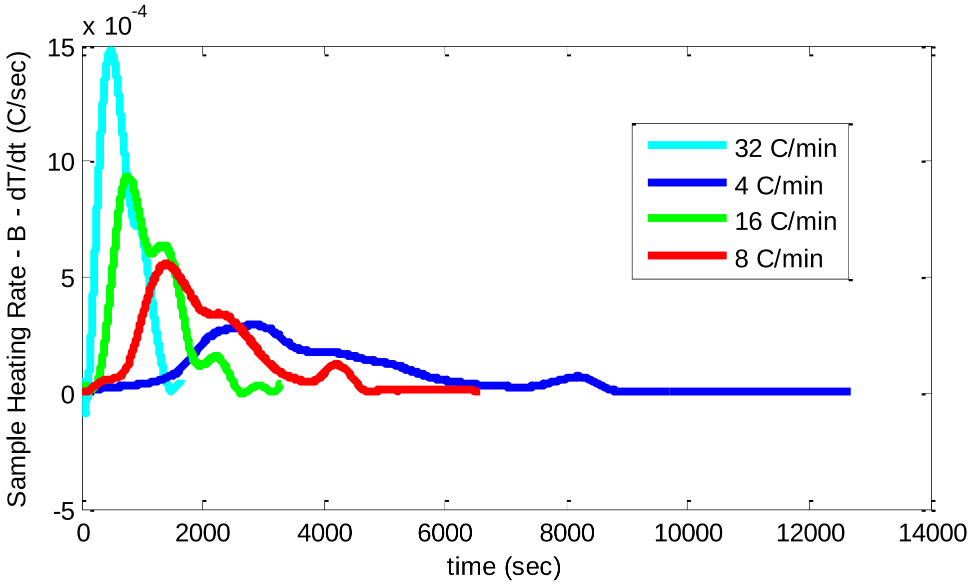

Figure B. 21 Reaction Rates of F-1 Sample in TGA Experiments

C. Matlab Codes for Filtering and Interpolation Operation

Savitzky-Golay Filtering

```
Sg=sgolayfilt(%sample heating rate%beta,5,10001);
Sg=sgolayfilt(%reaction rate%dadt,5,10001);
```

Interpolation Using Polynomial Fit

```
For i=31:1:40;
%plyval=polytool(alfa32(i*263:i*263+262),temp32(i*263:i*263+262),3
);
J=37;
A=polyfit(alfa32(j*263:j*263+262),temp32(j*263:j*263+262),3);
C=0.968;
D=0.980;
B=polyval(a,c:0.001:d);
Temperature=b';
A1=polyfit(alfa32(j*263:j*263+262),beta32smthd(j*263:j*263+262),3)
;
B1=polyval(a1,c:0.001:d);
Sample heating rate=b1';
A2=polyfit(alfa32(j*263:j*263+262),dadt32smthd(j*263:j*263+262),3)
;
B2=polyval(a2,c:0.001:d);
Reaction rate=b2';
End
```

D. Fitting of Time Vectors to Experimental Data

D.1. Fitting Integral Data

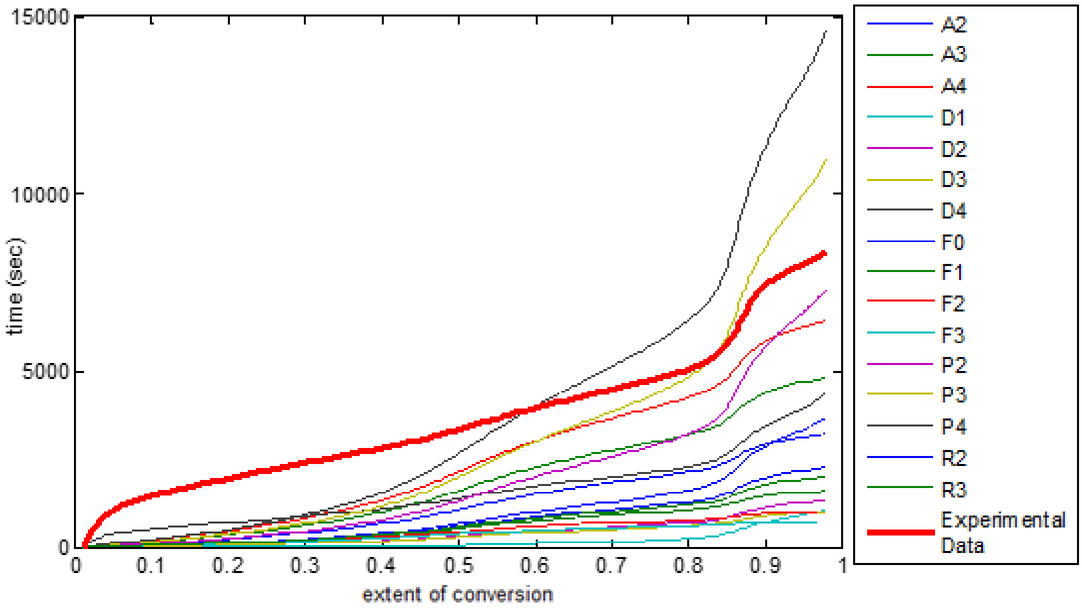

Figure D.1 Fitting integral time vectors to TGA profile of A-1 in 4 ºC/min experiment

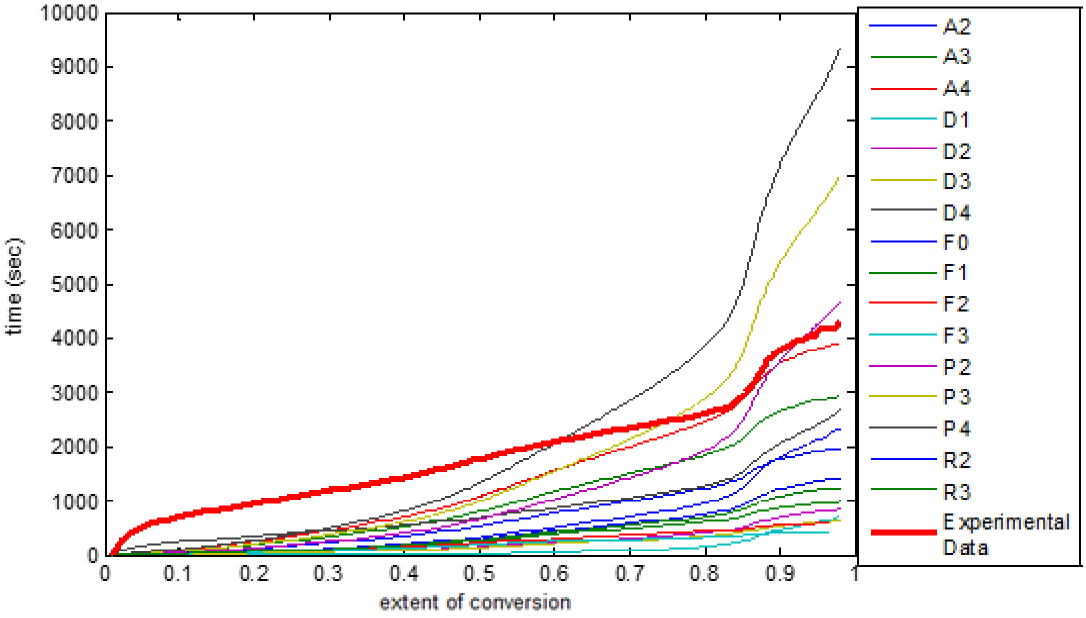

Figure D.2 Fitting integral time vectors to TGA profile of A-1 in 8 ºC/min experiment

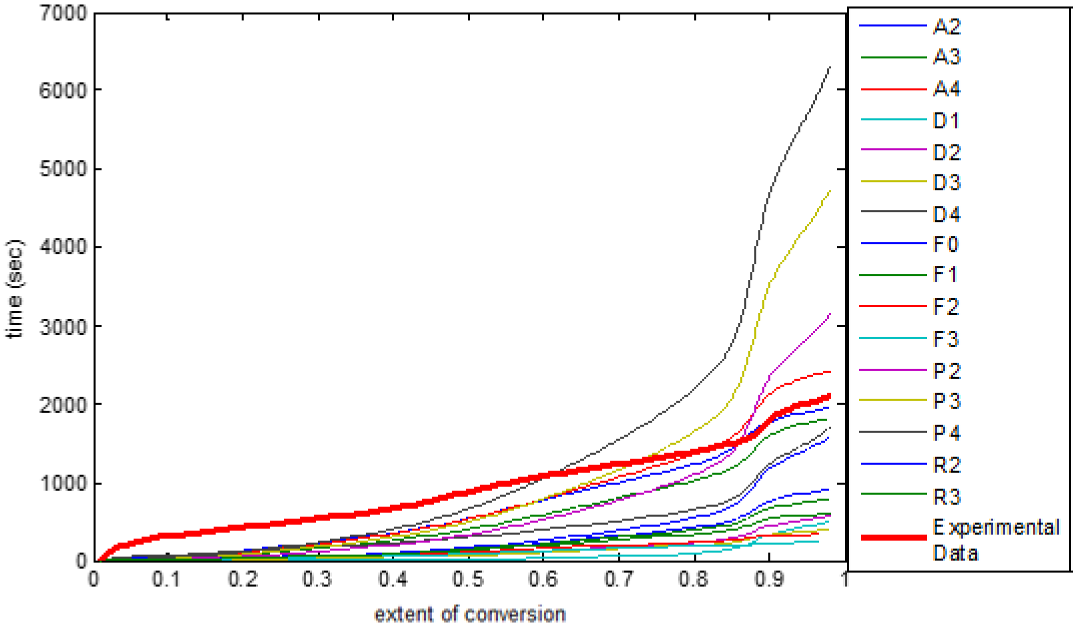

Figure D.3 Fitting integral time vectors to TGA profile of A-1 in 16 ºC/min experiment

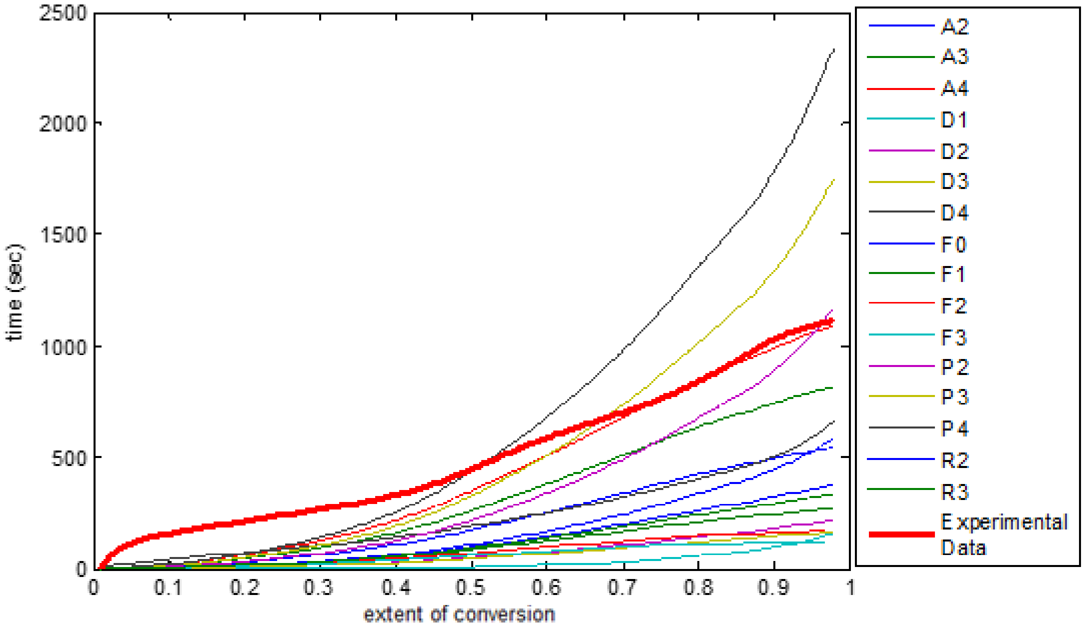

Figure D.4 Fitting integral time vectors to TGA profile of A-1 in 32 ºC/min experiment

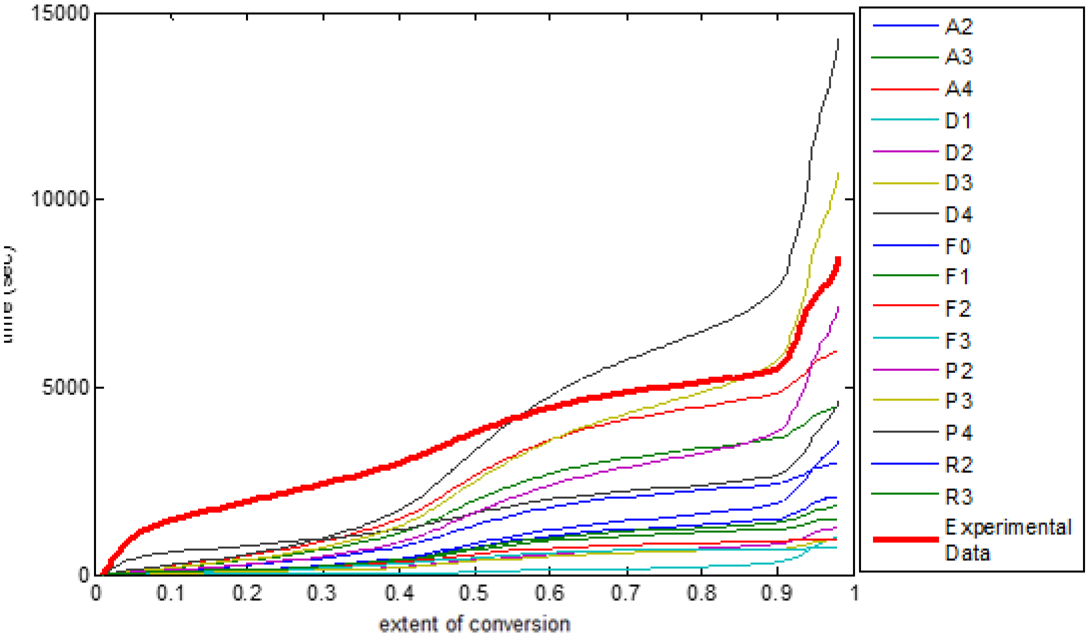

Figure D.5 Fitting integral time vectors to TGA profile of B-1 in 4 ºC/min experiment

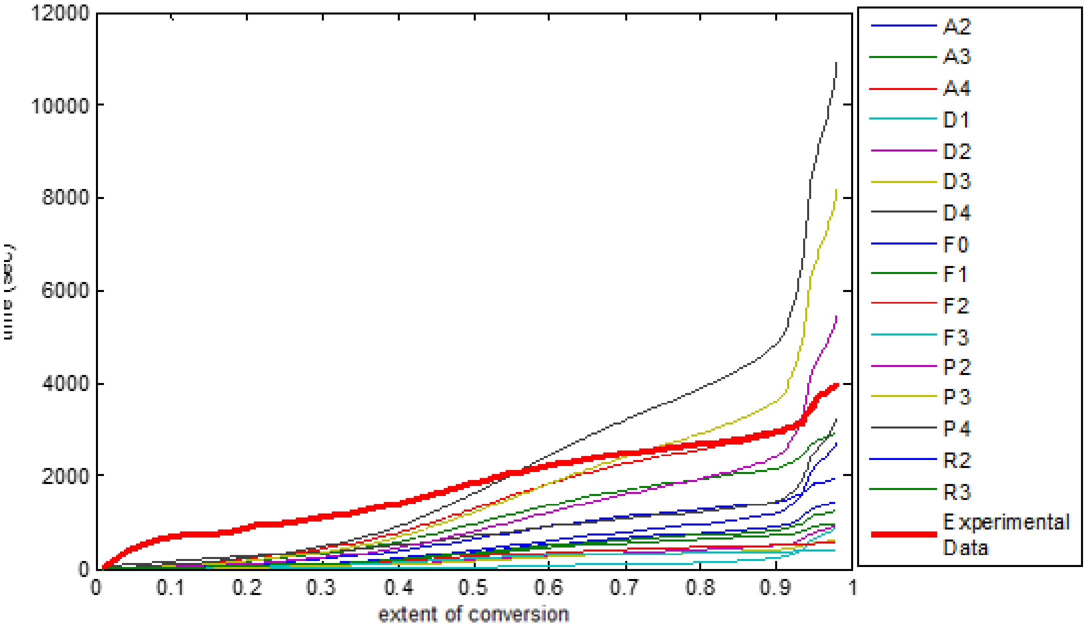

Figure D.6 Fitting integral time vectors to TGA profile of B-1 in 8 ºC/min experiment

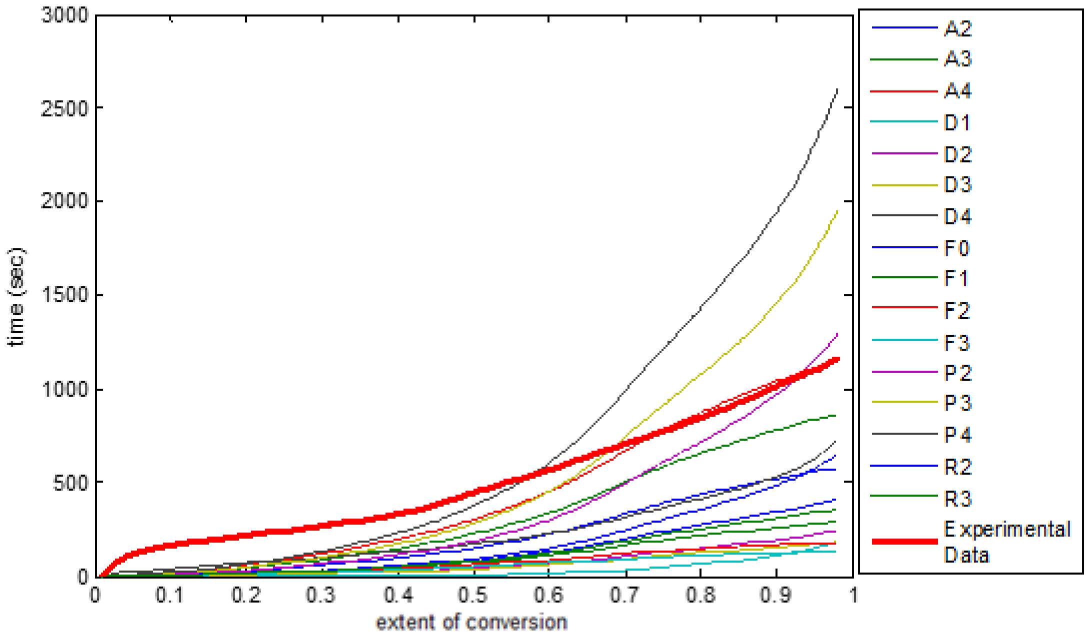

Figure D.7 Fitting integral time vectors to TGA profile of B-1 in 32 ºC/min experiment

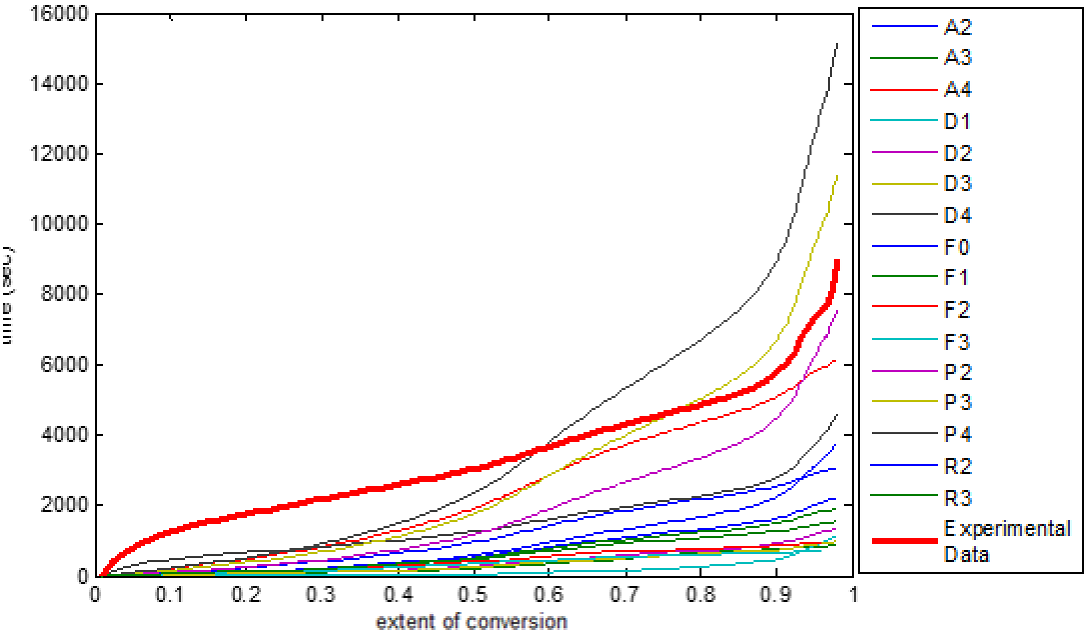

Figure D.8 Fitting integral time vectors to TGA profile of C-1 in 4 ºC/min experiment

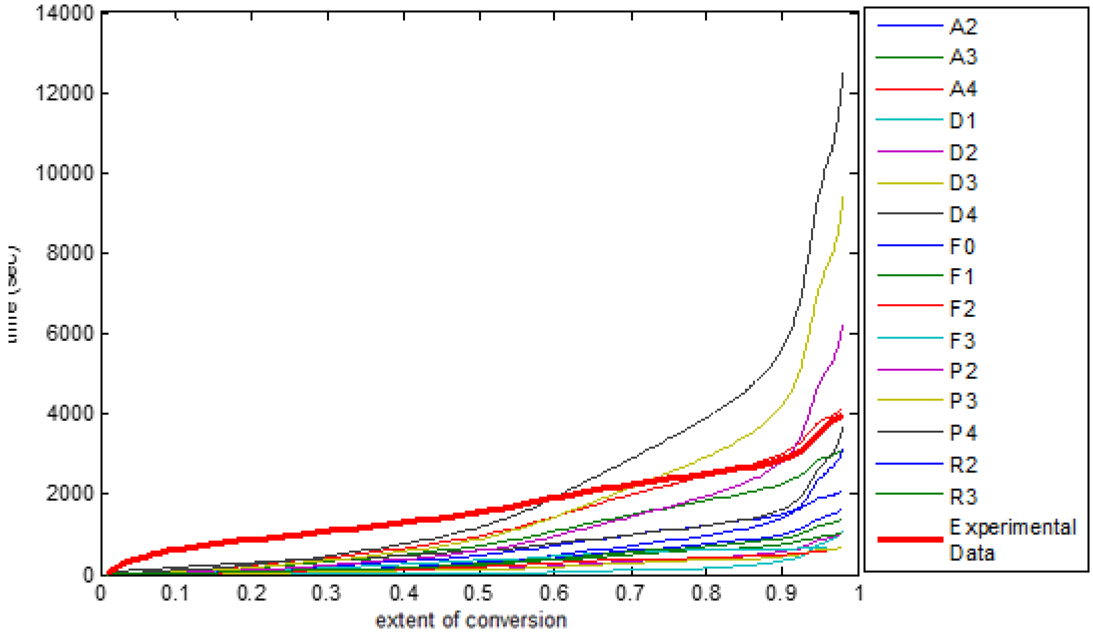

Figure D.9 Fitting integral time vectors to TGA profile of C-1 in 8 °C/min experiment

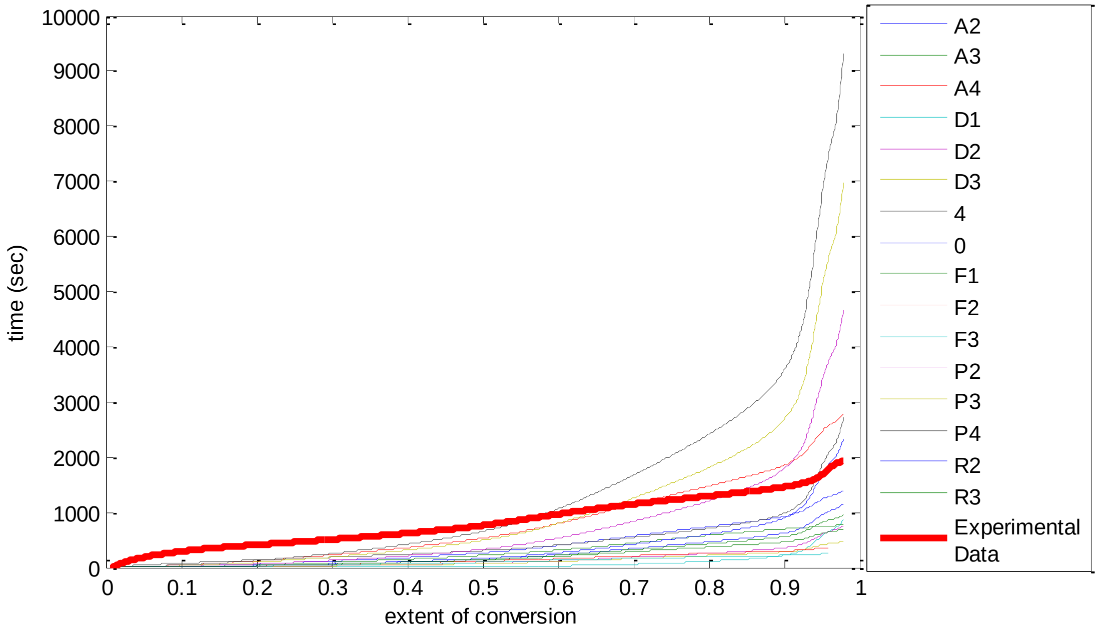

Figure D.10 Fitting integral time vectors to TGA profile of C-1 in 16 °C/min experiment

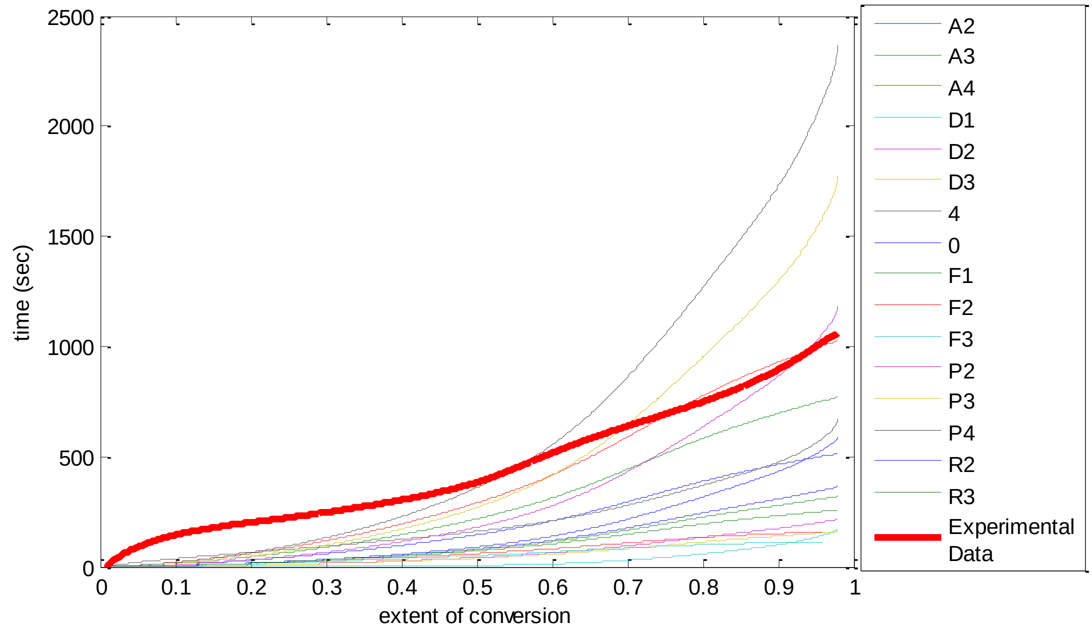

Figure D.11 Fitting integral time vectors to TGA profile of C-1 in 32 ºC/min experiment

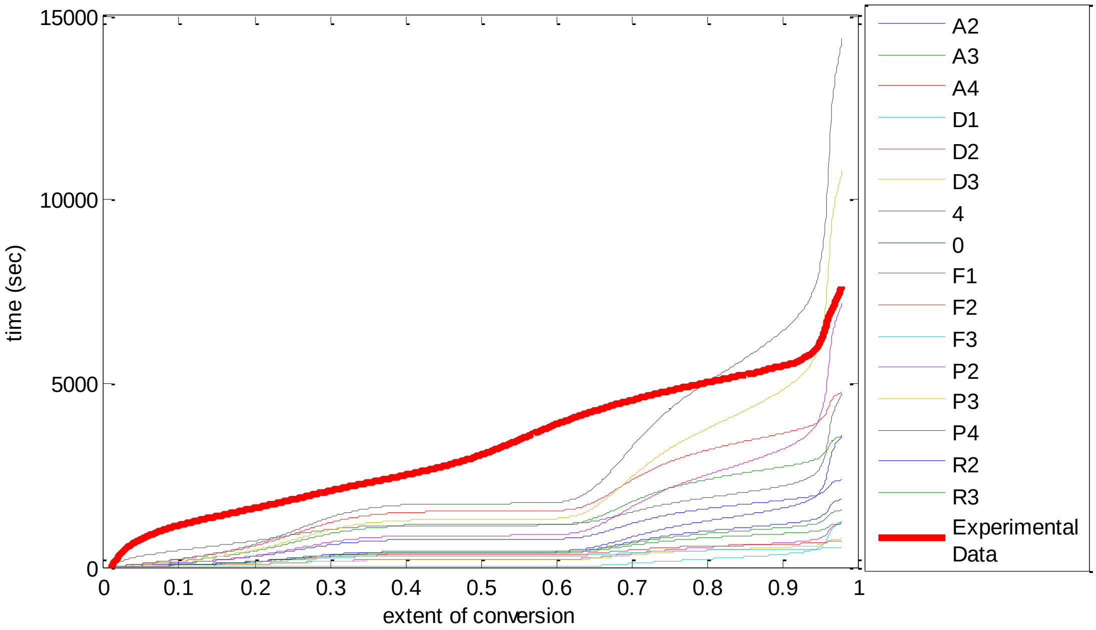

Figure D.12 Fitting integral time vectors to TGA profile of D-1 in 4 ºC/min experiment

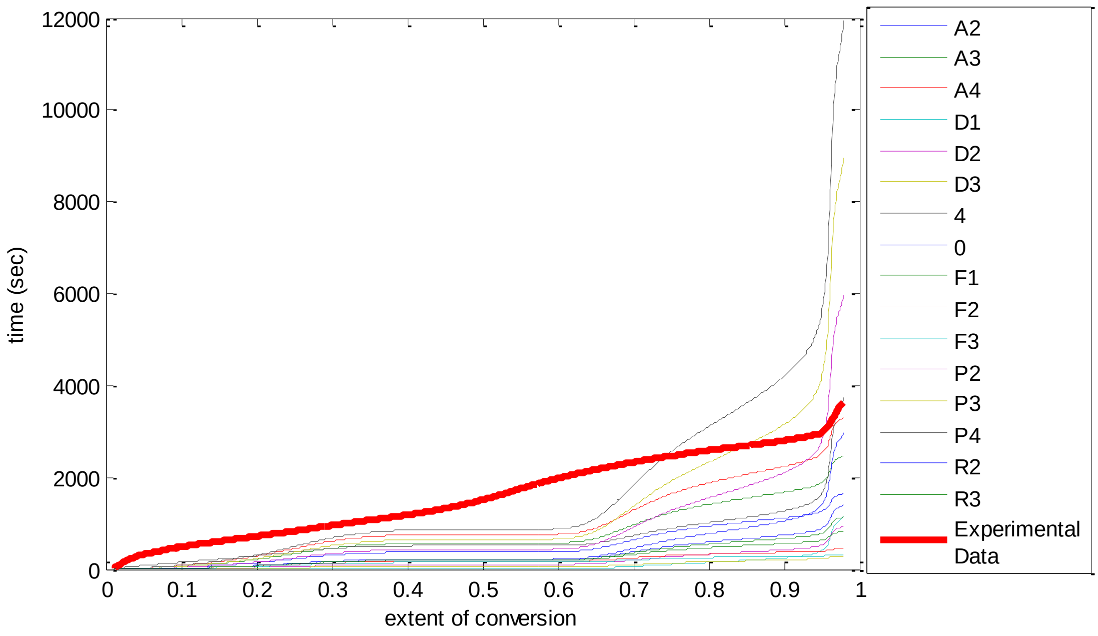

Figure D.13 Fitting integral time vectors to TGA profile of D-1 in 8 ºC/min experiment

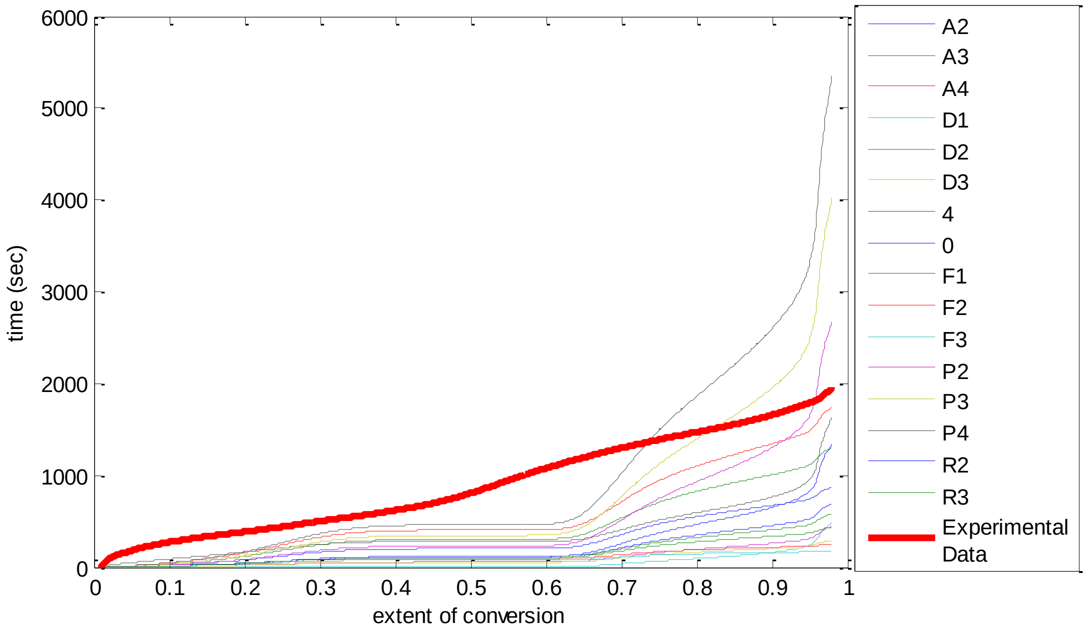

Figure D.14 Fitting integral time vectors to TGA profile of D-1 in 16 ºC/min experiment

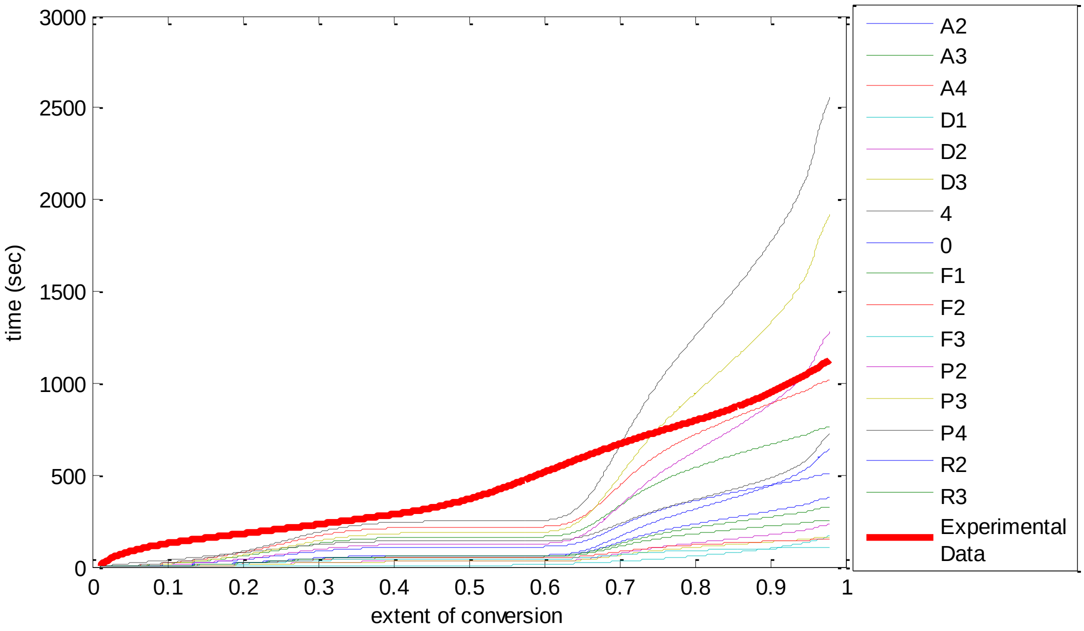

Figure D.15 Fitting integral time vectors to TGA profile of D-1 in 32 ºC/min experiment

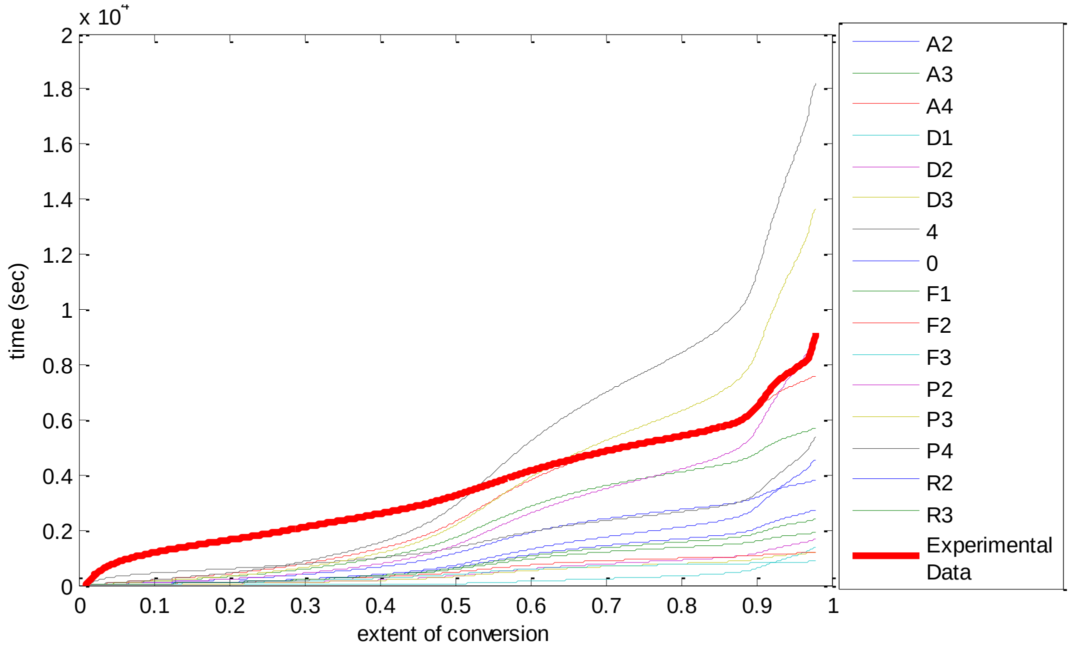

Figure D.16 Fitting integral time vectors to TGA profile of E1-1 in 4 ºC/min experiment

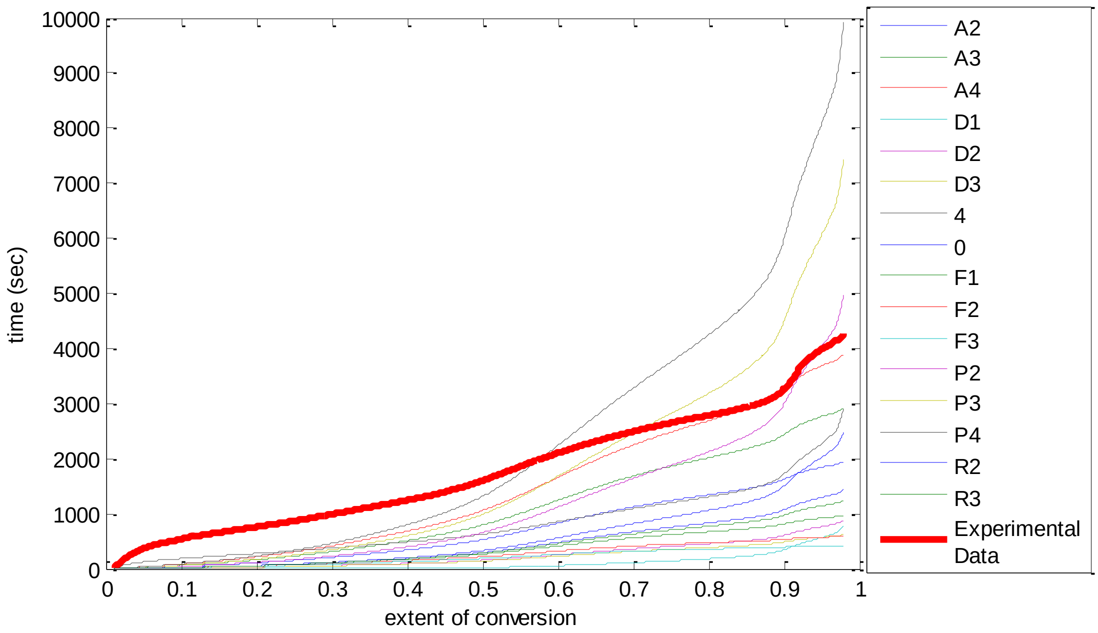

Figure D.17 Fitting integral time vectors to TGA profile of E1-1 in 8 °C/min experiment

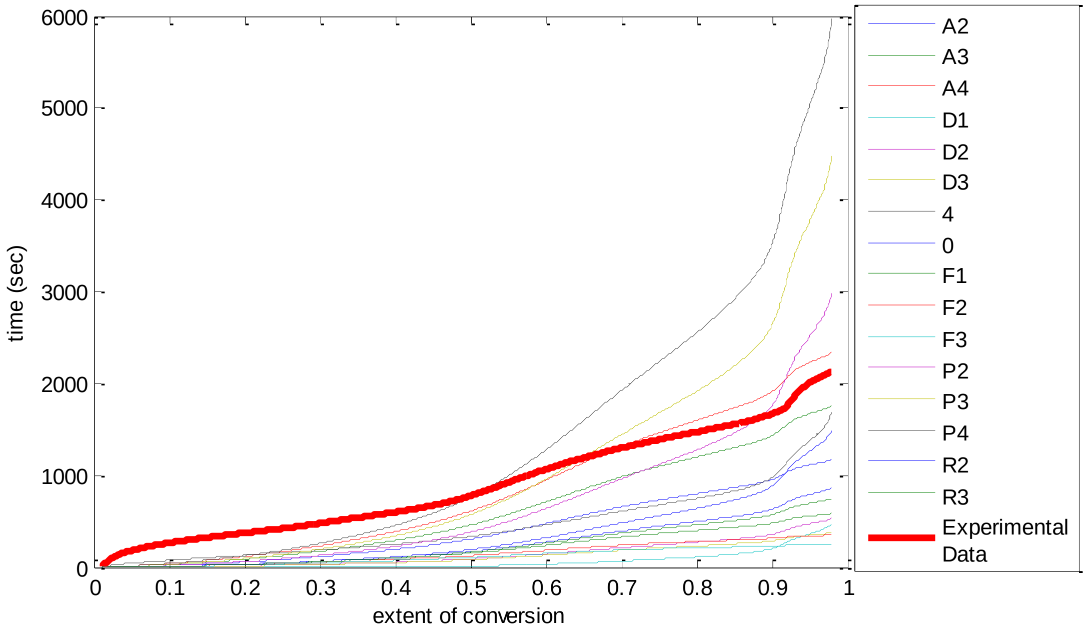

Figure D.18 Fitting integral time vectors to TGA profile of E1-1 in 16 °C/min experiment

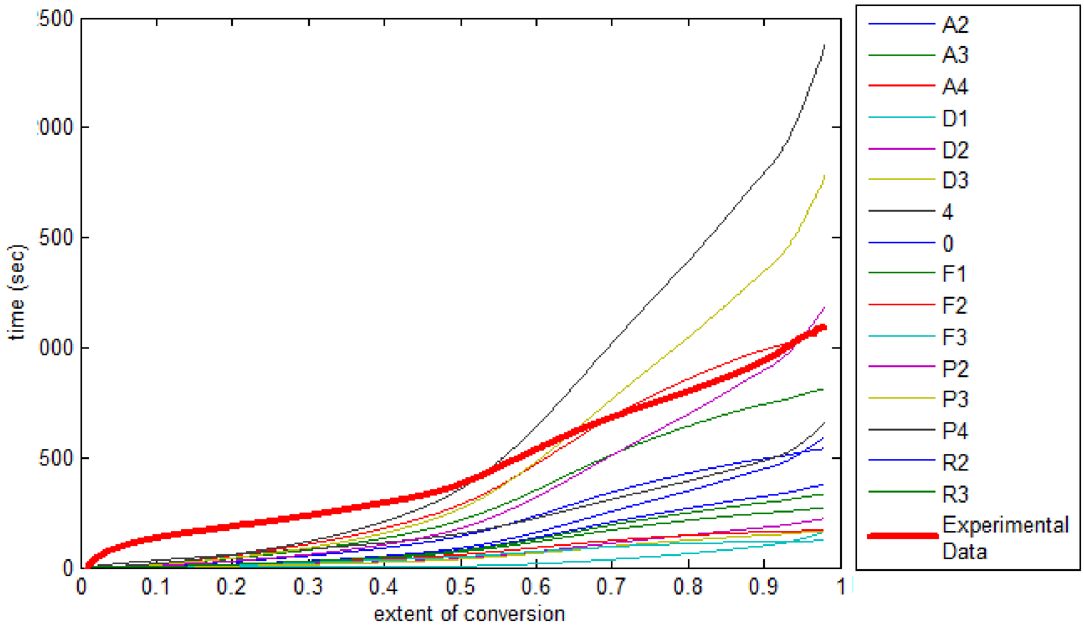

Figure D.19 Fitting integral time vectors to TGA profile of E1-1 in 32 °C/min experiment

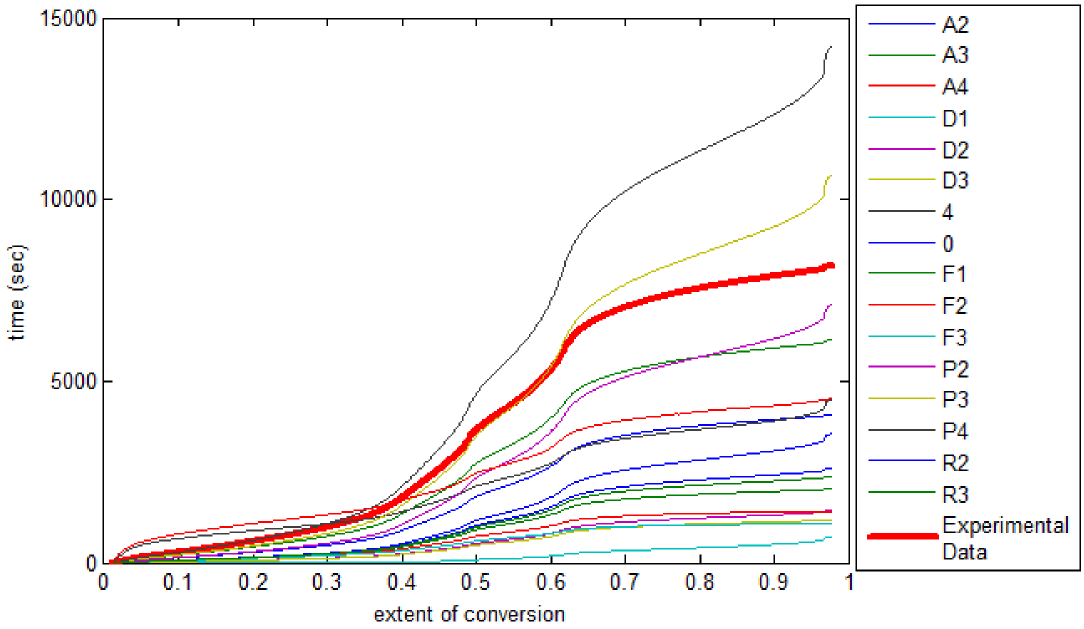

Figure D.20 Fitting integral time vectors to TGA profile of E2-1 in 4 °C/min experiment

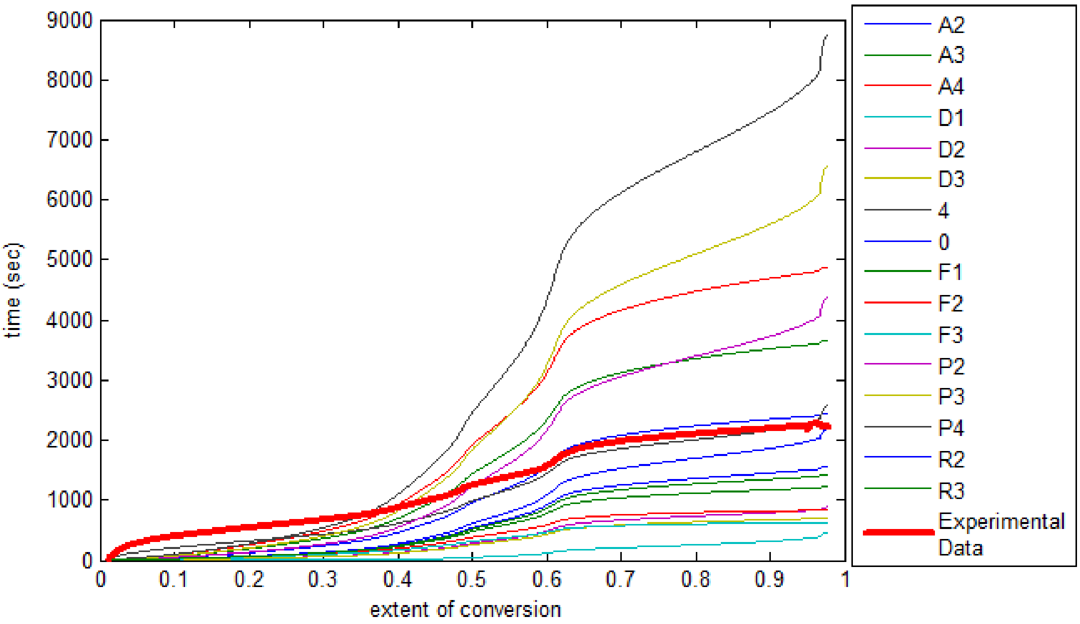

Figure D.21 Fitting integral time vectors to TGA profile of E2-1 in 8 ºC/min experiment

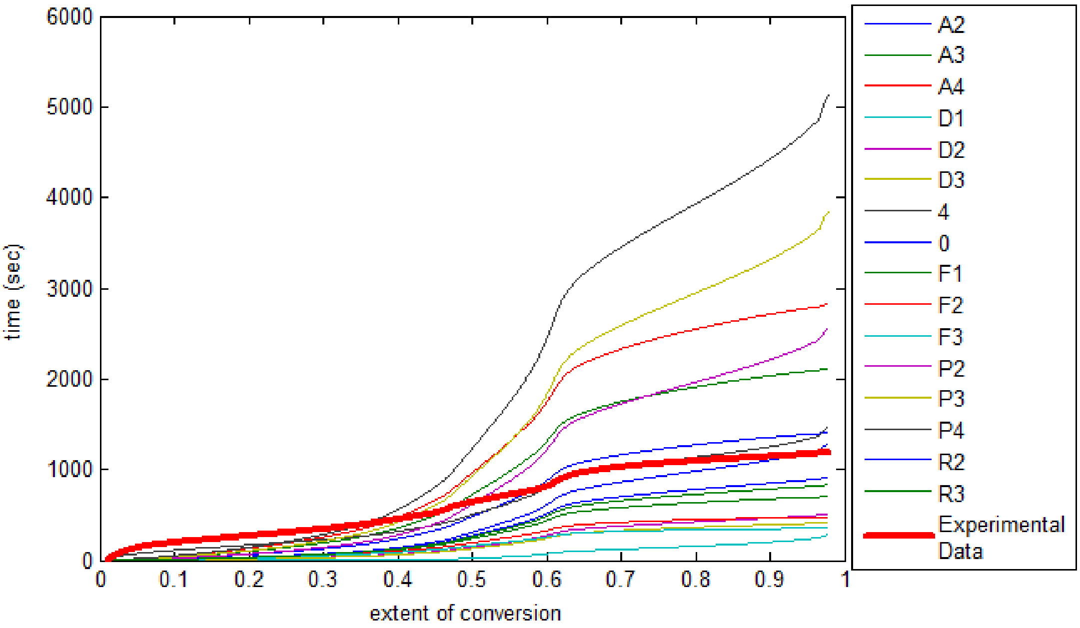

Figure D.22 Fitting integral time vectors to TGA profile of E2-1 in 16 ºC/min experiment

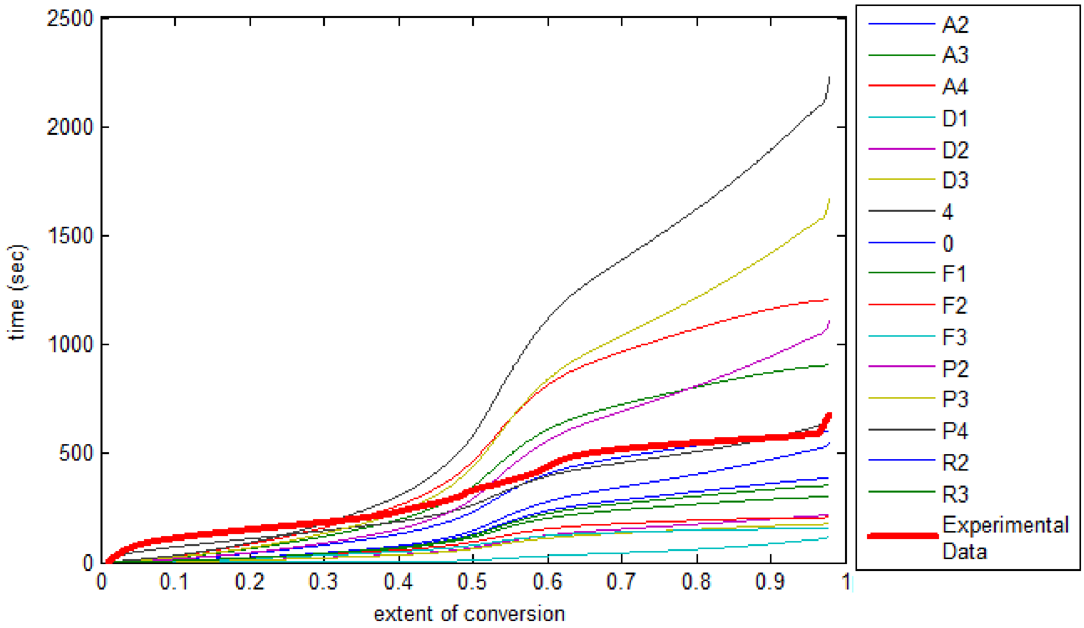

Figure D.23 Fitting integral time vectors to TGA profile of E2-1 in 32 °C/min experiment

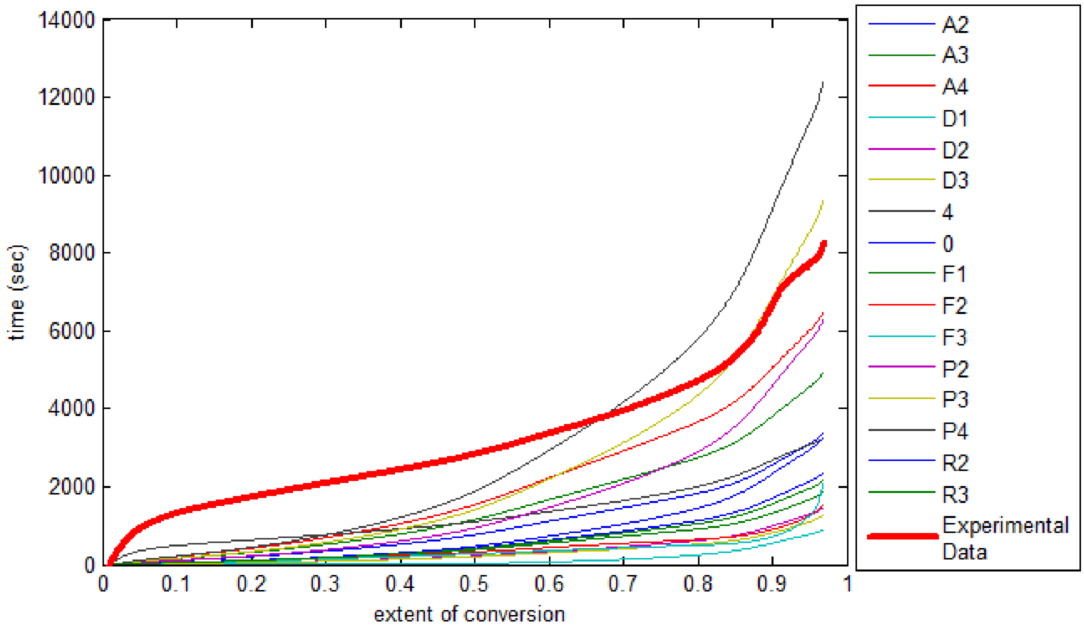

Figure D.24 Fitting integral time vectors to TGA profile of F-1 in 4 °C/min experiment

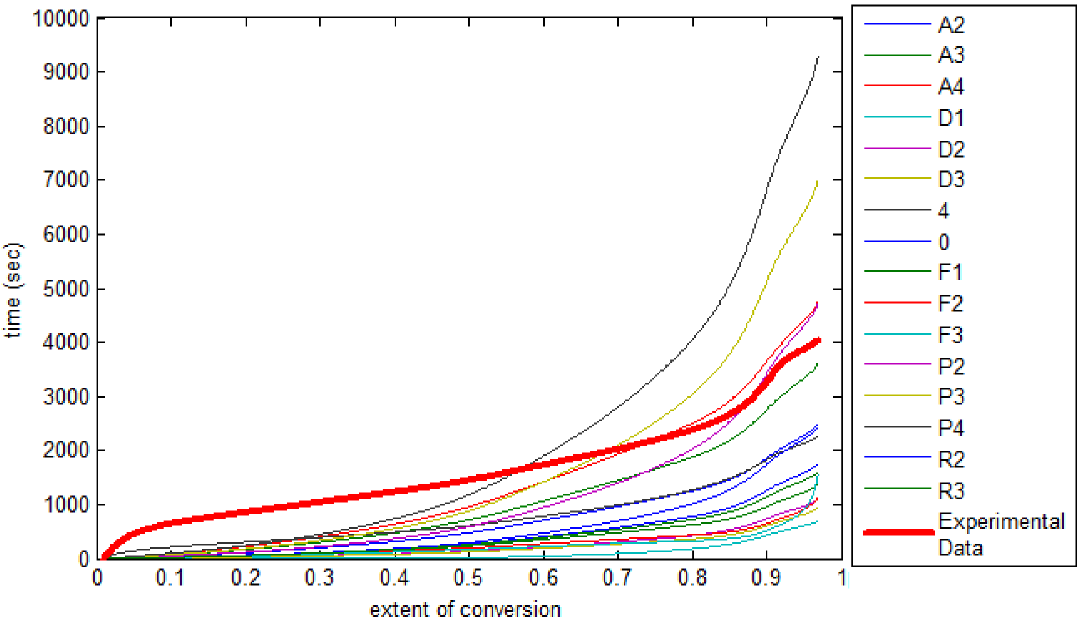

Figure D.25 Fitting integral time vectors to TGA profile of F-1 in 8 °C/min experiment

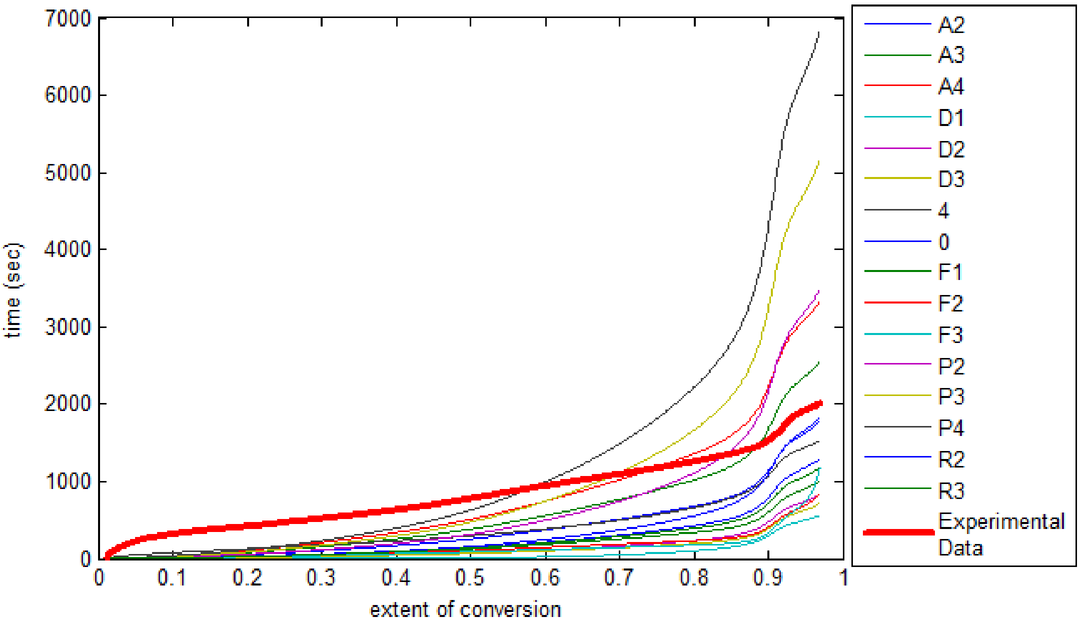

Figure D.26 Fitting integral time vectors to TGA profile of F-1 in 16 °C/min experiment

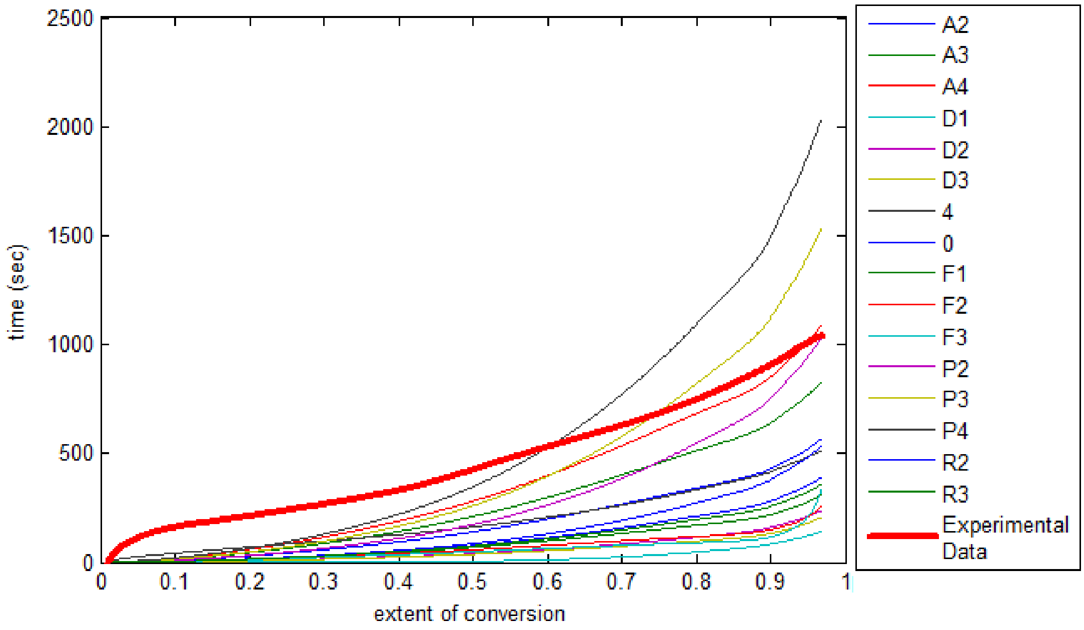

Figure D.27 Fitting integral time vectors to TGA profile of F-1 in 32 ºC/min experiment

D.2. Fitting Differential Data

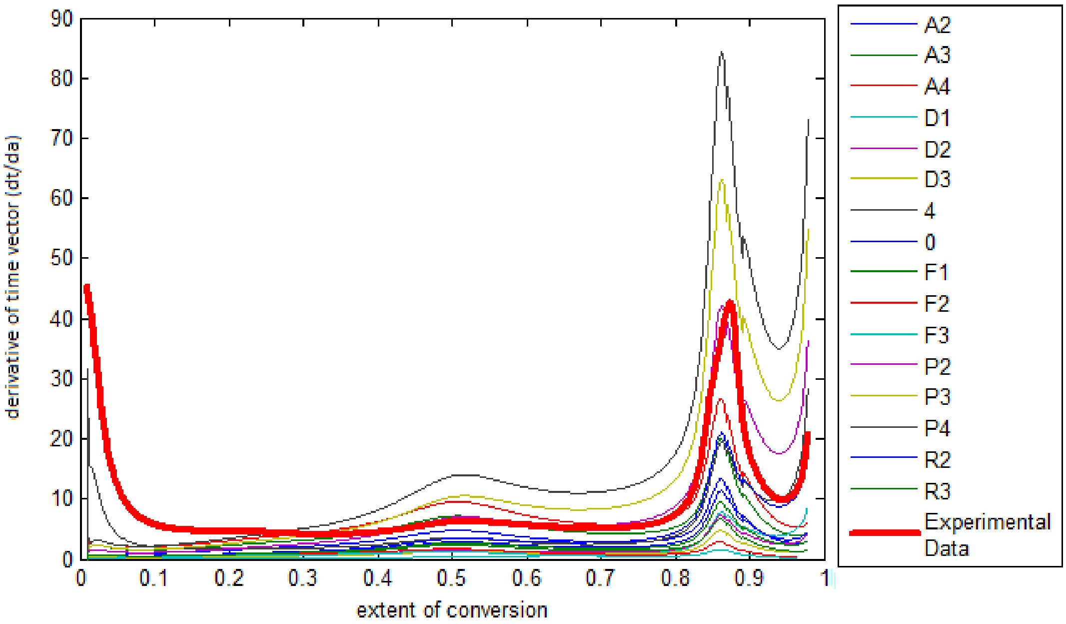

Figure D.28 Fitting differential time vectors to TGA profile of A-1 in 4 ºC/min experiment

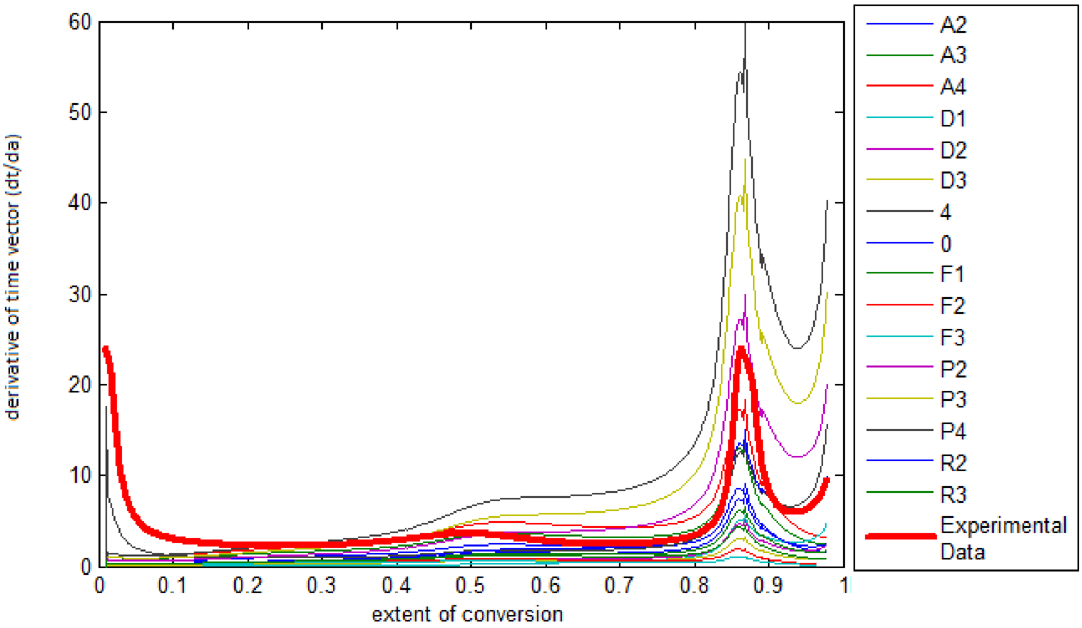

Figure D.29 Fitting differential time vectors to TGA profile of A-1 in 8 ºC/min experiment

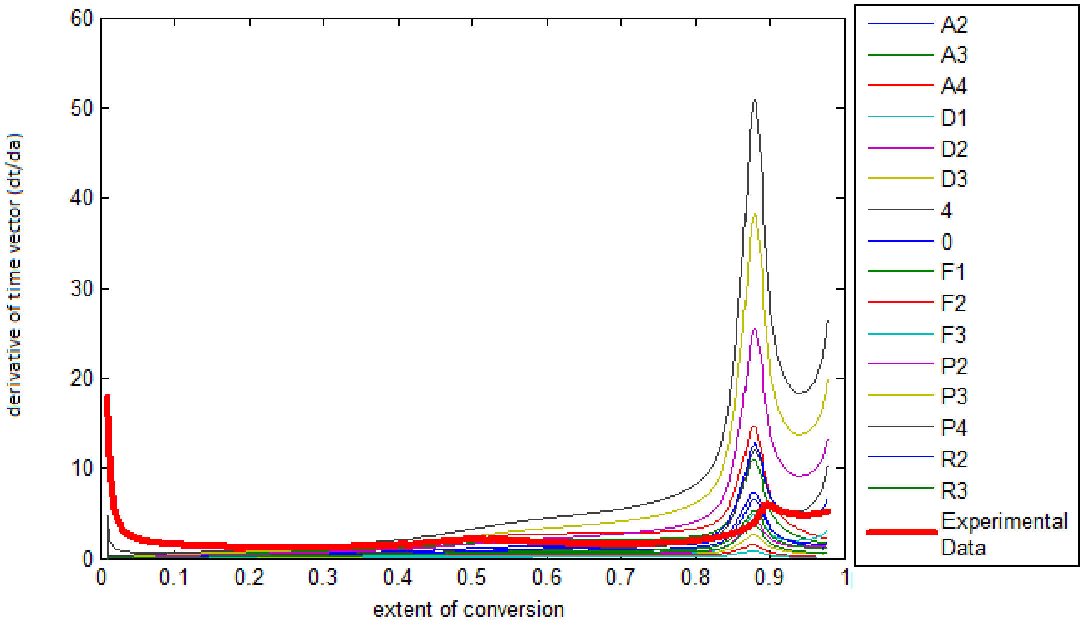

Figure D.30 Fitting differential time vectors to TGA profile of A-1 in 16 ºC/min experiment

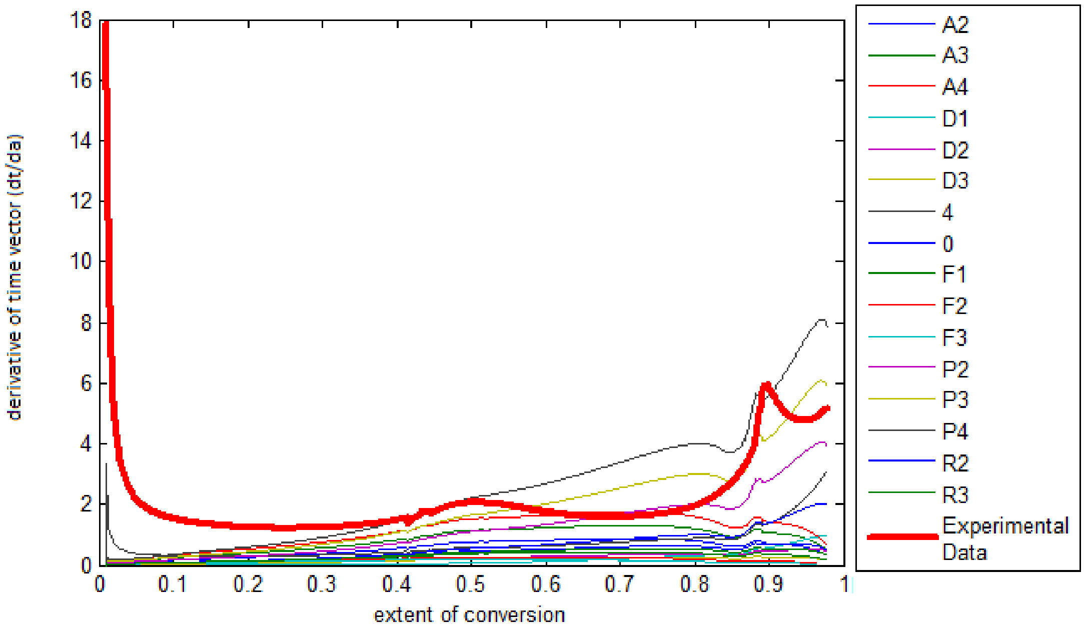

Figure D.31 Fitting differential time vectors to TGA profile of A-1 in 32 ºC/min experiment

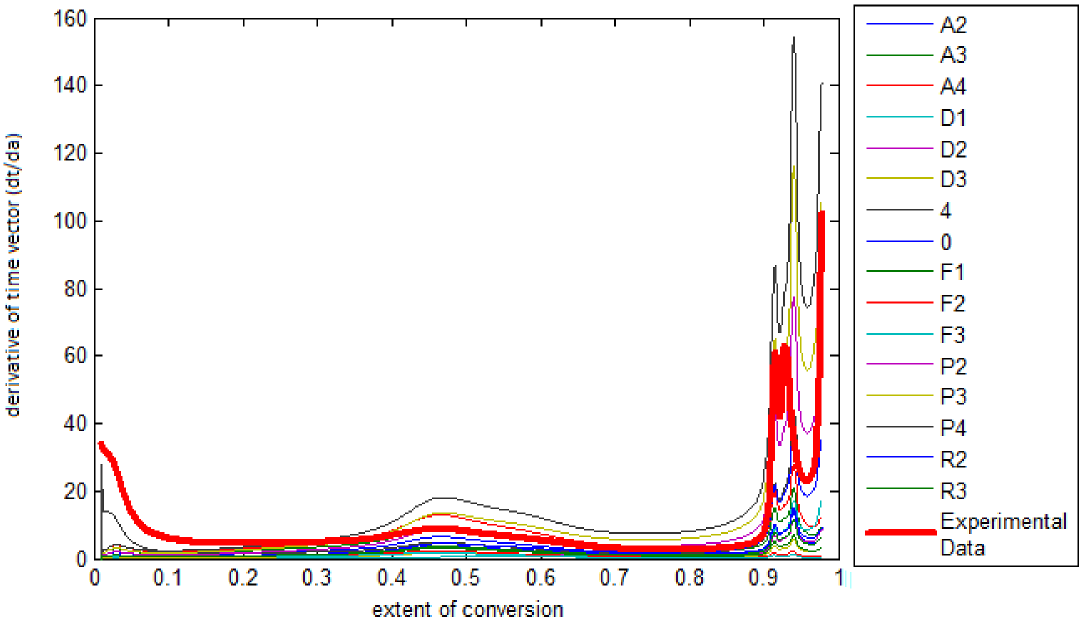

Figure D.32 Fitting differential time vectors to TGA profile of B-1 in 4 ºC/min experiment

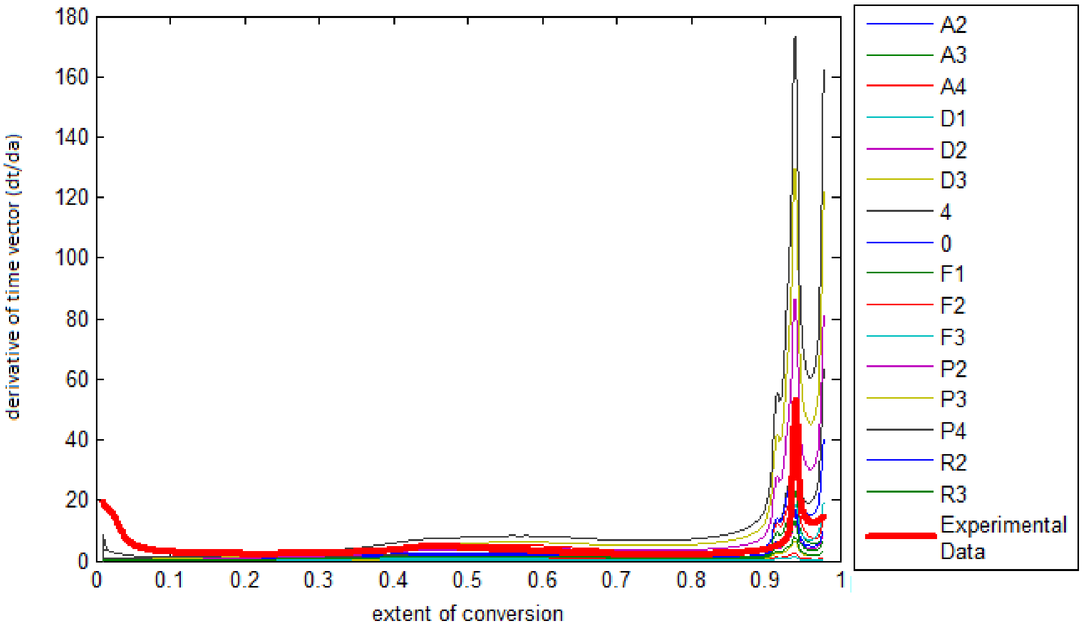

Figure D.33 Fitting differential time vectors to TGA profile of B-1 in 8 ºC/min experiment

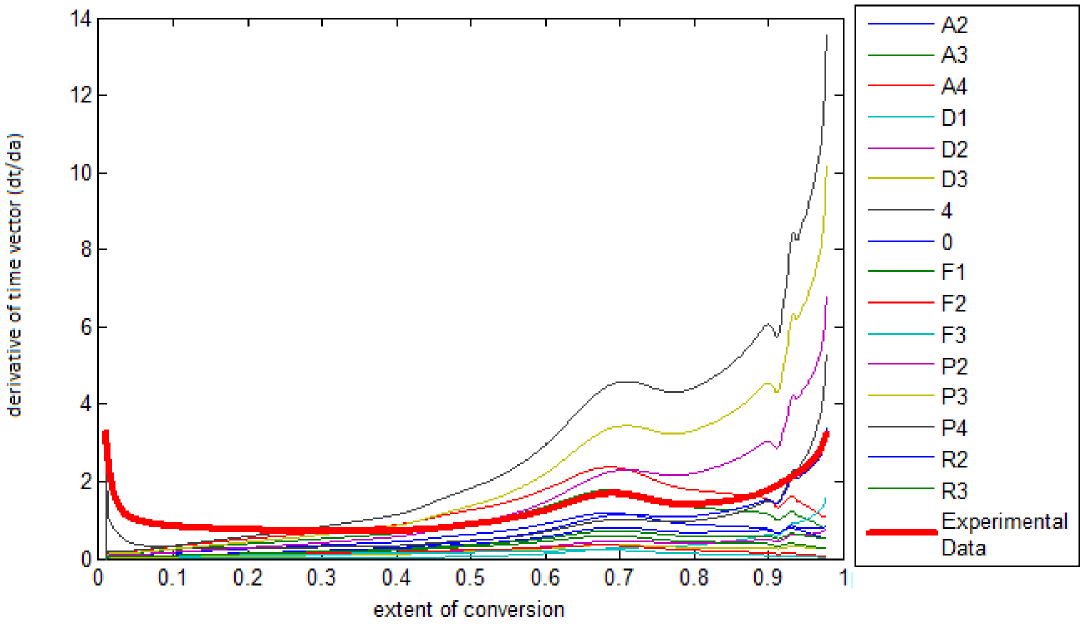

Figure D.34 Fitting differential time vectors to TGA profile of B-1 in 32 ºC/min experiment

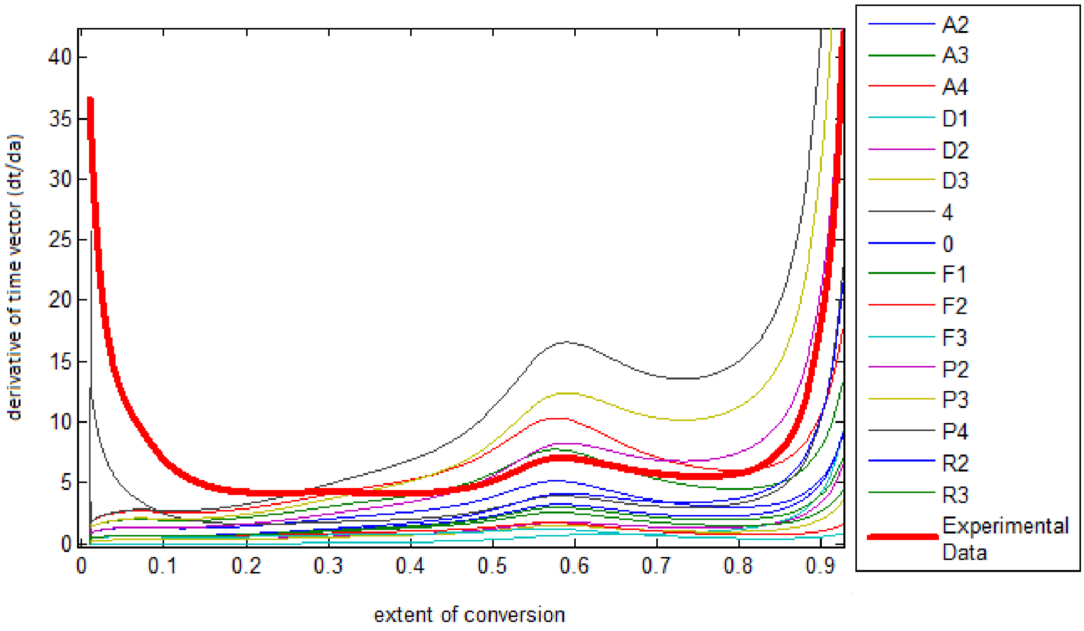

Figure D.35 Fitting differential time vectors to TGA profile of C-1 in 4 ºC/min experiment

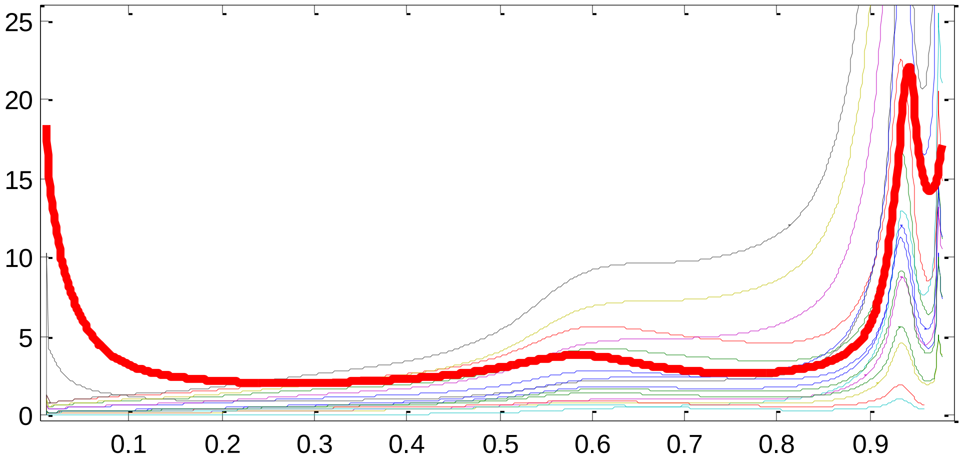

Figure D.36 Fitting differential time vectors to TGA profile of C-1 in 8 ºC/min experiment

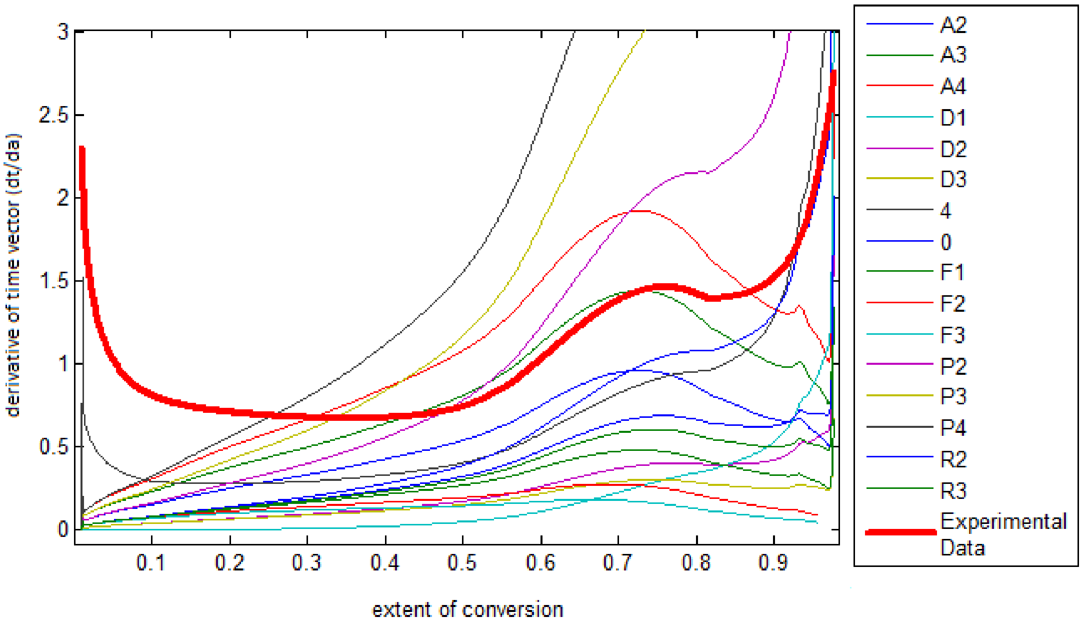

Figure D.37 Fitting differential time vectors to TGA profile of C-1 in 32 ºC/min experiment

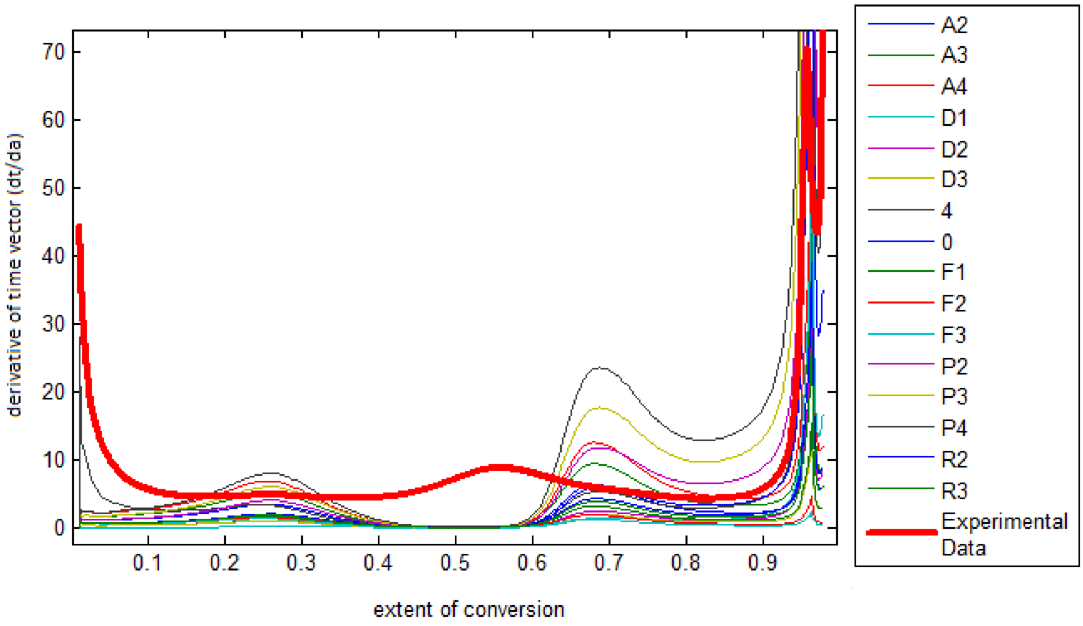

Figure D.38 Fitting differential time vectors to TGA profile of D-1 in 4 ºC/min experiment

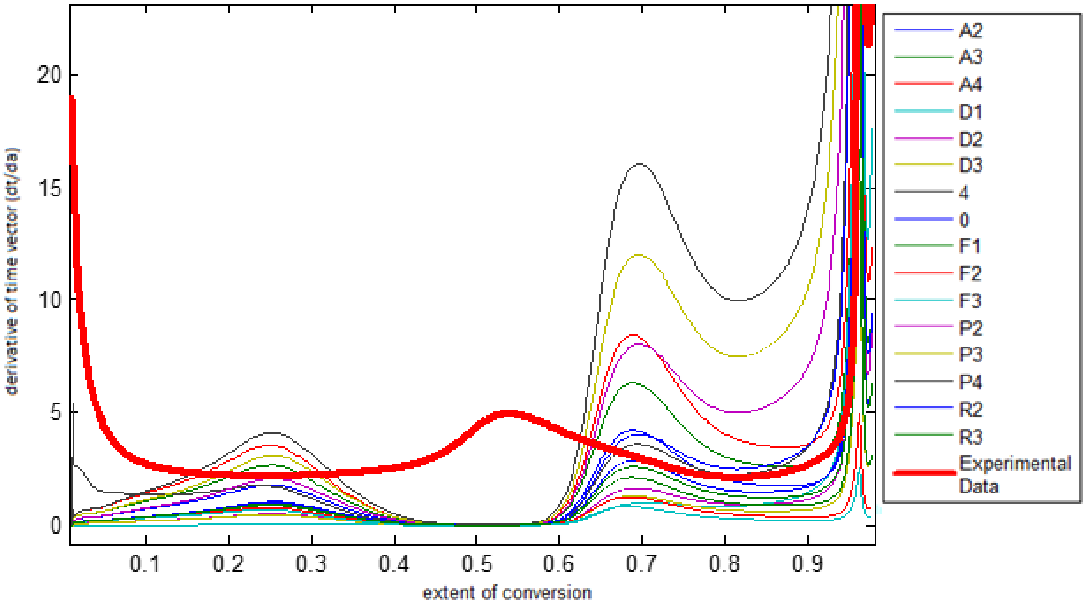

Figure D.39 Fitting differential time vectors to TGA profile of D-1 in 8 ºC/min experiment

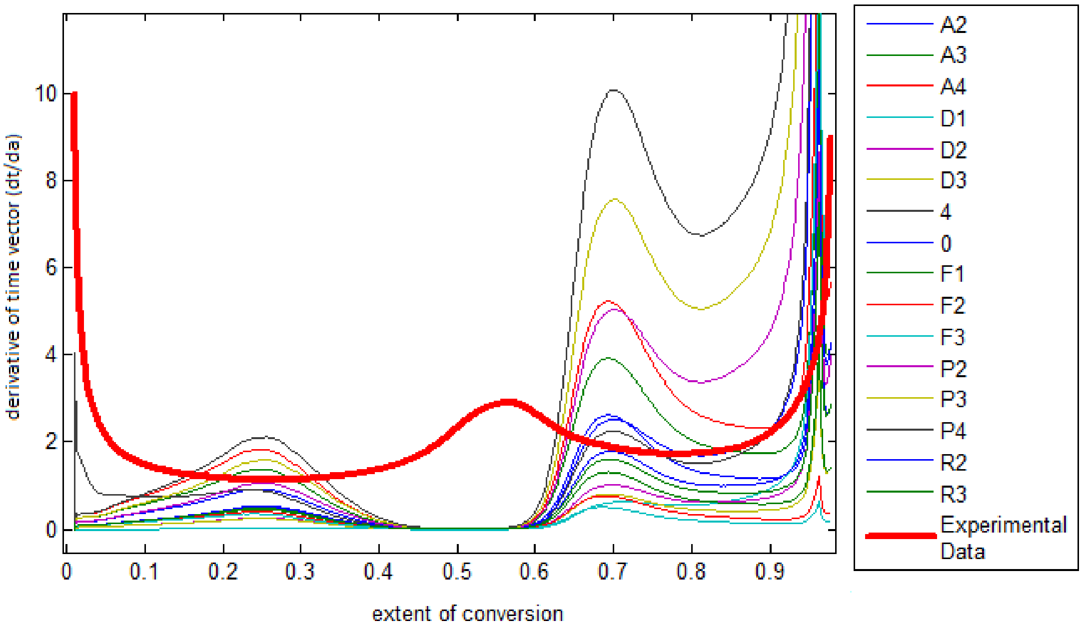

Figure D.40 Fitting differential time vectors to TGA profile of D-1 in 16 ºC/min experiment

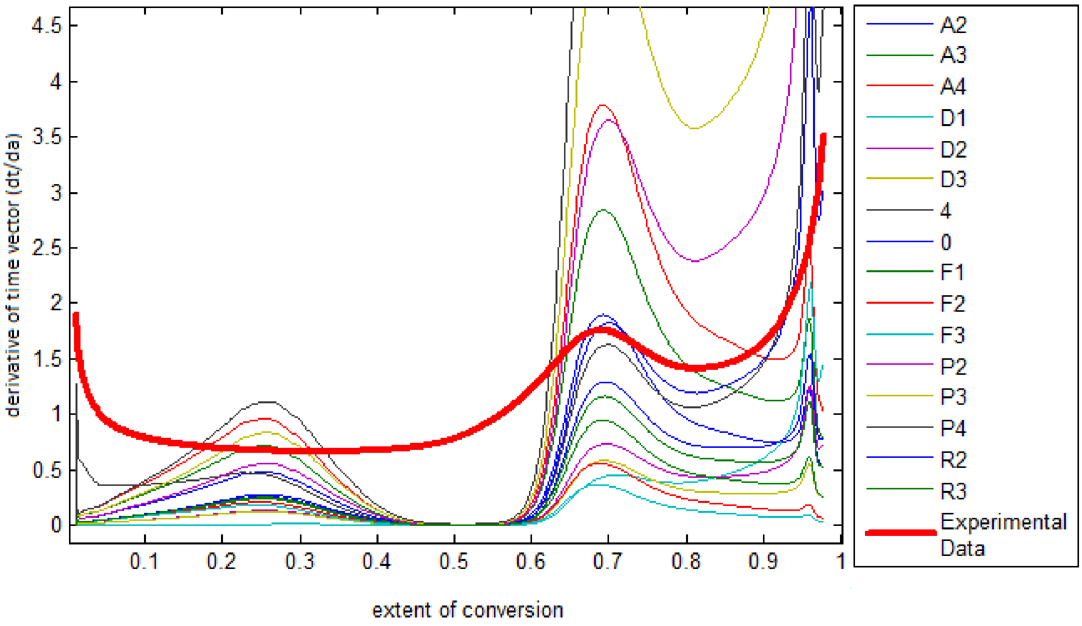

Figure D.41 Fitting differential time vectors to TGA profile of D-1 in 32 ºC/min experiment

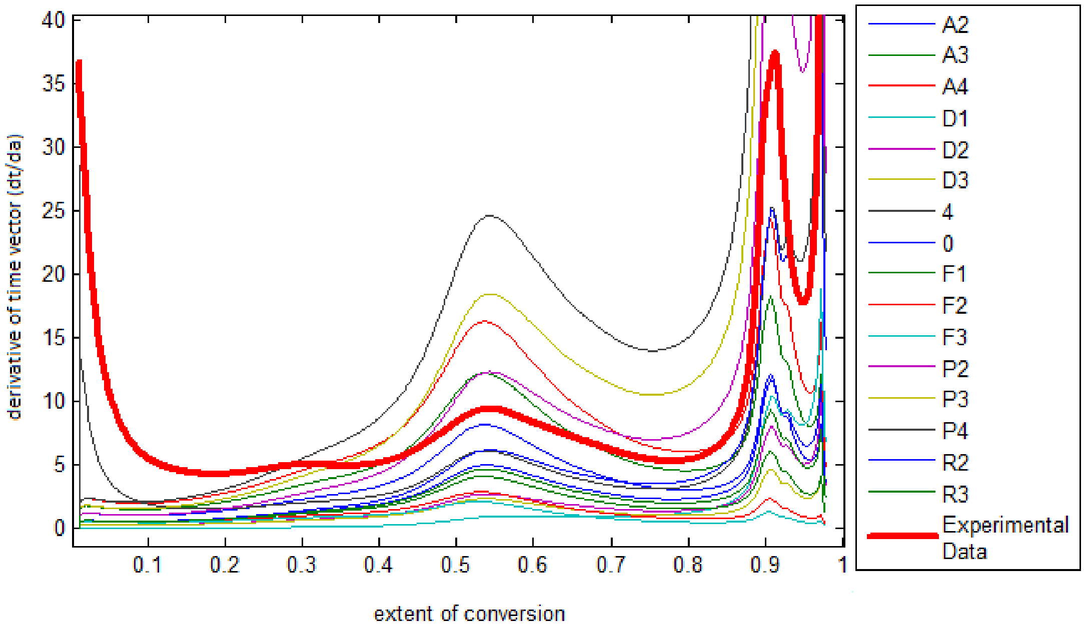

Figure D.42 Fitting differential time vectors to TGA profile of E1-1 in 4 ºC/min experiment

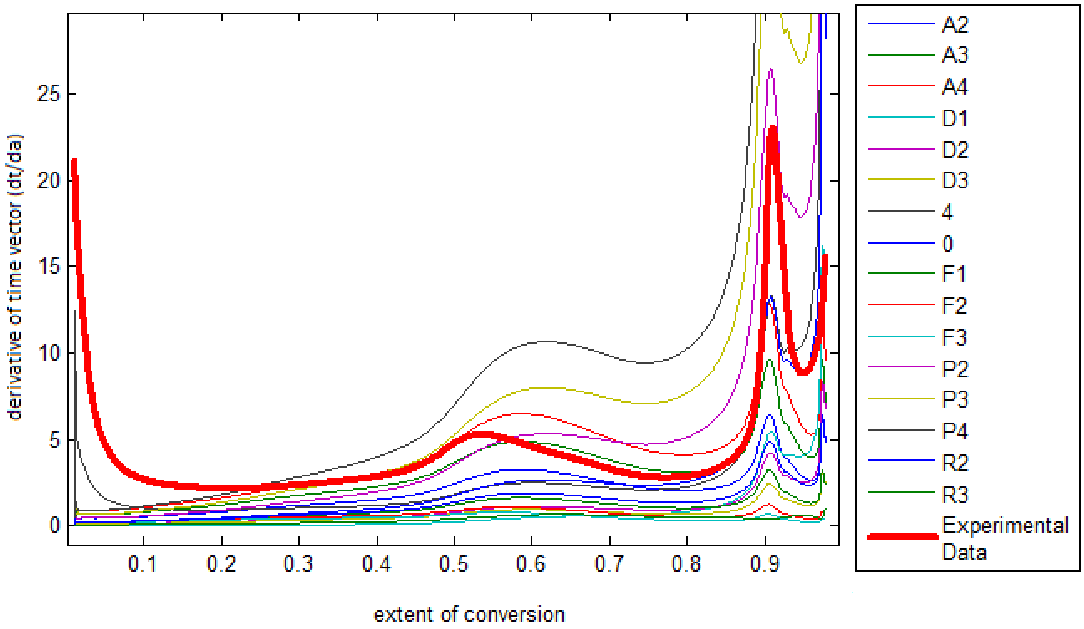

Figure D.43 Fitting differential time vectors to TGA profile of E1-1 in 8 ºC/min experiment

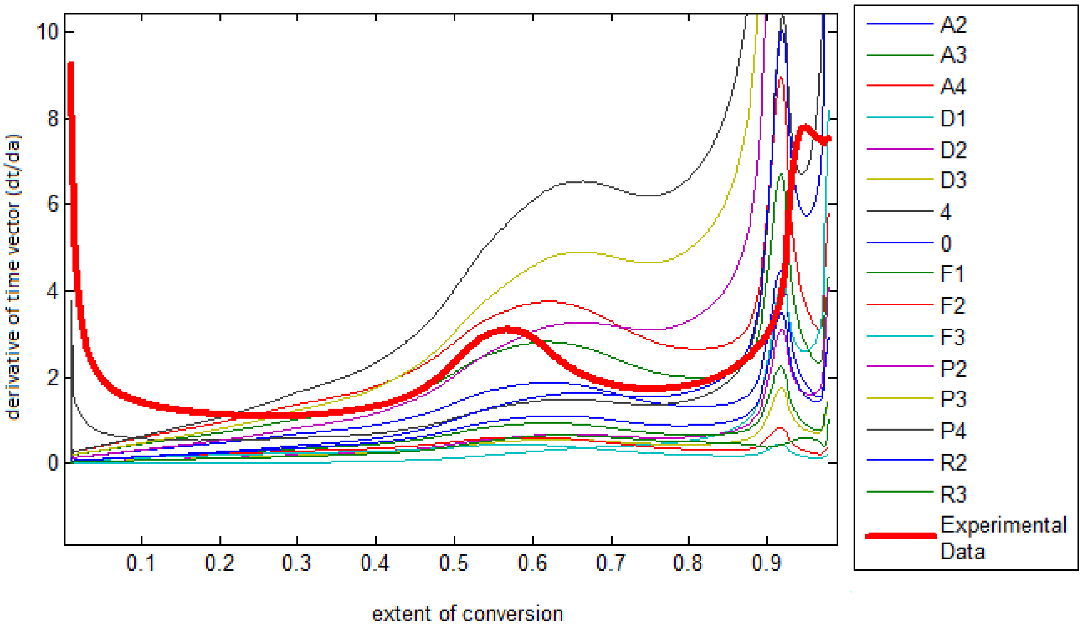

Figure D.44 Fitting differential time vectors to TGA profile of E1-1 in 16 ºC/min experiment

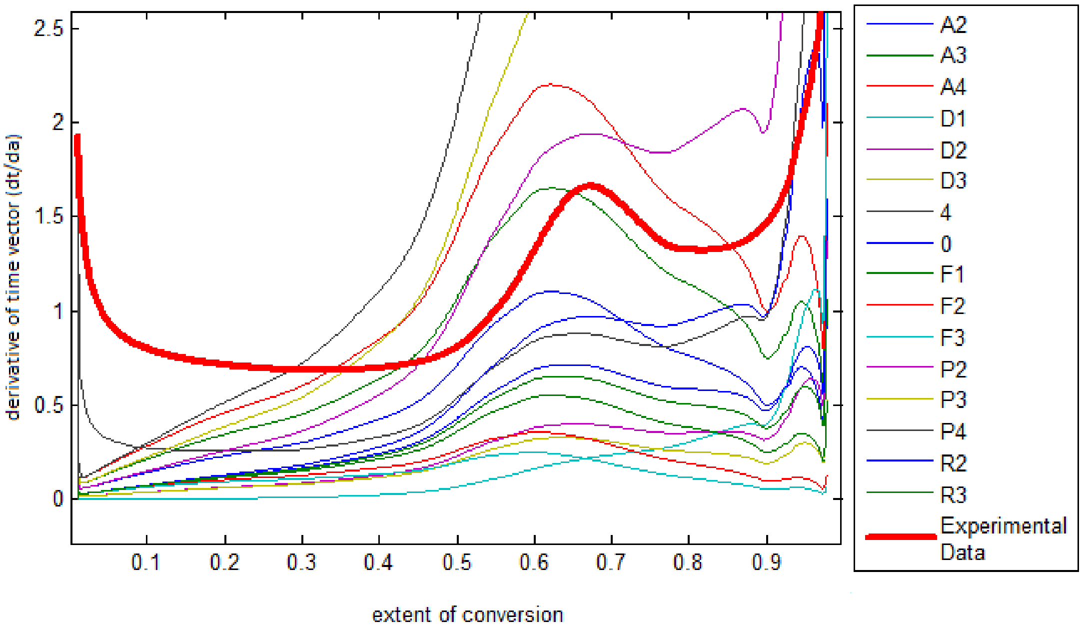

Figure D.45 Fitting differential time vectors to TGA profile of E1-1 in 32 ºC/min experiment

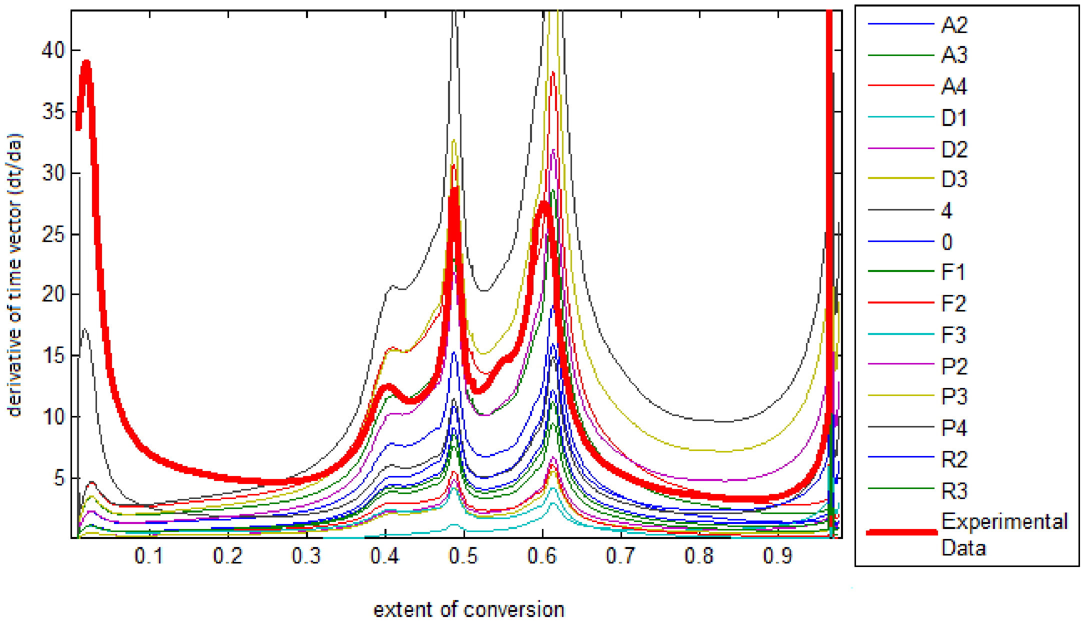

Figure D.46 Fitting differential time vectors to TGA profile of E2-1 in 4 ºC/min experiment

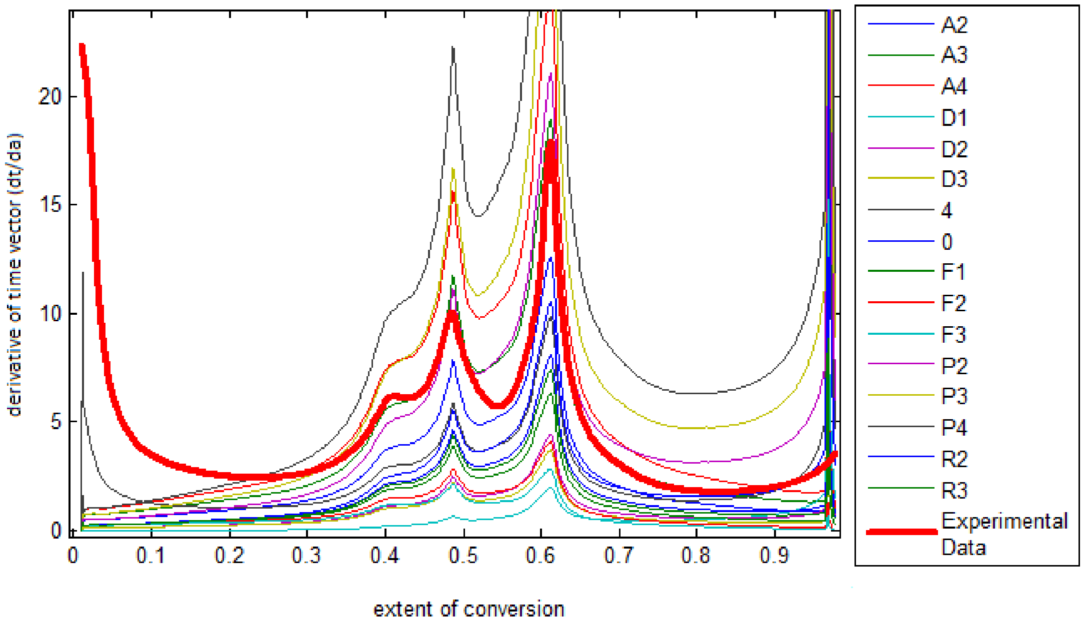

Figure D.47 Fitting differential time vectors to TGA profile of E2-1 in 8 ºC/min experiment

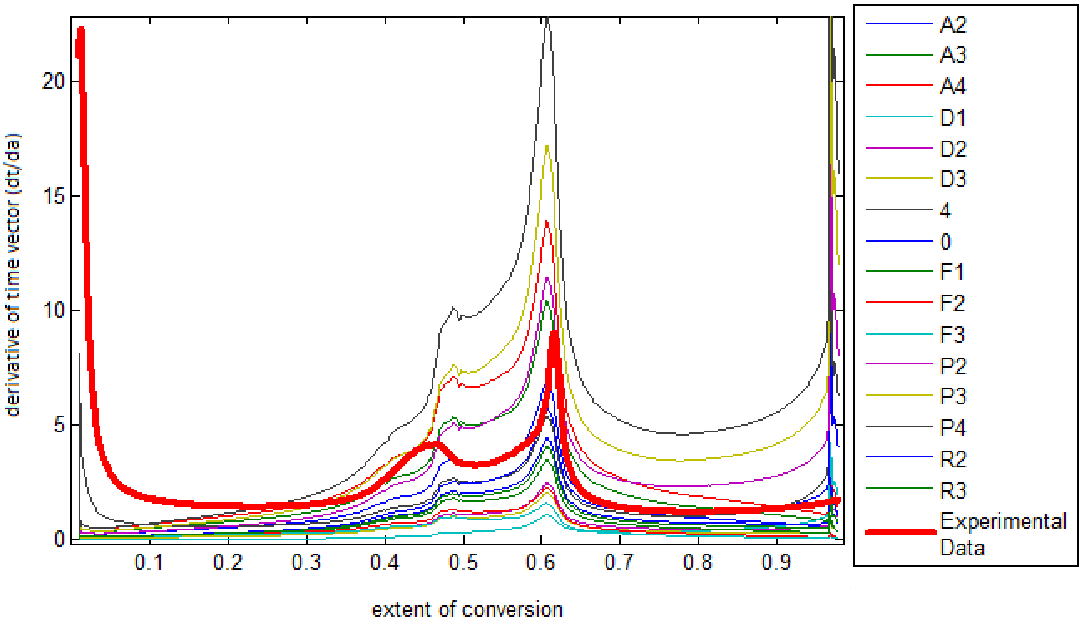

Figure D.48 Fitting differential time vectors to TGA profile of E2-1 in 16 °C/min experiment

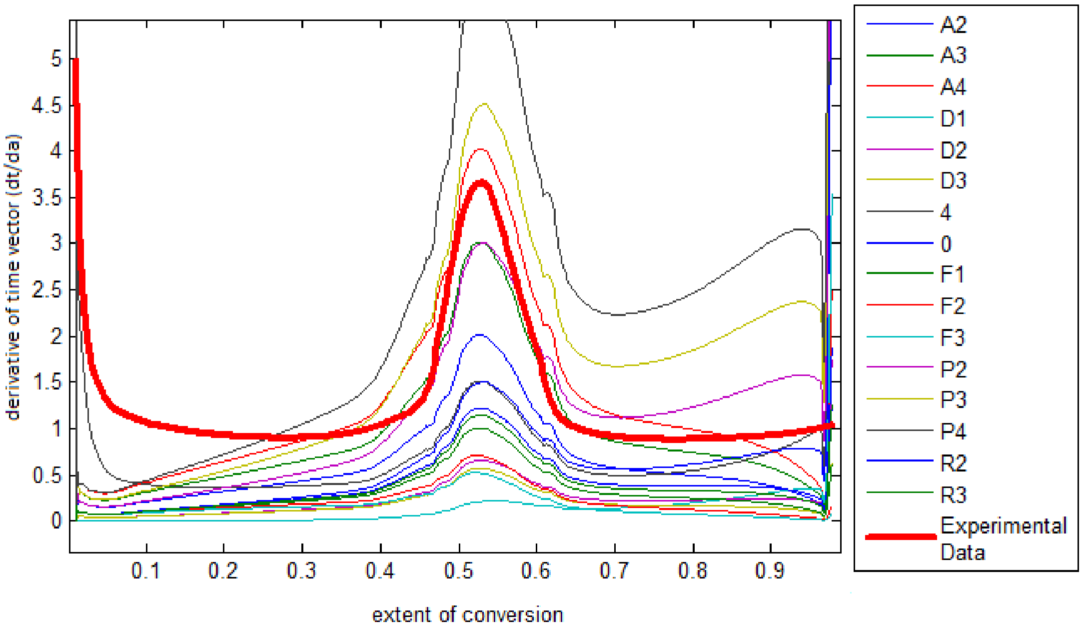

Figure D.49 Fitting differential time vectors to TGA profile of E2-1 in 32 °C/min experiment

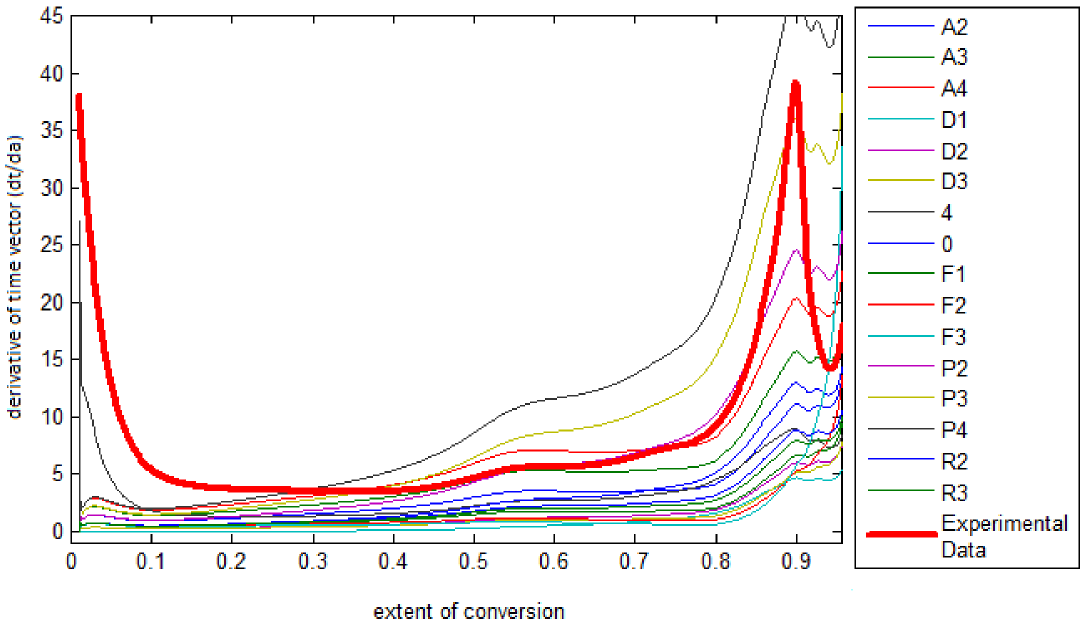

Figure D.50 Fitting differential time vectors to TGA profile of F-1 in 4 ºC/min experiment

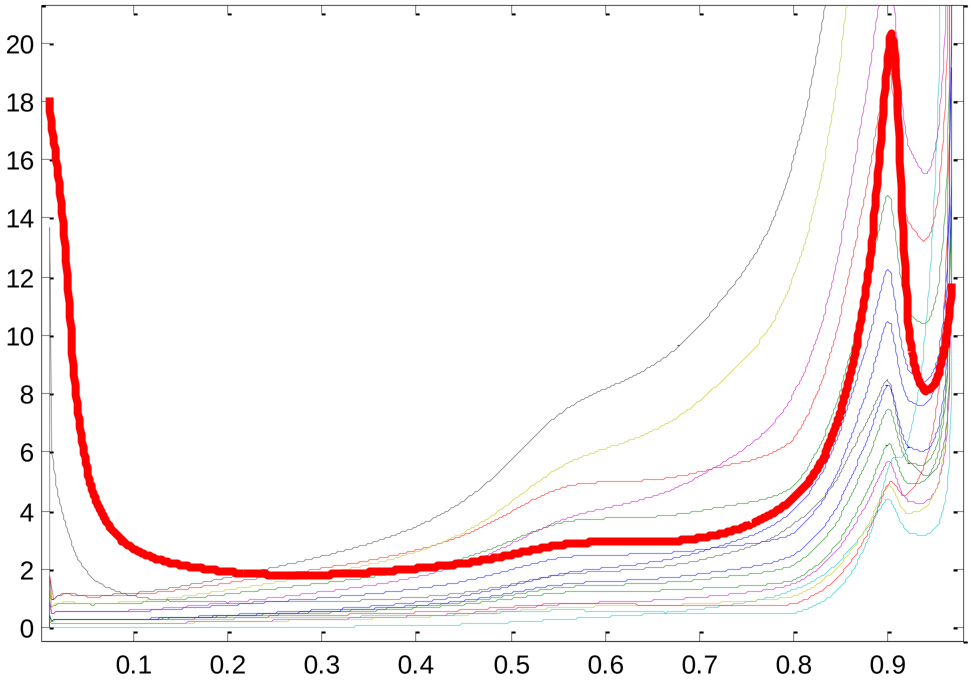

Figure D.51 Fitting differential time vectors to TGA profile of F-1 in 8 ºC/min experiment

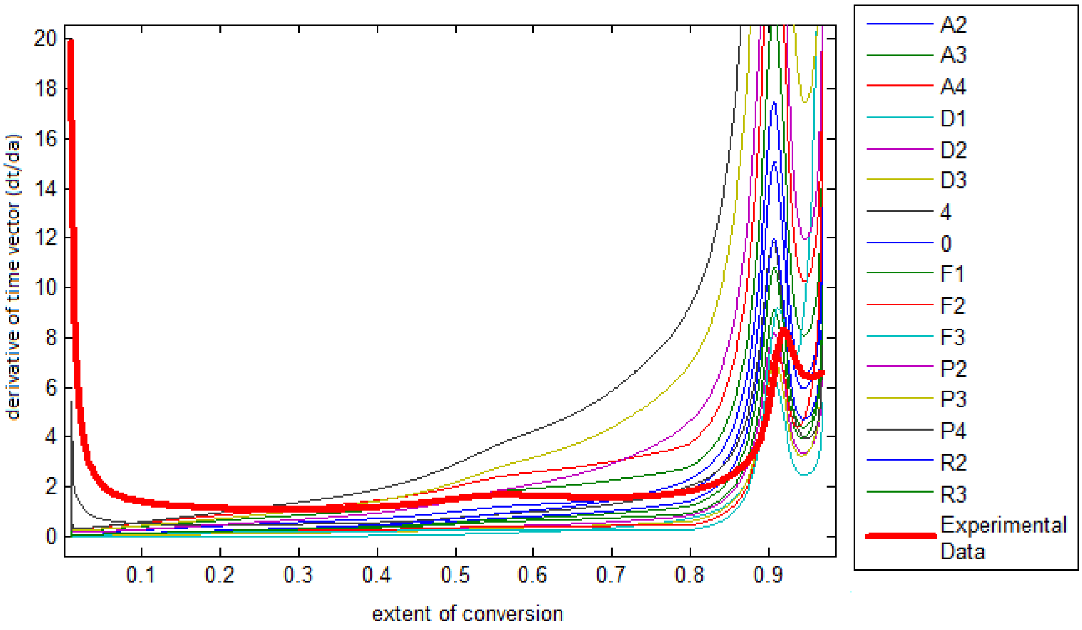

Figure D.52 Fitting differential time vectors to TGA profile of F-1 in 16 ºC/min experiment

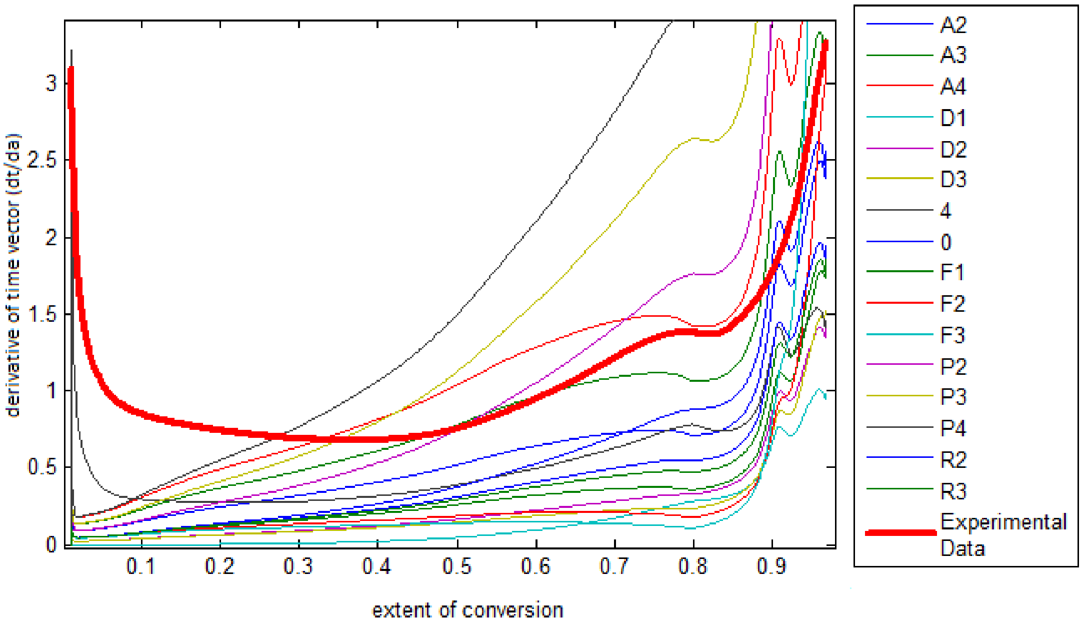

Figure D.53 Fitting differential time vectors to TGA profile of F-1 in 32 ºC/min experiment