

**Research Article**

## Effect of functional group distribution on combustion characteristics of chars from Afsin Elbistan lignite and RDF

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## ABSTRACT

RDF (Refuse Derived Fuel) and lignite from Afsin-Elbistan region were subjected to carbonization to produce their chars. For this purpose, these samples were heated from ambient to temperatures of 400, 500, 600, 700, 800, 900°C by a heating rate of 10°C/min in a tube furnace under nitrogen flow. Then, the chars were characterized in terms of the calorific values and the functional groups were investigated using FTIR (Fourier Transform Infrared Spectroscopy) technique. Also, some fuel blends where the chars of RDF and lignite are blended in different ratios were prepared. Effects of the charring process on the fuel properties of RDF and lignite were interpreted.

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### 1. Introduction

Future projections of Turkey in power generation show that the importance of lignites will be increased proportional to the increasing energy demand since oil and natural gas reserves in this country are seriously limited. Although, Turkey has large coal deposits in various coal ranks, low quality lignites account for the most part of the Turkish lignites. That is, low calorific value, high sulfur content, and high ash yield lignites are the most abundant natural primary energy sources. In addition to these disadvantages, fossil fuels consumption increases the CO<sub>2</sub> emission and triggers the greenhouse gases (GHG) formation and climate change. New technologies are actively being investigated to achieve emission reductions. Thus, the development of appropriate technologies for the evaluation of low-quality lignite potential must be one of the most important energy policies of our country [1]. For this reason, alternative energy sources must be found to meet the energy need of the industrialized world [2-4].

At the same time waste management is an important problem for the industrialized and urbanized countries.

Overpopulation and industrialization changes the consumption habits and Municipal Solid Waste (MSW) generation is increased [5-6]. When the wastes are used as alternative energy source, the energy, waste management and environmental problems can be avoided. MSWs are transformed to alternative fuel which is called Refuse Derived Fuel (RDF). RDF is the organic part of MSWs after separation of recyclable materials and its calorific value is considerably high [7].

RDF production from the MSW process starts with the separation of the recycled materials from the MSW, and then size of the separated waste is reduced by milling or shredding processes. Metal or glass particles are removed from finer wastes via air classification and magnetic separation steps. Homogenized wastes are dried to eliminate humidity in order to increase calorific value. At the end of the process wastes are packed to reduce volume. Pelletized fuels stored easily in order to their stable shapes [8-9]. RDF fuels are used in energy intensive areas such as cement, paper, chemical production industries or power generation [9-12]. Especially, RDF blends are suitable for rotary cement kiln in

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cement production power plants because of high flame temperatures. The use of RDF at the rotary kiln reduces the CO<sub>2</sub> emissions [13].

RDF fuels have high calorific values that are compatible with the lignitic coals. In this paper, RDF and Afsin-Elbistan lignite samples have been carbonized at different temperatures. In consequence of the calorific value measurements, the carbonization temperatures that produce the chars with the highest calorific value were assumed as the optimum carbonization temperatures for RDF and lignite, and the chars from these carbonization experiments were blended in different proportions to obtain the char blends. FTIR analysis of untreated RDF and lignite as well as their chars and char blends were carried out to determine the functional groups that have significant role on the fuel properties and the burning reactivities.

## 2. Material and Method

### 2.1 Materials

RDF was provided from Istanbul Metropolitan Municipality Odayeri Sanitary Landfill Area. Besides, the lignite sample was provided from Afsin-Elbistan region in Turkey. In this study, untreated main Afsin-Elbistan lignite coal sample (L) and RDF (R) were used and their chars were produced by carbonization at temperatures of 400, 500, 600, 700, 800, and 900°C.

### 2.2 Sample Preparation

RDF and lignite samples were dried under atmospheric conditions in open containers firstly and then these air-dried samples were put in an oven to eliminate the moisture completely. The dried samples were milled and sieved through Retsch AS200 sieve to get the particle size below 250 µm. Semicokes in other words chars which are the solid products of the carbonization experiments were produced by carbonization of the coal and RDF samples. That is, the carbonization process was performed under N<sub>2</sub> flow of 100 mL/min in a horizontal tube furnace by heating the sample from ambient to the final temperatures of 400, 500, 600, 700, 800, 900°C with a fixed heating rate of 10°C/min. Once the temperature reaches the final value, hold-time of 30 min at these temperatures was allowed. Then, the thermally treated samples were cooled down inside the furnace under nitrogen flow to avoid oxidation of the char. The char samples were kept in air-tight bottles to eliminate any interaction with oxygen. The chars will be hereafter named as L (lignite) or R (RDF) with the final temperature of carbonization. For an instance, L400 means the lignite char obtained at 400°C.



Figure 1. Horizontal tube furnace

### 2.3. Calorific Value Analysis

Considering the calorific values of these chars, the optimum carbonization temperatures were determined for lignite and RDF. Calorific values of samples were determined using IKA C2000 model calorimeter.

### 2.4. FTIR Analysis

Combustion characteristics of untreated samples, chars and char blends were investigated using thermal analysis method. FTIR (Fourier Transform Infrared Spectroscopy) technique was applied to untreated samples as well as the chars to specify the functional groups and interpret the effects of functional groups on the combustion behavior. FTIR analysis was conducted using Bruker Alfa-T FTIR device to determine the functional groups in the coal sample and its chars. For this purpose, the samples to be tested were mixed with potassium bromide (KBr) powders with a proportion of 1/100. Then, the specimens for FTIR were pressed between two 13 mm disks under 10 MPa pressure with KBr.

All the tests repeated several times to check the accuracy and the precision of the experimental results and the average values were taken.

## 3. Results and Discussion

The calorific values of char samples were determined using IKA C2000 calorimeter and the results were shown in Table 1 and indicated that the highest calorific values were obtained when the final temperature was 800°C for lignite while the corresponding temperature was 400°C for RDF. For this reason, we decided to produce char blends by simply mixing L800 and R400 chars in different proportions. Namely, the percentages of R400 changed in the interval of 10-50 wt% in these blends. This shows that the L800 was the dominant ingredient in these blends and R400 was used as an additive to increase the calorific value of the blends. Table 1 also gives the calorific values of these blends.

In this case, as the RDF char content of the blends increases, the thermal values increase. It has been thought that the RDF chars contribute to the coal chars, and as the blending ratio increases, the volatile matter content increases and the thermal values can be improved.

The FTIR spectra for Afsin-Elbistan lignite and its char samples are given in Figure 2. That is, there is evidence of O-H stretching bands at around 3000-3500  $\text{cm}^{-1}$  in Figure 2. The strong bands between 2800-2950  $\text{cm}^{-1}$  indicate the presence of methyl and methylene groups [14]. The bands between 1400-1600  $\text{cm}^{-1}$  indicates the aromatic C=C vibrations [15]. The peaks between 970-1250  $\text{cm}^{-1}$  indicate the C-O stretching vibrations and existence of alcohol or phenolic structures [16]. The peaks between 700-900  $\text{cm}^{-1}$  shows the ester groups' existence in the lignite samples [17].

Table 1. Calorific values of samples

Sample Name	Calorific Value (cal/g)
Lignite	2536
L400	2194
L500	2208
L600	2375
L700	2603
L800	2940
L900	2826
RDF	5424
R400	6623
R500	3382
R600	3359
R700	2983
R800	2902
R900	3094
10 R400+90 L800	3178
20 R400+80 L800	3570
30 R400+70 L800	3944
40 R400+60 L800	4252
50 R400+50 L800	4577

Figure 2 also shows the FTIR spectra of the chars in order to monitor the variations of functional groups due to carbonization at different temperatures. That is, the methyl and methylene groups could not be detected until carbonization is carried out at 500°C. This can be explained by the relatively enrichment of these constituents as a result of deoxygenation through partial devolatilization. The hydroxyl groups can be attributed to the moisture content of the samples. Besides, intensities of the derivations of etheric functional groups became stronger in L600 and L700 compared to L500. On the other hand, intensities of these groups lowered again in the cases of L800 and L900.

The intensities of the peaks at around 800 and 1400  $\text{cm}^{-1}$ , which may be resulted from the presence of aromatic C-H peaks, are highly distinctive in cases of L600 and L700. However, these peaks almost decayed in L800 that suggest the fact that aromatic structure was decomposed under high temperature effect. In addition, the intensity of aliphatic C-H peaks at around 2800  $\text{cm}^{-1}$  started to increase from L800.

Bonds in aromatic ring structures are relatively much stronger than straight-chain aliphatic bonds and accordingly high temperature is required for their breakdown. It is well-

known that high rank coals such as anthracites and bituminous coals are rich in aromatic ingredients, while low rank coals such as lignites are poor in aromatics. Instead, low rank coals are rich in aliphatic constituents. Thus, in L800 and L900, thanks to the straight-chain structures, given heat was enough to effect these bonds. In fact, two different phenomena determine the extent of the calorific values of the chars. One of them is in the favor of increase due to elimination of oxygen-rich volatiles. On the other hand, the other effect leads to decrease in the calorific value since severe disintegrations take place in the structure under elevated temperature conditions. That's why the calorific values of L600 and L700 are lower than that of L800 and L900 and the mentioned first phenomenon is more dominant at these temperatures. Besides, the calorific value of the L900 showed some decrease in comparison to L800 as carbonization temperature increased from 800°C to 900°C that predicts the fact that the second phenomenon is the governing phenomenon in the investigated temperature interval. FTIR spectra of the chars are in good agreement with the mentioned situations.

Figure 3 illustrates FTIR spectra of RDF and its chars basing on the absorbance intensities. That is, since RDF was already dried before the analyses and the chars were almost free of moisture, it is hardly difficult to detect the band at around 3500  $\text{cm}^{-1}$  that indicates hydroxyl (O-H) groups and is the characteristic bands of water. The peaks located in the region of 2800-3000  $\text{cm}^{-1}$  indicate the existence of C-H stretching in methyl and methylene groups. The macromolecular ingredients of biomass such as cellulose, lignin, and hemicellulose contain C-H bonds. On the other hand, plastic components found in RDF also contribute to these peaks [18]. Evaluation of HCl is indicated by peaks at 2600-3000  $\text{cm}^{-1}$  and the source of the HCl can be attributed to PVC in the RDF blends [14]. However, it couldn't be seen any peak in this range and this can be attributed to the fact that PVC had already been eliminated from MSW and the RDF used in this study is poor in PVC.

The medium-weak multiple bands at 1400-1600  $\text{cm}^{-1}$  indicate the aromatic C=C vibrations [19]. It is well-known that lignin that is the second most important ingredient in biomass after cellulose is the only aromatic material and these bands can be attributed to lignin found in biomass. The peaks in the range of 1200-1100  $\text{cm}^{-1}$  are related with the ether type structures such as cellulose and hemicellulose. In fact, C-O bonds in biomass are the most abundant bonds because of large amount of oxygen in biomass. Cellulose and hemicellulose have great contribution to these bands. Also, lignin contains C-O bonds. The source of these ligno-cellulosics is woody wastes, shells, barks, and agricultural remnants. Similarly, paper and paper products are very rich in celluloses [20].

Peak intensity of C-O bonds of about 1000  $\text{cm}^{-1}$ , indicating cellulosic structures, decreased at R400. Because

at this approximate temperature cellulose is degraded and thus an increase in the thermal value is expected. The highest thermal value of the R400 sample in the thermal value results confirms the FTIR results. The peaks appearing at  $1450\text{--}1600\text{ cm}^{-1}$  originate from aromatic C-H bonds. In addition, a decrease in peak intensity, which indicates C-H bonds, has been observed on the R400 sample with removal of the plastic volatile components, but as higher temperatures are reached, C-H bonds are again formed to form aromatic structures. The aromatic structures formed after R800 also degrade. Thus, the FTIR results confirm that there is a decrease in the thermal values after R400 and that the thermal value after R800 slightly increases.

Similarly, the FTIR spectra for the blends can be seen in Figure 4. It can be concluded that the FTIR spectra of the blends were closely affected from the proportions of the chars in the blends. As the content of RDF char in the blends increases, the C-H bonds, which represent aromatic structures seen around  $1400\text{ cm}^{-1}$ , are broken and the peak shrinks. The aromatic bonds, ie ring bonds, are much stronger than aliphatic bonds in straight chain structures and require high energy to break. As the RDF char content increases, the increase in thermal values confirms the FTIR results.

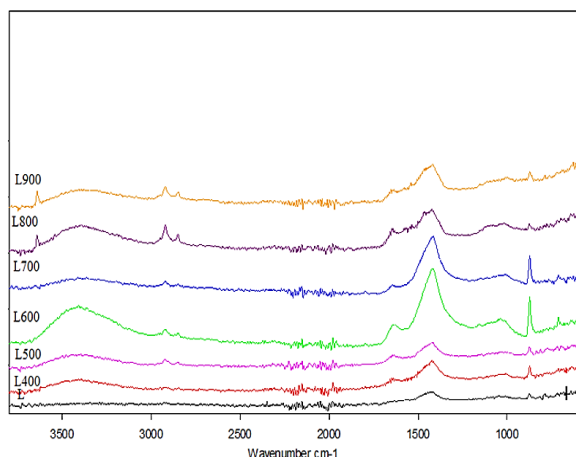


Figure 2. FTIR spectra of lignite and char samples

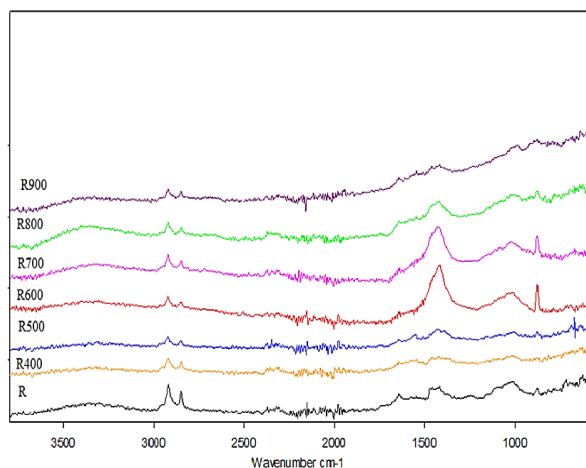


Figure 3. FTIR spectra of RDF and char samples

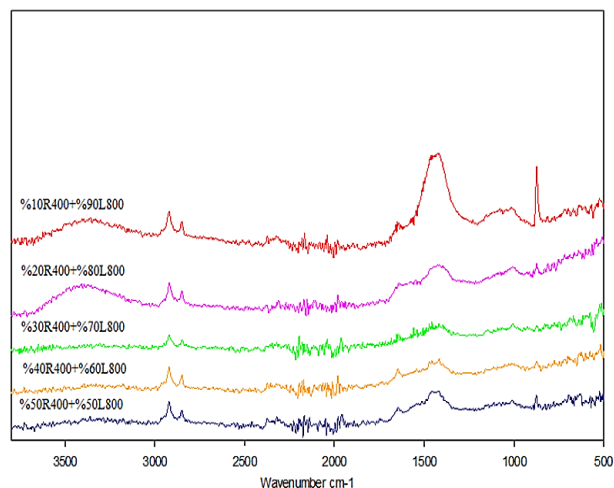


Figure 4. FTIR spectra of char blends

#### 4. Conclusions

RDF samples have higher calorific values than the Afsin-Elbistan lignite coal. When the RDF samples are carbonized at  $400^{\circ}\text{C}$ , the highest calorific value is reached. However, increasing the carbonization temperature beyond the  $400^{\circ}\text{C}$  has detrimental effects on structure and consequently it leads to reductions in the calorific value. Therefore,  $400^{\circ}\text{C}$  can be regarded as the optimum temperature for carbonization of RDF and the chars of RDF can be produced at this temperature. In addition, the char blend that has a composition of 50% of R400 and 50% of L800 is the optimum composition in terms of the calorific value and the sustainability of the fuel. The FTIR spectra of the untreated RDF and lignite, their chars, and the char blends showed the presence of several functional groups including O-H, C-H, C-O, C=C. The intensities of these bands are highly influenced from the carbonization temperature.

This study revealed that carbonization of lignite affected not only the calorific values of the carbonized chars but also the functional groups found in these chars are highly influenced from the carbonization temperature. Namely, the intensity of a given bond in FTIR spectrum was determined by the relative abundancy of the other bonds. That is, the stages of drying, devolatilization, and even further devolatilization of the forming char during carbonization need different temperature regions and heat requirements in such thermal treatment studies. Accordingly, some peaks on FTIR spectrum became either decayed or intensified depending on the temperature applied during the carbonization process.

As a result of the experimental studies, Afsin Elbistan lignite coal and RDF produced high thermal value fuel. It has been thought that the improvement of the thermal values can be made as the contribution of the RDF char on the coal char and the ratio is increased.

## Nomenclature

- L* : Lignite  
*R* : RDF  
 RDF : Refuse Derived Fuel

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