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APPLIED SCIENCES

(DOCTOR OF PHILOSOPHY THESIS)

**PYROLYSIS OF SCRAP TYRES AND EVALUATION
OF PYROLYTIC CHAR**

Sermin ÖNENÇ

Supervisor: Prof. Dr. Jale YANIK

Chemistry Department

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Jüri Üyeleri:

Jüri Başkanı : Prof. Dr. Jale YANIK
Raportör Üye : Doç. Dr. Tamer KARAYILDIRIM
Üye : Prof. Dr. Serap ALP
Üye : Prof. Dr. Hayati OLGUN
Üye : Prof. Dr. Suat UÇAR

İmza



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EÜ Lisansüstü Eğitim ve Öğretim Yönetmeliğinin ilgili hükümleri uyarınca Doktora Tezi olarak sunduğum “Pyrolysis of Scrap Tyres and Evaluation of Pyrolytic Char” başlıklı bu tezin kendi çalışmam olduğunu, sunduğum tüm sonuç, doküman, bilgi ve belgeleri bizzat ve bu tez çalışması kapsamında elde ettiğimi, bu tez çalışmasıyla elde edilmeyen bütün bilgi ve yorumlara atıf yaptığımı ve bunları kaynaklar listesinde usulüne uygun olarak verdiğimi, tez çalışması ve yazımı sırasında patent ve telif haklarını ihlal edici bir davranışımın olmadığını, bu tezin herhangi bir bölümünü bu üniversite veya diğer bir üniversitede başka bir tez çalışması içinde sunmadığımı, bu tezin planlanmasından yazımına kadar bütün safhalarda bilimsel etik kurallarına uygun olarak davrandığımı ve aksinin ortaya çıkması durumunda her türlü yasal sonucu kabul edeceğimi beyan ederim.

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Sermiye Öner

ÖZET**ÖMRÜNÜ TAMAMLAMIŞ LASTİKLERİNİN PİROLİZİ VE
PİROLİZ KATISININ DEĞERLENDİRİLMESİ**

ÖNENÇ, Sermin

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Bu tez çalışmasında, ömrünü tamamlamış otomobil lastiği, ömrünü tamamlamış kamyon lastiği, sintine suyu ve yağlı çamur gibi tehlikeli atıkların çevresel ve ekonomik fayda sağlayan ürünlere dönüştürülmesi incelenmiştir.

İlk deney bölümünde, bu tür atıkların yakıtlar veya aktifleştirilmiş karbonlar gibi faydalı ürünlere dönüştürülmesi için en uygun işlemlerden biri olan piroliz işlemi uygulanmıştır. Buna ek olarak, ömrünü tamamlamış lastiklerin ve yağlı atıkların birlikte piroliz deneyleri gerçekleştirilmiştir. Piroliz ürünlerinin kalorifik değerleri; katı ürünler için yaklaşık 28 MJ/kg, sıvı ürünler için yaklaşık 43 MJ/kg olarak bulunmuştur.

İkinci deney bölümünde ömrünü tamamlamış otomobil lastiğinin pirolizinden elde edilen kokun aktif karbon olarak kullanımı araştırılmıştır. Kokun aktivasyonu amacıyla; siklik aktivasyon, kimyasal aktivasyon ve fiziksel aktivasyon yöntemleri kullanılmıştır. Aktifleştirilmiş kokların yüzey özelliklerinde belirgin gelişmeler saptanmamıştır.

Çalışmanın son bölümünde; ömrünü tamamlamış otomobil lastiğinin ve piroliz katısının yanma davranışları termogravimetrik analizör ve lab-scale reaktör kullanılarak incelendi. Ayrıca, kokun diğer karbonlu maddelerle (liniyit ve tavuk gübresi koku) birlikte yanması da incelenmiştir. Yakıt karışımlarına tavuk gübresinin ilavesi SO_x salınımını önemli ölçüde azaltmıştır.

Anahtar kelimeler: Ömrünü tamamlamış lastikler, yağlı atıklar, tavuk gübresi, piroliz, aktifleştirme, yanma.



ABSTRACT**PYROLYSIS OF SCRAP TYRES AND EVALUATION OF
PYROLYTIC CHAR**

ÖNENÇ, Sermin

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The conversion of hazardous wastes such as scrap car tyre, scrap truck tyre, bilge water and oily sludge into products providing environmental and economic benefits were studied in this thesis.

In the first experimental section, pyrolysis process which is one of the most convenient processes for the conversion of these kinds of wastes into useful products such as fuels or activated carbons was applied. In addition, co-pyrolysis experiments of scrap tyres and oily wastes were also carried out. High heating calorific values of the pyrolysis products were found to be around 28 MJ/kg for chars and 43 MJ/kg for oil.

The utilization of the char, obtained from pyrolysis of scrap car tyre, as activated carbon was investigated in the second experimental section. For the purpose of activation of the char; cyclic activation, chemical activation and physical activation methods were used. No significant improvement on the surface properties of the activated chars was observed.

In the last section of the study; combustion behaviours of the scrap tyre and its char were investigated by using thermogravimetric analyser and lab-scale reactor. In addition, the co-combustion of the char with the other carbonaceous matters (lignite and poultry litter char) were also investigated. Addition of poultry litter char into fuel blends led to significant reduction of the SO_x emissions.

Keywords: Scrap tyres, oily wastes, poultry litter, pyrolysis, activation, combustion.



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1. INTRODUCTION

Every product that we use for facilitate our life has cost but the greatest price will be paid for environmental pollution unless precautions such as recycling, converting into useful products, and etc. are not taken after the end of their life. Precautions have also to be taken for wastes which are composed from during the production. Along with the importance of these precautions, waste management is became one of the serious topic for environmental protection. Besides of the recycling and converting into useful products, landfill can be seen as another solution. However, landfill is supposed to be the last option for the waste management in environment safety. Even if it has to be used for the management it should be compelled with the requirements of Directive 1999/31/EC on the landfill of waste. According to the landfill directive, some wastes may not be accepted in a landfill such as liquid waste, flammable waste, explosive or oxidising waste, scrap tyres, hospital and other clinical waste which is infectious (European Commission, 1999).

Correspondingly, increasing number of motor vehicles in the world is a major concern, because, every year, servicing this type of transport leaves a huge amount of various waste materials such as scrap tyres. According to the recent statistics, each year a worldwide accumulation of scrap tyres exceeds 20.2 million tons (over 1 billion units) and over 24 million tons of used engine oils are collected (Jonusas and Miknius, 2015). Approximately 65% of scrap tyres go to landfill or they are illegally dumped or stockpiled. The conversion processes of scrap tyres have difficulties since tyre is produced with the objective of degradation resistant which is gained by the vulcanization process. Thusly, tyre does not degrade easily in landfills. On the other side, tyre provides high quality reprocessing products, due to long-chain hydrocarbons content which consist of natural rubber (10–30%), styrene–butadiene rubber (30–50%), butadiene rubber (up to 30%). In the consequence of both, environmental concerns and energy requirement led to increase the interest in treatment of such wastes (Alkhatib et al., 2015).

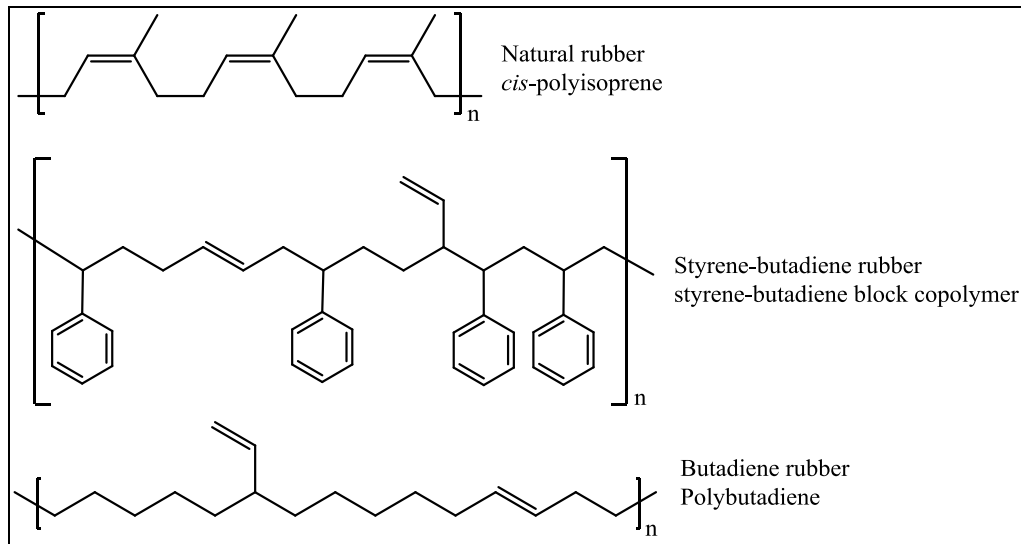


Figure 1.1. Formulation of NR, SBR, and BR.

In addition to these type of pollution in land, there are other types of wastes such as bilge water and oily sludge which are very harmful wastes for open oceans and coastal waters. The existences of these wastes threat the marine environments. They are collected in specific storage cells in ships during their routes. After fill up all cells with these oily wastes, they have to be discharged to keep the balance of ships. Discharges of these oily wastes are limited by the Annex I of MARPOL 73/78. These harmful wastes are discharged to storage area in harbours, against payment.

Scrap tyres without any separation and grinding can be used as decorative products. But these utilizations are not enough to compensate the massive amount of scrap tyre wastes. Thusly, studies are focused on other kinds of utilization which are carried out after separation of the steel parts and grinding. These powdered scrap tyres can be used as asphalt modifier (Wang et al., 2015) and sub-ballast layer material for rail way construction (Signes et al., 2016). In addition, they are also used for the production of rubber containing products such as vehicle mudguards, carpet padding, floor mats, composites (Chandaran et al., 2016; Abu-Jdayil et al., 2016), and polymer blends (Karger-Kocsis et al., 2013; Ramarad et al., 2015; 2017). On the other side, they are valuable wastes for the cement industry. They can be used as energy supplies during the combustion process of cement production because of their high calorific values (Giugliano et al., 1999;

Mut et al., 2015; Nakomcic-Smaragdakis et al., 2016). The combustion process of scrap tyre should be a controlled combustion process due to release of harmful gas emissions such as NO_x, SO_x, PHAs (polycyclic aromatic hydrocarbons) and etc. during the process (Nakomcic-Smaragdakis et al., 2016; Conesa et al., 2016). Therefore thermal degradation methods such as pyrolysis (Rodriguez, 2001; Leung et al., 2002; Li et al., 2004; Boxiong et al., 2007; Wang et al., 2007; Kwon and Castaldi, 2009; Choi et al., 2016) and gasification (Donatelli et al., 2010; Molino et al., 2013; Kandasamy and Gokalp, 2015) gain importance for the conversion of energy from scrap tyre. These methods are also more favourable conversion processes with regard to the cost efficiency. The products obtained from these processes can be used as intermediate products. For example, Molino et al. (2013) were carried out steam gasification process firstly and then they activated the char obtained from gasification in the second step. They were reported that the higher heating value of syngas obtained from steam gasification process is around 10.8 MJ/Nm³ and this value was found to be sufficient for activation of char obtained from the gasification. They also reported that the activated char obtained from gasification was found to be higher Cd (II) adsorption capacity compared to commercial activated carbon which were used in the study. Likewise, the solid product obtained from pyrolysis can be used as fuel (Leung and Wang, 1998) which is defined as intermediate products while it can be used as carbon black (Pantea et al., 2003) and activated carbon (Hoseinzadeh et al., 2012) which are defined as final product. Liquid and gas products are mainly used as fuel (Dogan et al., 2012; Koc and Abdullah, 2014).

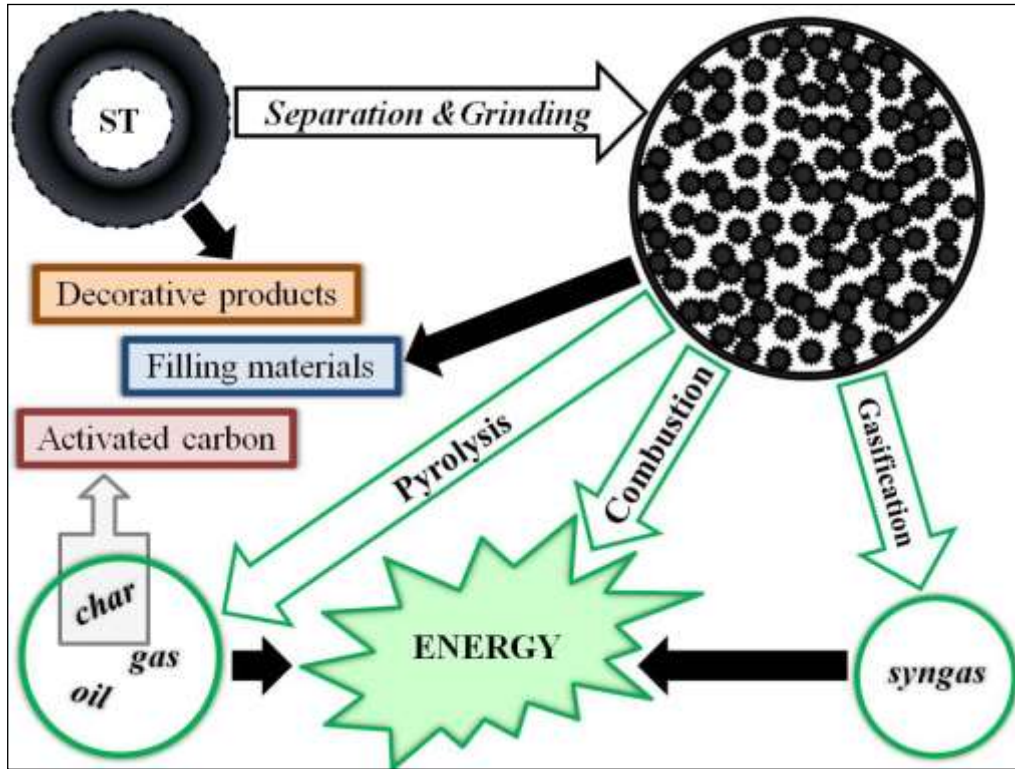


Figure 1.2. The scheme of the utilization of scrap tyres.

The oily wastes, generally, BW and OS can be disposed by combustion process. But this process can be caused secondary pollution due to harmful gas emissions such as NO_x , SO_x and CO_x . For this reason, several treatment methods such as wet air oxidation (Bernal et al., 1999), ultra filtration (Karakulski et al., 1998), electrochemical methods (Korbahti and Artut, 2010; Carlesi et al., 2015) can be used for treatment of bilge water. These methods are sufficient for obtaining of bilge water which is proper in terms of the international standard discharge levels. On the other side, conversion processes such as biodegradation (Nievas, 2006; Marchut-Mikolajczyk et al., 2015) and thermal degradation (Sinag et al., 2010; Ma and Li, 2012; Liu et al., 2012; Liu et al., 2014) were studied for these kinds of wastes. From the point of energy recovery, thermal degradation processes can be more favourable.

1.1. Pyrolysis

Pyrolysis which is a thermal degradation process based on decomposition of carbon rich materials by heating under the oxygen free atmosphere. The volatile

products, namely oil and gas products are obtained during pyrolysis while the solid product, namely char, is obtained as residue after pyrolysis process. Depending on the feedstock, these products can be used as feed stocks for petrochemicals or as fuels.

Pyrolysis, is one of the convenient process for conversion of hazardous wastes such as scrap tyre (Fernandez et al., 2012, Ucar et al., 2005a) and oily wastes (Fang et al., 2016; Sinag et al., 2010; Liu et al., 2009, Shie et al., 2003; Schmidt and Kaminsky, 2001). Because of its high amount of fixed carbon content, scrap tyre has higher calorific value than biomass and some kinds of coal. Besides the high amount of sulphur content is main concern due to release of harmful gas emissions (SO_x) during combustion process. Thusly, pyrolysis can be considered as the major alternative for production of useful chemicals and fuels.

The gas composition obtained from pyrolysis of the scrap tyre is consisted of major amount of hydrocarbons (mainly methane, ethane, butadiene, and acetylene) and minor amounts of CO and CO_2 (Siva et al., 2013). And its higher heating value is around 37 MJ/m^3 (Kandasamy and Gokalp., 2015). The liquid product, oil, obtained from pyrolysis of scrap tyre is consist of a mixture of aliphatic and aromatic hydrocarbons (Mastral et al., 2000; Ucar et al., 2005a; Onenc et al., 2012; Siva et al., 2013; Martinez et al., 2013b). And its higher heating value is around 44 MJ/kg (Siva et al., 2013). The oil was examined as an alternative energy source for diesel engine in several studies (Dogan et al., 2012; Koc and Abdullah, 2014). The mixtures of oil obtained from pyrolysis of scrap tyre and commercial diesel in different ratios (from 10% to 90 %) were examined by using diesel engine by Dogan et al. (2012). They were reported that the addition of oil obtained from scrap tyre in blends led to decreased CO emissions while increased the NO_x emissions (depending on engine speed). They were also reported that the oil had no effect on engine power whether reducing or enhancing. Differently from this study, Hita et al. (2015) studied to improve the fuel properties of the oil by hydrocracking and hydrotreating processes and using the $\text{PtPd/SiO}_2\text{--Al}_2\text{O}_3$ catalyst.

Differently from volatile products obtained from pyrolysis, the char can be utilized as carbon black (Pantea et al., 2003) or activated carbon (Hoseinzadeh et al., 2012; Danmaliki and Saleh, 2016; 2107). Activation of char obtained from pyrolysis of scrap tyre can be carried out in two different activation process which are physical activation (Ucar et al., 2005b; Hadi et al., 2016) and chemical activation (Antoniou and Zabaniotou 2015; Aftab et al., 2016). And then the usability of the activated char as activated carbon can be estimated by its porous structure and textural properties.

Co-pyrolysis process is pyrolysis of two or more different kinds of feed stocks together. This process is carried out for the purpose of finding out the presence of any synergic effect between feed stocks. The synergic effect is desired due to leads to reduction of activation energy for degradation or increasing of product yields. In literature, number of studies related to co-pyrolysis of scrap tyre with oil wastes (Ucar et al., 2007; Siva et al., 2013; Janusas and Miknius, 2015) or biomass (Uzun and Yaman, 2014) or coal (Kriz and Brozova, 2007; Bicakova and Straka, 2016) were present. The increasing of oil yields by the addition of scrap tyre in blends were noted in related studies.

1.2. Combustion

Combustion of the wastes is one of the promising process for energy recovery. Furthermore this process provide to disposal of wastes. In literature, numerous studies about combustion of scrap tyres (Atal and Levendis, 1995; Larsen et al., 2006), plastic wastes (Cooke et al., 2003), agricultural (Christensen and Livbjerg, 1996; Miranda et al., 2011; Sommersacher, 2012; Forbes et al., 2014) and animal wastes (Abelha et al., 2003; Billen et al., 2014b; 2014c; 2015) were published.

The main concern about the combustion of wastes is harmful gases emissions (SO_x , NO_x and etc.) releasing during the process. Particularly, release of SO_x emissions during combustion of scrap tyres is high amount because of its S content which is related from vulcanization process (Mut et al., 2015). In contrast to this, amount of SO_x and NO_x emissions released from the combustion of

biomasses such as agricultural and animal wastes are low. Therefore, biomasses can be used for reduction of harmful emissions via co-combustion with wastes which can cause release of these emissions (Abelha et al., 2003). Moreover, reduction of harmful emissions by co-combustion of biomass and coal was reported (Sahu et al., 2010).

On the other side, ash composition of wastes can caused various problems such as agglomeration, low ash melting point, sintering, fouling and etc. during the combustion process (Sommersacher et al., 2012; 2013). Ash composition can be balanced with combustion of proper wastes together and ash related problems can be obviated (Lynch et al., 2013a; 2013b). Consequently, co-combustion can be a promising process for both kind of problems ash related and harmful emissions.

In addition to environmental benefits of co-combustion of coal and such wastes, this process provides economic benefits by the utilization of these wastes as alternative fuels.



2. PYROLYSIS OF SCRAP TYRES AND OILY WASTES

In the pyrolysis section of this thesis, four different types of wastes were used as feedstock for the tests. Scrap car tyres (CT) and scrap truck tyres (TT) were used as petroleum derived wastes while bilge water (BW) and oily sludge (OS) were used as oily wastes from ships.

To investigate the effect of temperature on pyrolysis products, the scrap tyres were pyrolyzed at three different temperatures (400°C, 500°C and 700°C). In the co-pyrolysis experiments, scrap car tyre, truck car tyre, bilge water oil and oily sludge were pyrolyzed together in different ratio. The blends were prepared in proportion of 9:1, 8:2, 7:3, 6:4, 1:1 of CT/BW, CT/OS, TT/OS.

For each experiment, solid residue (char), oil (pyrolytic oil) and aqueous phase fraction yields were determined by weight and the gas fraction yield was calculated by difference. The gas composition was analysed by GC-TCD and GC-FID. Hydrocarbon composition of pyrolytic oils was investigated by H^1 -NMR. The fuel characteristics of oil and wastes were determined using standard analysis methods, such as simulated distillation curve, viscosity, specific gravity, flash point, ash, water, volatile matter and elemental analysis. The elemental composition and heating value of solid products were determined using standard methods.

2.1. General Information

Economic and environmental reasons steer us to find solutions about the utilization of hazardous wastes such as scrap tires, bilge water and oily sludge while environmental regulatory authorities are increasingly concerned about the possible adverse effects of these kinds of wastes. Thermal decomposition of these kinds of wastes appears as beneficial process for recovery. As one of the thermal decomposition process, pyrolysis of scrap tires and oily wastes are still ongoing studies.

Lifetime of tyre in a landfill is estimated between 80 and 100 years. As a thermoset polymer, tyre has irreversible bonds after vulcanization on the purpose of become an enduring material. Thermoset polymers cannot be melted or separated into chemical components which were formed them. Usage of scrap tyre take a place in many energy applications power plants, tyre manufacturing facilities, cement kilns, and pulp and paper production among others. Pyrolysis also titled thermal distillation or thermolysis is a thermochemical treatment that allows breaking apart chemical bonds via the thermal composition under non-oxidative conditions. This thermochemical treatment can be used for feedstock recycling transforming solid wastes into high calorific fuels, chemicals, monomers or other valuable materials (Martinez et al., 2013a).

Understanding of rubber structure can be an informative study for prediction of product compositions from thermal degradation of rubber based materials. Typical, polymer structures consist of carbon atoms linked by different kinds of bonds. Identification of basic characteristic of rubber by carbon-carbon double bonds was reported. Thermal decomposition process leads to formation of monomers of the original rubber molecule besides free radicals which are highly reactive (Dodds et al., 1983). During natural rubber pyrolysis process, which is one of the thermal decomposition processes, Diels-Alder mechanism is an alternative suggestion for dimer formation as a result of monomer recombination (Groves and Lehrle, 1991). Dimerization leads formation of limonene which is detected as abundant product (approx. 12%). Besides Diels-Alder mechanism, formation of limonene via cyclisation is also reported (Mastral et al., 2000). According to Pakdel et al. (2001), thermal decomposition of polyisoprene in the scrap tyre formed as isoprene radicals via beta-scission mechanism and these isoprene radicals are transformed to isoprene molecules in the gas phase and then dimerization of isoprene molecules are occurred in the gas phase. They also mentioned that dimerization rate can be changed by pyrolysis conditions such as temperature, pressure and time. The pyrolysis of scrap tyres was studied in a pilot-scale rotary kiln by Li et al (2004). They reported that primary pyrolysis reactions were formed between 250 °C and 520 °C and then primary volatiles gave the secondary post-cracking reaction between 600 °C and 800 °C. The liquid product was a mixture of aliphatic and aromatic hydrocarbons and solid product was rich

in carbon. Similarly, the liquid product obtained by previous studies (Mastral et al., 2000; Rodriguez et al., 2001; Laresgoiti et al., 2004; Ucar et al., 2005a; Onenc et al., 2012; Siva et al., 2013; Martinez et al., 2013a) consisted of aliphatic and aromatic hydrocarbons.

Besides scrap tyre pyrolysis, there are several studies revealed the potential of pyrolysis as a recovery method for waste oils. Ahmad et al. (2016) investigated catalytic conversion of spent lubricating oil (SLO) in purpose of produce diesel-like fuels by pyrolysis process in presence of barium ferrite catalyst. They obtained the liquid product having similar properties with diesel fuel. Wang et al. (2007) studied the thermal degradation behaviour of oil sludge by TG/MS. They reported that pyrolysis reaction of oil sludge started at about 200 °C and the maximum evolution rate was observed between the temperatures of 350-500 °C. The using of catalyst/additives (FCC catalyst, NaOH and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and high pyrolysis temperature (≥ 500 °C) promoted the pyrolysis conversion (less solid residue production), while did not improve oil product. In another study related to catalytic pyrolysis of waste machinery oil, the catalysts (HZSM-5 and Ni/SiO_2) led to an increase in gas yield and formation of oil having fewer amounts of aromatics (Sinag et al., 2010). Microwave pyrolysis was also used to treat and recycle the waste automotive engine oil (Lam et al., 2010b). The significant amounts of valuable products, such as gaseous hydrocarbons with light olefins, and liquid hydrocarbon oils containing BTX (the mixture of benzene, toluene, xylene etc.) and benzene derivatives, were obtained by microwave-induced pyrolysis of automotive oils.

Co-pyrolysis of wastes is another approach for waste valorisation (Ucar et al., 2007) explored the co-pyrolysis of scrap tyre with waste lubricant oil (WLO). The addition of WLO in the pyrolysis of scrap tires was aimed at obtaining extra oil. The results showed that co-pyrolysis with WLO produced more oil than pyrolysis of tyres alone. Jonusas and Miknius (2015) investigated the effect of the mixture composition on the yield and properties of products obtained from co-pyrolysis of scrap tyre with used engine oil. The results showed that the engine oil as an additive in the co-pyrolysis of tyre had a positive effect on the yield of the liquid product, which increased from 39.4 to 60.2% (w/w). The majority of metal

deposition was observed in the solid product and increased amount of used engine oil in the blend, co-pyrolysis gave a lower amount of metals in the liquid phase. In co-pyrolysis of scrap tyres with lignite (Onay and Koca, 2015), co-pyrolysis favoured of pyrolysis oil product in terms of both quality and quantity. The maximum of synergetic effect from the point of the oil yield was observed for the blend containing 10% of lignite, the oil yield increased by 11.8%. It was postulated that this synergism was driven mainly to formation of aromatic compounds and asphaltenes. The blends with a low rank coal and a bituminous waste were also co-pyrolyzed to modify the composition of the oil from the pyrolysis of the scrap tyre (Acevedo and Barriocanal, 2014). The results showed that the amount of aliphatic in oil was increased by adding a coal and the amount of aromatics in oil increased by co-pyrolysis with a bituminous waste.

In our previous studies, we investigated the catalytic co-pyrolysis of scrap tyres with oily wastes in a glass reactor (Onenc et al., 2012) and in a fixed bed reactor (Siva et al., 2013). The use of catalysts led to production of light products in pyrolysis oils. The results obtained showed that co-pyrolysis of oily wastes with scrap tires could be an environmentally friendly way for the transformation of hazardous wastes into valuable products such as chemicals or fuels.

2.2. Material Methods

2.2.1. Material

Scrap car tyre (CT) and scrap truck tyre (TT) as petroleum derived wastes, oily sludge (OS) and bilge water (BW) as oily wastes were supplied from Gerence Yapı Malzemeleri Madencilik ve Taşımacılık San. Tic. Ltd. Şti..

The collected scrap tyres were categorised according to the kind of vehicle which they did belong to then they were separated from the steel parts and grinded approximately the size of 2-3mm. Scrap tyres were prepared for pyrolysis process by the way that was explained above.

Bilge water are located at the vessel's gravitational low point and contains everything from engine oil, fuel, wash water (containing soap, oil and other organic material), lake, ocean, sea or river water. Oil sludge is in the form of mud-like residue inside the bottom of a fuel tank or fuel residue that accumulates on the fuel filter before it reaches the main engine. Oil sludge also contains the residual waste oil products such as those resulting from the purification lubricating oil from main or auxiliary machinery or separated waste oil from bilge water separators or oil collected in drip trays, and waste hydraulic and lubricating oils. The some properties of wastes are given in Table 2.1.

Table 2.1. Properties of wastes.

	Car Tire	Truck Tire	Oily Sludge	Bilge Water Oil
<i>Proximate analysis (as received, wt%)</i>				
Moisture	-	-	17.8	10.2
Volatile matter	62.3	63.9	79.7	89.5
Fixed carbon	29.0	28.8	2.0	3.5
Ash	8.7	7.3	0.5	1.0
<i>Ultimate Analysis (dry, %wt)</i>				
C	77.1	77.7	69.8	79.4
H	6.6	7.1	10.3	12.0
N	0.4	0.4	0.3	-
O*	14.3	13.2	18.5	7.7
S	1.6	1.6	1.1	0.9
Viscosity (SUS), at 100°C	-	-	1900	9.8
HHV**, MJ/kg	36.9	38.0	39.8	29.2

* calculated from difference.

** High heating value.

2.2.2. Methods

2.2.2.1. Pyrolysis and co-pyrolysis process

Pyrolysis reactor was of a fixed bed design and of stainless steel 6cm diameter 21cm high and could contain up to 100 g of samples. In a typical run, the samples of 100 g were placed into the reactor. The system was heated at a rate of 7 °C min⁻¹ to the desired temperature, and held at that temperature for 1 hour. The volatile products were swept by nitrogen gas or pyrolysis atmosphere from reactor to collection flasks. Following the condensation distillate in first trap at room

temperature, no condensable gases were passed through the lead nitrate solution (10 wt%) containing traps. Experimental set up is shown in Figure 2.1.

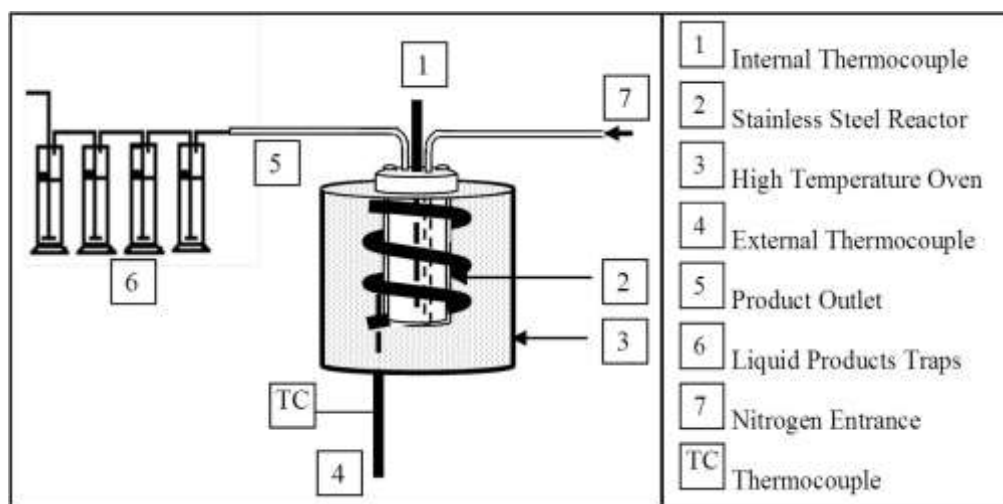


Figure 2.1. The scheme of pyrolysis process.

For each experiment, the char (pyrolysis carbon residue), pyrolytic oil (pyrolysis oil) and aqueous fraction were determined by weight and the pyrolytic gas (pyrolysis gas) yield was calculated from difference.

2.2.2.2. Analysis of wastes

The main characteristics (elemental analysis, proximate analysis and calorimetric value) of wastes were determined according to standard analysis method (ASTM D5291-96, ASTM D3174-04, ASTM D3175-89 and ASTM D240-02). The thermal degradation behaviour were investigated by thermogravimetric analyser (TGA).

Thermogravimetric analysis was performed by on a Perkin Elmer Diamond TG/DTA thermogravimetric analyzer under N_2 atmosphere. The flow rate of purge gas was kept at 200 mL/min. The sample was heated from the ambient temperature up to 800 °C with a heating rate of 10 °C/min.

2.2.2.3. Analysis of liquid products

The fuel properties of pyrolytic oils were determined by using the following standard methods: The specific gravity (ASTM D4052-96), the kinematic viscosity (ASTM D445), the flash point (ASTM D93), the gross calorific value (ASTM D240-02) and the water content (ASTM D6304-04).

The pyrolytic oils were analyzed by gas chromatography with a flame ionization detector (GC-FID) using a Hewlett-Packard 6890 series GC. HP-5 capillary column (30 m length 0.32 mm diameter coated with cross-linked 5% phenylmethylsiloxane at a thickness of 0.25 mm) was used in the GC system. The GC oven was programmed from 40 to 280 °C at 5 °C min⁻¹ with a final holding time of 30 min. The data obtained from GC-FID analysis were used to draw the simulated distillation curves of pyrolysis and co-pyrolysis oils according to ASTM D2887.

¹H nuclear magnetic resonance (¹HNMR) spectra of pyrolytic oils were recorded with a Varian AS 400 Mercury instrument using CDCl₃ as solvent; the obtained data were used to determine the hydrocarbon types of the oils (Myers et al., 1975).

2.2.2.4. Analysis of gas products

Gaseous products were analyzed by refinery gas analyzer (Agilent 7890A). The system has five valves and three detectors (FID, TCD1 and TCD2). The pyrolysis gas composed of C1 (methane), C2 (ethane, ethylene), C3 (propane), C4 (n-butane and derivatives), CO₂, CO and H₂ was determined by GC analyzer.

2.3. Result and Discussions

2.3.1. Thermal degradation behaviours of wastes

Thermal degradation of scrap car tyres (CT) and scrap truck tyre (TT) under nitrogen atmosphere occurred in a wide temperature range (200 °C– 500 °C) due

to the complex composition of wastes (Figure 2.2). Scrap tyres also contain plasticizers and other additives, besides natural rubber (NR), butadiene rubber (BR) and styrene butadiene rubber (SBR). The decomposition of additives starts at 200 °C; the main composition starts around 290 °C, which is related to degradation of rubbers. The maximum degradation rates were observed around 380 °C for both scrap tyres.

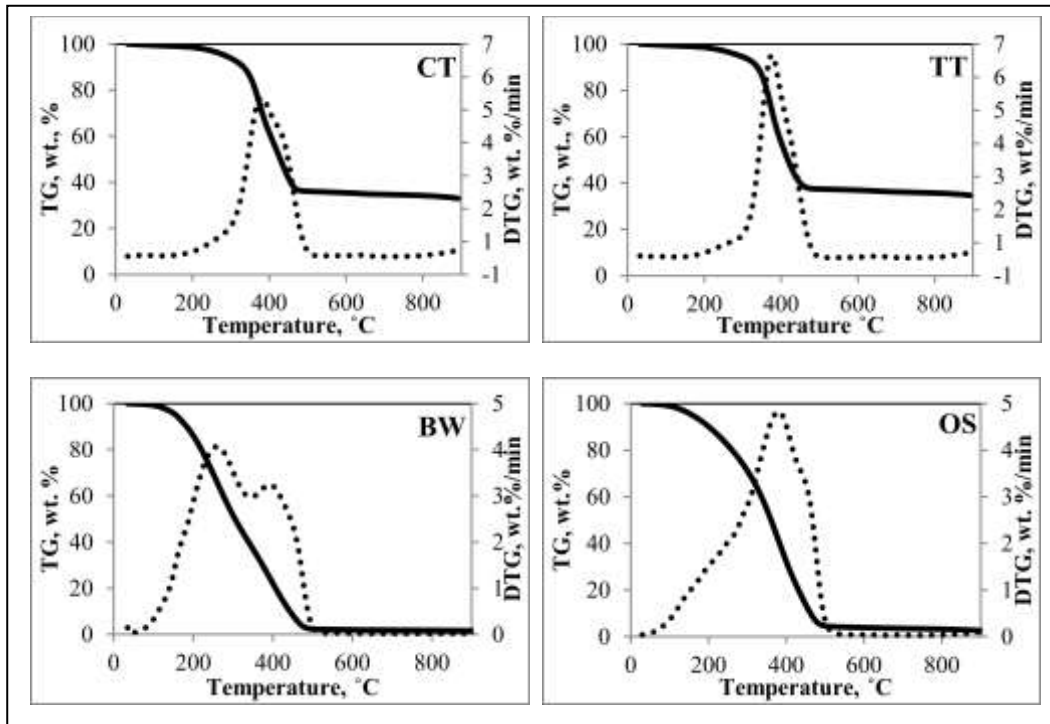


Figure 2.2. TG and DTG curves for CT, TT, BW, OS.

On the other hand, the decomposition of oily waste started as soon as heating starts, due to the loss of water. The bilge water (BW) degraded in two main degradation steps with maximum degradation rates at 235 °C and 370 °C, respectively. However, the OS was decomposed in one stage with maximum degradation rate at 360 °C.

2.3.2. Effect of pyrolysis atmosphere

In pyrolysis experiments, at first we investigated the effect of pyrolysis atmosphere on product yield and the properties of pyrolytic oil and char. For this purpose, pyrolysis of CT were carried out at the temperature of 500 °C for 1 h

under different atmosphere, namely N_2 and self-generated. In former case, N_2 gas was passed through the system during pyrolysis. In case of self-generated atmosphere, N_2 gas was passed through the system till when the temperature of the inside of reactor reached 100 °C. And then N_2 gas was closed and pyrolysis took place under self-generated atmosphere. Product yields from both two pyrolysis processes are given in Table 2.2. Product yields has found similar with the results obtained by other researchers (Ucar et al., 2005a; Williams and Brindle, 2003; Boxiong et al., 2007).

As seen from Table 2.2, there was no difference between self-generated and N_2 atmosphere pyrolysis with regards to pyrolysis yields. Similarly, elemental composition and hydrocarbon types of pyrolytic oils (Figure 2.3) did not changed depending on the pyrolysis atmosphere (Table 2.3).

Table 2.2. Product distributions from pyrolysis of CT under self-generated and nitrogen atmosphere, wt. %.

	Char	Pyrolytic oil	Aqueous phase	Pyrolytic gas
Self- generated atmosphere	39.4	48.7	2.5	9.4
Nitrogen atmosphere	39.7	49.5	2.0	8.8

Table 2.3. Ultimate analysis and calorific value of pyrolytic oils obtained from CT pyrolysis under self-generated and nitrogen atmosphere.

	Ultimate analysis, wt. %					HHV, MJ/kg
	C	H	N	S	O*	
Self generated atmosphere	81.1	9.7	0.5	0.7	8.0	43.6
N_2 atmosphere	79.4	9.4	0.5	0.9	9.9	43.6

*calculated by differences

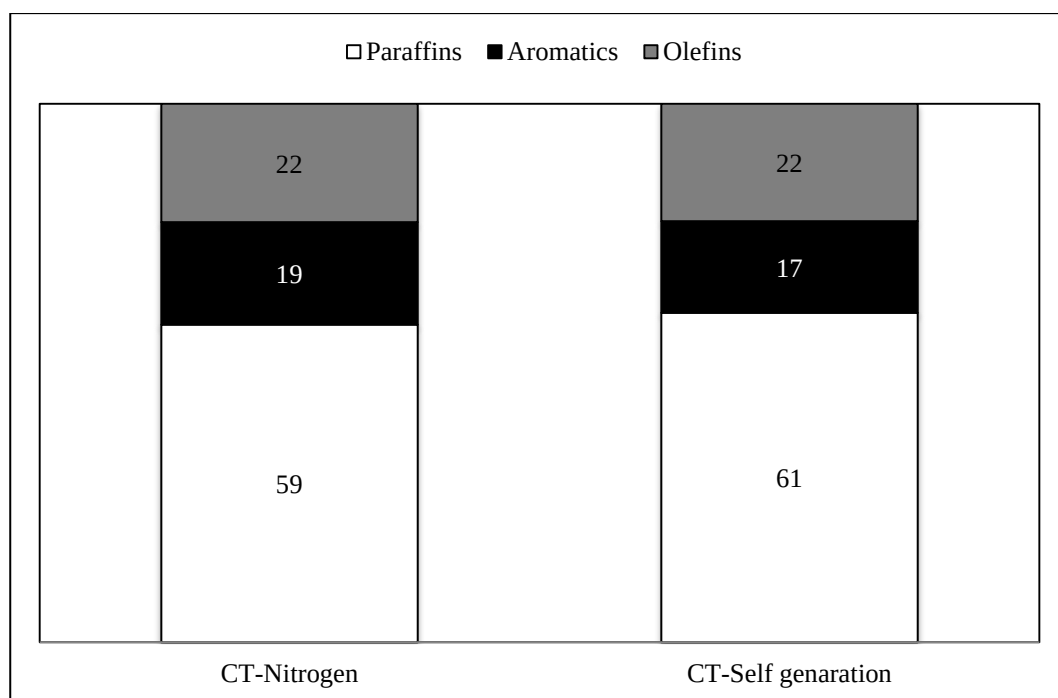


Figure 2.3. The amount of hydrocarbon types in pyrolytic oils obtained from CT pyrolysis under self-generated and nitrogen atmosphere (vol., %).

However, pyrolysis atmosphere effect the elemental composition of char (Table 2.4). Char from self-generated pyrolysis process had lower C amount and calorific value than char from pyrolysis of CT under N_2 atmosphere. The reason might be that repolymerization of primary degradation products under self-generated or nitrogen swept prevents the removing of oxygenated degradation products from pyrolysis reactor. The ash amounts of chars were found be around 18 wt. %.

Table 2.4. Ultimate analysis and calorific values of chars obtained from CT pyrolysis under self-generated and nitrogen atmosphere.

	Ultimate analysis, wt %				HHV, MJ/kg
	C	H	N	S	
Self-generated atmosphere	59.9	0.6	0.2	2.5	28.4
N_2 atmosphere	70.0	1.3	0.1	2.1	28.0

From the point of industrial application, self-generated pyrolysis were chosen as pyrolysis process in further experiments.

2.3.3. Pyrolysis of scrap tyres

The effect of temperature on the yields and properties of products from scrap tyre pyrolysis was investigated at three different temperatures (400 °C, 500 °C and 700 °C). These temperature range were chosen as based on TGA results. As seen from the table 2.5, the yields of pyrolytic oils were increased and char yields were decreased by increasing the pyrolysis temperature from 400 °C to 500 °C for both wastes. Further increase in temperature (from 500 °C to 700 °C) had no effect on product yields. This result is similar with the previous publications (Laresgoiti et al., 2000; 2004).

Table 2.5. Product distributions from pyrolysis of scrap tyres at different temperatures, wt., %.

	Temperature, °C	Char	Pyrolytic oil	Aqueous phase	Pyrolytic gas
CT	400	52.7	30.9	3.4	13.0
	500	38.0	49.0	1.2	11.8
	700	39.2	47.1	1.6	12.1
TT	400	51.5	29.7	5.1	13.7
	500	40.9	45.8	2.7	10.6
	700	37.3	47.4	1.1	14.2

The hydrocarbon types in pyrolytic oils were given in Figure 2.4. Oil samples were named as following the “scrap tyre – pyrolysis” sequence (e.g. CT - 500 stands for pyrolysis of CT at 500 °C). The temperature had no considerable effect on pyrolytic oil composition. Although hydrocarbon types in pyrolytic oil from pyrolysis of TT at 500 °C was different from that of CT at 500 °C, pyrolytic oils obtained at 700 °C from TT and CT were similar (Figure 2.4). It is interesting that the temperature differently affected the pyrolytic oil composition for each tyre. Thus, in case of TT, the increase in temperature led to increase paraffin content while decrease olefin content. In contrast, in case of CT, the increase in temperature led to decrease paraffin content while increasing olefin content (Figure 2.4). It is worthy that pyrolytic oils had high olefin content. According to Myer’s formula, d- limonene, which is one of the degradation compounds of isoprene, was considered as olefin. It was reported that 86.5 % of olefin contents in pyrolytic oil of tyres come from d- limonene (Onenc et al., 2012).

Simulated distillation analysis provided information about the boiling point distribution of hydrocarbons in pyrolytic oil. The pyrolysis temperature above 400 °C has no effect on boiling point distribution of hydrocarbons in pyrolytic oils. As seen from Figure 2.5, pyrolytic oils were lighter than commercial diesel but heavier than commercial gasoline.

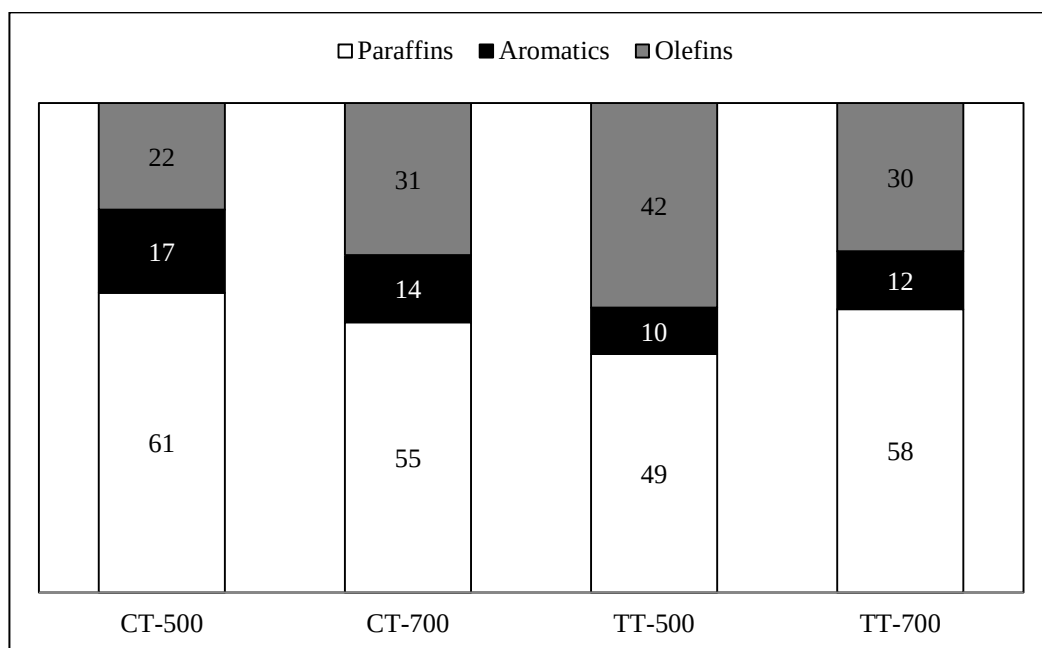


Figure 2.4. The amount of hydrocarbon types in pyrolytic oils obtained from CT and TT pyrolysis at 500 °C and 700 °C (vol., %).

According to boiling point temperature, fractions of pyrolytic oils were described as light nafta for < 93 °C, heavy naphta for 93-204 °C, light gas oil for 204-343 °C and heavy gas oil for > 343 °C. Fraction of pyrolysis oils from CT and TT pyrolysis are presented in Figure 2.6. For comparison purpose, fraction of commercial diesel and commercial gasoline were also presented in the same figure. The main fraction in all pyrolytic oils was heavy naphta. Its content in TT-oils was increased by increasing temperature from 400 °C to 500 °C, whereas its content in CT-oils was not changed. The light gas oil fraction in all pyrolytic oils was decreased by increasing temperature from 400 °C to 500 °C.

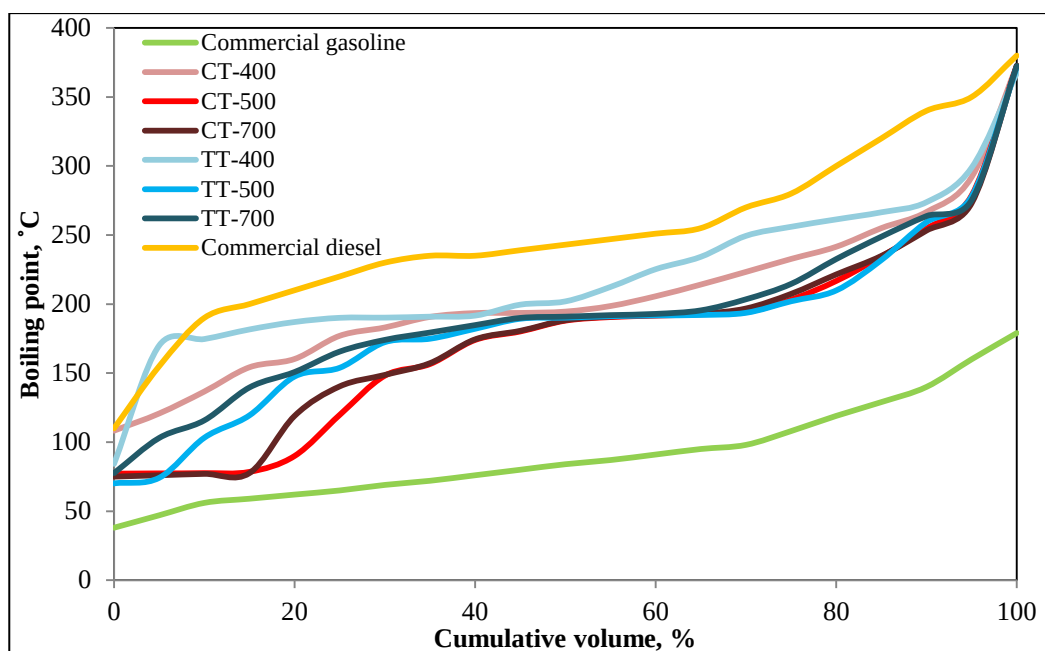


Figure 2.5. Simulated distillation curve of pyrolytic oils obtained from pyrolysis of CT and TT at 400 °C, 500 °C and 700 °C.

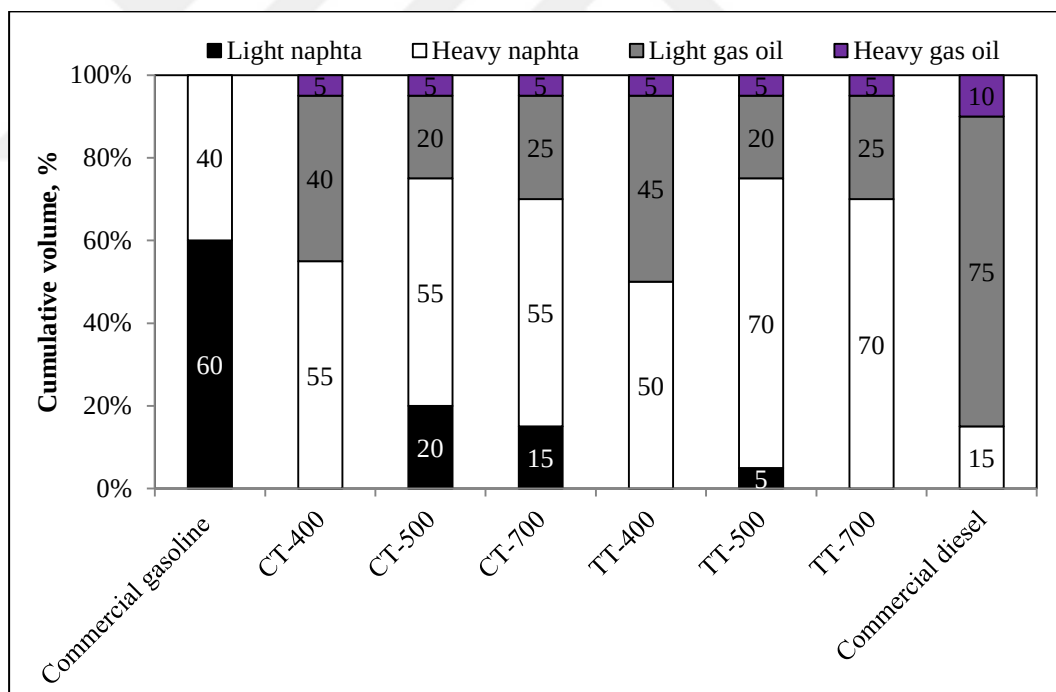


Figure 2.6. Fractions of pyrolytic oils obtained from CT and TT pyrolysis at 400 °C, 500 °C and 700 °C.

Above results showed that the pyrolytic oils obtained both 500 °C and 700 °C has similar composition. And also product yields from two temperatures were

same. From the point of process economy, the temperature of 500 °C was optimized as pyrolysis temperature. The main fuel characteristics of oils and chars obtained from pyrolysis of tyres at 500 °C were determined according to standards methods and given in Table 2.6 and 2.7. There was no difference in elemental composition and heating value of pyrolytic oils. It should be noted that although the oils have high heating value (as petroleum fuels), their sulphur content were high.

Table 2.6. Ultimate analysis and calorific values of pyrolytic oils obtained from pyrolysis of CT and TT at 500 °C.

	Ultimate Analysis, wt. %					HHV, MJ/kg
	C	H	N	S	O	
CT	81.1	9.7	0.5	0.7	8.0	43.6
TT	77.5	9.3	0.5	0.7	12.0	43.2

In contrast to pyrolytic oils, carbon content of the chars was different (Table 2.7). TT char had higher carbon content than CT char, showing more aromatic structure in char. The thermal degradation of SBR (which was present in TT) yielded a char having more condensed aromatic structure. The content of sulphur in char from CT is 61.5 % of total sulphur in scrap tyre. However, the content of sulphur in char from TT is 74.1 % of total sulphur in scrap tyre. The reason might be that the difference in the ash components between TT and CT. As known from literature some inorganic in tyre bind the sulphur formed during pyrolysis (Ogasawara et al., 1987; Darmstadt et al., 1995; Mastral et al., 1999; Leung et al., 2002).

Table 2.7. Ultimate analysis and calorific values of chars obtained from pyrolysis of CT and TT at 500 °C.

	Ultimate analysis, wt. %				HHV, MJ/kg
	C	H	N	S	
CT	59.9	0.6	0.2	2.5	28.4
TT	69.3	0.7	0.2	2.9	28.6

Pyro-gas from pyrolysis of CT and TT have similar composition, there was almost no differences between them (Table 2.8). The gaseous products are mainly composed of C1, C2, C3, C4 and H₂. As expected, the C4 amount was highest due to the butadiene contents in rubbers.

Table 2.8. Composition of gas products obtained from pyrolysis of CT and TT at 500 °C.

	C1	C2	C3	C4	CO ₂	CO	H ₂	HHV, MJ/Nm ⁻³
CT	15.1	9.6	4.6	47.9	7.2	3.1	12.6	49.8
TT	15.9	9.1	4.8	46.1	5.2	2.6	16.3	48.5

2.3.4. Pyrolysis of Oily Wastes

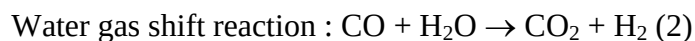
The oily wastes from ships (BW and OS) were pyrolyzed at 500 °C and under self generation atmosphere, which are optimized conditions in previous sections (2.3.2, 2.3.3). Products yields are shown in Table 2.9. The pyrolytic oil yields from pyrolysis of oily wastes were found higher than that of other researches based on pyrolysis of oil sludge (Wang, 2007) and waste machine oils (Moliner et al., 1997; Lam et al., 2010a; b, Sinag et al., 2010).

Table 2.9. Product distributions from pyrolysis of oily wastes, wt. %.

Waste material	Char	Pyrolytic oil	Aqueous phase	Pyrolytic gas
Oily sludge (OS)	2.4	70.4	6.7	20.5
Bilge water oil (BW)	1.3	89.7	0.7	8.3

*contained ~ 90% water.

Pyrolysis of BW produced more oil and less gas than that of OS. It was noted that the aqueous phase yield was less than predicted one, by considering water amounts in oily wastes (Table 2.1). The reason might be that the water in oily wastes was consumed by following reactions during pyrolysis.



The composition of pyrolytic oils was characterized in terms of hydrocarbon types and boiling point distribution of hydrocarbons. Hydrocarbon types of OS and BW pyrolytic oils were given in Figure 2.7. Oil samples were named as following the “waste type – oil” (e.g. OS - oil stands for pyrolytic oil obtained from OS pyrolysis). In contrast to pyrolytic oils from scrap tyres, pyrolytic oils from OS and BW consisted of mainly paraffinic hydrocarbons. Regarding to results from boiling point distribution (Figure 2.8), pyrolytic oils from OS and BW pyrolysis had heavier fraction than commercial gasoline. OS-oil had lighter fraction than commercial diesel while BW-oil had similar boiling point distribution with commercial diesel. Both OS-oil and BW-oil had mainly light gas oil (Figure 2.9).

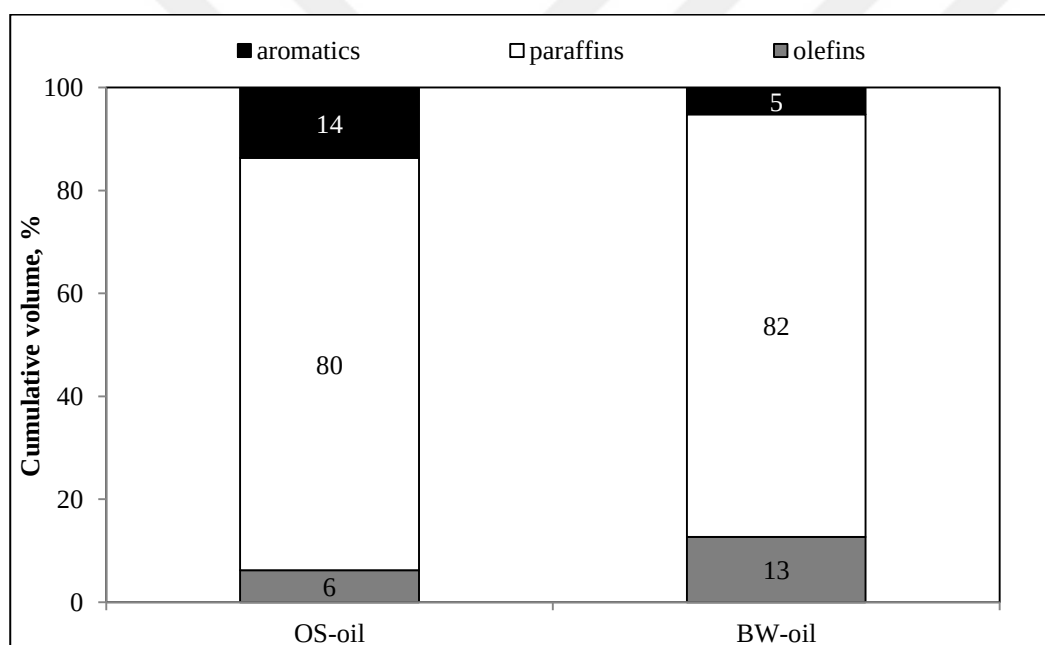


Figure 2.7. The amount of hydrocarbon types in OS-oil and BW-oil (vol., %).

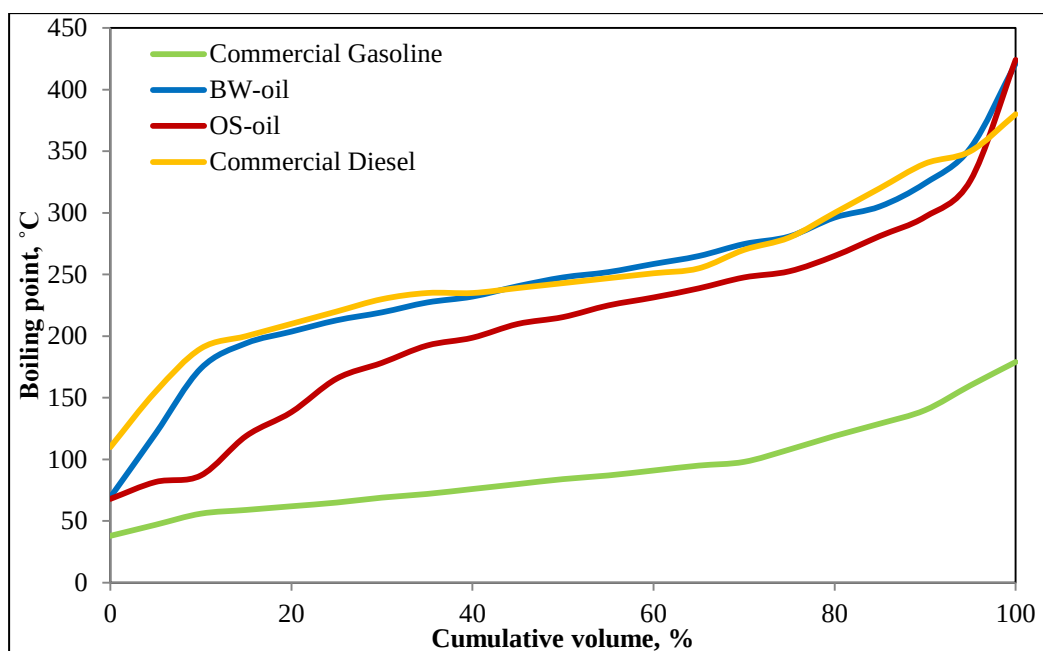


Figure 2.8. Simulated distillation curves of OS-oil and BW-oil.

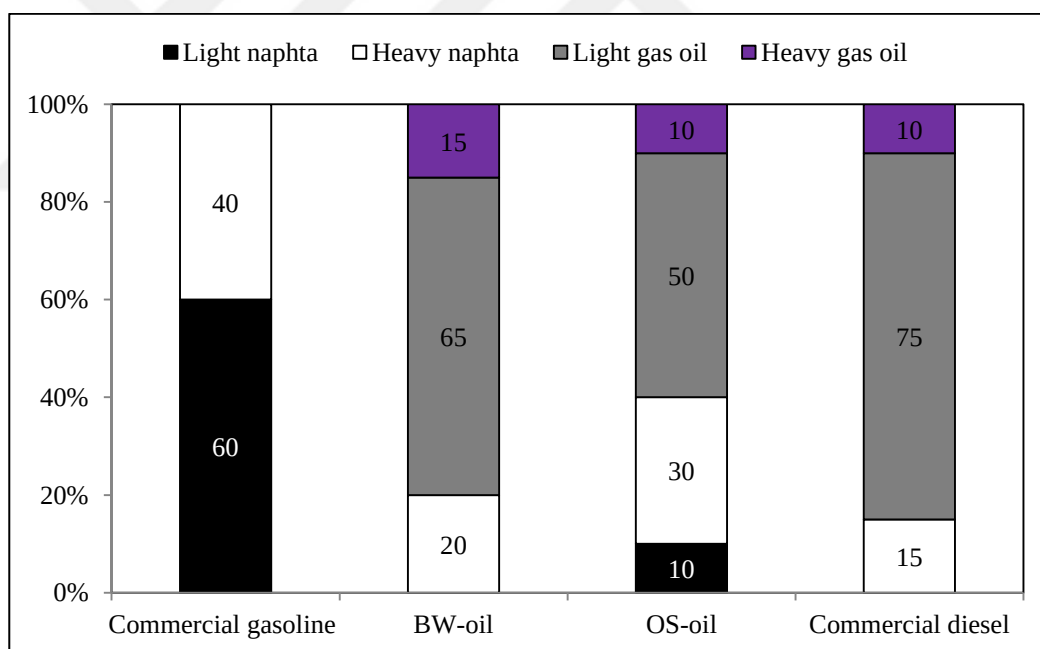


Figure 2.9. Fractions of pyrolytic oils obtained from BW and OS pyrolysis.

Some fuel characteristics of pyrolytic oils obtained from oily wastes are presented in Table 2.10. Compare to pyrolytic oils obtained from scrap tyres, pyrolytic oils from oily wastes had lower amount of O and S. Absence of N in pyrolytic oils of oily wastes was other different property from pyrolytic oils of scrap tyres.

Table 2.10. Ultimate analysis and calorific value of pyrolytic oils obtained from oily wastes pyrolysis.

	Ultimate analysis, wt. %					HHV, MJ/kg
	C	H	N	S	O	
OS-oil	81.5	12.9	-	0.2	5.4	45.4
BW-oil	83.2	13.1	-	0.2	3.5	45.5

Since oily wastes are generated from engine room, the metals are one of the important pollutants in oily wastes. Because of this, we determined the metal contents of both wastes and pyrolytic oils. The results are presented in Table 2.11. Pyrolytic oils had lower metal content than that waste oils, these results suggested that metals were held in chars during pyrolysis. Metal content in the oily wastes could be vaporized during pyrolysis process then they might condense in the pyrolytic oil or stay in the gas product as chloride compounds and metallic form. On the other hand, depending on metal type such as Cu, Ni, Pb, Zn, and Fe (P 65%), they could be retained in the char (Lam et al., 2010a).

Table 2.11. Metal contents in OS, BW and their pyrolytic oils.

Heavy metal, ppm	OS	Pyrolytic oil of OS	BW	Pyrolytic oil of BW
Ag	<3	<3	<3	<3
Al	6	<3	44	<3
B	<3	<3	<3	<3
Ba	<3	<3	<3	<3
Ca	388	<3	1800	<3
Cd	<3	<3	<3	<3
Cr	<3	<3	<3	<3
Cu	<3	<3	<3	<3
Fe	62	<3	170	<3
Mg	<3	<3	29	<3
Mn	<3	<3	<3	<3
Mo	<3	<3	<3	<3
Na	15	<3	33	<3
Ni	<3	<3	12	<3
P	102	<3	215	<3
Pb	<3	<3	<3	<3
Sn	12	<3	39	<3
Ti	<3	<3	<3	<3
V	35	<3	66	<3
Zn	<3	<3	55	<3

The gas product from pyrolysis of oily wastes consisted of mainly hydrocarbon gases (Table 2.12). OS derived gaseous products contained more amounts of C1 than that of BW, while BW derived gaseous products contained more amounts of C4. Moreover, pyrolysis gases had high calorific values because of low content of CO_x. We claimed that the energy requirements of the pyrolysis process can be provided by gas products.

Table 2.12. Composition of gas products obtained from pyrolysis of oily wastes.

	C1	C2	C3	C4	CO ₂	CO	H ₂	HHV*, MJ/Nm ³
OS	37.2	21.5	7.7	21.2	2.0	0.6	9.9	40.4
BW	18.3	21.6	8.2	36.5	2.8	0.7	12.0	48.4

Fuel characteristics of chars were not determined because of their very low yield (2.4% and 1.3% for OS and BW in respectively).

2.3.5. Co-pyrolysis of waste materials

Co-pyrolysis experiments were carried out with a blend containing scrap tyre and oily wastes at 500 °C and under self-generation atmosphere, which are optimized conditions in previous sections (2.3.2, 2.3.3). The five blends of scrap tyre/oily wastes (9:1, 8:2, 7:3, 6:4, 1:1) were used.

Products yields from co-pyrolysis of CT/OS blends are shown in Table 2.13. Predicted values were also given in the same table to understand the synergic effects in co-pyrolysis process. Predicted values were donated as t-char, t-oil, t-gas, etc.

In co-pyrolysis experiments (except the blend 1:1), we obtained aqueous phase in emulsion form. It may be hypothesized that the surfactants in oily waste led to formation of oil-water emulsion. Because of this, experimental oil yields were lower than predicted one and experimental aqueous phase yields were more than predicted one. Jonusas and Miknius (2015) studied on thermolysis of scrap tyre and used engine oil blends and they noted that the oil yield was increased to

60 % by increasing ratio of used engine oil in blends. For the blend 1:1, we observed no formation of emulsion and experimental pyrolytic oil yields were higher than predicted one and experimental aqueous phase yields were less. On the other hand, experimental gas yields were slightly lower than predicted one.

Table 2.13. Product distributions from co-pyrolysis of CT/OS blends, wt. %.

	char	t-char	oil	t-oil	aqueous	t- aqueous	gas	t-gas
CT/OS (9:1)	37.4	35.9	45.4	50.2	9.4	3.7	7.8	10.2
CT/OS (8:2)	32.8	32.3	47.7	51.6	10.6	5.0	8.9	11.1
CT/OS (7:3)	31.6	28.8	43.4	53.0	15.6	6.2	9.3	12.0
CT/OS (6:4)	27.3	25.3	40.7	54.5	22.2	7.4	9.9	12.8
CT/OS (1:1)	24.2	21.8	66.2	55.9	0.6	8.6	9.1	13.7

Although we observed synergetic effect in product yields, no synergetic effect was observed in oil composition for the some blends (9:1, 8:2, 1:1). For the blends of 7:3 and 6:4, co-pyrolysis produced oil containing more olefins than predicted one. As expected, the paraffinic hydrocarbon amount of oils increased by increasing amount of oily wastes in blend (Figure 2.10). Overall, the amounts of olefin content in co-pyrolysis oils was less than that of scrap tyre derived oils and amount of paraffinic hydrocarbon was more. This shows that the co-pyrolysis of scrap tyres with the oily wastes had a positive synergetic effect on quality of oil.

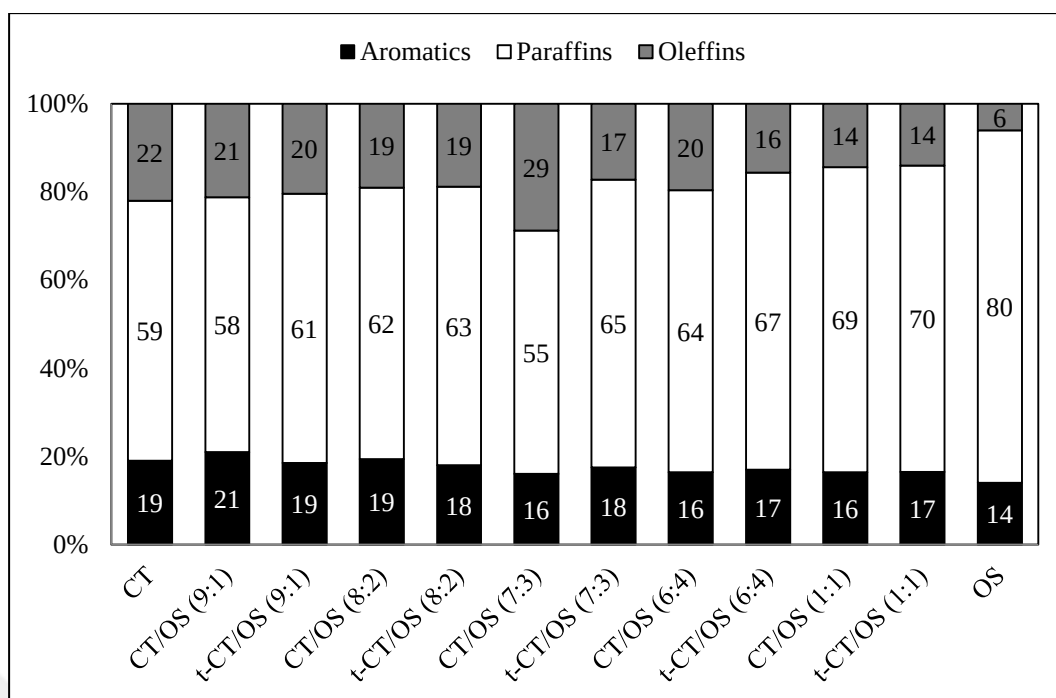


Figure 2.10. The amounts of hydrocarbon types in CT/OS co-pyrolytic oils and their calculated values.

Some fuel characteristics of co-pyrolytic oils are presented in Table 2.14. For comparison purpose, the oil obtained from pyrolysis CT and OS alone are also given in same table. Elemental composition and calorific value of oils didn't significantly change depending on blend ratio. And no synergetic effect was observed from the point of elemental composition and calorific value of oils.

Table 2.14. Ultimate analysis and calorific values of co-pyrolytic oils obtained from CT/OS co-pyrolysis.

	Ultimate analysis, wt.%					HHV, MJ/kg
	C	H	N	S	O	
CT	81.1	9.7	0.5	0.7	8.0	43.6
CT/OS (9:1)	80.8	10.0	0.4	0.9	8.0	43.7
CT/OS (8:2)	81.9	10.5	0.3	0.8	6.4	43.6
CT/OS (7:3)	81.6	10.9	0.5	1.7	5.3	43.9
CT/OS (6:4)	83.0	11.1	0.5	1.0	4.3	44.1
CT/OS (1:1)	78.9	11.0	0.5	1.0	8.6	43.6
OS	81.5	12.9	-	0.2	5.4	45.4

In contrast, the addition of OS to CT effected the elemental composition of chars. The carbon content of chars was decreased by increasing amount of OS in blend (Table 2.15). High heating values of the chars from co-pyrolysis of CT/OS had similar values which were around 27.8-28.4 MJ/kg.

Table 2.15. Ultimate analysis of co-pyrolytic chars obtained from CT/ OS co-pyrolysis, wt., %.

	C	H	N	S
CT/OS (9:1)	76.7	0.7	0.4	2.8
CT/OS (8:2)	70.2	0.9	0.4	2.3
CT/OS (7:3)	67.8	1.4	0.6	1.8
CT/OS (6:4)	66.3	1.4	0.6	2.3
CT/OS (1:1)	67.3	1.5	0.6	2.2

The co-pyrolysis experiments were also carried out with the mixture of TT and OS. Products yields from co-pyrolysis of TT/OS blends are shown in Table 2.16. Predicted values were also given in the same table to understand the synergic effects in co-pyrolysis process. Predicted values were donated as t-gas, t-char, t-oil, etc.

In these group experiments, as in case of co-pyrolysis CT/OS, we obtained aqueous phase in emulsion form. The oil yields were not significantly changed depending on blend ratio. However, aqueous phase amount increased and char yield decreased by increasing amount of OS in blend. For the blends containing more than 20 wt. % OS, experimental gas yields were lower than predicted one and experimental aqueous phase yields were more.

Table 2.16. Product distributions from co-pyrolysis of TT/OS blends, wt., %.

	char	t-char	oil	t-oil	aqueous	t- aqueous	gas	t-gas
TT/OS (9:1)	35.8	34.7	51.5	52.1	3.0	2.9	9.7	10.3
TT/OS (8:2)	33.9	31.3	51.6	53.3	5.6	4.2	8.9	11.2
TT/OS (7:3)	30.0	27.9	50.3	54.5	11.0	5.5	8.8	12.0
TT/OS (6:4)	26.1	24.5	55.2	55.7	9.4	6.8	9.3	12.9
TT/OS (1:1)	23.2	21.2	52.6	57.0	14.9	8.1	9.3	13.7

The composition of gas products from co-pyrolysis of TT/OS is given in table 2.17. Comparison purpose, gas product composition from TT and OS pyrolysis alone are also presented in Table 2.17. It is difficult to a generalization on the synergic effects related to gas composition. However, it is clear that the all gasses derived from co-pyrolysis had high calorific value due to their high amount hydrocarbon gas contents. In addition, the amounts of CO from all blends were higher than predicted values. The reason might be due to the decarbonylation effect of carbon black (derived TT) on the degradation products derived from OS.

Table 2.17. Composition of gas products obtained from co-pyrolysis of TT/OS blends.

	C1	C2	C3	C4	CO ₂	CO	H ₂	HHV, MJ/Nm ⁻³
TT	15.9	9.1	4.8	46.1	5.2	2.6	16.3	48.5
TT/OS (9:1)	13.7	7.0	4.1	48.3	3.8	9.8	13.3	49.0
TT/OS (8:2)	18.6	9.5	4.9	34.1	2.7	7.9	22.4	40.9
TT/OS (7:3)	20.1	11.4	5.5	34.0	2.9	8.3	17.8	42.1
TT/OS (6:4)	17.0	9.0	4.5	42.1	4.0	11.6	11.9	45.9
TT/OS (1:1)	20.4	11.2	5.3	39.5	3.3	8.6	11.7	45.6
OS	37.2	21.5	7.7	21.2	2.0	0.6	9.9	40.4

Another group co-pyrolysis experiments were carried out with CT/BW blends. Product distributions of co-pyrolysis of CT/BW are presented in Table 2.18. It is clearly seen that there is no synergic effect from the point of product yields in co-pyrolysis experiments for the blends containing more than 20 % BW. For the blends containing 10 and 20 wt. % BW, the gas yields were higher than predicted one while oil yields were lower. It is interestingly, in contrast to CT/OS blends, the yields of aqueous phase were similar to predicted values.

Table 2.18. Product distributions from co-pyrolysis of CT/ BW blends, wt., %.

	char	t-char	oil	t-oil	aqueous	t- aqueous	gas	t-gas
CT/BW(9:1)	36.8	35.6	48.5	52.7	2.3	2.4	12.5	9.3
CT/BW(8:2)	32.3	31.8	52.7	56.7	2.8	2.3	12.2	9.2
CT/BW(7:3)	27.5	28.0	60.5	60.8	2.1	2.1	9.9	9.1
CT/BW(6:4)	23.3	24.2	64.4	64.8	1.8	2.0	10.6	9.0
CT/BW(1:1)	19.9	20.4	70.7	68.8	0.5	1.9	8.9	9.0

The composition of gases from co-pyrolysis of CT/BW is given in Table 2.19. The synergy related to gas composition was also observed for the blends containing 10 and 20 wt. % BW. For these blends, the amounts of H₂ and C1 were higher than predicted values, while C4 amounts were lower. McGregor et al. (2010) reported that carbonaceous materials showed activity in the catalytic dehydrogenation and oxidative dehydrogenation of light alkanes.

Table 2.19. Composition of gas products obtained from co-pyrolysis of CT/BW blends.

	C1	C2	C3	C4	CO ₂	CO	H ₂	HHV, MJ/Nm ⁻³
CT	15.1	9.6	4.6	47.9	7.2	3.1	12.6	49.8
CT/BW (9:1)	22.6	13.1	4.7	28.9	3.3	1.4	26.0	39.0
CT/BW (8:2)	21.8	15.6	5.5	34.3	3.9	1.6	17.5	44.0
CT/BW (7:3)	18.0	14.4	5.5	43.0	5.8	2.3	11.2	48.9
CT/BW (6:4)	16.1	14.4	5.6	45.9	6.5	2.5	9.0	50.8
CT/BW (1:1)	22.4	21.4	7.1	34.8	2.6	0.9	10.8	47.4
BW	18.3	21.6	8.2	36.5	2.8	0.7	12.0	48.5

The composition of co-pyrolytic oils was characterized in terms of hydrocarbon types and boiling point distribution of hydrocarbons. Hydrocarbon types of co-pyrolytic oils obtained from the waste tyre/oily waste (1:1) blends were given in Figure 2.11. Oil samples were named as following the “blend type – oil” (e.g. CT/OS - oil stands for oil obtained from CT/OS co-pyrolysis). Co-pyrolytic oil from CT/BW blend contained higher amounts of paraffinic hydrocarbons and less amount of olefin and aromatic hydrocarbons than that from blend containing OS. Although type of oily wastes effected the hydrocarbon type in co-pyrolytic oil, the boiling point distribution of pyrolytic oils from CT/OS and CT/BW had similar (Figure 2.12). Both two co-pyrolytic oils contained 45-50 % naphtha fraction and 45-50 % light gas oil fraction.

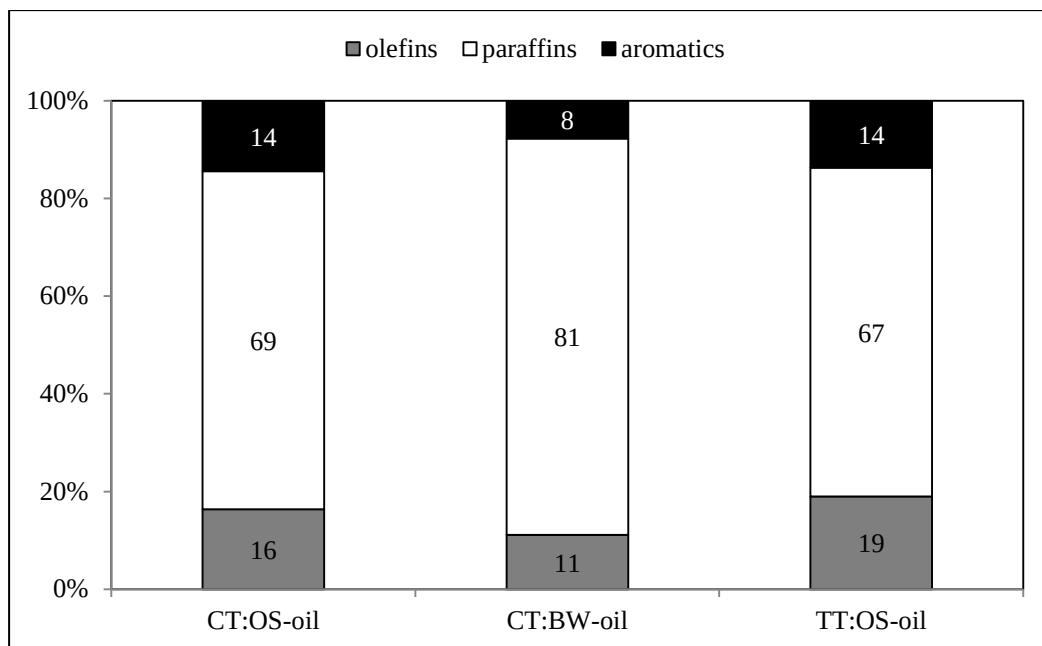


Figure 2.11. The amount of hydrocarbon types in co-pyrolytic oils (vol., %).

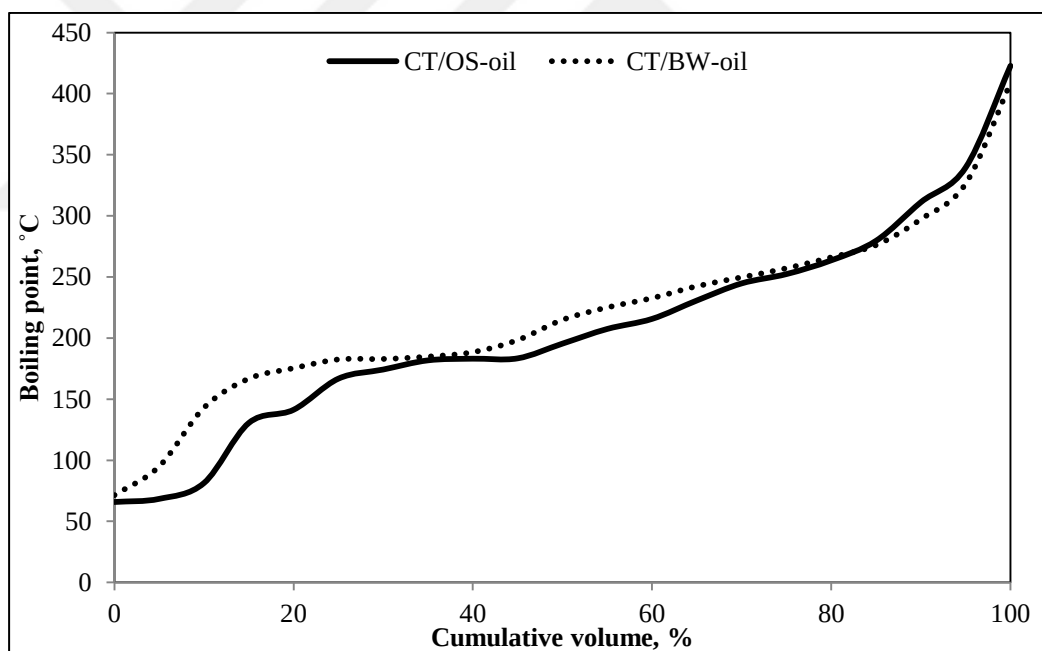


Figure 2.12. Simulated distillation curves of co-pyrolytic oils.

2.4. Conclusion

In this part of thesis, pyrolysis of scrap tyres, oily wastes and their blends were carried out. Pyrolysis temperature was optimized by the pyrolysis experiments performed with scrap tyres. Optimum temperature was selected as

500 °C from the point of yield and composition of pyrolytic oil and process economy. The pyrolysis of CT and TT produced the oil with yields of 49.0 wt % and 45.8 wt. %, respectively. These oils consisted of mainly paraffinic hydrocarbons, 61 % for CT and 49 % for TT. The pyrolysis of OS and BW produced the oil with yields of 70.4 % and 89.7 %, respectively. It was an important observation that the concentration of metal impurities (< 0.3 ppm) in pyrolytic oils derived from oily wastes was significantly lower than those in the feedstock. It was suggested that metals retained in the char. The oils from oily wastes had more paraffinic character than that from scrap tyres, 82 % for BW and 80 % for OS. The pyrolytic oil produced from pyrolysis of scrap tyres mostly contained heavy naphtha fraction, whereas pyrolytic oils obtained from pyrolysis of oily wastes mostly contained light gas-oil.

Although pyrolysis of oily wastes produced fewer char (around 2 wt. %), the char yields from pyrolysis of scrap tyres were 38.0 wt % for CT and 40.9 wt % for TT. The calorific value of chars can be compared with high quality coal. But their sulphur contents were high (2.5-2.9 wt %). The high sulphur content is the main drawback in its utilization as fuel. But it can be used as energy source for heating of the pyrolysis process with a proper emission control device. In addition, high ash content limits its use as carbon black, required a demineralization process.

In addition to pyrolysis experiments, co-pyrolysis of wastes were studied in attempt to investigate synergic effect on pyrolysis products. Co-pyrolysis experiments were carried out with the blends of CT/OS, TT/OS and CT/BW at 500 °C. The ratio of scrap tyre to oily wastes varied between 9:1 and 1:1. In the co-pyrolysis of scrap tyres with oily wastes, synergic effect varied with type of oily waste and blend ratio. From the point of product yields, there was no synergy for CT/BW blends while synergic effect was observed in CT/OS blends, decreasing in oil yield. For the CT: oily wastes blend, the paraffinic content remarkably increased while aromatic content decreased in the presence of BW. However, hydrocarbon compositions were not significantly changed in the presence of OS. For the TT: oily waste blend, the olefin content in co-pyrolytic oil was significantly lower than that in pyrolytic oil obtained from TT pyrolysis. The

co-pyrolytic oils had heavier hydrocarbons than pyrolytic oil. The co-pyrolytic oils from the CT and oily wastes blends contained 45-50 % naphtha fractions while the pyrolytic oil from CT contained 75 % naphtha fraction.

As conclusion, oily wastes can be co-proceeding with scrap tyres. The gas products from pyrolysis and co-pyrolysis had high calorific values. They can be used as fuel to provide the energy requirements of the pyrolysis process. All pyrolytic and co-pyrolytic oils have lighter compounds than commercial diesel and have a similar calorific value with commercial diesel. But they need to be distilled to fractions such as naphtha, gas oils etc. and each fractions should be upgraded before used as fuel.





3. ACTIVATION OF CHAR

In this section of thesis, investigation was focused on the activation of the char obtained from CT pyrolysis was investigated to obtain activated char. For this purpose, two methods namely dry and wet, were used. Dry methods include cyclic activation and CO₂ activation. Cyclic activation is partial oxidation of char. It was performed in the pyrolysis reactor under N₂ and air flow. Activation with CO₂ was carried out in pyrolysis reactor at 900 °C under CO₂ atmosphere. Wet methods include H₂O₂ and HNO₃ activation methods. In H₂O₂ activation, char was treated with H₂O₂ using two different ways: One of them was carried out under reflux at room temperature for 24 h, the other one was carried out in the autoclave. In HNO₃ activation, char was treated with HNO₃ solution (30 %) at room temperature for 20 min. The activated chars were characterized following analysis; methylene blue removal, iodine number, fourier transform infrared (FT-IR), scanning electron microscopy (SEM) and elemental analysis.

3.1. General Information

Due to its high surface area and porous structure, the activated carbon is a widely used material for treatment of waste waters and hazardous gas emissions. Wastes such as scrap tyres have a potential to be used as precursors in activated carbon production (Abdelbassit et al., 2017; Danmaliki and Saleh, 2016; 2107; Betancur et al., 2009; Brady et al., 1996). The usage of scrap tyre as activated carbons provides an interesting concept, controlling the pollution with a waste material.

In literature, several studies were carried out to production of activated carbon from scrap tyre using chemical (Al-Rahbi and Williams, 2016; Aftab et al., 2016; Antoniou and Zabaniotou 2015) and physical activation methods (Helleur et al., 2001; Hadi et al., 2016; Ucar et al., 2005b; Teng et al., 1995). Tanthapanichakoon et al (2005) studied the production of activated carbons from scrap tyre using both two methods and investigated their liquid-phase adsorption–desorption characteristics. In physical activation, scrap tyre was activated by

steam at 850 °C. In chemical activation, scrap tyre was activated by HCl (1M) treatment. Porous properties of activated carbons and their adsorption capacities for phenol and commercial dyes (Black 5 and Red 31) were investigated. For comparison purpose, porous properties and adsorption characteristics of commercial activated carbon (CAL; Calgon Co. Ltd., USA) was also investigated. It was reported that the prepared activated carbon had almost same micropore volume and BET surface area with commercial activated carbon. But the activated carbons had larger mesopore volume and higher dyes adsorption capacities than the commercial activated carbon.

In another study, Aftab et al. (2016) produced the activated carbon from scrap tyre char by the chemical activation using the mixture of HCl and HNO₃ solutions (in the proportion of 1:1). Porous properties and colour removal capacity of activated char were investigated. Congo red dye was used as adsorbates in the experiments. BET surface area of the activated carbon was found to be 172.6 m²/g. and maximum dye removal capacity of activated carbon was found to be 98.6%. They concluded that the activated carbon obtained from scrap tyre char was a good adsorbent for removal of the textile dye from water.

As differently from the study of Aftab et al., Al-Rahbi and Williams (2016) were carried out the chemical activation method by using alkali agents. In their study, KOH, K₂CO₃, NaOH and Na₂CO₃ were used for the chemical activation of the char. And NO adsorption capacity of the activated carbon were determined. The activation process of impregnated chars with alkali agents were carried out at 900 °C for 3 hours under N₂ atmosphere. The highest NO adsorption capacity in the low temperature (25 °C) was found for the char activated with KOH treatment. And the NO removal efficiency was noted to be 75%. On the other side, the chars activated with K₂CO₃, NaOH and Na₂CO₃ treatment showed lower efficient on NO removal. They reported that the NO adsorption capacity of the activated chars decreased in the order of alkali impregnation as KOH > K₂CO₃ > NaOH > Na₂CO₃.

The chemical activation of the char by using alkali agent was also investigated by Antoniou and Zabaniotou (2015). The impregnated char with

KOH in a ratio of 4:1 was heated up 850 °C under N₂ atmosphere in tubular reactor. BET surface area and yield were determined for the activated char, 402.39 m²/g and 60 % in respectively.

In literature, the physical activation of the char obtained from scrape tyre pyrolysis is more common, comparing to other activation process. Hadi et al. (2016) was used to steam for physical activation of the char. They investigated the effect of steam activation on textural properties of the char for different reaction time (2, 4, 6 h) and temperature (900, 925, 950, 975 °C). They noted that the increase in reaction time and temperature led to increase in the burn off value due to development of micro and mesopores. The surface area was increased from 32 m²/g to 732 m²/g by steam activation. Although the activated char was obtained from steam activation at 975 °C for 6 h had the maximum surface area, the burn off value was found to be highest. Thus, the optimum operating conditions for steam activation was reported as the temperature of 975 °C and reaction time of 4 h.

Helleur et al. (2001) was carried out the physical activation process of char obtained from scrap tyre pyrolysis at 900 °C. The activation processes were carried out at 900 °C for steam and CO₂ activation and at 750 °C for O₂ activation. The activated chars had similar surface areas (about 250 m²/g) and these values were substantially higher than that of raw char (91 m²/g). Methylene blue and phenol adsorption capacities of chars were also higher than that of raw char. On the other hand, Cu²⁺ adsorption capacity of the raw char was found to be higher than that of activated chars. In addition, they also observed that burn off and iodine number of activated chars was increased by the increase in activation time. It was reported that the activated char produced from CO₂ activation at 900 °C for 420 min was found to have maximum burn off value (38 %) and maximum iodine number (302 mg/g).

According to study of Teng et al. (1995), the activated chars produced from CO₂ activation found to have lower specific surface area (~ 170 m²/g) and higher burn off value (~ 50 %). But the calculated specific surface area was noted as 1000 m²/g on the basis of ash free char. For the purpose of reduction of the ash

influence on surface area, Ucar et al. (2005b) carried out the activation process in two steps. Firstly, they demineralised the char with HCl (the solution of 10 %) and then carried out the CO₂ activation process. The non-demineralised char was also activated for comparison purpose. The activation processes with CO₂ were carried out at 900 °C for 2, 4, 6 and 8 hours. They observed that BET surface area increases with increasing process time. BET surface area of demineralised-activated char (204 m²/g) was determined to be slightly lower than that of non-demineralised-activated char (240 m²/g). However homogeneous distribution of particles was observed on the demineralised char surface.

As differently from above methods, Heras et al. (2009) studied the cyclic activation method. In this method, each cycle was consisted of a chemisorption stage and a desorption stage. At chemisorption stage, the partial oxidation of char was carried out under air atmosphere at low temperature (210 °C). Then desorption stage was carried out under nitrogen atmosphere at higher temperature (550 °C and 750 °C). This stage provides the elimination of the oxidized structure from the main structure thus the formation of porous structure. They reported that, after 15th cycle, BET surface areas were found to be 156 m²/g and 239 m²/g for desorption at 550 °C and 750 °C, respectively. Meanwhile, the burn off values were detected as 17.4 % for desorption at 550 °C and 22.3 % for desorption at 750 °C. They suggested that the activated chars produced from cyclic activation method might be used as catalytic supports in liquid phase applications due to its granular activated structure. During the cyclic activation of scrap tyre char, the effect of particle size and desorption temperature on burn off value and BET surface area was investigated by Heras et al. (2012). For this purpose they carried out the activation process by using chars with three different particle size (1, 2, and 3 mm) and desorption temperatures at 550, 650 and 750 °C. In study, the temperature of 210 °C was used for all chemisorption stage. The highest burn off value (~ 45 %) and surface area (~ 600 m²/g) were observed for the largest particle size and at medium desorption temperature in case of 20th cycle of activation.

Heras et al. (2014) also investigated the cyclic liquid-phase oxidation. The liquid-phase oxidation experiments were carried out by using HNO₃, H₂O₂ and

ammonium persulphate. Then desorption stage was carried out at 650 °C under nitrogen atmosphere. They observed that the effect of oxidizing agent on textural improvement increased in the order of HNO₃, H₂O₂, and ammonium sulphate. After 15th cycle, BET surface area was around 400 m²/g for H₂O₂ and 750 m²/g for HNO₃. The burn off values was around 63 - 90%. They concluded that compared to cyclic activation with air, liquid phase cyclic activation leads to higher surface area and pore volume, but at the expense of higher burn-off.

3.2. Material and method

3.2.1. Cyclic activation

The char was loaded in the pyrolysis reactor and heated to desired temperature (200, 225, 250, 275 and 300 °C) under N₂ flow (25 mL/min). When the temperature reached to the desired temperature, N₂ flow was switched to air flow (80mL/min) and hold under these conditions for desired time (1, 3 and 5 h). And the air flow was switched to N₂ flow (100mL/min) and temperature increased to 500 °C and holds this temperature for 2 hours.

3.2.2. CO₂ activation

The char was loaded in the pyrolysis reactor and heated to 900 °C under N₂ flow (50 mL/min). When the temperature reached to 900 °C, N₂ flow was switched to CO₂ flow (360 mL/min) and hold for 210 min. After that, the reactor was cooled to room temperature under N₂ flow. The activated char was donated as AC-CO₂.

3.2.3. H₂O₂ activation

H₂O₂ activation was carried out with two methods. In first method, approximately 10 g of char was treated with 100 mL of H₂O₂ (30%) solution for overnight at room temperature. After oxidation treatment, the supernatant was separated by filtration and the residual solid (activated char) was washed with

distilled water, then oven-dried at 110 °C for overnight. The activated char was named as AC-H₂O₂-R. In second method, char and 50 mL of H₂O₂ (30%) solutions was placed in an autoclave (V = 100 mL). After sealing, the reactor was purged with N₂ for three times to remove air. Then, the autoclave was heated to 200 °C and hold for 2 h and 4 h. Then, the autoclave was cooled down to room temperature by a fan. After the gas product was released, reactor content was filtered, the solid residue was washed with distilled water, then oven-dried at 110 °C for overnight. Activated chars were donated as AC-H₂O₂-2 (activated for 2 h) and AC-H₂O₂-4 (activated for 4 h).

3.2.4. HNO₃ activation

Approximately 50 g of char was treated with 500 mL of HNO₃ (30%) solution for 20 min. at room temperature. After oxidation treatment, the supernatant was separated by filtration and the residual solid (activated char) was washed with distilled water, then oven-dried at 110 °C for overnight. The activated char was named as AC-HNO₃. In second step, AC-HNO₃ was loaded in the pyrolysis reactor and heated to 750 °C under N₂ flow (100 mL/min) and hold for 2 h. After that, the reactor was cooled to room temperature under N₂ flow. The activated char was donated as AC-HNO₃-des.

3.2.5. Analysis of activated chars

The elemental composition and iodine number of chars were determined according to standard analysis methods (ASTM 5291-96, ASTM D4607-94). Surface chemistry of chars was investigated by using FT-IR spectroscopy. The methylene blue adsorption capacity of the chars was determined according to literature (Raposo et al., 2009).

The surface area of chars was measured by multi point BET (Brunauer-Emmett-Teller) analysis and the nitrogen adsorption isotherms at 77°K were used for the measurements. The micropore volumes and the external area were calculated by the t-plot approach.

3.3. Results and Discussions

3.3.1. Cyclic activation

The cyclic activation is a method carried out cycle by cycle and each cycle is consisting of two stages which are namely chemisorption and desorption. The sample collected from the first cycle is used at the second cycle to be reactivated. Cycles are carried out until the desired product is obtained thus this activation method provides controlled activation of the char. This activation also provides to obtain the activated char having higher surface area with lower burn off value.

In this study, air was used as an activating agent at the chemisorption stage. The activation time and activation temperature gain importance since the char surface was activated by the oxygen in the air in this stage. For this purpose, to investigate the effect of activation time and activation temperature on the pore development, chemisorption stage was carried out under different conditions. Then in the following stage, desorption stage which was carried out at 500 °C under N₂ atmosphere for 2 hours, the aim was the formation of porous structure by removing the activated parts on the char surface.

3.3.1.1. Effect of the chemisorption temperature

In the cyclic activation process, at first we investigated the effect of the chemisorption temperature on yield and surface characteristics of activated char. For this purpose, activation of char was carried out at 200, 225, 250, 275 and 300 °C under air flow for 2h. The activated chars were named as following the “activated char – activation temperature” sequence (e.g. AC - 250 stands for cyclic activation of the char at 250 °C under air flow). The non-activated char was named as "N". The Methylene blue number (MB_N) of the raw char and activated chars were determined and given in the Table 3.1 along with the burn off values. Methylene blue number (MB_N) is defined as the maximum amount of methylene blue (in mg) adsorption of 1g activated carbon in liquid phase. The MB_N of the activated chars were found to be substantially lower amount than that of activated carbons (over 300 mg/g) reported in the literature (Djahed, 2016; Xin-hui, 2014).

It was observed no activation temperature effect on MB_N , even the temperature was reached up 300 °C. For activated chars, except AC-250, burn off values slightly increased with increasing chemisorption temperature.

Table 3.1. Variation of the methylene blue number and burn off values of activated chars with chemisorption temperature.

	N	AC-200	AC-225	AC-250	AC-275	AC-300
MB_N (mg/g)	21.1	22.5	21.8	22.3	23.1	23.9
Burnoff, %	-	1.9	2.0	1.9	2.1	2.4

Textural properties of the char and activated chars such as specific surface area (S_{BET}), external surface area (S_{ext}), total pore volume (V_{tot}), micropore volume (V_{mic}) and mesopore volume (V_{mes}) were presented in Table 3.2. The value of the mesopore volume was calculated from differences of total pore volume and micropore volume. Although S_{BET} values were increased by increasing chemisorption temperature from 200 °C to 300 °C, these values were not significant. Similarly, no improvement in pore volumes was observed by the increasing chemisorption temperature.

Table 3.2. Variation of the textural properties of activated chars with chemisorption temperature.

	S_{BET} (m ² /g)	V_{tot} (cm ³ /g)	S_{ext} (m ² /g)	V_{mic} (cm ³ /g)	V_{mes} (cm ³ /g)
N	52.5	0.63	52.5	-	0.63
AC-200	62.9	0.63	62.3	-	0.63
AC-250	62.4	0.62	60.7	-	0.62
AC-300	66.8	0.63	62.0	0.01	0.63

3.3.1.2. Effect of the chemisorption time

To investigate the effect of the chemisorption time on activated char properties, a series of chemisorption experiments was carried out at 250 °C for 1, 3 and 5 hours. As seen from the Table 3.3, MB_N of the activated chars were slightly increased by increasing of chemisorption time, while burn off values was

unchanged. The slight increase in the values of MB_N was not to be notable for any improvement of surface characteristics.

Table 3.3. Variation of the methylene blue number and burnoff values of activated chars with chemisorption time.

Time, h	-	1	3	5
MB_N (mg/g)	21.1	24.6	25.5	26.2
Burn off, %	-	2.1	2.1	2.1

According to results from this section and previous section (3.3.1.1), the temperature of 250 °C and the time of 1 hour were taken as optimum chemisorption conditions for further experiments.

3.3.1.3. Repeated cyclic activation

In the cyclic activation of the scrap tyre char, chemisorption-desorption steps repeated five times. After each cycle, the residue was weighed and approximately 2 g activated char was taken for analysis. As seen from the Table 3.4, Burn off slightly increased by repetition of activation, but although the increasing value of burnoff were linearly dependent on the cycle number, cyclic activation had no effect on MB_N of the activated chars. The MB_N of the activated chars even after five cycle was lower compare to activated carbons reported in literature (Djahed, 2016; Xin-hui, 2014).

Table 3.4. Variation of the methylene blue number and burn off values of activated chars with cycle number.

Cycle number	1st	2nd	3rd	4th	5th
MB_N (mg/g)	24.6	21.5	20.4	22.1	22.0
Burn off, %	2.1	3.5	3.8	4.3	4.6

The textural properties of the activated chars obtained from the 1st cycle to the 5th cycle were presented in the Table 3.5. In studies of Heras et al. (2009; 2012), they reported the S_{BET} areas as over 100 m²/g for activated chars after the fifth cycle. But we observed that S_{BET} areas were around 50-70 m²/g for activated chars in our study. Regarding to these results, we can say that textural properties

showed slight improvement until the 3rd cycle but after that, from 3rd cycle to 5th cycle, this improvement was disappeared by the possible destruction of existing pore structure.

Table 3.5. Textural properties of activated chars obtained from cyclic activation.

Cycle number	S_{BET} (m ² /g)	V_{tot} (cm ³ /g)	S_{ext} (m ² /g)	V_{mic} (cm ³ /g)	V_{mes} (cm ³ /g)
1st	58.5	0.65	58.5	0.00	0.65
3rd	68.8	0.65	63.7	0.01	0.64
5th	51.2	0.66	51.2	0.00	0.66

The surface chemistry of chars were analysed by FT-IR spectroscopy. FTIR spectrums were presented in the Figure 3.1. The spectrum of chars displays a number of bands centred at 3565, 1500, 960 cm⁻¹ which were ascribed to stretching (v) (O–H, C=C, and C–O) vibrations. The stretching vibration of OH groups can come from phenol groups (Diaz and Griffiths, 2000). The stretching (v) (C=C, and C–O) vibration at 1500- 960 cm⁻¹ might be the sign of the skeletal vibrations in aromatic rings (Troca-Torrando et al., 2011). Unreasonably, the peaks around 2342 cm⁻¹ which ascribed to stretching (v) (C=O) vibrations of CO₂ was observed (Gerakines et al., 1995). The effect of cyclic activation methods on surface chemistry of activated chars could not be observed.

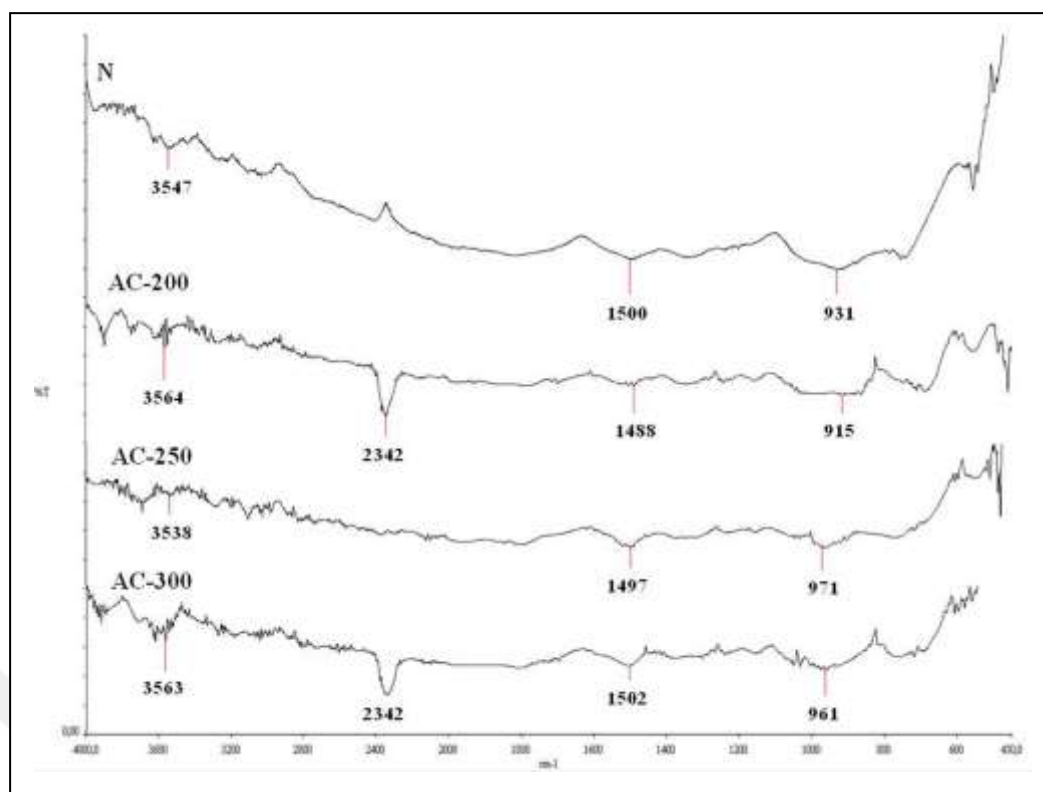


Figure 3.1. FT-IR spectrum of chars obtained from cyclic activation.

3.3.2. Chemical and physical activation

The improvement of the surface characteristics of the char was investigated comparatively by using chemical activation and physical activation. The elemental compositions and ash amounts of the chars obtained were presented in the Table 3.6. Ash amounts of AC-H₂O₂-R and AC-HNO₃-des were lower than that of raw char. It is notable that ash amount of AC-CO₂ was considerable higher than that of raw char. This is reasonable because some part organics in char was removed during CO₂ treatment resulting of increasing in fraction of inorganics. Chemical activation led to decrease in sulphur amount in char due to the dissolving of sulphur compounds during chemical treatment. Another point of interest is the fact that the activated chars obtained from H₂O₂ treatment at 200 °C and HNO₃ treatment contained oxygen.

Table 3.6. Ultimate and ash analysis of chars.

wt., %	None	AC-H ₂ O ₂ -R	AC-H ₂ O ₂ -2	AC-H ₂ O ₂ -4	AC-CO ₂	AC-HNO ₃	AC-HNO ₃ -des
C	77.46	83.05	77.91	77.58	62.02	76.60	83.33
H	0.64	0.74	0.76	0.85	0.16	0.73	0.44
N	0.32	0.33	0.27	0.42	0.14	0.91	0.64
S	1.72	0.19	0.08	0.12	1.56	0.21	0.16
O*	-	-	2.44	0.65	-	2.14	2.23
Ash	19.86	15.69	18.54	20.38	36.12	19.41	13.20

The textural properties of the activated chars obtained from chemical and physical activation were presented in the Table 3.7. It is clearly seen that chemical activation led to no notable improvement of textural properties.

Table 3.7. Textural properties of chemically and physically activated chars.

	S _{BET} (m ² /g)	V _{tot} (cm ³ /g)	S _{ext} (m ² /g)	V _{mic} (cm ³ /g)	V _{mes} (cm ³ /g)
N	52.5	0.63	52.5	-	0.63
AC-H ₂ O ₂ -R	62.5	0.70	62.6	-	0.70
AC-H ₂ O ₂ -2	60.5	0.74	60.5	-	0.74
AC-H ₂ O ₂ -4	50.7	0.78	50.7	-	0.78
AC-CO ₂	119.7	0.85	72.8	0.02	0.83
AC-HNO ₃	59.3	0.08	17.2	0.03	0.05
AC-HNO ₃ -des	64.0	0.07	64.0	-	0.07

As seen from the table, the activated char obtained from CO₂ activation had highest surface area, 119.7 m²/g. But this value was significantly lower than that of activated chars produced in a previous study (Mui et al., 2004).

The iodine number of activated chars was given in the Table 3.8. For comparison purpose, the iodine number of raw char was also given. The iodine number is defined as the maximum amount of iodine (in mg) adsorption of 1g activated carbon in liquid phase. Although the iodine number is defined as an porosity indicator for activated carbons, it was also noted in the standard test method (ASTM D4607-94) that this indicator cannot be generalized. According to results from Table 3.7 and Table 3.8, there were no correlation between textural properties and the iodine numbers. However, the amount of iodine number of AC-CO₂ could be noted as the highest value.

Table 3.8. Iodine number of the chars

	None	AC-H ₂ O ₂	AC-CO ₂	AC-HNO ₃	AC-HNO ₃ -des
Iodine no.	967.6	987.2	1026.8	960.9	1006.3

Regarding with comparison study above, we could say that the chemical activation methods reduced the sulphur and ash content of activated chars. On the other hand, the physical activation with CO₂ was found to be more effective on the porosity development of chars than chemical activations.

The FT-IR spectrums of chars obtained from chemical and CO₂ activation were given in the Figure 3.2. Likewise char activated with cyclic activations, the spectrum of chars displays a number of bands around 3600, 1500, 930 cm⁻¹ which were ascribed to stretching (ν) (O–H, C=C, and C–O) vibrations. The stretching vibration of OH groups can come from phenol groups. The stretching (ν) (C=C, and C–O) vibration might be the sign of the skeletal vibrations in aromatic rings. In addition, the peaks around 2342 cm⁻¹ which ascribed to stretching (ν) (C=O) vibrations of CO₂ was observed, meaninglessly. The effect of chemical activation and CO₂ activation methods on surface chemistry of activated chars could not be observed.

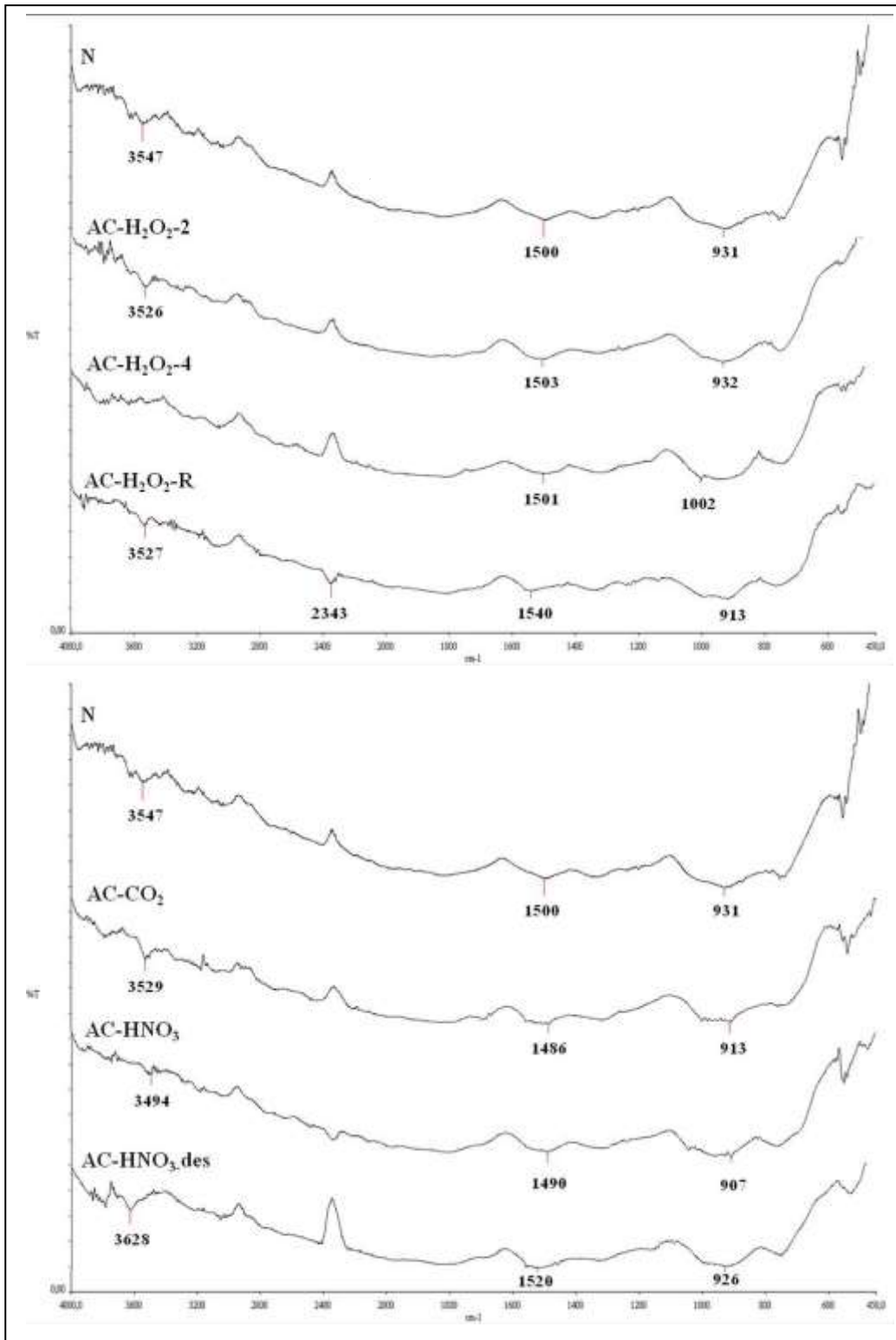


Figure 3.2. FT-IR spectrums of chars obtained from chemical and CO_2 activation.

3.4. Conclusion

In this section of thesis, activation of the char obtained from scrap car tyre was investigated by different methods, chemical activation, physical activation and cyclic activation method.

Both cyclic activation and chemical activation methods led to no notable improvement on the surface characteristics of the activated chars. But, these methods led to decrease in sulphur and inorganic amounts in char due to the dissolving of inorganics and sulphur compounds during chemical treatment. On the other hand, the physical activation with CO₂ was found to be more effective on the porosity development of chars than chemical activations.



4. CHARACTERISTICS AND SYNERGISTIC EFFECTS OF CO-COMBUSTION OF CHAR DERIVED SCRAP TIRE WITH COAL AND CARBONACEOUS WASTE.

In this section of the study; combustion behaviours of the scrap tire and its char were investigated by thermogravimetric analyser and lab-scale reactor. In addition, the co-combustion of the scrap tyre with the other carbonaceous matters (lignite and poultry litter) were also investigated.

4.1. General Information

In literature, a number of study related to possible usage area of char obtained from scrap tyre (STC) are present, such as an activated carbon production (Teng et al., 2000; Miguel et al., 2002; Hoseinzadeh et al., 2012), carbon black (Pantea et al. 2003) and production of SiC/Si₃N₄ nanocomposite (Rajarao et al., 2015). Nonetheless the utilization of the char as carbon sources for production of activated carbon is limited due to presence of additives comes from tyre manufacture. On the other hand, the char could be used as fuel due to its' high calorific value (about 30.5 MJ/kg). Interestingly, only one report on combustion of STC has come across in literature. Leung and Wang (1998) investigated the combustion behaviour of the scrap tyre and its' char by using thermogravimetric analyzer (TGA). They observed only one distinct peak (at the temperature of 450-620 °C) from DTG curve and assumed that only one reaction occurs during STC combustion. In contrast to STC, combustion of ST has been studied by many researchers.

Juma et al. (2007) investigated the combustion behaviours of ST by (TGA). The effect of the temperature and O₂ concentration on the combustion of ST was studied. The temperature of 512 °C was detected as the ignition temperature which was increased by increasing volume of O₂ concentration. The significant reduction of the reaction time was observed by the increasing temperature and decreasing O₂ concentration. Some of the experiments were carried out in two stages; ST was pyrolyzed under nitrogen atmosphere at the first stage and then the combustion process was carried out under different oxygen concentrations

(volume of 5%, 10% and 15%). The mass loss of the ST was determined as 52-55 % at the pyrolysis stage and 30 % at the combustion stage. On the other hand, Larsen et al. (2006) studied the effect of particle size of ST on combustion by using macro TGA. They noted that larger particle diameters and lower temperatures led to increase in devolatilization time, during combustion process. The effect of particle size, temperature (in the range of 700-1000 °C) and O₂ concentration (in the range of 5 to 21 volume %) on combustion of was also investigated by Nielsen et al. (2012) in the pilot scale rotary kiln reactor. They reported that the particle size of ST was of small importance for the tyre char conversion time, but temperature and O₂ concentration had important effect on char oxidation.

As known, main problem of ST combustion is fuel gas emissions. Kwon and Castaldi (2012) studied the ST combustion by using TGA and GC/MS under various oxygen concentrations (volume of 7-30%). The significant mass loss (~55%) was detected around 300–500 °C, where the thermal degradation rate was almost independent of oxygen concentrations due to simultaneous volatilization and oxidation. They suggested that formation of PAHs, which were derived from the thermal degradation of SBR and IR (polyisoprene) in ST, occurred at relatively low temperatures (350 -500 °C). Because of this, combustion temperature should be high enough to avoid a long retention time for completing of char burnout. Kandasamy and Gokalp (2015) reported that significant amounts of CO, CO₂, and SO₂ were release at combustion processes and the majority of condensable gases such as aromatic compounds and alcohols were released during the pyrolysis stage. Combustion of the ST in the high-temperature rotary drum was studied by Mut et al. (2015). In the study, the effect of volatile content and particle size on SO₂ emissions released from the combustion of scrap tyre was investigated. They observed that SO₂ emissions increased with the decreasing particle size. They suggested, the formation of volatiles get easier by faster heating of smaller particles and consisted volatiles lead to increase in SO₂ release. In addition, they observed the increase in SO₂ emissions by the increase in volume of O₂ concentration. Yu et al. (2016) studied the volatilization behaviour of heavy metals derived from pyrolysis and combustion of ST at different heating rates and temperatures. For heavy metal release, combustion at low-heating rate showed

improvement compare to combustion at rapid-heating. They observed the decreasing in emissions rate of Zn and Pb for slow-heating combustion and they suggested that the reason might be formation of stable metal compounds which were formed by reaction with the additives, such as kaolin and calcium. It also suggested that the adsorption of Zn and Pb by these additives is another cause for the reduction in emission rates.

In another study, combustions of ST and coal were comparatively investigated by Levendis et al. (1996). The NO_x emissions from ST were lower than that from coal (by a factor of 3), reflecting its lower nitrogen content. In contrast, the SO_2 emissions from ST were more than that from coal (by a factor of 2). PAH emissions from both ST and coal were varied depending on combustion conditions. At fuel-lean conditions ($\phi < 0.6$), ST combustion produced no detectable PAHs, but at $\phi > 0.6$, PAHs emission increased substantially. Generally, PAH emissions of ST were found to be 1.5-2 times higher than those of coal.

To minimize the emissions from ST combustion and to improve the combustion characteristics of some fuels, co-combustion of ST with carbonaceous materials was studied by some researchers. Co-combustion of ST with coal in the pilot scale vertical furnace was investigated by the Biagini et al. (2002). It was observed that SO_2 emission increased with the tire/coal ratio in the feed, because of the high S content of the blend, but the experimental data were lower than the predicted values. They concluded that co-combustion of ST was feasible using a low NO_x burner.

Co-combustion of ST with high ash coal was studied by using TGA (Xiangguo et al., 2006). The effects of ST addition into coal on combustion parameters were investigated. The addition of ST improved the combustion characteristics of coal, decrease in the ignition temperature and increase in the maximum weight loss rate. They concluded that the co-combustion of ST with low qualified coal is feasible.

Giere et al. (2006) reported the results of gas emissions from combustion of two type fuels in stoker boilers, coal and a mixture of 5 % ST and 95 % coal. They observed that the present of ST in fuel increased the Zn emission because of the high Zn content of ST. They reported that the addition of ST had no effect on the emissions of SO₂ and NO_x while led to decrease in CO emissions slightly.

Zaharia et al. (2009) studied the combustion of blends of ST + metallurgical coke (MC) (10:90, 20:80, 30:70; ST:MC) in a drop tube furnace at 1200 °C. Because of the high volatile content of the ST, faster weight loss and increased char burn out was observed during the combustion of blends. They suggested that efficiency of an Electric Arc Furnace Steel making is increased a certain extent when the coke was partially replaced by ST.

Singh et al. (2009) carried out reburning and co-combustion experiments using tyre rubber and two different coals in a down-fired combustor. In reburning experiments, they obtained low levels of NO emissions (up to 80 % reduction) using a lower volatile coal as the primary fuel and tyre rubber as the reburn fuel. The co-combustion of tyre rubber with coal also decreased NO emission depending on the reactivity of coal. They noted that emissions of SO₂ was increased with the addition of tyre rubber at the ratio over 12 %. In their study relating to co-combustion of tyre rubber with coal (Singh et al., 2011), they observed also the NO_x reduction and an increase in SO₂ in co-combustion of tyre rubber with coal. The same research group (Singh et al., 2013) investigated slagging and fouling behaviour of the residual ashes obtained from co-combustion of coal and ST blends. The mineral matter composition of the ashes obtained from combustion and co-combustion were determined by using X-ray fluorescence (XRF) and inductively coupled plasma-optical emission (ICP-OES). The slagging and fouling characteristics was calculated by use of fusibility correlations. It was reported that ash derived from co-combustion showed minimal risk of slagging and fouling.

Wu et al. (2013) investigated the combustion characteristics of a Spanish coal and a South Africa coal blended with four types of carbonaceous wastes at three different mass fractions by using TGA. The carbonaceous wastes lowered

ignition temperatures at higher blending fraction levels. The combustion characteristics showed improved combustion performance for the blends when compared with that of coal only. It was mentioned that there was notable synergistic effects during co-combustion.

The poultry litter wastes become an environmental problem due to the raw poultry litter is not able to be used in land as fertilizer since it is caused to eutrophication (Kelleher et al., 2002). For this problem, several solutions such as composting (Georgakakis and Krintas, 2000), combustion (Lynch et al., 2013a; 2013b; 2014; Billen, 2014a; 2014b; 2014c), gasification (Taupe et al., 2016; Pandey et al., 2016), hydrothermal carbonization and pyrolysis (Kantarli et al., 2016) etc. were presented in literatures. Kelleher et al. (2012) asserted that the use of poultry litter as a fuel is one option for poultry litter management, although it has low calorific value. They reported the low melting point of ash produced from combustion is another disadvantage of the process. On the other side, the high calcium content of ash was representing as an advantage leading the reduction of harmful emissions such as NO_x and SO_x during combustion process. They stated that fluidised bed combustor can be used for the direct combustion of poultry litter.

Lynch et al. (2013a) examined the suitability of poultry litter as fuel for use in fluidized bed combustor. The amount of residue obtained from combustion of poultry litter was measured as 9 %. They noted that the residue is consist of 110 g/kg elemental phosphorus and 170 g/kg potassium and the residue with these content can be used as nutrient substitute for mineral fertilizer. They suggested that adequate dust collector should be employed for minimising the emissions released from combustion of poultry litter, during energy recovery. Although the residue obtained from combustion of poultry litter is valuable product in the case of utilization as fertilizer due to containing minerals, during the combustion process this containing can be caused the ash-related problems.

The possible problems relating to combustion residue from poultry litter was discussed by several researchers (Billen, 2014a; 2014b; 2014c; Lynch, 2013b; 2014). Poultry litter is known as one of the P-rich biomass fuel and the P is

mainly present in forms of HPO_4^{2-} or $\text{H}_2\text{PO}_4^{1-}$ salts which are inclined to react with Ca or CaO salts in the ash. These reactions lead the formation of $\text{Ca}_3(\text{PO}_4)_2$ which caused the reduction of the Ca silicates in the ash. At this point, Ca/K equilibrium gain an importance. The reducing of Ca in the form of Ca silicates lead to increase of K silicates which have the lower ash melting point. Billen et al. (2014b) found a solution for reducing the formation of K silicates which caused the low ash melting point. They introduced the additional CaCO_3 to the combustion process and provided the formation of CaO which react with silicates instead of K. Thus, by the formation of Ca silicates, the ash melting point reached the higher temperature. Lynch et al. (2013b) observed that the coarse ash was consisted of mainly alkali-Ca-phosphates while the fine fraction was formed of K_2SO_4 and KCl. In addition, the major content of slag phase (95%) determined as SiO_2 and K_2O . And the rest of slag composition was mostly contained Al_2O_3 , K_2SO_4 , and Na_2O . Heavy metal composition is also one of the ash-related problems and was investigated by the Lynch et al. (2014). They reported that the most of the heavy metals was associated with the fine ash particles after combustion. They concluded that the utilization of residue obtained from combustion of poultry litter as a fertilizer was found to be acceptable under the Sewage Sludge Directive.

Billen et al. (2015) proposed one option for poultry litter; combustion with subsequent recycling of the ash. They had also reported that electricity produced from the combustion of poultry litter more beneficial compare to combustion of coal since the saving fossil fuels, low emissions, no waste water, and recycling of P and K.

The co-combustion of poultry litter with coal and carbonaceous materials is also present in literature. The combustion experiments of the poultry litter and peat blend at the ratio of 1:1 was studied in the fluidised bed combustor by Abelha et al (2003). The feeding problem was observed due to humidity rate of fuel above the 25%. The secondary air flow was introduced to the combustion system for improvement of the combustion. Thus, the emissions of CO and NO_x had been reduced by introducing the secondary air flow. Although the low ash melting point of poultry litter had been representing as a disadvantage, the Ca content of

the ash had retained the emission of SO_x which is one of the undesirable emissions to be able to formed during the combustion. They reported that the K and Cl and minor amount of heavy metals (Cd, Cu, Ni, Pb, Cr, Mn and Zn) are detected in ashes collected from cyclones.

Toptas et al (2015) investigated the co-combustion of coal and torrefied poultry litter by using thermogravimetric analyzer. Burnout performance improvement for lignite was observed during the co-combustion. They suggested that poultry litters could be useful for coal/biomass co-combustion systems. In another study, the combustion behaviours of poultry litter, coal and their blends in different proportion were investigated by using thermogravimetric analyzer (Yurdakul, 2016). The synergetic effect was observed during co-combustion. Compared to poultry litter and blends, the reactivity of the coal had the lowest value and the reactivity of the blends reduced by the addition of coal.

4.2. Material and Methods

4.2.1. Materials

The fuels used in this study included the char derived scrap tyre (STC), a Turkish lignite-LIG (from the Soma basin, Turkey), poultry litter (PL), char derived poultry litter (PLC) and their blends. Poultry litter was provided were provided by a local farm. Poultry litter char was obtained by pyrolysis of poultry litter in fixed bed pyrolysis reactor at 500°C with $10^\circ\text{C min}^{-1}$ heating rate under N_2 atmosphere. Scrap tyre char was obtained by pyrolysis of scrap car tyres at 500°C (Section 2.2.1.). The coal/STC, coal/PLC and STC/PLC blends were prepared by physical mixing in the rate of 1:1.

Prior to combustion experiments, the oven dried fuels was ground to particle size less than $250\ \mu\text{m}$. and then they were stored in sealed containers until use. The some properties of fuels used in this study are listed in Table 4.1.

4.2.2. Methods

4.2.2.1. Thermal Gravimetric Analysis

Combustion characteristics of fuels used were determined by a thermal gravimetric analyser (NETZSCH STA 409 CD) under air atmosphere. The sample with a mass of 50 mg, approximately, was heated from room temperature up to 105 °C after wait for 1 hour at this temperature, it was heated up to 1200°C with a heating rate of 20 °C min⁻¹ under air flow with a flow rate of 100 mL. min.⁻¹. Weight loss and weight loss rate were continuously recorded during the process. Two repetitions were run for each sample.

The combustion parameters, such as burnout temperature (BT), ignition temperature (IT), and combustion reactivity were calculated from TG/DTG curve according to literature (Park and Jang, 2012). Burnout temperature is the temperature at which the rate of weight loss become smaller than 1 wt.%/min. The ignition temperature was determined based on the temperature at which the DTG had its peak value and the corresponding slope to the intersection with respect to the TG profile. The combustion reactivity of sample is considered directly proportional to the maximum rate of mass loss, whereas it is inversely proportional to the corresponding peak temperature. The use of both two properties in a parameter provides an average of fuel reactivity. In this study, mean reactivity, R_m , was calculated based on the literature (Park and Jang, 2012).

4.2.2.2. Lab-scale reactor tests

Lab-scale reactor consisted of a cylindrical retort (height, 35 cm; inner diameter, 12 cm), which was heated electrically and controlled by two separated proportional –integral –derivative (PID) controllers (Figure 1). The fuel was put in a cylindrical holder of 100 mm height and 95 mm inner diameter. The material of the reactor wall and sample holder was silicon carbide, which was inert under reducing and oxidizing conditions; therefore, the wall did not react with the fuel, ash, and flue gas. The mounting and vessel for the fuel bed were placed on the plate of a scale. The scale was mechanically separated from the retort by a liquid

sealing (synthetic thermal oil: Therminol 66). The scale was used to determine the weight loss of the sample. With this setup, it was possible to continuously measure the mass reduction of the sample during combustion. The sample was introduced into the preheated reactor which was at 450°C for section 2 while the section 1 was at 800°C. The test conditions for all test runs performed with the lab-scale reactor are shown in Figure 4.1.

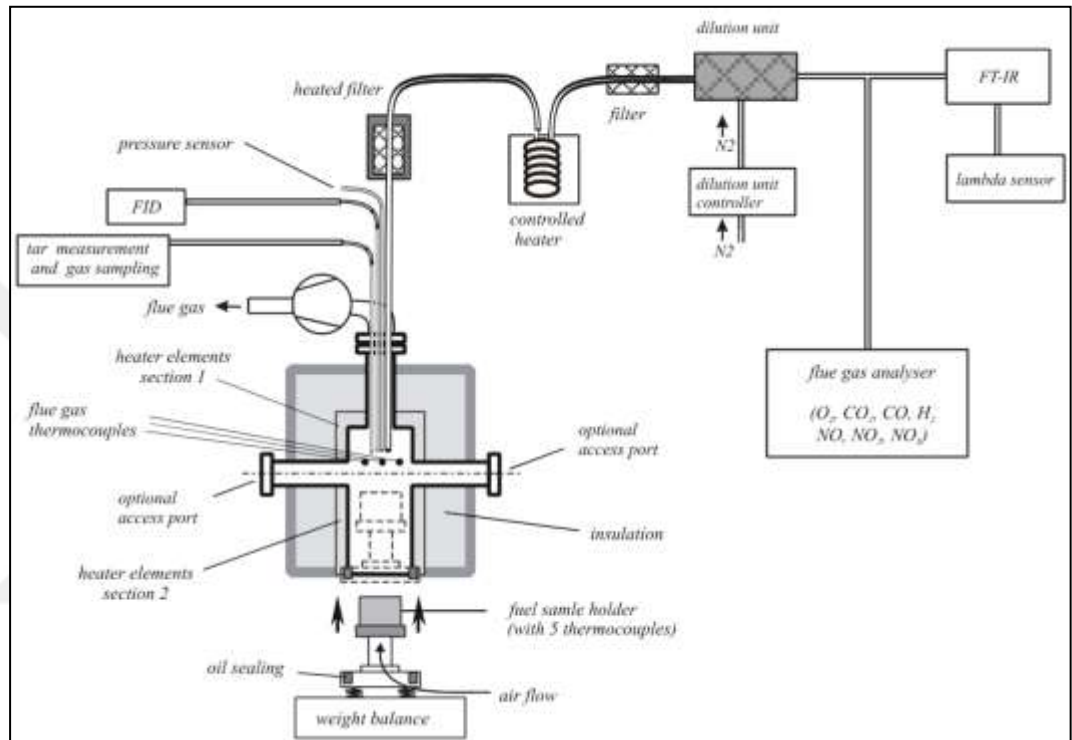


Figure 4.1. Scheme of the Lab-scale reactor.

The following measurements/analyses were performed during each of the combustion test runs: (1) Mass decrease of the fuel over time (balance). (2) Concentrations of flue gas species over time: (i) Determination of CO₂, H₂O, CO, CH₄, NH₃, HCN, N₂O, and basic hydrocarbons was performed with a multi-component Fourier transform infrared (FTIR) spectroscopy device (Ansyco Series 447). (ii) The O₂ and H₂ concentrations were measured with a multi-component gas analyzer (Rosemount NGA 2000). This device used paramagnetism as a measurement principle for O₂ detection and a thermal conductivity detector (TCD) for H₂ detection. (iii) The amount of total hydrocarbons (C_xH_y) was determined with a flame ionization detector (FID, Bernath Atomic 3005), which detected organic compounds by ionization in a burning H₂ flame. (iv) Wideband λ

sensor (O_2). (v) A nitric oxides (NO_x) was calculated by difference (fuel N – ($NH_3 + HCN$)). (3) Temperature measurements over time: (i) Five thermocouples in the fuel bed (three different heights NiCr – Ni). (ii) Thermocouples in the gas phase (NiCr – Ni). (4) Analysis of the biomass fuel used and residual ash produced. The data of the fuel analysis and the residual ash analysis as well as the weight measurements of the fuel sample and the ash sample could be used to calculate the elemental release to the gas phase. This was performed by calculating the mass balance for every relevant element as well as the total ash.

The same experimental setup has been used for the investigation of different kind of biomass (e.g., wastes and residues from agriculture and the food industry, short rotation coppices, and energy crops) (Sommersacher et al., 2012).

4.2.2.3. Analyses

The moisture content of fuel samples was determined according to Ö NORM CEN/TS 14774 (determination of the weight loss during drying at $105\text{ }^{\circ}\text{C}$ until a constant weight is reached). The ash content was estimated according to CEN/TS 14775 by determination of the loss of ignition at $550\text{ }^{\circ}\text{C}$. The determination of C, H, and N contents of biomass fuels was done according to Ö NORM CEN/TS 15104 by combustion and subsequent gas-phase chromatographical separation and measurement in an elemental analyzer (Vario EL 3, Elementar). The determination of chlorine was carried out according to Ö NORM CEN/TS 15289, applying a digestion step based on bomb combustion in oxygen and absorption in NaOH (0.05 molar), followed by a measurement by ion chromatography (ISC 90, Dionex).

The major and minor elements in fuels was determined by multi-step pressurized digestion of the fuel with HNO_3 (65%)/HF (40%)/ H_3BO_3 (Multiwave 3000, Anton Paar), followed by measurement by inductively coupled plasma–optical emission spectroscopy (ICP –OES, Arcos, Spectro) or inductively coupled plasma –mass emission spectroscopy (ICP –MS, Argilant 7500, Agilent), depending upon detection limits.

Expect Cl, the same methods as described for the fuel analysis was applied for the determination of major and minor elements in ash. The Cl content was measured by ion chromatography (ISC 90, Dionex) after elution for 24 h with deionized water.

4.3. Results and Discussion

4.3.1. Characteristics of the Fuels

The properties of fuels used in combustion experiments were given in Table 4.1. The volatile and ash contents varies significantly among the fuels investigated, which suggests significant different combustion characteristics of individual coal, wastes, chars and their blends.

Table 4.1. Some properties of fuels.

	ST	STC	PL	PLC	LIG
<i>Proximate analysis, wt. %, dry basis</i>					
Ash	7.66	20.12	19.64	41.74	24.25
Volatile matters	62.77	3.41	66.47	18.02	38.30
Fixed Carbon	29.57	76.47	13.89	40.24	37.45
FC/VM	0.47	22.43	0.21	2.23	0.98
<i>Ultimate analysis, wt. %, dry basis</i>					
C	81.54	77.27	39.35	47.22	53.05
H	7.10	0.68	4.97	1.75	4.11
N	0.33	0.29	3.55	3.51	1.35
S	1.73	2.45	0.77	0.89	1.32
<i>Ash analysis, wt. %, dry basis</i>					
TOC*	4.90	1.65	0.82	0.08	0.81
TIC**	1.60	1.08	2.00	0.98	0.16

*Total organic carbon

**Total inorganic compounds

As expected, the chars had higher ash content than raw wastes, but lower volatile content. It should be noted that char derived scrap tyre had considerably less amount volatile compounds. Therefore STC is difficult to be ignited and burns difficulty compared with other fuels. The scrap tyre and its char contained high sulphur, which is used as vulcanization agent. For this reason, the SO_x

emissions are expected to be over the emission limits. Co-combustion of STC with coal looks more promising way in its utilization as fuel. On the other hand, the high nitrogen content for poultry litter and its char suggests a possibility increase in NO_x emission during combustion. In combustion process, ash composition is a critical parameter. The alkali compounds lead to slagging and fouling in the boiler. Due to the higher concentration of K and Ca in poultry litter and its char, it is expected that their fouling tendency and slagging index are high. The blending of PL and PLC may result in noticeable decrease in NO_x emission and in slagging/fouling risk in the boiler.

4.3.2. Combustion experiments with thermal gravimetric analyzer

The behaviour of wastes and their chars in air atmosphere with $20\text{ }^\circ\text{C min}^{-1}$ heating rate was studied in the first series of experiments.

In case ST combustion, one strong peak was seen in the range of 224 to 464 $^\circ\text{C}$ and one broad peak in the range of 666 to 1079 $^\circ\text{C}$ corresponding to the formation of volatiles and char combustion, respectively (Figure 4.2). The total weight loss was 52 % in volatilization step and 36 % in char combustion step. For STC, combustion process started at higher temperatures (at 406 $^\circ\text{C}$) due to the very low volatile matter in STC. The linear weight loss was observed during combustion process and no obvious peak was seen. It looks that the char oxidation step was overlapped with decomposition of inorganics (Zn and Si compounds). About 60 % of total weight loss occurred in combustion of STC, the residue was ash.

In case of PL, the volatilization step and the char combustion step occurred at different temperature ranges, the one strong peak (around 400 $^\circ\text{C}$) was observed in volatilization step. The weight loss was 48 % in volatilization step and 42 % in char combustion step. For PLC, The broad peak between 320-697 $^\circ\text{C}$ showed that volatilization step was overlapped with char oxidation step (Figure 4.3). The second strong peak at 932 $^\circ\text{C}$ was related to decomposition of inorganics. The total weight loss in combustion of PLC was 73 %. The reason higher residue amount from chars compared to their raw material was high ash content in chars.

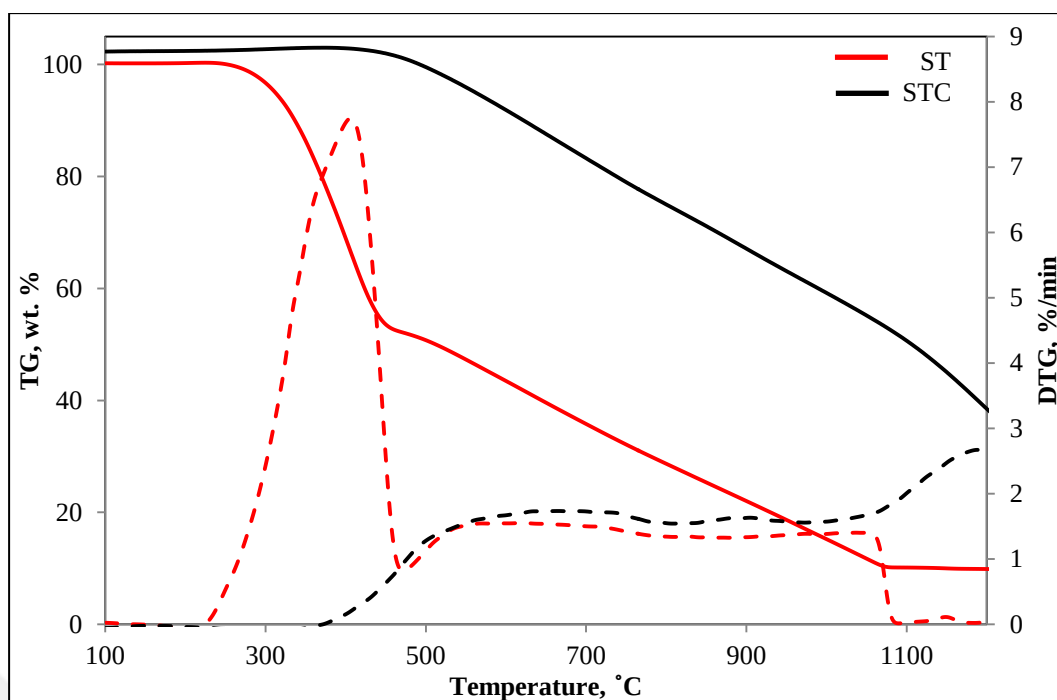


Figure 4.2. TGA - DTG profiles of ST and STC in air.

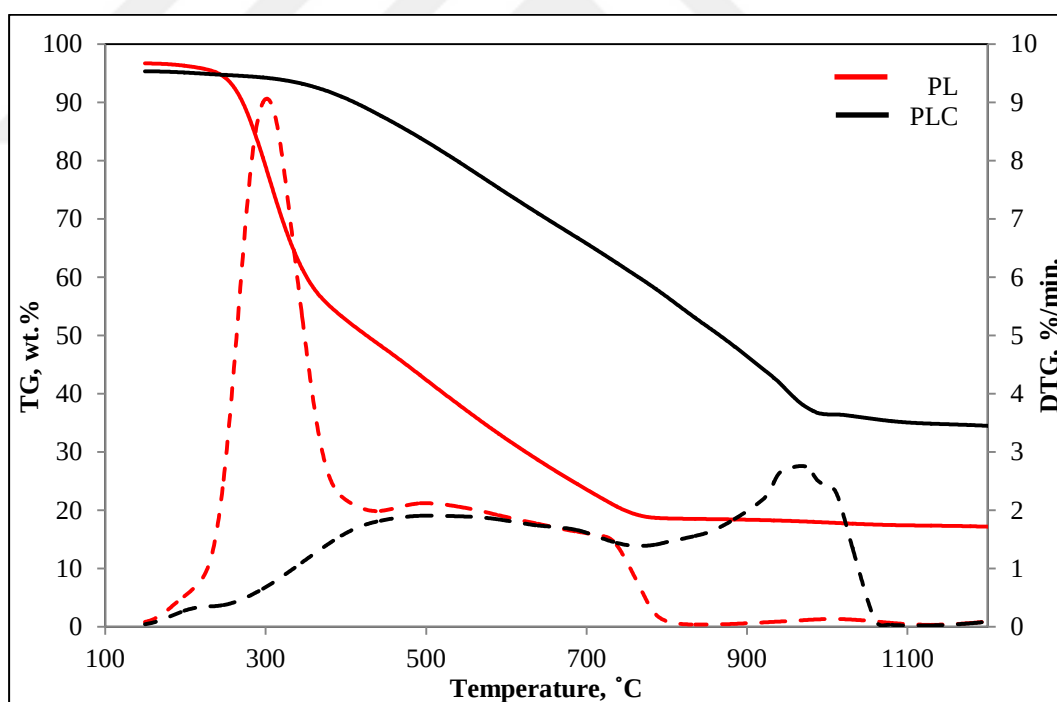


Figure 4.3. TGA - DTG profiles of PL and PLC in air.

The TGA/DTA thermograms in Figure 4.4 show the difference between the combustion properties of lignite and chars. The combustion profile of lignite was similar to those of PLC. Differently, the strong peak at 932 °C related to

decomposition of carbonates was observed in PLC char. It is clearly seen that combustion rate of lignite was higher than that of chars. The reason might be high volatile amount in lignite.

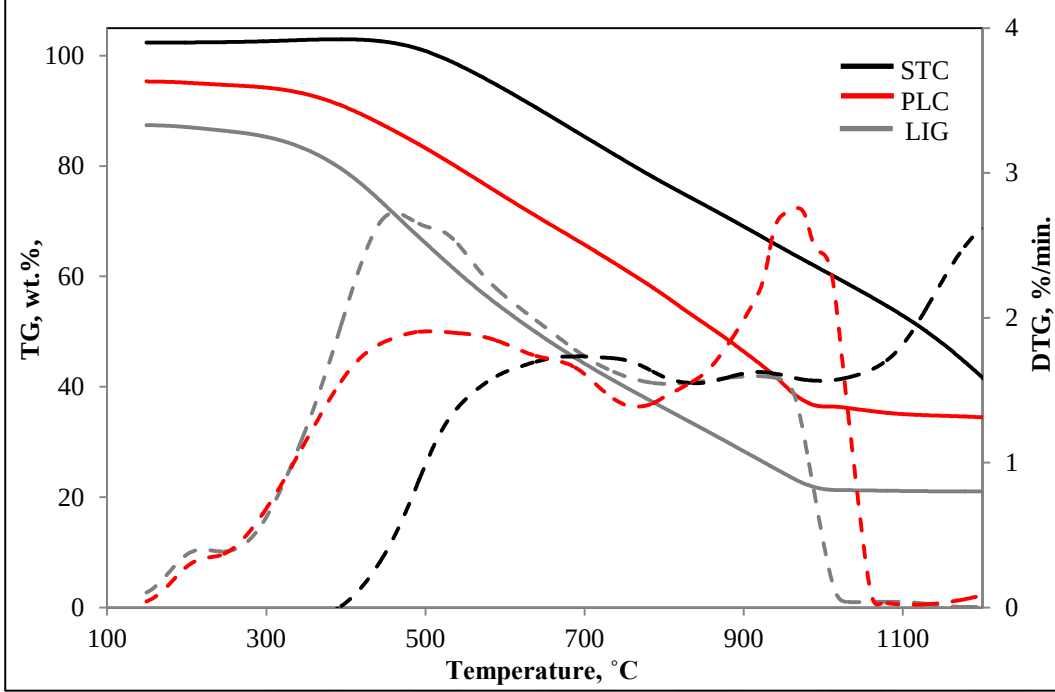


Figure 4.4. TG and DTG curves for STC, PLC and LIG.

In practice, the co-combustion plants are used generally with a blend containing around 10% biomass or wastes (Toptas et al., 2015). However, the use of char instead of raw material provides a technical option for high substitution ratios of biomass/waste in the co-combustion system (Li et al., 2012). In this thesis, the chars obtained from STC and PLC was chosen for co-combustion experiments.

TG and DTG curves of the STC/LIG, STC/PLC and PLC/LIG blends were given in the Figure 4.5, Figure 4.6 and Figure 4.7 respectively. To see the interaction between lignite and chars, the theoretical TGA and DTG curves were calculated using Eq. 4.1 and Eq. 4.2, respectively. The theoretical curves represent the sum of the curves for individual components in the blend.

$$\text{weight loss \%} = 0.5 (\text{weight loss, \%})_{\text{lignite}} + 0.5 (\text{weight loss, \%})_{\text{char}} \quad (\text{Eq. 4.1})$$

$$(\text{dm/dt})_{\text{sum}} = 0.5 (\text{dm/dt})_{\text{lignite}} + 0.5 (\text{dm/dt})_{\text{char}} \quad (\text{Eq. 4.2})$$

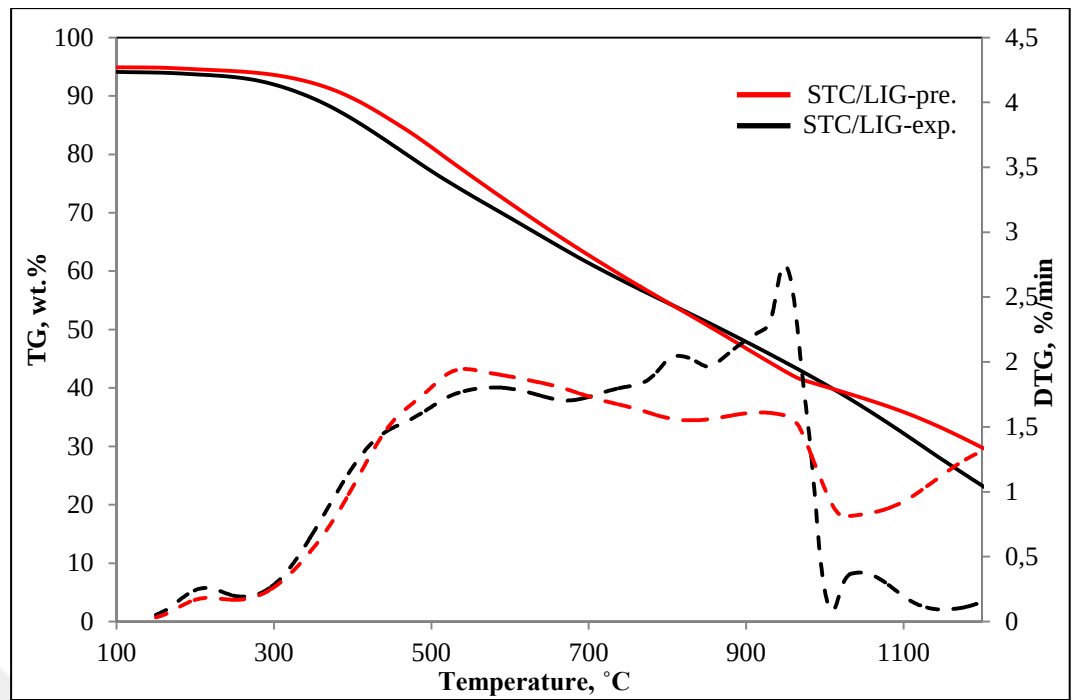


Figure 4.5. TG and DTG curves for STC and LIG blend which is called as STC/LIG.

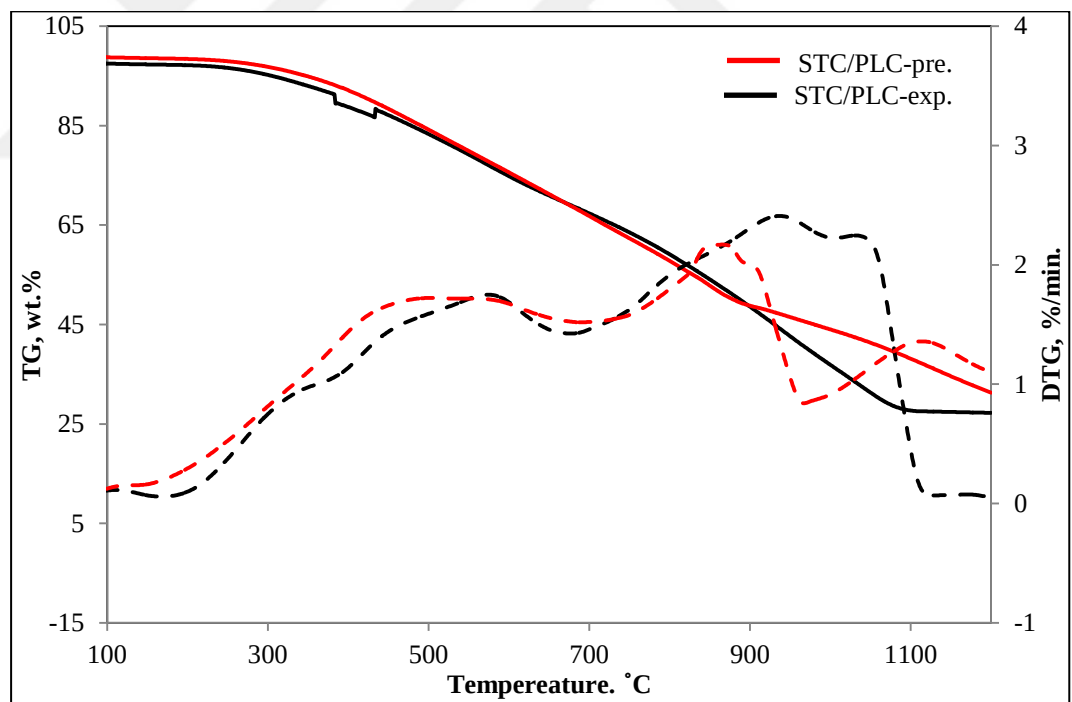


Figure 4.6. TG and DTG curves for STC and PLC blend which is called as STC/PLC.

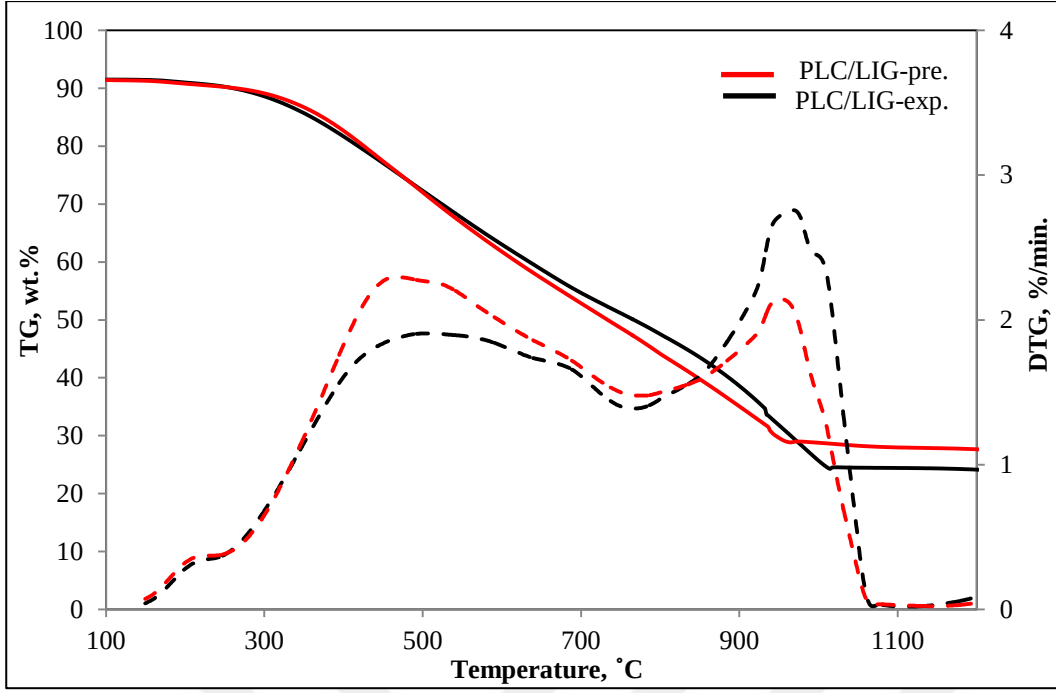


Figure 4.7. TG and DTG curves for PLC and LIG blend which is called as PLC/LIG.

The TGA/DTG curves for blends showed additivity behavior in volatilization and combustion steps. It should be noted that synergetic effect was observed at high temperatures corresponding to decomposition of inorganics. Decomposition rates at high temperatures were higher than predicted one.

The combustion parameters were calculated from TG/DTG curve based on the literature (Miranda et al., 2011; Toptas et al., 2015). Ignition temperature (IT) is a point at which the weight loss rate is $1\% \text{ min}^{-1}$. Burnout temperature (BT) is a point at which the rate of weight loss become smaller than $1 \text{ wt.}\%/\text{min}$. The reactivity (R) was calculated by following equation:

$$R (\% \text{ min}^{-1} \text{ K}^{-1}) = 100 \text{ DTG}_{T_p} T_p^{-1} \quad (\text{Eq. 4.3})$$

Where, DTG_{T_p} is maximum combustion rate ($\% \text{ min}^{-1}$) and T_p is peak temperature ($^{\circ}\text{K}$). Table 4.2 shows the combustion characteristics of lignite, wastes and their chars. Due to the high volatile contents, the ignition temperature and T_{max} of chars are higher than that of raw material. BT of chars is also higher than that of raw materials. It is interesting to note that we could not determine BT for STC, because even at 1200°C , combustion process has not ceased. STC had

also lowest combustion reactivity. The ignition and burnout temperatures of PLC/LIG blend are very close to that of lignite. However, it might be expected the inorganics in PLC could catalyse the combustion of lignite, lowering in BT of blend. In case of STC/LIG blend, the ignition temperature of blend is higher than that of lignite alone but lowers than that of STC alone, which shows that in the initial phase of combustion there was an interaction between the blend components. In contrast to STC alone combustion, we could calculated BT of STC/LIG blend. This shows an interaction between the lignite and STC during combustion. From the data in Table 4.3, it is clearly seen that addition of char (STC and PLC) to lignite caused lowering of reactivity (anti-synergistic effect).

Table 4.2. Combustion characteristics of fuels and their blends.

	ST	STC	PL	PLC	LIG	STC/ PLC	STC/ LIG	PLC/ LIG
Ignition Temperature, °C	267	477	211	310	309	432	356	311
Burnout Temperature, °C	1069	nd*	732	952	990	1080	956	1000
Peak Temperature, °C	408	690	270	479	487	647	553	480
Maximum combustion rate, min ⁻¹	7.8	1.7	10.2	1.9	2.6	1.8	1.8	1.9
Reactivity, %min ⁻¹ .K ⁻¹	1.14	0.18	1.88	0.25	0.35	0.19	0.22	0.25

*not determined

However, in literature, the synergistic effects were reported for coal–chars derived biomass blends (Goldfarb and Liu, 2013; Kastanaki and Vamvuka, 2006; Farrow et al., 2013; Sarkar et al., 2014).

We can conclude that the synergies in co-combustion process is difficult to predict due to the interactive effects varied with the characteristics of the components in blend, such as heterogeneity, nature and distribution of reacting species etc. (Sahu et al., 2010).

4.3.3. Lab-scale test results

Lab-Scale reactor provided to continuously measure the weight reduction of the fuel during combustion (volatilization and char oxidation steps). The top of reactor was heated to 800 °C and bottom of the reactor was heated to 450 °C.

After the system reached steady state at desired temperatures, the fuel was introduced into the reactor. During experimental run, the temperature inside reactor self-increased due to the combustion. Because of rapid heating of fuel introducing into the reactor, combustion experiments can be well-comparable to the real combustion processes. In this experimental system, chars, lignite and their blends were used as fuel.

4.3.3.1. Reaction time, mass loss and ash residue

The O₂ concentration has been used as an indicator for estimation of combustion time. When the main fuel decomposition phase starts, O₂ concentration in the flue gas decreased, and then dropped to 0. During char combustion step, O₂ concentration in the flue gas started slowly increasing. The flue gas consisted of only O₂ at the end of combustion. After the combustion, the residue was weighed. Table 4.3 shows the combustion time and the percent of ash residue (based on feed fuel).

Table 4.3. Combustion time and ash residue amounts.

Sample	PL	PLC	ST	STC	LIG	PLC/ STC	PLC/ LIG	STC/ LIG
Combustion time, min.	82	62	96	74	107	72	71	124
Estimated aerosol, %	0.58	1.45	0.40	2.08	0.22	2.68	0.31	1.21
Bottom residue, %	17.83	38.81	7.87	17.31	17.92	26.12	31.63	17.58

In contrast to combustion experiments using TGA, the combustion time of STC was lower than that of lignite. The reason might be differences between the experimental systems. In case of combustion with TGA, fuel was heated gradually from room temperature to 1200 °C. However, in Lab-Scale reactor, fuel was rapid heated. In the test runs, the fuel bed temperature measured varied with the fuel time. The mass loss of fuel during test runs was monitored versus time.

Mass loss of STC, PLC and LIG combustion was given in Figure 4.8. For PL, PLC and ST, mass loss started at 200th sec. and decreased sharply. On the other hand, the main mass loss was observed after 2000th sec. and 1600th sec. for lignite and STC.

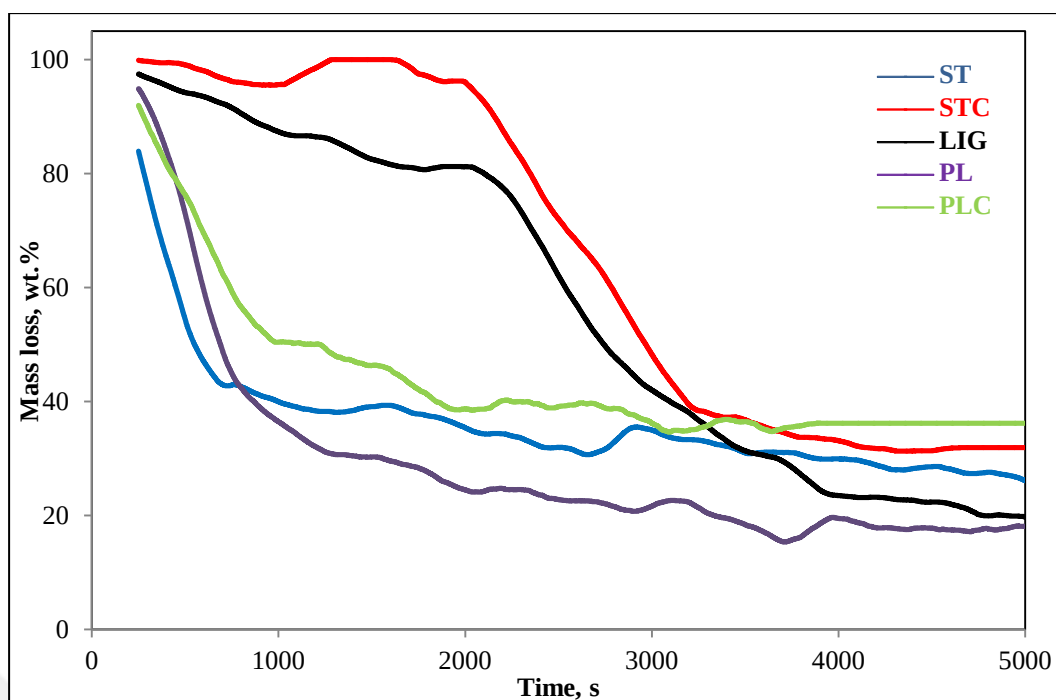


Figure 4.8. Mass losses during the combustion of fuels used in study.

To see the interaction between lignite and chars, the theoretical mass losses were calculated for blends. The experimental and predicted mass losses versus time were given Figures 4.9, 4.10 and 4.11. As seen in Figure 4.9, there was no synergic effect in the co-combustion of lignite with STC. However, the synergic effect in the co-combustion of lignite with PLC is clearly observed from the Figure 4.10, increasing mass loss rate. Similarly, for PLC/STC blend, mass loss rate was higher than predicted one. The reason is that inorganics (alkali metals) in PLC might catalyse the combustion of lignite and STC.

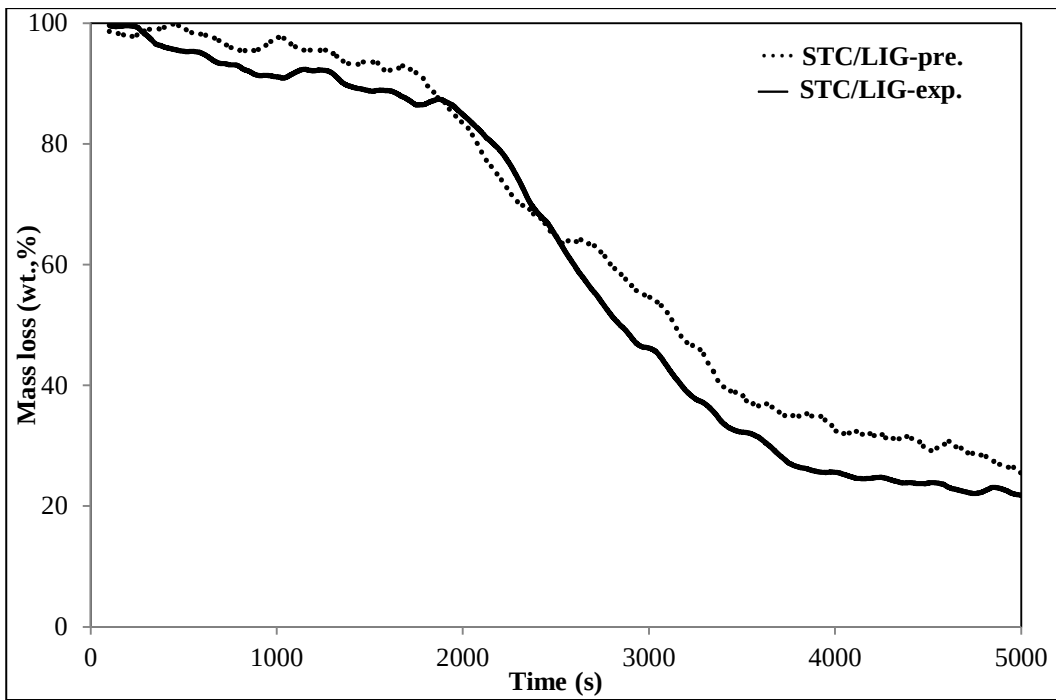


Figure 4.9. Predicted and experimental mass loss during co-combustion of STC/LIG.

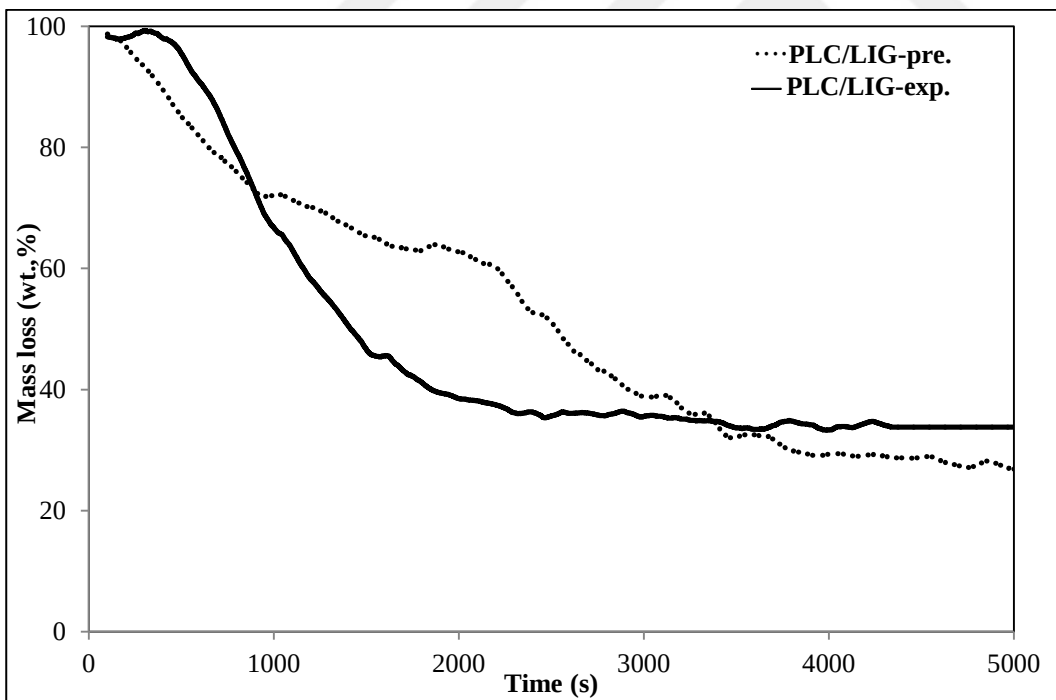


Figure 4.10. Predicted and experimental mass loss during co-combustion of PLC/LIG.

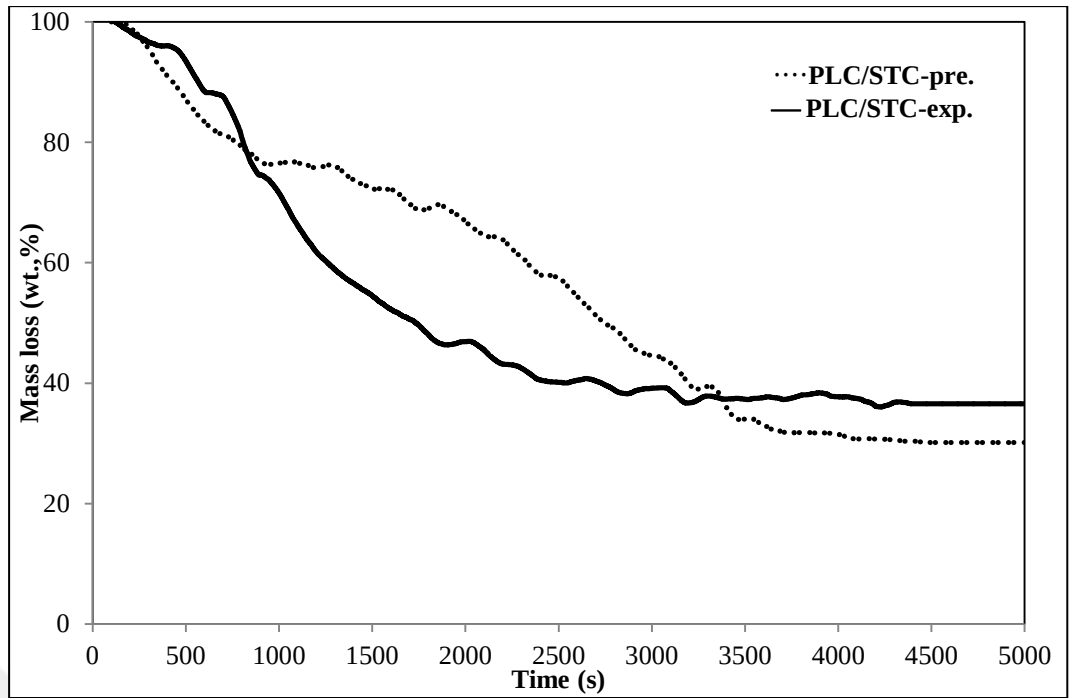


Figure 4.11. Predicted and experimental mass loss during co-combustion of STC/PLC.

4.3.3.2. CO_x, hydrogen and hydrocarbon gaseous emissions

Figure 4.12 shows the concentrations of CO₂, CO, H₂O, H₂ and O₂ in flue gas depending on the time for ST combustion. As seen from Figure 4.12, the release of volatiles and charcoal gasification started in the 2nd sec of the experiment and the stage was continue until the 500th sec. After this period, the combustion of charcoal started which can be indicated by the significantly increasing CO₂ amount. As expected, during the combustion phase, the O₂ concentration increased and the CO₂ concentration decreased. The ending of combustion stage can be indicated by the reaching of O₂ concentration up to initial value (about 4950th sec). During this phase, the highest fuel bed temperature was detected at 870 °C. The hydrocarbon composition of ST was mainly consisting of CH₄ and it was given in the Appendix 1. The CH₄ concentration was determined to be 75.7 g in the gas composition obtained from the combustion of 1 kg ST. This means that 6.96 % of C was converted to CH₄ during combustion. Besides of the CH₄, H₂ and H₂O were also determined in the flue gas. The maximum concentration of H₂ and H₂O were measured, 24283 and 140722 ppm respectively.

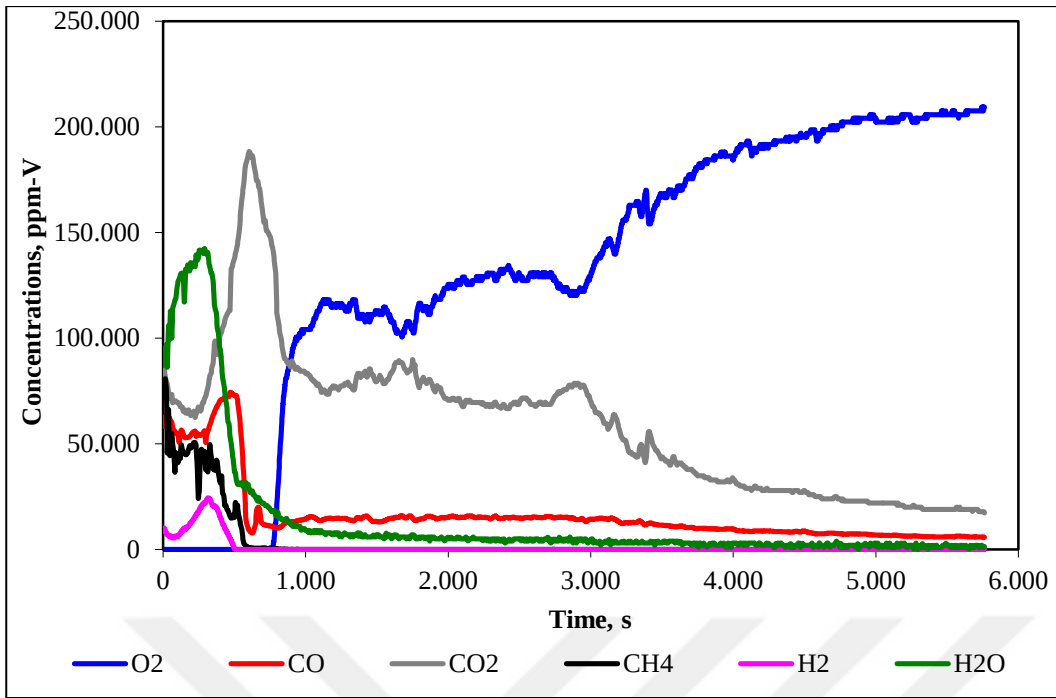


Figure 4.12. Variation of gas emissions during combustion of ST.

The combustion time for STC was about 4500 sec which can be seen from Figure 4.13. After 1000th sec from the start of the test, fuel combustion started, indicated by decreasing O₂ concentrations and increasing CO₂ concentrations in the flue gas. The main decomposition phase started with a rapid increase in CO₂ and CO. In early stage of combustion, minor amounts of H₂ (max. 200 ppm) and H₂O (max. 28293 ppm) were measured in the flue gas. After 2000th sec, the O₂ concentration dropped to 0. Mainly CO₂ and CO was measured in the flue gas. The minor amounts of hydrocarbons (mainly CH₄) were also measured (Appendix 2). After 2654th sec, the CO concentration decreased and dropped to zero at 3270th sec. At 3186th sec, the inflection point of the CO₂ trend was reached. At this point, the devolatilization was almost completed, and charcoal combustion became dominate (Sommersacher et al., 2016). Charcoal combustion phase is characterized by smaller amounts of CO and increasing CO₂ concentrations in the flue gas as well as slowly increasing O₂. During this phase, the temperature measured was 1217 °C, which was typically the highest fuel bed temperature.

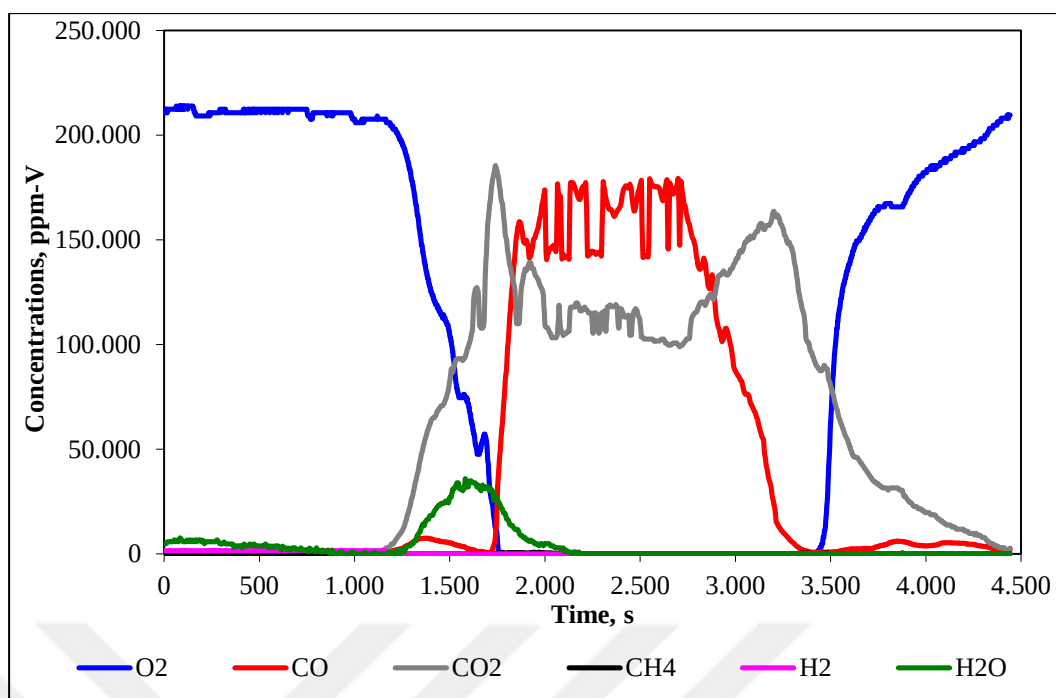


Figure 4.13. Variation of gas emissions during combustion of STC.

According to flue gas composition obtained from combustion of PL, the release of volatiles and charcoal gasification started at the 2nd sec of the experiment and the stage was continue until the 602th sec (Figure 4.14). The combustion of charcoal started as the following stage, which can be indicated by the significantly increasing CO₂ amount. This stage was continue from the 602th sec to 2642th sec. The hydrocarbon gasses were in small quantities and consisted mostly of CH₄ (Appendix 3). Compare to flue gases obtained from ST and STC combustion, the H₂ and H₂O concentrations in the flue gas were high and found to be at the maximum concentrations of 34090 and 242300 ppm, respectively. During this phase, the highest fuel bed temperature was detected at 919 °C.

The combustion time of PLC was shorter than that of STC, it was about 3600th sec. The main decomposition phase started at 200th sec at which the O₂ concentration dropped to 0 (Figure 4.15). In contrast to STC combustion, H₂O and H₂ concentrations in the flue gas were high, 194124 and 22788 ppm, respectively. At 1014th sec, the devolatilization was almost completed. The highest temperature measured was 902 °C. As in the case of STC, the minor amounts of hydrocarbons (mainly CH₄) were also measured (Appendix 4).

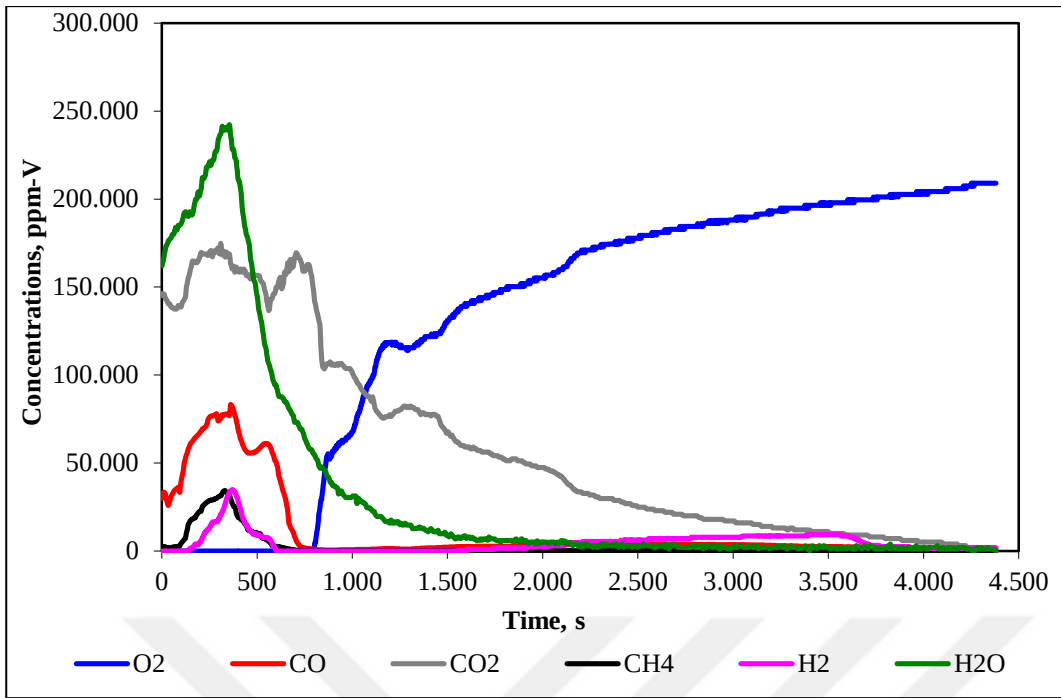


Figure 4.14. Variation of gas emissions during combustion of PL.

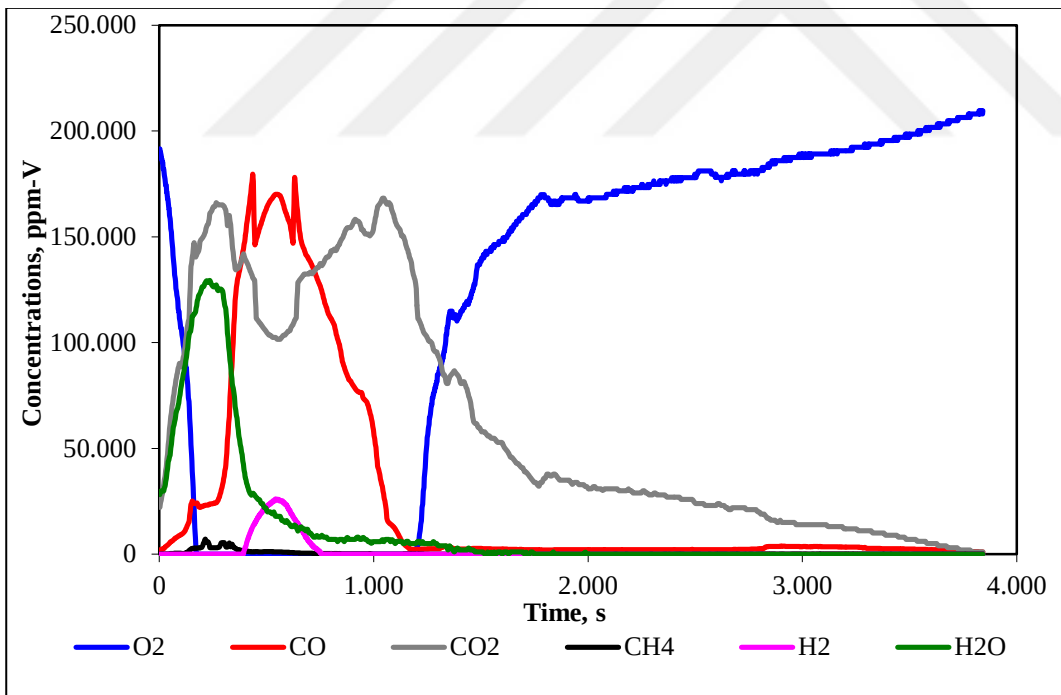


Figure 4.15. Variation of gas emissions during combustion of PLC.

The highest combustion time was measured in combustion of lignite, 6500 sec (Figure 4.16). The main decomposition phase started after 2200th sec. Typically the highest fuel bed temperatures, in this case 995 °C are measured. It

should be noted that maximum concentration of H_2O measured was higher than that of CO_2 and CO . The inflection point of the CO_2 trend was reached at 3472th sec. The hydrocarbons (mainly CH_4) were also measured in flue gas (Appendix 5). The maximum H_2O , H_2 and CH_4 concentrations measured was high comparing to PLC and STC combustion.

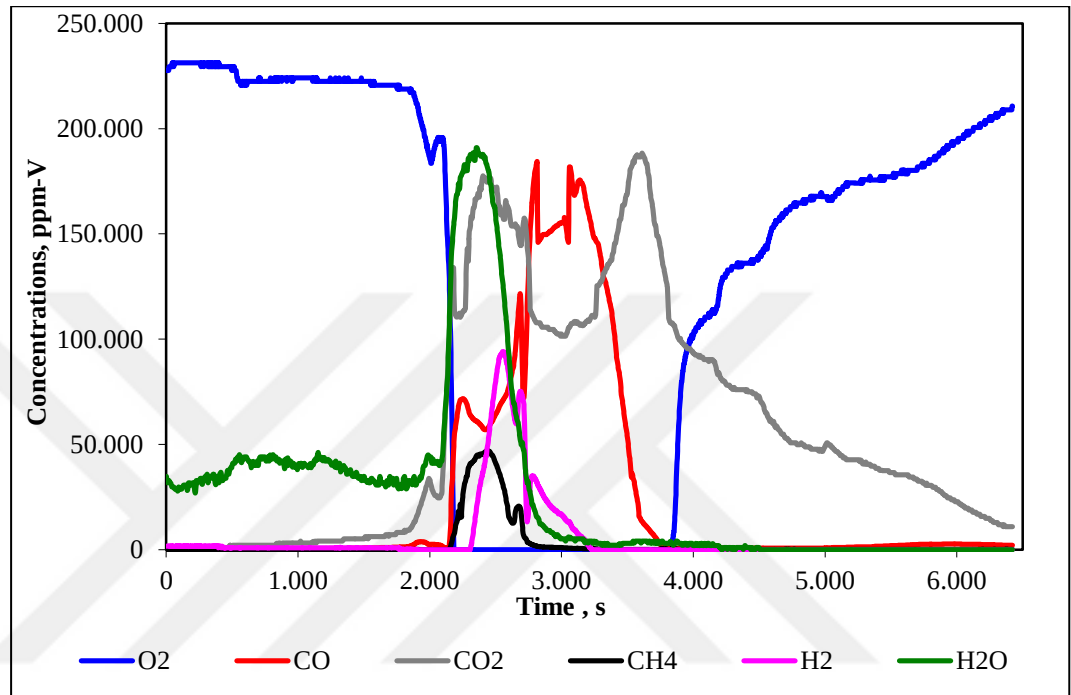


Figure 4.16. Variation of gas emissions during combustion of lignite.

In case of STC/LIG blend, the combustion time was about 6500th sec, which is the same with lignite (Figure 4.17). The main decomposition phase started at 2000th sec, which is the same with PLC. These results show that there was no additive effect in both combustion time and main decomposition starting time. The highest fuel bed temperature measured was 1095 °C. This value was approximately predicted value for blend. Less amount of hydrocarbon emissions were also observed during combustion experiments. Variation of hydrocarbon emissions during co-combustion of STC/LIG were given in Appendix 6.

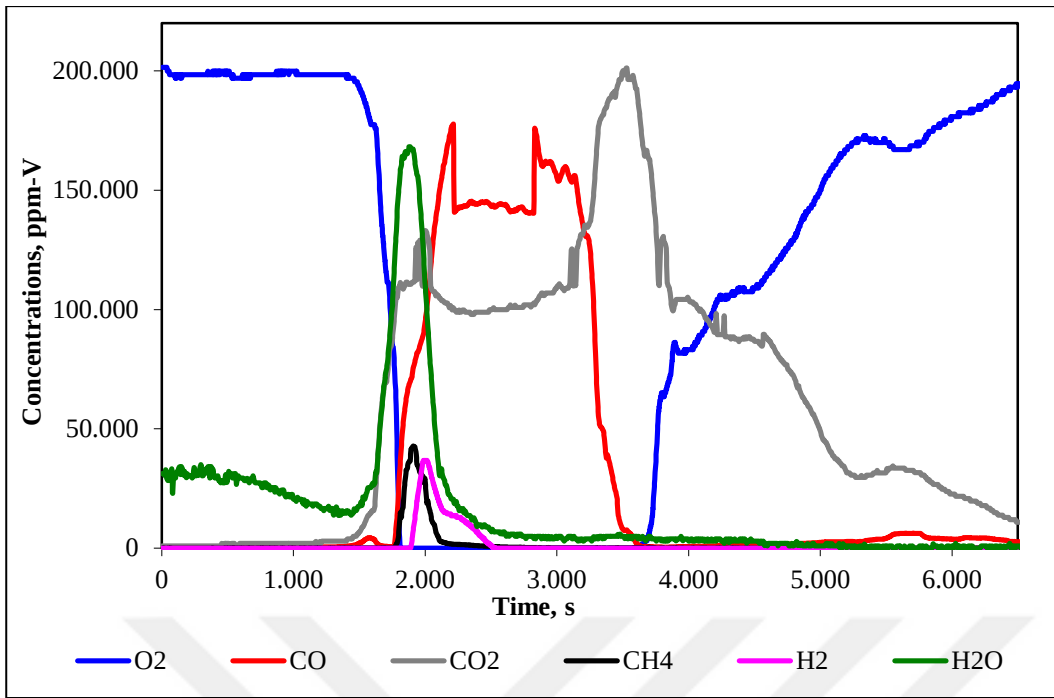


Figure 4.17. Variation of gas emissions during co-combustion of STC-LIG.

For the STC/PLC blend, the combustion time was about 4400th sec, which is the same with STC (Figure 4.18). The main decomposition phase started at 2000th sec, which is the same with PLC. This value is very late compare to single combustion of PLC, which shows that STC led to retarding in decomposition of PLC. The highest fuel bed temperature measured was 1202 °C. This temperature is very close to that in the single combustion of STC. Variations of hydrocarbon emissions during co-combustion of STC/PLC were given in Appendix 7.

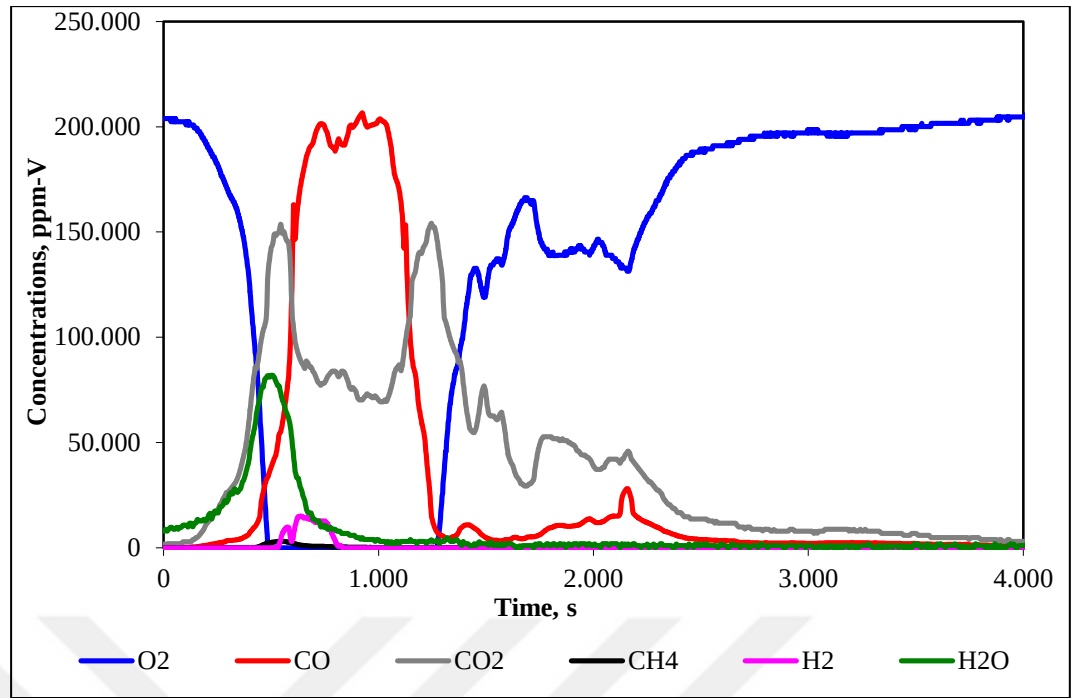


Figure 4.18. Variations of gas emissions during co-combustion of STC/PLC.

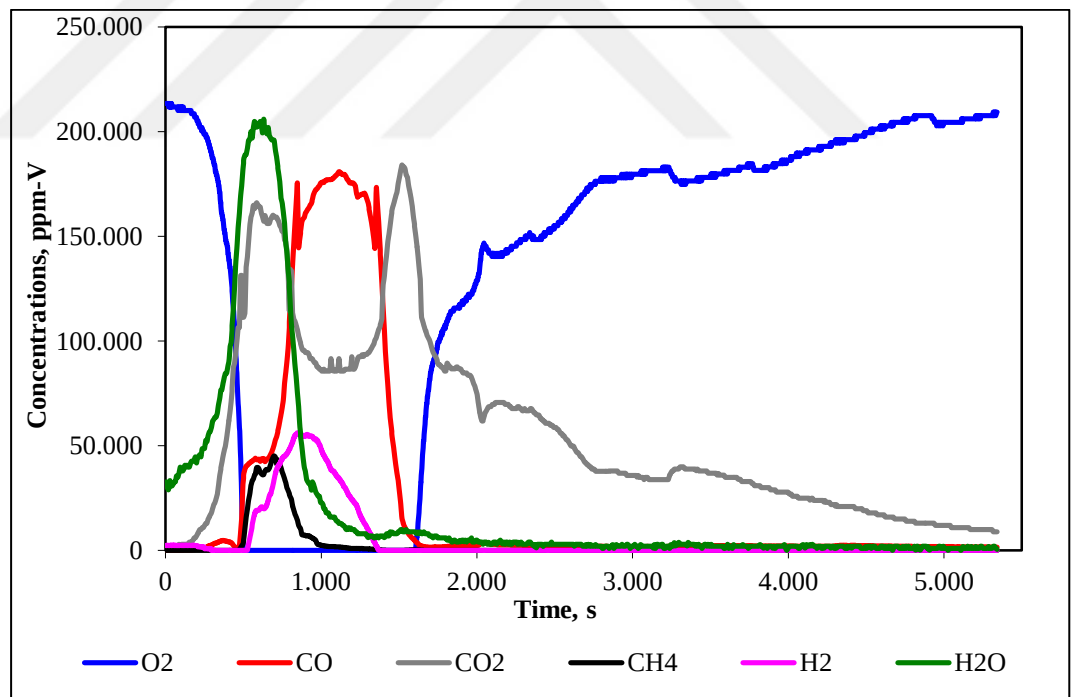


Figure 4.19. Variations of gas emissions during co-combustion of PLC/LIG.

For the PLC/LIG blend, the combustion time was about 5500th sec, which is shorter than lignite alone (Figure 4.19). The main decomposition phase started at 2000th sec, which is the same with lignite. This value is very late compare to

single combustion of PLC, which shows that lignite led to retarding in decomposition of PLC. The highest fuel bed temperature measured was 1078 °C. This temperature is higher than that in the single combustion of PLC and lignite. Variations of hydrocarbon emissions during co-combustion of PLC/LIG were given in Appendix 8.

4.3.3.3. Nitrogen gases emission

As known, nitrogen in fuel is released as NO, NO₂, HCN, NH₃ and N₂. In this study, concentrations of NH₃, HCN, N₂O in flue gas was measured using a multi-component Fourier transform infrared (FTIR) spectroscopy and concentrations of NO and NO₂ was calculated by difference (fuel N – (NH₃+HCN)). In combustion processes, the formation of NO_x (NO + NO₂) is well known, which can be formed from molecular nitrogen in the combustion air and from the fuel-N. However, it is recognized that the major source of NO_x in solid fuel combustion systems, at where temperature is below 1300 °C, is the oxidation of fuel-bound nitrogen (Jones et al., 1999). In this study, it is expected that measured NO_x came from the fuel-N, because the combustion temperatures were low for formation from molecular nitrogen in air. In combustion, the fuel N is distributed between the volatiles and the char bound nitrogen depending mainly on the fuel structure and the temperature. The inorganic species in fuel may also affect the fuel nitrogen conversion (Tchapda and Pisupati, 2014). It has been reported that the pyrolysis of nitrogen containing species in coals result in mainly HCN, while amine type functional groups (in biomass) would provide a possible source of NH₃ (Tchapda and Pisupati, 2014). Both the HCN and NH₃ compounds are oxidized further to NO_x, NH₃, can also act reducing agents similarly as in the thermal DeNO_x process (Oliva et al., 2000). More than 80 wt. % of nitrogen in fuel released as NO_x (Figure 4.20). The less than 0.3 wt. % of nitrogen in fuel was released as HCN while less than 3.6 wt. % of nitrogen in fuel was released as NH₃ (except ST and PL). But, in case of PL and ST, the conversions of N-fuel to N-NH₃ emission were 17.6 wt.% and 10.9 wt.%.

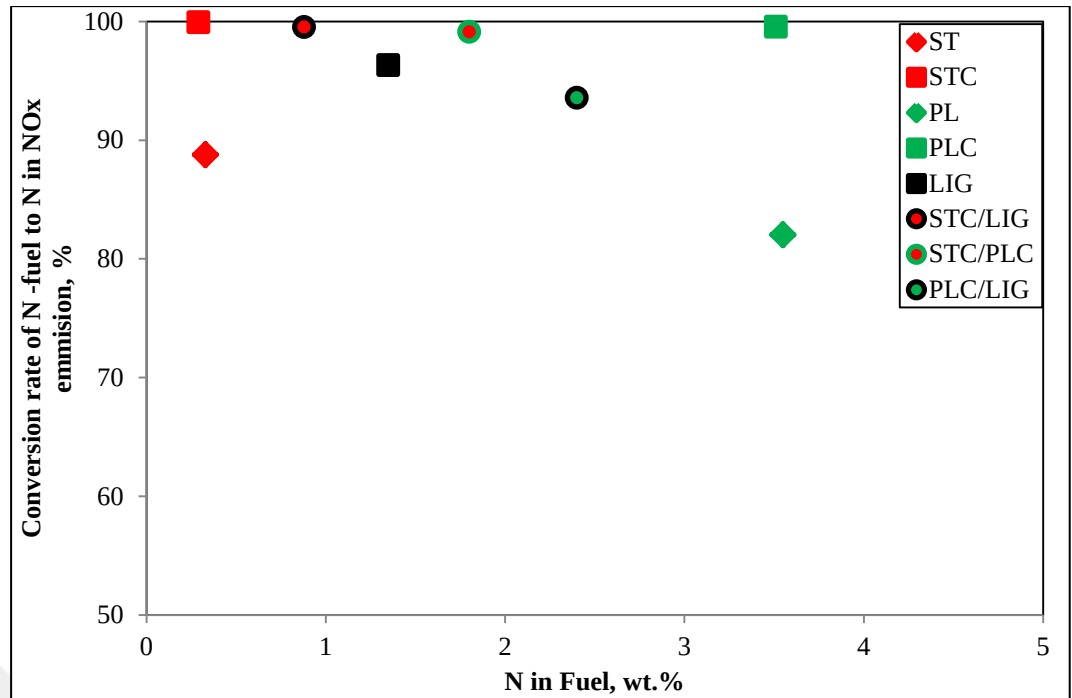


Figure 4.20. Conversion rate of N in fuel to N in NO_x dependent upon the N content of fuels.

On the other hand, there is a linear correlation between N in NO_x emissions and the N content of fuel (Figure 4.21), the NO_x emissions increase with the N content of the fuel. This result in agreement with the results found in Ref. Sommersacher et al. (2012) who investigated combustion-related problems for lignocellulosic biomasses. It is worth nothing to notice that NO_x emission from PL was lower than that from PLC, although they have similar N content. This might be due to the increasing of NO destruction reactions with NH₃ (DeNO_x process).

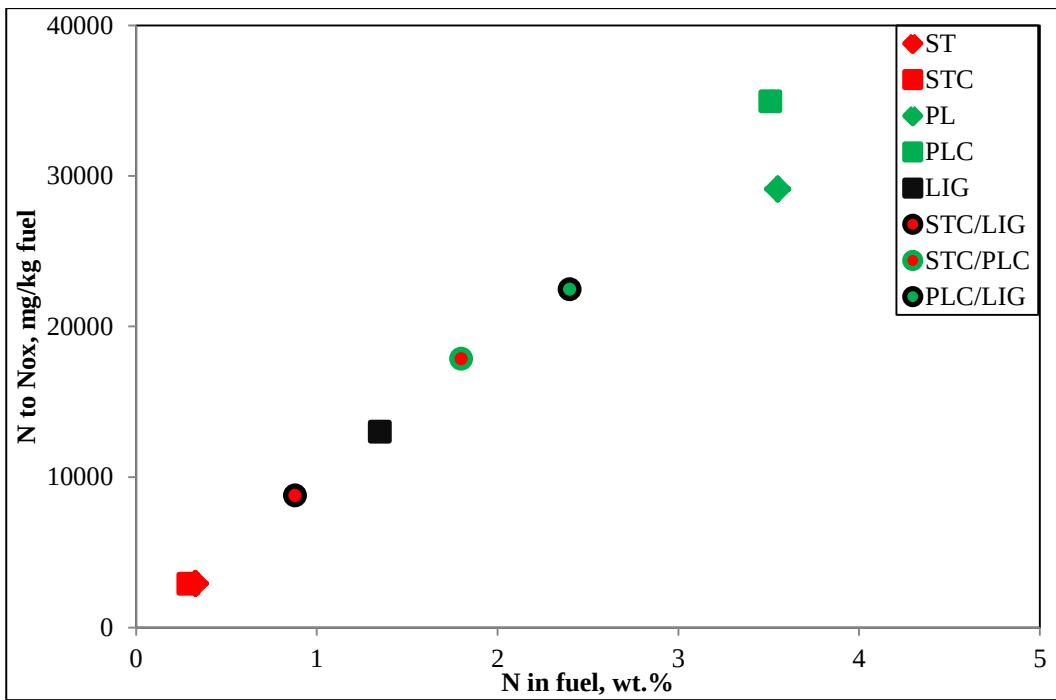


Figure 4.21. NOx emissions dependent upon the N content of fuels.

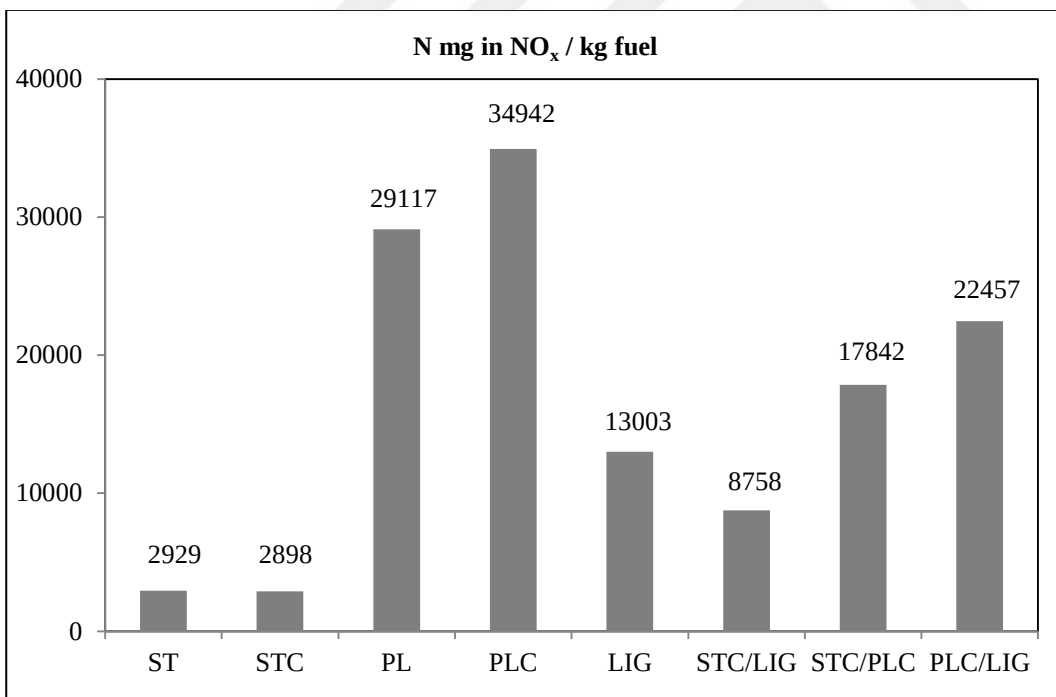


Figure 4.22. Conversion of N in 1kg fuel to N mg in NOx emission.

4.3.3.4. SO₂ emission

The SO₂ emissions from combustion depend on several parameters, such as combustor type, fuel type, combustion temperature and pressure etc. The SO₂ was mainly released during the devolatilization step; however, it was also liberated during char combustion. SO₂ (g) released during the volatilization phase likely occurred because of the oxidation of organic sulphur in the fuel (Dayton et al., 1999). The SO₂ (g) released during the char combustion phase is due to the decomposition of inorganic alkali metal sulphates at high temperatures. Total emissions of SO₂ varied significantly between the different fuels (Figure 4.23). As seen from Figure 4.23, there is no correlation between fuel sulphur and SO₂ emission. The formation of SO₂ and other S compounds in gas phases will be discussed in Section 4.3.3.5.1.

For PLC containing blends, the SO₂ releases are not proportional to the mixing ratio of the fuels and to the emissions properties of the respective fuels. The experimental SO₂ releases were much lower than the predicted ones (Table 4.4). This is in agreement with the previous studies. The co-combustion of biomass with coal can reduce the SO₂ emissions due to the alkali and alkali earth metals in biomass (Spliethoff and Hein, 1998; Nussbaumer, 2003).

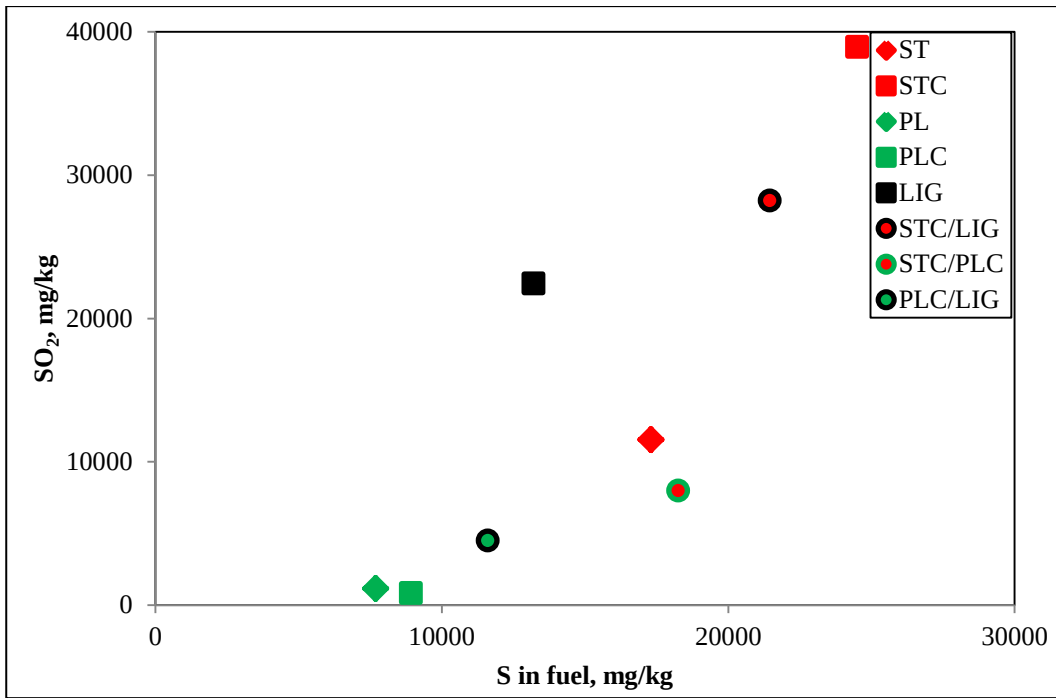


Figure 4.23. SO₂ emission versus S concentration of the fuel.

Table 4.4. Experimental and predicted SO₂ values from combustion of blends, mg /kg fuel.

	Experimental	Predicted
STC/LIG	28226	26071
STC/PLC	7995	19886
PLC/LIG	4493	7015

4.3.3.5. Aerosol emissions

Although the use of biomass as fuel offers a number of environmental and economic benefits, their use can cause serious ash-related problems, such as agglomeration, corrosion, fouling, and slagging, due to their high levels of alkali metals and Cl contents. Because of this, in most existing co-combustion power plants, the biomass can only be blended with coal at relatively low ratios to avoid the ash-related problems. The behaviour of alkali metals during combustion is well known. The K, Na, S, Cl, Zn, and Pb are semi-volatile and volatile, these elements are release to gas phase during combustion and react with each other resulting in ash-forming vapours (Sommersacher et al., 2012). These vapours are

deposited leading the ash-related operational problems. There is numerous studies on the pollutant emissions and release of alkali metals during combustion and co-combustion of biomass, especially lignocellulosic biomass (Sommersacher et al., 2012; 2013; 2015b; 2016; Li et al., 2014; Brunner et al., 2002; Vassilev et al., 2013; Kortelainen et al., 2015). The release of alkali metals depend on the temperature conditions in the fuel bed and the inorganic composition of the fuel, especially the ratios of Si/K, Cl/S, and Cl/K (Kortelainen et al., 2015).

In this section of experiments, we investigated the emission levels from combustion of ST, STC, PL, PLC, and lignite and co-combustion of STC/PLC, STC/LIG, and LIG/PLC to gain knowledge about the use of these types of fuels/fuel mixtures in small-scale boilers.

The distribution of ash-forming elements between bottom ash and fly ash was studied for Ca, Si, Mg, K, Na, Zn, Pb, S, Cl, P, Fe, Al and Ba. For each element, the amount of element in aerosol, as per mg of fuel combusted, was calculated using the data from analysis of fuel and residual ash as well as the weight of the fuel sample and the residual ash. The amount of each element in aerosol (fly ash + gas emissions) and residual ash are given in Table 4.5. The amount of elements in fuels is also given in the same table. The percentage retention on ash after combustion for the elements studied is presented in Figure 4.24. During combustion process, K, Na, Zn and Pb can be formed chlorides, sulphates, and oxides of themselves as results of reaction with Cl and/or S (Brunner et al., 2002).

As expected, the lead in the fuel was volatilized (Figure 4.24) in almost every case; the one exception was ST combustion. The 75 % of lead in fuel was retained on ash after combustion in case of ST combustion. The reason might be combustion temperature, which was the lowest temperature (870 °C) observed during combustion among others. Regarding alkali release, most part of alkali in fuel was retained on combustion residue. The inorganic components in the fuel and the temperature of fuel bed affect the release of alkali metals. As known from literature, K released to gas phase, in the form of, mainly, KOH and KCl, and minor amount as K₂SO₄ and K₂CO₃ (Joller et al., 2005; Knudsen et al., 2004).

There are two system (K-Ca-Si and K-Ca-P), which are relevant K-release from fuel to gas phase (Billen et al., 2014a). The K-release decreased when K is incorporated into silicate or phosphate structures. It has also been reported (Sommersacher et al., 2012) that when the molar Ca/Si ratio increased, CaO react with SiO_2 and K release to gas phase. On the other hand, the K release is decreased by the increasing of P content in fuel. The presence of Fe, Al, S etc. in fuel also affects the alkali release (Li et al., 2014).



Table 4.5. Inorganic contents of fuels, residues and aerosols.

		Ca	Si	Mg	K	Na	Zn	Pb	S	Cl	P	Fe	Al	Ba	Ti
ST	Fuel, mg/kg	2790	19600	281	464	485	15700	21	17300	363	171	446	550	6	348
	Residue, mg/kg fuel	2628	17387	233	464	485	13532	17	2274	63	135	446	544	6	47
	Aerosol, mg/kg fuel	162	2213	48	0	0	2168	4	15026	300	36	0	6	0	301
STC	Fuel, mg/kg	7100	46200	637	863	1210	38300	43	24500	732	320	783	1310	12	131
	Residue, mg/kg fuel	7100	46200	615	863	1117	21984	0	1870	196	320	783	1310	12	119
	Aerosol, mg/kg fuel	0	0	22	0	93	16316	43	22630	536	0	0	0	0	12
PL	Fuel, mg/kg	24700	20800	6870	31100	3360	513	0	7690	5790	12100	1080	746	29	732
	Residue, mg/kg fuel	21217	19256	5937	27101	3031	465	0	4136	4580	10591	653	704	25	38
	Aerosol, mg/kg fuel	3483	1544	933	3999	329	48	0	3554	1210	1509	427	42	4	694
PLC	Fuel, mg/kg	53500	33800	15000	70700	7880	1180	0	8920	11900	29400	1400	1410	62	89
	Residue, mg/kg fuel	51622	33800	13857	62490	7452	1180	0	8500	10751	28140	1400	1324	61	89
	Aerosol, mg/kg fuel	1878	0	1143	8210	428	0	0	420	1149	1260	0	86	1	0
LIG	Fuel, mg/kg	6920	51500	2260	4300	0	23	8	13200	62	252	7660	33400	154	910
	Residue, mg/kg fuel	5773	38524	1761	3404	0	23	0	604	20	252	6433	24189	127	717
	Aerosol, mg/kg fuel	1147	12976	499	896	0	0	8	12596	42	0	1227	9211	27	193
STC/LIG	Fuel, mg/kg	7800	39350	1609	2220	680	22313	36	21450	519	328	5145	14465	78	507
	Residue, mg/kg fuel	6135	39350	812	1537	680	14310	0	1934	9	200	4659	13537	60	318
	Aerosol, mg/kg fuel	1665	0	796	683	0	8002	36	19516	510	127	486	928	18	188
STC/PLC	Fuel, mg/kg	33895	42850	8074	31835	4085	22780	32	18250	5685	12248	2040	2130	45	196
	Residue, mg/kg fuel	26638	33950	7025	26638	3761	16401	0	11517	2379	12248	1175	1178	35	94
	Aerosol, mg/kg fuel	7257	8900	1048	5197	324	6379	32	6733	3306	0	865	952	10	102
PLC/LIG	Fuel, mg/kg	34305	43700	8835	32985	3405	493	7	11600	5334	12180	5395	15065	108	486
	Residue, mg/kg fuel	31408	40485	8835	32578	3405	493	0	6737	3985	12180	4713	14897	88	389
	Aerosol, mg/kg fuel	2897	3215	0	407	0	0	7	4863	1349	0	682	168	19	96

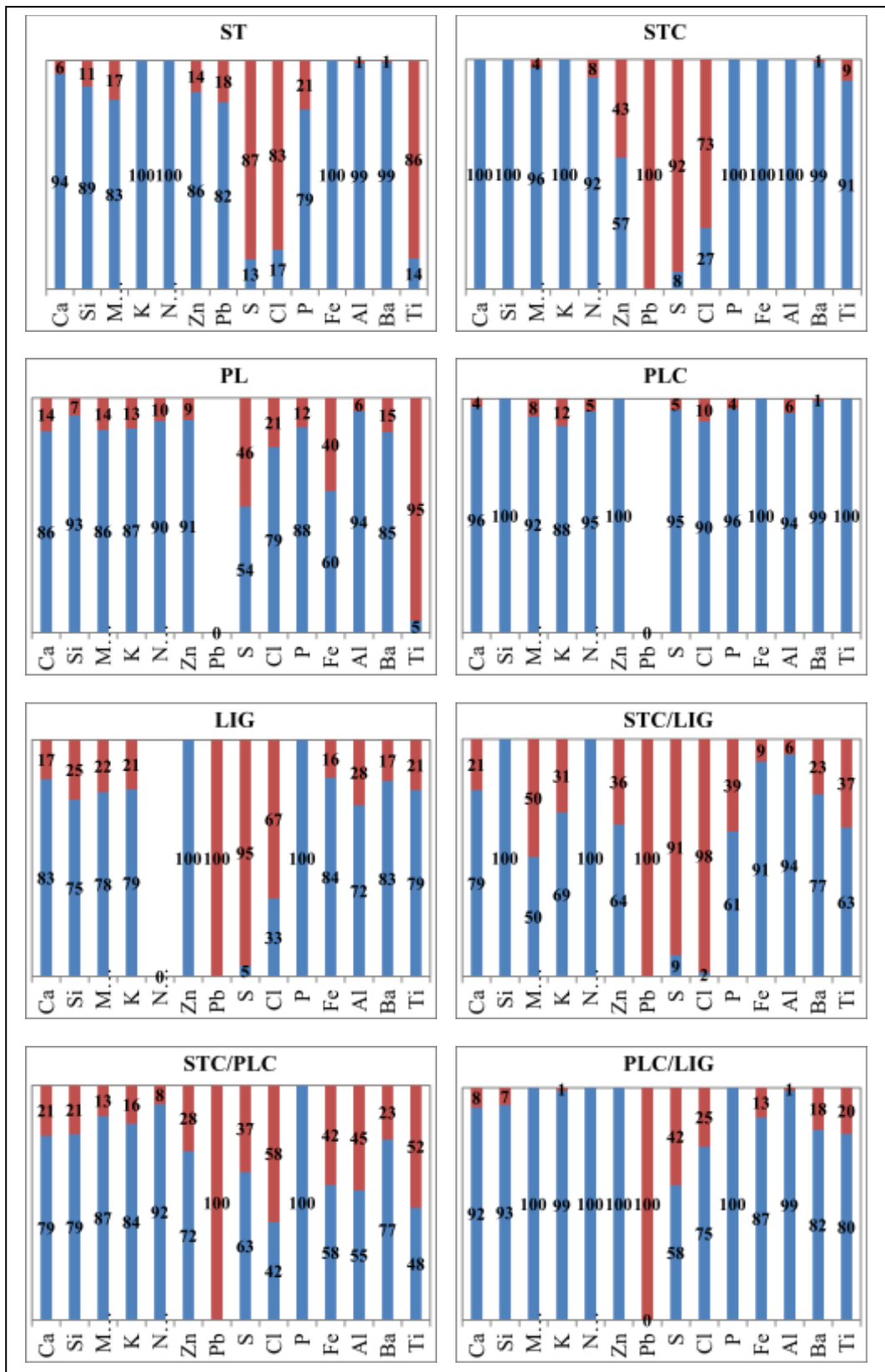


Figure 4.24. Percent distribution of elements in aerosol (■) and in residue (■).

Release of S to the gas phase.

The sulphur in fuel is released not only as SO_2 , also alkali sulphates which are risk for heat exchanger fouling and corrosion problems. For the fuels tested in this study (except PLC and PLC containing blend), the amount of S release shows a correlation with amount of S in fuel.

In case of PLC, although it had higher sulphur amount than PL, the S release during combustion of PLC was lower than S release from PL. The reason may be that the calcium and phosphor contents of PLC were higher than that of PL. It was reported that a total of 20-25 % of the calcium in the fuel remained in bottom ash, as CaSO_4 during combustion of bark and pulp and paper mill sludge in a pilot-scale circulating fluidized bed reactor (Lind et al., 2006). For the PLC containing blends (PLC/LIG and PLC/PTC), the S release is not proportional to the mixing ratio of the fuels. The experimental sulphur releases were lower than the predicted ones (Table 4.6). This is possible reason is that the SO_2 released during the combustion of lignite and the Ca in PLC binds to form non-volatile CaSO_4 . In contrast to PLC containing blend, for STC/LIG, the experimental sulphur releases were slightly lower than the predicted ones (Table 4.6).

Table 4.6. The amount of sulphur release during co-combustion, mg/ kg fuel.

	experimental	predicted
STC/LIG	19516	20063
STC/PLC	6733	11525
PLC/LIG	4863	6508

Linear correlation between S release and S concentration of fuels with the exception of PLC and PLC blends can be seen clearly from the Figure 4.25. The reason of the non linear correlation for these fuels could be the CaSO_4 formation which was also mentioned above.

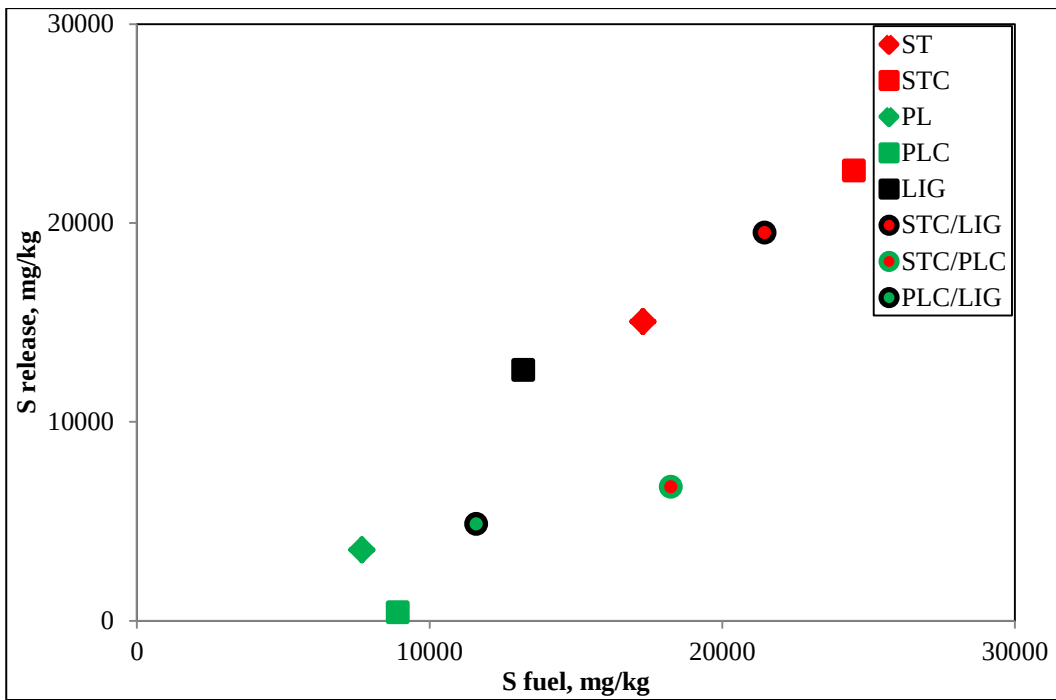


Figure 4.25. S concentration of the fuel versus S release to the gas phase.

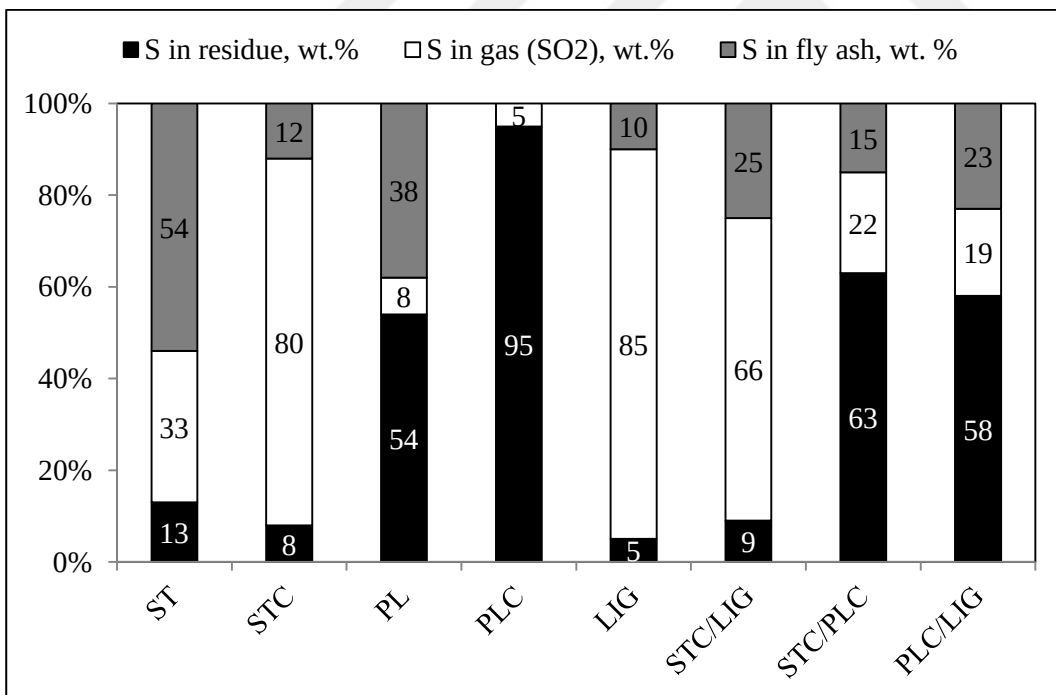


Figure 4.26. Distribution of sulphur in fuels into residue, fly ash and gas as SO₂.

Distribution of sulphur in fuels into residue, SO_2 gas and aerosol is given in Figure 4.26. For STC, Lignite and STC/LIG, most of sulphur in fuel released as SO_2 . Not surprisingly, 85 % of fuel S was released as SO_2 during combustion of lignite. It is worth nothing that the main part of S released appeared in aerosol for ST, whereas the S released mainly as SO_2 in case of STC. Probably reason is the form of S in fuel. Thus, S in ST present in the form of organic sulphur compounds while some part of sulphur in STC present as ZnS .

Release of Cl to the gas phase.

The release of Cl species in fuel during combustion, mainly alkali chloride, HCl , and or fine alkali metal chloride, is concerned for aerosol formation and corrosion risk. (Muller et al., 2006; Brunner et al., 2002; Christensen and Livbjerg, 1996; Knudsen et al., 2004). The earlier studies showed that amount of Cl release was related to Cl content in fuel. In contrast, there is no linear correlation between Cl release and fuel Cl in this study (Figure 4.27).

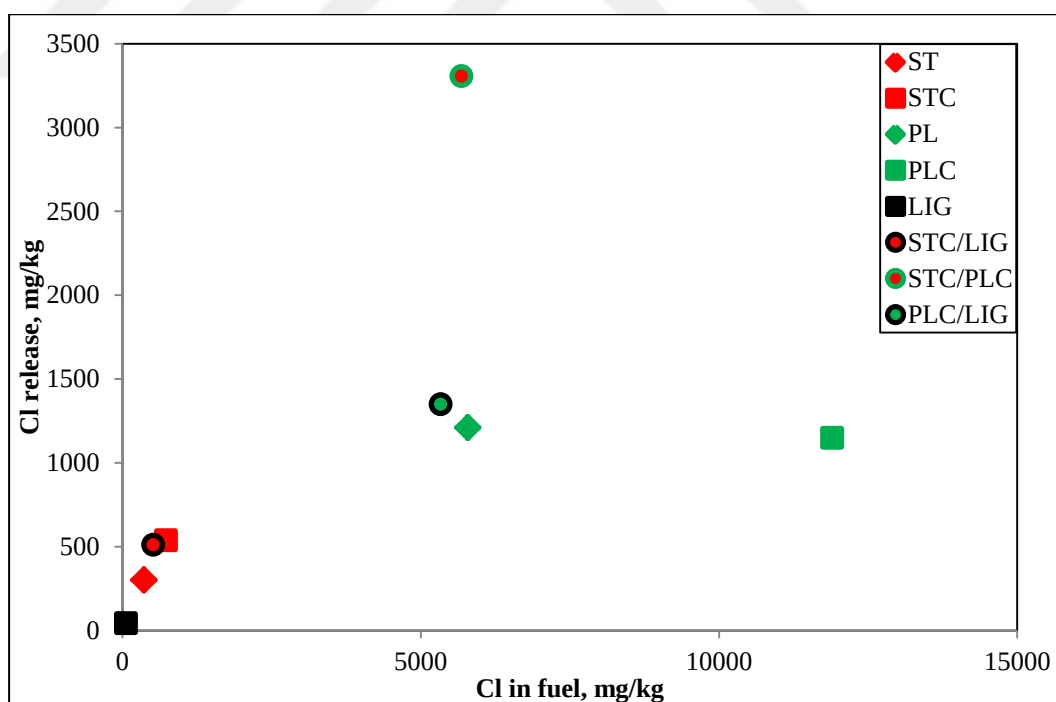


Figure 4.27. Cl concentration of the fuel versus Cl release to the gas phase.

This shows that the Cl release strongly depend upon other inorganic constituents in fuels. Cl release was very low for PL, PLC and PLC containing

blends; approximately 21 % for PL, 10 % for PLC, 25 % for PLC/LIG and 58 % for STC/PLC. By considering high P content in these fuels, it can be speculated that phosphorus may enhance Cl retaining in the ash.

4.3.3.6. Fuel indexes: Evaluation of combustion properties of fuels

The ash composition in fuel provides to predict the combustion related problems. In this study, the combustion properties of fuels tested were evaluated by using of some fuel indexes for lab- scale combustion system. The definition and evaluation of these fuel indexes have been discussed in a previous papers (Sommersacher et al., 2012; 2015a). The fuel index results obtained from lab-scale combustion system can be used for grate combustion plants.

Effect of molar Si/K ratio on the K release.

The molar Si/K Ratio in fuel is an indicator for the K release, the high ratio decreases K release due to the formation of potassium silicates (Knudsen et al., 2004). But, figure 4.28 shows that no linear correlation between K release and the Si/K ratio. For example, although Si/K ratio for lignite was much higher than that for PL and PLC, K release was higher. The reason was high P in PL and PLC, leading to formation of potassium phosphates which are present in the bottom ash. For PLC/LIG, compared with the predicted K release, the release of K was much less. This might be that due to reactions of lignite K with PLC P. More interestingly, the highest K release was observed for combustion of STC/LIG which have high Si/K ratio and low P amount in fuel. The possible explanation might be the fact that formation of calcium silicates instead of potassium calcium silicates due to the high Ca/Si ratio (Sommersacher et al., 2012). On the other hand, Ca and Mg have a priority on binding with Si compare to K, by that way, K release may be increased with increasing amount of Ca and Mg (Risnes et al., 2003).

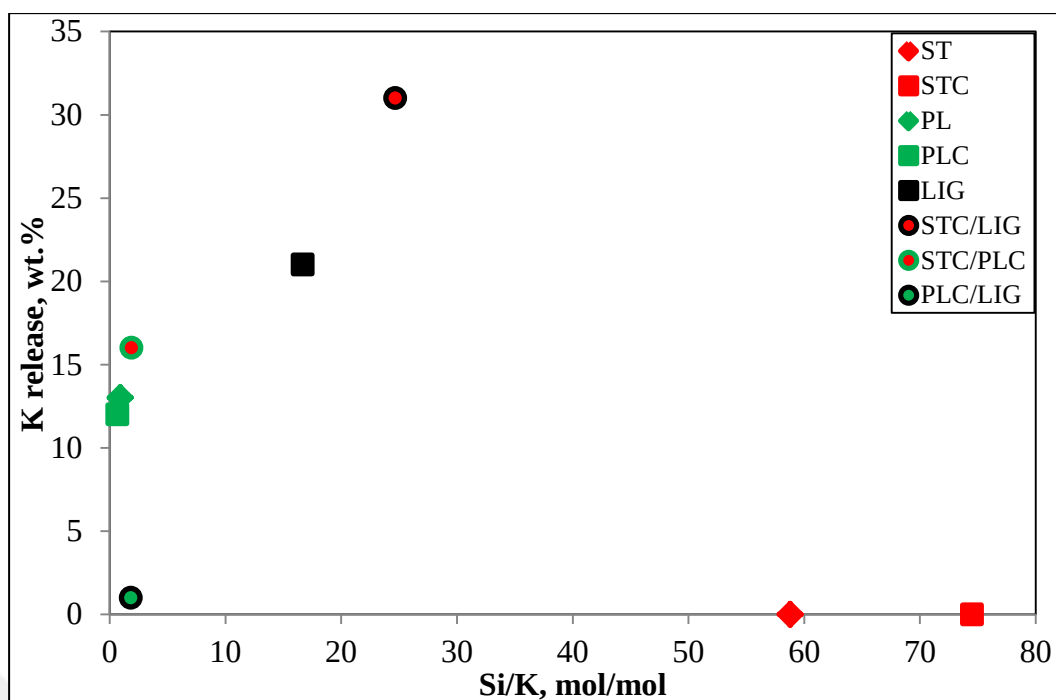


Figure 4.28. Molar Si/K ratio versus K release for wastes.

Molar 2S/Cl ratio as an indicator for high temperature corrosion risks.

The presence of chlorine in a biomass fuel tends to enhance the vaporization of alkali metals as chlorides and HCl and increases corrosion risk. Although several different corrosion mechanisms have been suggested in the literature, three mechanisms are proper for biomass combustion units (Sommersacheret al., 2012): 1) the direct attack of gaseous HCl or Cl₂ to metal surface and form volatile metal chlorides, 2) the alkali sulphate and/or alkali chloride melt formed dissolve the protecting oxide layer on the heat exchanger surface, 3) the attack of Cl released by the sulphation of alkali metal or heavy metal chlorides to the heat exchanger surface, called as active oxidation. Generally, high temperature corrosion in boilers can be explained “active oxidation” mechanism.

Chlorine content in the fuel affects volatilization behaviour of alkalis and certain heavy metals. Hence, increasing chlorine content in the fuel is expected to increase aerosol concentration. Sulphur in fuel released as SO₂ and alkali sulphates. In addition, alkali metal sulphates are formed from gas phase compounds by the sulphation of alkali metal/or heavy metal chlorides. Sulphation

reaction is slower but is still significant in deposits (Lind et al., 2006). Therefore, the 2S/Cl ratio in the fuel is considered as an indicator for high-temperature corrosion risk (Sommersacher et al., 2012). Molar ratios of the 2S/Cl in fuels used versus aerosol emissions were given in Figure 4.29.

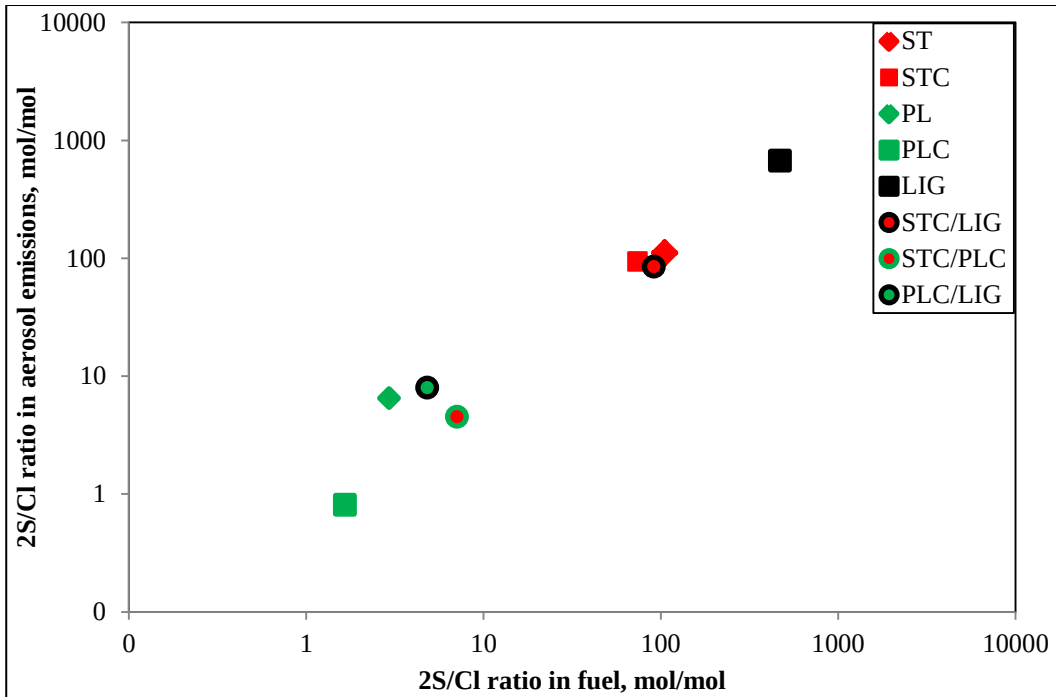


Figure 4.29. Molar ratios of the 2S/Cl between fuel and aerosol emissions for the combustion and co-combustion reactions.

As seen Figure 4.29, there is a correlation between the 2S/Cl ratios in fuel and aerosol. High 2S/Cl ratios shows the presence of the protective sulphate layer on the heat exchanger surface. It is suggested that the 2S/Cl has to be at least 8 for negligible chlorine levels in deposits on the heat exchanger surface. If 2S/Cl ratios is greater than 4 but less than 8, minor corrosion risks is expected. Figure 4.29 shows that STC/PLC and PLC/LIG show minor corrosion risk while lignite, ST, STC and STC/LIG show negligible risk of high temperature Cl. But risks of high temperature Cl are high for PL and PLC.

Molar (K + Na)/[x(2S + Cl)] ratio.

Molar (K + Na)/[x(2S + Cl)] Ratio can be used for the prediction of the SO_x and HCl emissions. Sulphates and chlorides of Mg and Ca can be formed as well

as formation of alkaline sulphates and chlorides. Cl and S give a reaction with these elements in the gaseous phase which they are in the form of SO_x and HCl.

In the molar $(\text{K}+\text{Na})/[\text{x}(2\text{S}+\text{Cl})]$ ratio, the x factor is described as the average of K and Na release rates in relation to average of S and Cl release rates. The molar ratio of $(\text{K}+\text{Na})/[\text{x}(2\text{S}+\text{Cl})] > 1$ shows that released alkaline metals are surplus. The prediction for the value > 1 has to be very small amount HCl and SO_x emissions as a result of S and Cl bounding in the ash. If the value is < 1 , high amount of HCl and SO_x emissions are to be predicted.

SO_x conversion was decreased by the increasing molar ratio of $(\text{K}+\text{Na})/[\text{x}(2\text{S}+\text{Cl})]$ which can be seen from figure 4.30. Because of the high K content, decreasing of the SO_x conversion was expected for the PLC blends. A less amount of decreasing was occurred compare to envisaged amount.

Conversion of Cl in fuel to HCl emissions are given in the figure 4.31 for each fuels. Cl conversion was significantly decreased by the presence of the PLC in blends which can be clearly seen from figure 4.31. On the other hand, there is no linear correlation between Cl conversion and molar $(\text{K} + \text{Na})/[\text{x}(2\text{S} + \text{Cl})]$ ratio.

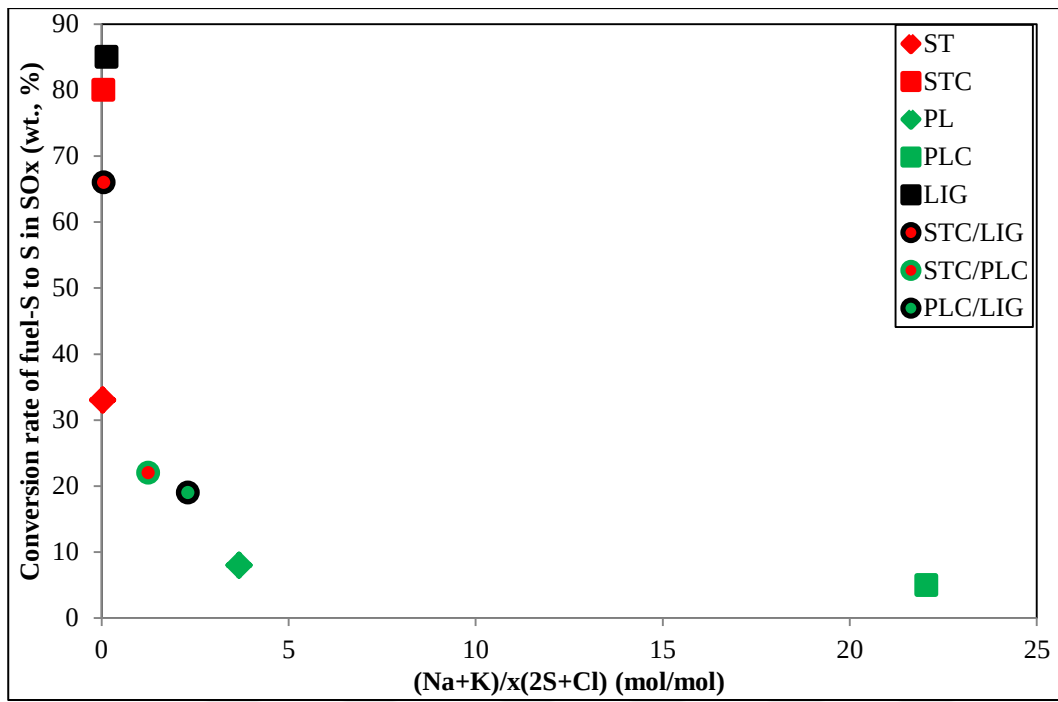


Figure 4.30. The effect of $(\text{K}+\text{Na})/[\text{x}(2\text{S}+\text{Cl})]$ ratio on the conversion of S fuel to SO_x .

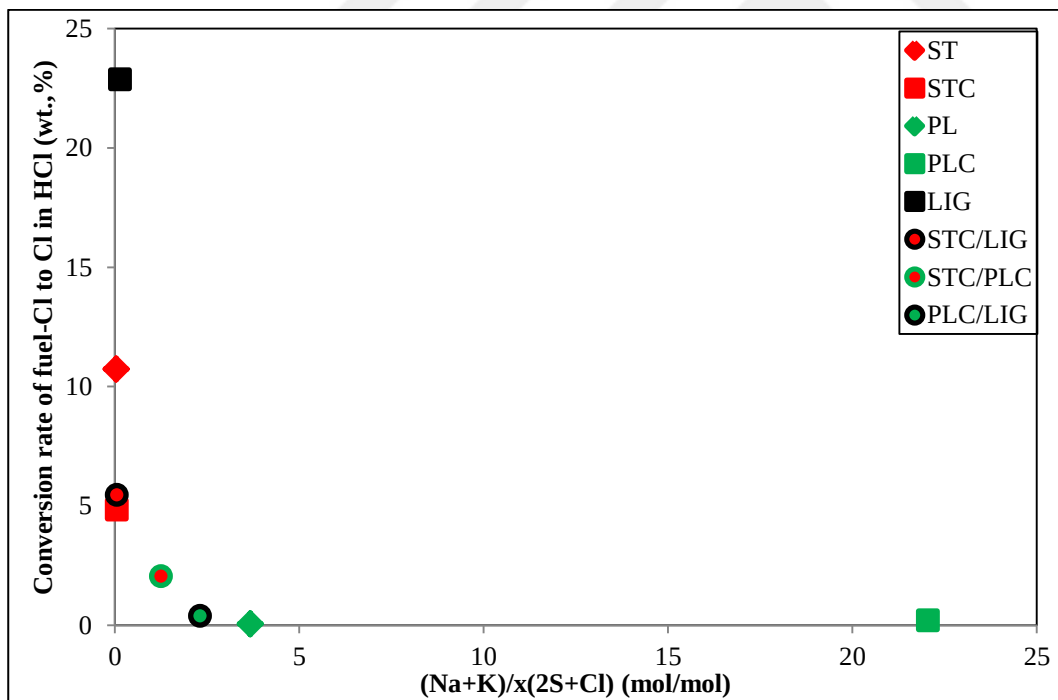


Figure 4.31. The effect of $(\text{K}+\text{Na})/[\text{x}(2\text{S}+\text{Cl})]$ ratio on the conversion of Cl fuel to HCl.

Fuel index for the prediction of slagging problem

Slagging is one of the most common causes for poor performance in coal fired boilers. The main contributions to slagging come from the inorganic material in the fuel, depending on ash melting. For coals, engineering indices, which are accepted as an industrial standard, are used as a guideline for the characterization of ash slagging (McLennan, 2000). One of them is based on the bulk ash chemistry, the ratio of basic to acidic oxides in ash; $(\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}) * \text{S} / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)$ Index I. S is % sulphur in dry coal. The slagging potential of fuel decreases with decreasing of below ratio.

This index must be upgraded for biomass fuels, because biomass has variable chemical and phase-mineral composition and these characteristics differ significantly in comparison with those of coal. Behaviour of inorganic matter during biomass combustion has been well reviewed by Vassilev et al. (2013). K, Si, Ca and Mg play significant role the slagging tendency in the bottom ash. The increase in the molar $\text{Si}/(\text{Ca} + \text{Mg})$ ratio, Index II, in fuel decreases the ash-melting (sintering) temperature.

Sommersacher et al. (2012) postulated a fuel index (molar $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg})$) to predict the sintering behaviour for P- and K-rich fuel. They found a linear correlation given between the molar $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg})$ ratio, Index III, and the ash-sintering temperature. The decrease in molar $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg})$ ratio increases the ash-melting (sintering) temperature.

In this study, we tested different type of fuels; coal, coal like waste and biomass. Because of this, we used different slagging indices. The results are presented in Table 4.7. For ST, LIG, STC and STC/LIG, the $(\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{K}_2\text{O} + \text{Na}_2\text{O}) * \text{S} / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2)$ ratio was used. The other indices gave irrelevant result, as expected, for them. PLC and PLC containing blends, the molar $\text{Si}/(\text{Ca} + \text{Mg})$ ratio and the molar $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg})$ gave different result. By considering the high P and K contents in fuel, we accepted the value of $(\text{Si} + \text{P} + \text{K})/(\text{Ca} + \text{Mg})$ ratio to predict the sintering behaviour. From the data in Ref. Sommersacher et al. 2012 and 2013, we may speculate that the ash

melting temperatures for PL, PLC and PLC containing blends are higher than 1000 °C.

Table 4.7. The molar ratios of (Si)/(Ca+Mg) and (Si+P+K)/(Ca+Mg) in fuels.

	ST	STC	PL	PLC	LIG	STC/ LIG	STC/ PLC	PLC/ LIG
Si/(Ca+Mg)	-	-	0.82	0.62	-	-	1.30	1.28
(Si+P+K)/(Ca+Mg)	-	-	2.14	2.03	-	-	2.32	2.29
(Fe₂O₃+CaO+MgO+K₂O+Na₂O)*S/ (SiO₂+Al₂O₃+TiO₂)	0.31	0.44	-	-	0.25	0.54	2.89	1.28

From the data obtained, we can say that ST, STC and STC/LIG have low slagging potential (McLennan et al., 2000). For the PLC containing blends, Index I calculated is also given in Table 4.7. According to Index I, STC/PLC is seen to have high slagging potential whereas PLC/LIG has medium slagging potential.

4.4. Conclusions

In this section of the thesis, combustion behaviours of the scrap tyre, scrap tyre char (STC) and their blends with coal (LIG) and poultry litter were investigated by using TGA analyzer and lab-scale reactor. Combustion properties such as ignition temperature (IT), burnout temperature (BT), peak temperature (T_{max}), maximum combustion rate, reactivity, volatilization and char oxidation step were determined by using TGA while the emissions released from combustion process and its relation with ash composition of wastes were investigated by using lab-scale reactor system.

Due to the high volatile contents, IT, T_{max} , BT of poultry litter and scrap tyre were found to be lower than that of their chars. STC had the lowest reactivity compare to other fuels. It is interestingly, BT could not be detected for STC since the combustion did not complete due to its ash composition with high degradation temperatures (over 1200 °C). However, for STC/LIG blend, BT temperature was found to be detectable in contrast to combustion of STC alone and IT of the blend was observed as higher than that of lignite while lower than that of STC alone.

The interactions between lignite and chars (STC and PLC) were observed, the addition of chars caused to decrease in the reactivity of lignite.

From the point of mass loss rates during combustion in lab-scale reactor, no synergic effect was observed for lignite and STC blend. However, for lignite and STC blend and PLC/STC blend, the synergic effect was observed due to the alkali metals in PLC, which catalyse the combustion of lignite and STC.

For all fuel, the hydrocarbon gasses in flue gas were in small quantities and consisted mostly of CH_4 . More than 90 wt. % of nitrogen in fuel (except ST and PL) released as NO_x . The minor amounts of NH_3 and also HCN were also detected in flue gasses. There was a correlation between the NO_x emissions and fuel-N. NO_x emissions increased with the N content of the fuel. There was no correlation between fuel sulphur and SO_2 emission. For PLC containing blends, the SO_2 emissions were much lower than the predicted ones.

Regarding the aerosol emissions (ash-forming vapours), the lead in the fuels (except ST) was almost volatilized. In case of ST combustion, the 75 % of lead in fuel was retained on ash. The most part of alkali in fuel was retained on combustion residue, whereas most of chlorine (except STC/PLC blend) was volatilized.

Based on the fuel index, following results were derived; ST, STC and STC/LIG had low slagging potential and PLC/LIG has medium slagging potential, but STC/PLC had high slagging potential.

5. CONCLUSION

The main objective of this study is conversion of hazardous wastes such as scrap car tyre, scrap truck tyre, bilge water and oily sludge into economic and environmental friendly products. For this purpose, in the first experimental section, namely "pyrolysis of scrap tyres and oily wastes", pyrolysis and co-pyrolysis processes of these wastes were carried out and products obtained from these processes were investigated comprehensively. Then, in the second experimental section, namely "activation of the char", activation of the char obtained from scrap car tyre were studied with the aim of investigation of utilization area of the char as active carbon. At the last experimental section, namely "Characteristics and synergistic effects of co-combustion of char derived scrap tyre with coal and carbonaceous waste", co-combustion experiments of chars and coal were carried out. In this part of thesis, char of poultry litter was used as carbonaceous material and the effect of this char on the combustion characteristics of coal and char obtained from scrap tyre was investigated.

In first experimental section, pyrolysis of scrap tyres, oily wastes and their blends were carried out. From the point of yield and composition of pyrolytic oil and process economy, optimum temperature was selected as 500 °C. The yield of pyrolytic oils obtained from TT, CT, OS and BW were found to be 49.0 %, 45.8 %, 70.4 % and 89.7 % respectively. These oils consisted of mainly paraffinic hydrocarbons, 61 % for CT, 49 % for TT, and over 80% for pyrolytic oils obtained from oily wastes. The metal content of oily wastes feedstock (< 0.3 ppm) were retained in their chars. The amounts of char obtained from oily wastes are less than 2 % while chars obtained from TT and CT were found to be 38.0 % and 40.9 %, respectively. Although the calorific value of chars obtained from scrap tyres were similar to high quality coal, their sulphur contents were high (2.5-2.9 wt %). In addition to limited combustion due to high sulphur content, high ash content limits their use as carbon black, required a demineralization process. Co-pyrolysis experiments were carried out with the blends of CT/OS, TT/OS and CT/BW. The anti-synergic effect on oil yields obtained from co-pyrolysis of CT/OS was observed. In the case of co-pyrolysis of CT/BW, the addition of BW into blends led to reduction of the aromatic content while it led to increasing of

the paraffinic content. Co-pyrolytic oils obtained from TT: oily waste blend found to be significantly lower than that of TT pyrolytic oil.

According to result from this part of thesis is that pyrolytic gases and pyrolytic oils obtained from both pyrolysis and co-pyrolysis had high calorific value. But differently from pyrolytic gasses, pyrolytic oils should be upgraded before used as fuel.

In the second experimental section, activation of the char derived from scrap car tyre was carried out by using chemical activation, physical activation and cyclic activation methods. From the point of improvement of surface characteristic, physical activation of char with CO₂ was found to be more promising compare to other activation methods.

In the third experimental section, combustion behaviours of the scrap tyre, scrap tyre char and their blends with coal and poultry litter char were investigated by using TGA analyzer and lab-scale reactor. Furthermore, the effect of ash composition of feedstocks on the ash related problems and released emissions were investigated. According to TGA results, combustion behaviour of STC such as IT, BT and reactivity showed improvement by the co-combustion process. In contrast to this, the addition of chars (STC and PLC) caused to decrease in the reactivity of lignite. In case of lab-scale reactor results, the alkali metal composition of the PLC showed catalytic effect on combustion behaviour of STC and LIG. And the most part of alkali in fuels was retained on combustion residue, whereas most of chlorine (except STC/PLC blend) was volatilized. The decreasing of SO_x emissions with addition of PLC into blends were observed. As expected, during the combustion of all fuels (except ST and PL), the N composition of fuels were mainly released as NO_x emissions. Additionally, the release of NO_x emissions were increased with the increase in N amount of fuels. According to ash composition of fuels; ST, STC, STC/LIG had low, PLC/LIG had medium and STC/PLC had high slagging potential.

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APPENDIX

Appendix1. Variation of hydrocarbon emissions during combustion of ST.

Appendix 2. Variation of hydrocarbon emissions during combustion of STC.

Appendix 3. Variation of hydrocarbon emissions during combustion of PL.

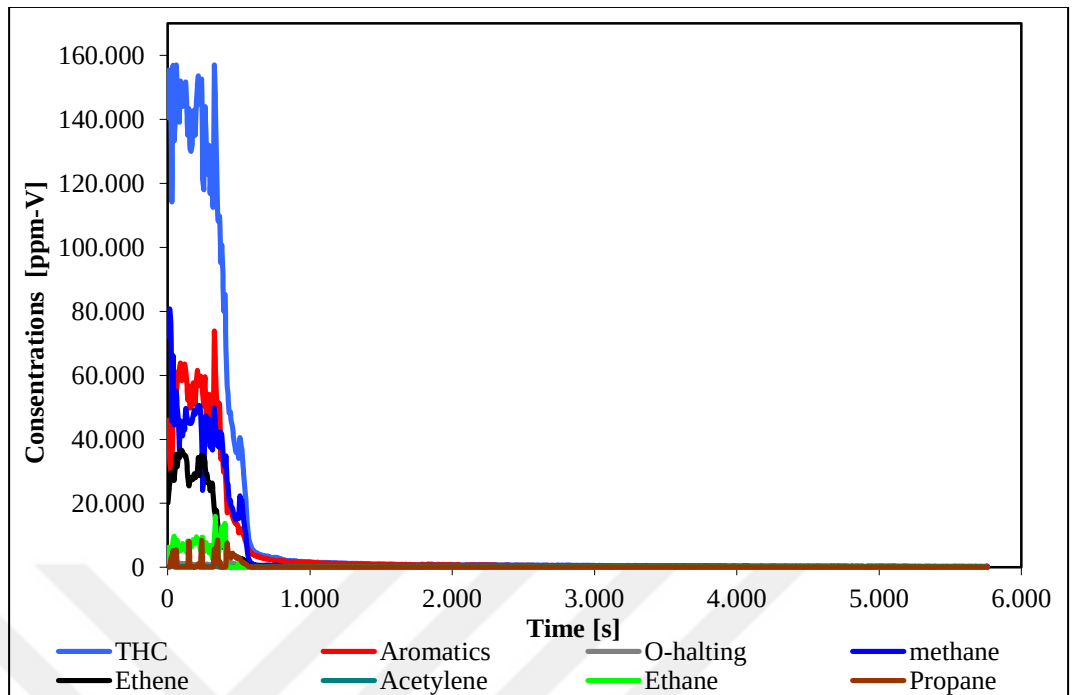
Appendix 4. Variation of hydrocarbon emissions during combustion of PLC.

Appendix 5. Variation of hydrocarbon emissions during combustion of lignite

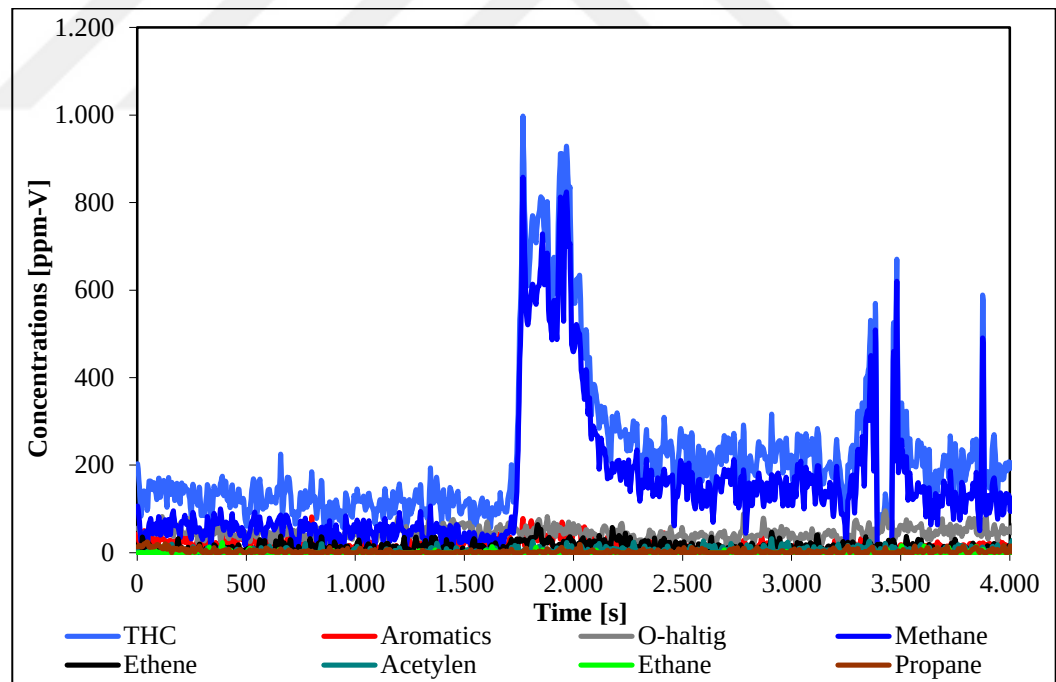
Appendix 6. Variation of hydrocarbon emissions during co-combustion of STC-LIG

Appendix 7. Variation of hydrocarbon emissions during co-combustion of STC-PLC

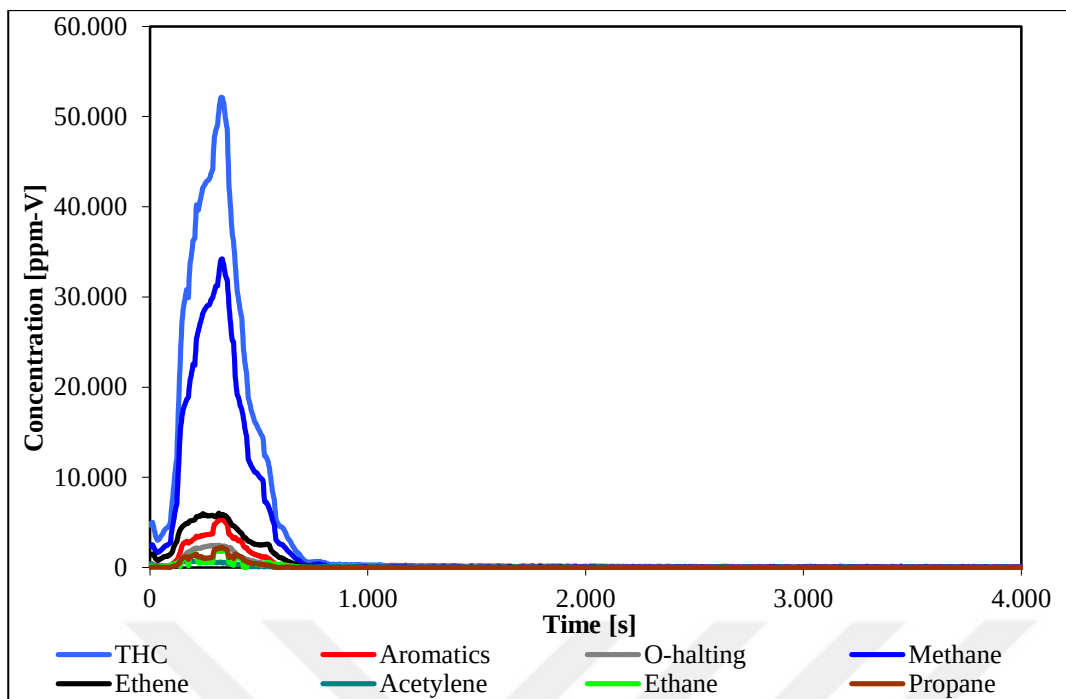
Appendix 8. Variation of hydrocarbon emissions during co-combustion of PLC-LIG.



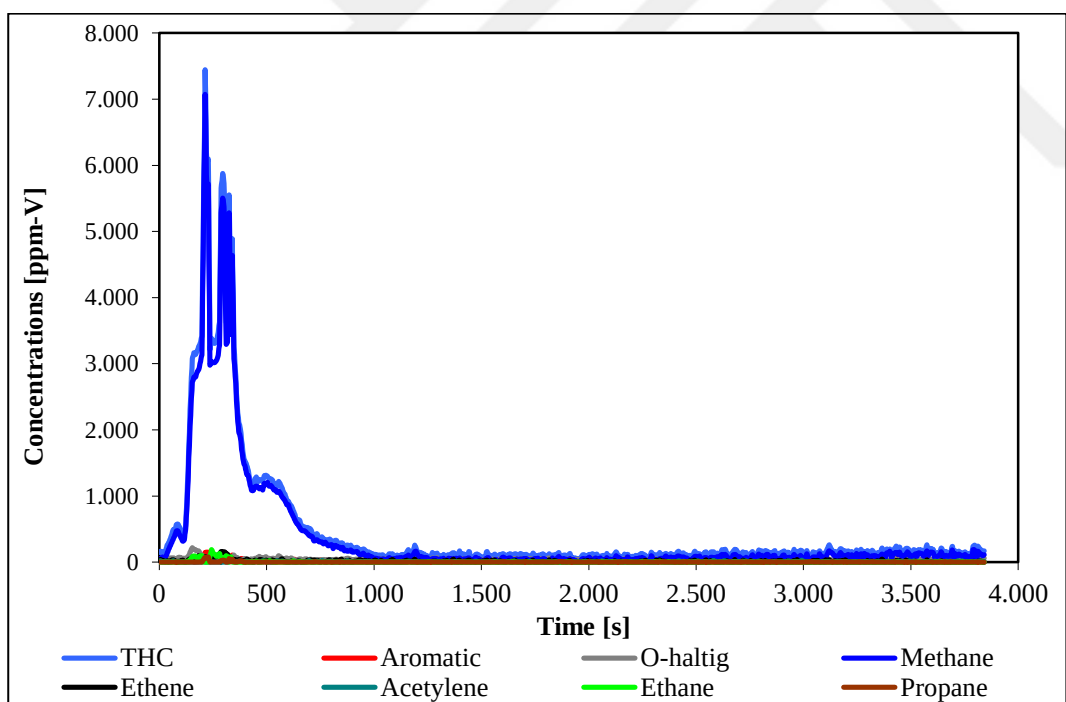
Appendix1. Variation of hydrocarbon emissions during combustion of ST.



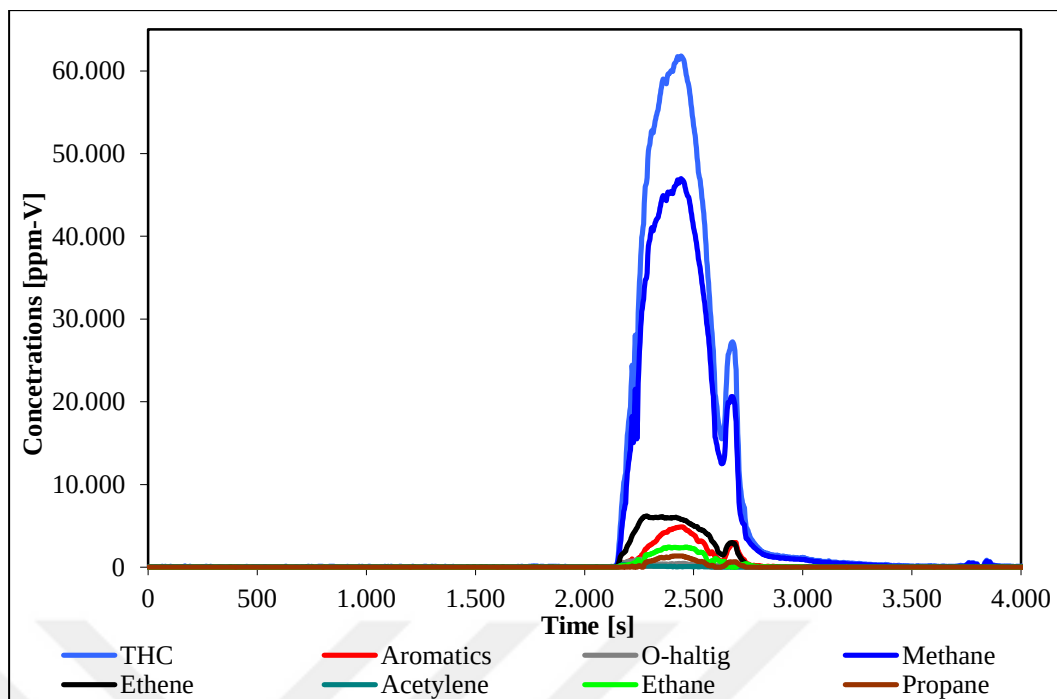
Appendix 2. Variation of hydrocarbon emissions during combustion of STC.



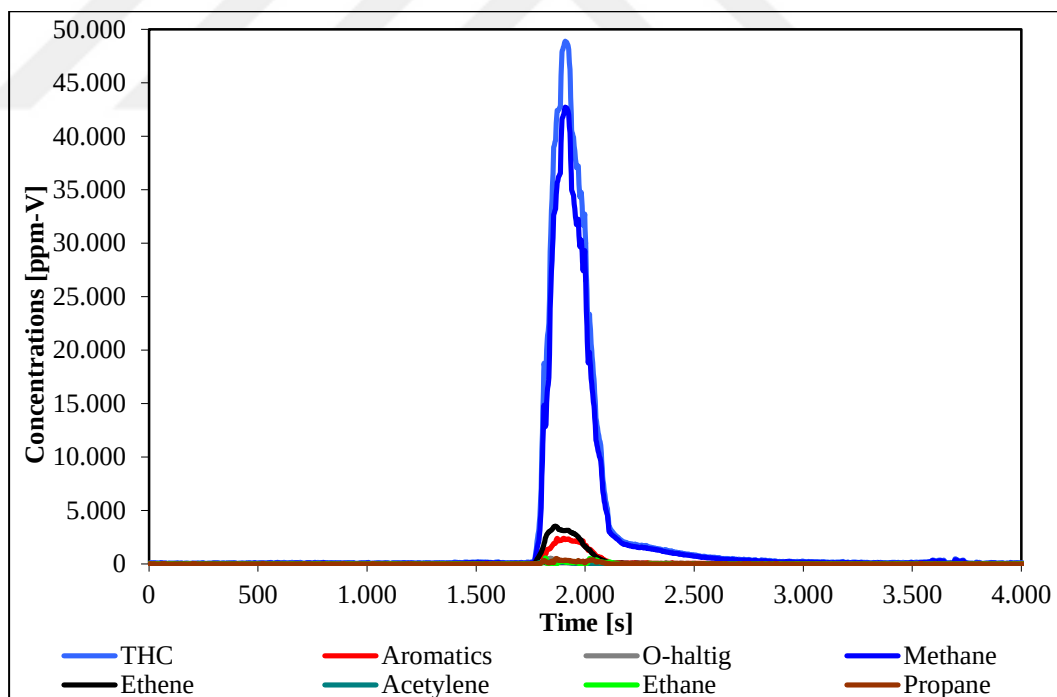
Appendix 3. Variation of hydrocarbon emissions during combustion of PL.



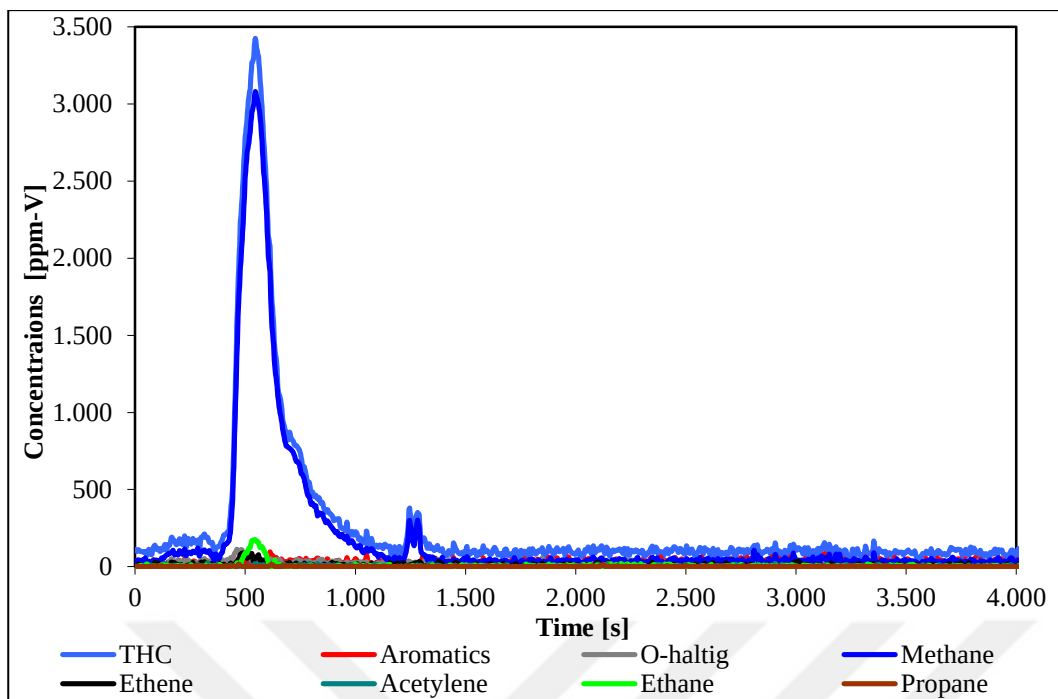
Appendix 4. Variation of hydrocarbon emissions during combustion of PLC.



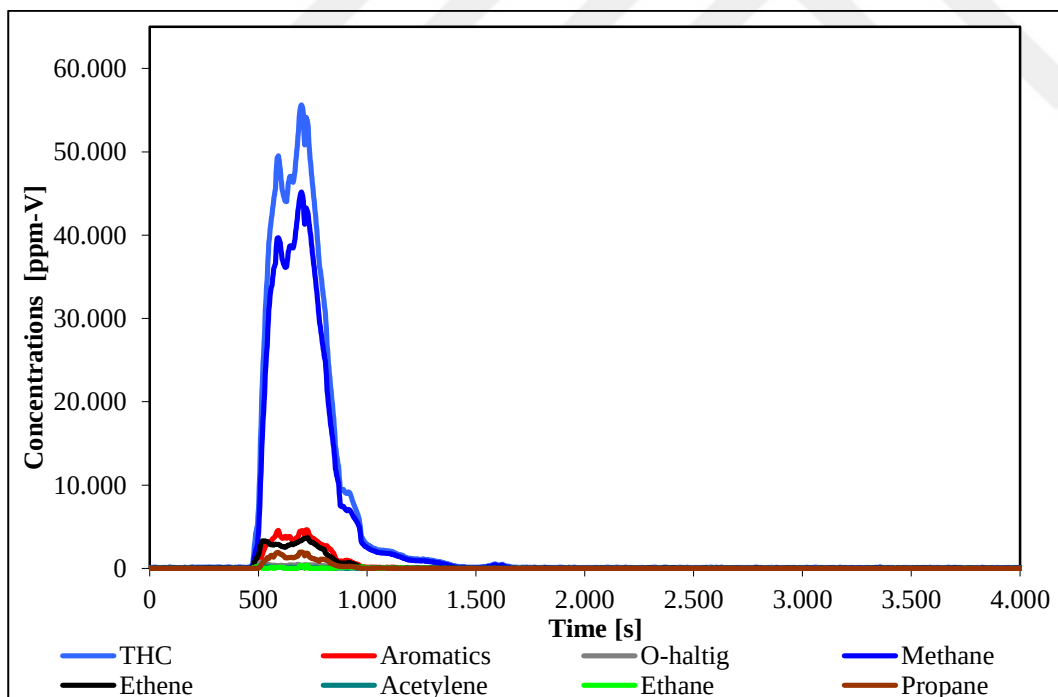
Appendix 5. Variation of hydrocarbon emissions during combustion of lignite.



Appendix 6. Variation of hydrocarbon emissions during co-combustion of STC-LIG.



Appendix 7. Variation of hydrocarbon emissions during co-combustion of STC-PLC



Appendix 8. Variation of hydrocarbon emissions during co-combustion of PLC-LIG.