

Effect of Solvent Swelling on the reactivity of demineralized Turkish Lignite

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ABSTRACT

In this research, effect of demineralization and solvent swelling on pyrolysis kinetics was investigated. The experiments were carried out to investigate the effects of solvent swelling with different solvents, such as THF, Pyridine and DMSO after demineralization with HCl, HNO₃ and HF successively. To calculate the activation energies of lignite sample during pyrolysis, TGA analyses were performed with raw and swollen samples at 5, 10 and 20° C/min heating rates. Coast-Redfern model was used for the determination of kinetic parameters. According to the results, the macromolecular structure of lignite was affected from these hydrogen bonding solvents. So, the activation energies of swollen samples found to be less than the raw lignite sample for all heating rates. The reactivity of lignite samples can be ordered as follows; DMSO swollen sample > Pyridine swollen sample > THF swollen sample. Activation energy of DMSO swollen lignite sample is 10.62 kJ/mole whereas activation energies of pyridine swollen and THF swollen sample are 17.83, 25.76 kJ/mol, respectively at a heating rate of 10° C/min. The results indicated that, solvent swelling has catalytic effect on pyrolysis kinetics.

Key words: Demineralization, Solvent Swelling, Kinetics, Pyrolysis

I. INTRODUCTION

Coal which is composed mainly of carbon, hydrogen and oxygen is a combustible, sedimentary, organic rock. Coal is abundant and can be found on each part of the world. It is estimated that, coal will provide energy to human being approximately more than 100 years. Being consumed in the production of electricity and important for in steel industry and cement production, coal is indispensable for us today. Unfortunately, it is not renewable and also pollutant. Efficient usage or minimizing damage on environment caused by coal is essential. In Turkey, the reserves of coal are mainly lignite and this corresponds to 1.6% of world reserves. As a result of exploration activities in the last ten years, Turkish lignite reserves have reached more than 14 billion tones [1]. Unfortunately, lignite has low calorific value and high mineral content in Turkey. Although a small part of lignite has medium calorific value, most of them has the low calorific value between 1100 to 4500 kcal/kg [2]. Although its low calorific, lignite is mainly used in power stations in Turkey and causes an environmental pollution.

Turkey is energy dependent country. Necessary precautions should be taken to reduce its energy dependence besides decrease pollution. For this purpose, upgrading prior to use, lignite is essential. There are various studies for upgrading the properties of coal in the literature [2], [3], and [4]. This can be achieved with physical and chemical methods. The effectiveness of upgrading methods is strictly based on coal or lignite chemical and physical

properties. In contrast to cost of operation, chemical methods are generally much effective than the physical methods. The chemical methods may be acid leaching, alkali leaching under high pressure and at elevated temperatures, leaching by molten caustic baths [5]. Lignite has high ash and high mineral matter in Turkey. The minerals are of pyrite, carbonates, silicates, sulfates, oxides, chlorides, hydroxides and more. So, direct use of lignite is inefficient during thermal processes such as combustion, pyrolysis, gasification or liquefaction. Since, high yield cannot be obtained during conversion and also it will cause pollution and corrosion or fouling in the equipment.

Acid leaching is one of the most common upgrading methods for fossil fuels. During the treatment of coal with acids, acid and/or water soluble parts of mineral are dissolved in the solution [3]. So, demineralized organic structure which contains less mineral matter can be obtained. Carbonates and many oxides, sulphates, sulphides, many zeolite etc. are soluble in HCl. Demineralization degree is 28 and 19 wt.% for Boragolia and Ledo coal in 10% HCl treatment, respectively. Beside this, demineralization degree with successive treatment with alkali and acid increased from 40.57 and 40.35 % to 50 and 44 wt.%, respectively [7]. Treatment of minerals increased with increasing acid concentration. The removal of organic sulfur from Boragolia and Ledo coal samples increased from 5.8 and 8.9% to 26.7 and 31.4%, inorganic sulfur from 74.1 and 85.0% to 94.0

and 94.6%, and ash from 19.9 and 14.6% to 45.0 and 43.0%, respectively, on acidification of the peroxide solution [8].

Coal has complex macromolecular network structure and composed of organic and inorganic materials which are joined by cross-linked hydrogen and van der Waals bonds. The macromolecular structure is important for conversion processed due to its high porous structure. It is very important to have sufficient information about the coal matrix before conversion processes. One of the techniques to define the complex structure of coal is solvent swelling. It has provided useful insight into the structure of a number of bituminous coals and has also been used to provide valuable information about the course of both pyrolysis and conversion reaction [9]. During the swelling process, solvent dissolve and swell the coal. At the end of swelling, coal molecules dissociate, rearrange and re-associate in lower free energy conformations probably in a different molecular structure. This means that the swollen coal molecular structure is not the same as that of raw coal. After treatment with HCl, the bond structure in the lignites was affected by removing some cations in the chelate structures or breaking some of ether or ester bonds [10, 11].

Increasing depletion of high quality coal reserves caused the effective usage low rank coal for environment and economy. During the thermal conversion processes of coal, the selectivity of the products may be high; the reaction mechanism can be controlled. There are numerous researches about pretreatment of fossil fuels such as demineralization or solvent swelling. The aim of this study is to describe the reaction mechanism during pyrolysis after successive demineralization and solvent swelling of lignites. For this purpose, treated lignite samples were subjected to TGA analysis at different heating rates, reaction mechanism was found and kinetic parameters were calculated.

II. EXPERIMENTAL

The investigations were performed with lignite samples which were taken from the deposit in Soma province in Turkey. For experiments, these samples were first crushed and ground in a jaw mill until the desired particle size was obtained. Then the samples were sieved to obtain a < 0.1 mm fraction and dried at 105° C under N₂ atmosphere. Proximate and ultimate analyses of raw lignite sample were given in Table 1.

Demineralization of Lignite

1 gr of lignite samples (LIG) were demineralized with 20% HCl, 5% HNO₃ and 40 % HF, successively. At the end of each demineralization step, IR Spectras were recorded between 4000 and 400 cm⁻¹ using a Shimadzu Model spectrometer,

Spectra of the raw and demineralized lignite samples are given in Figure 1.

Solvent Swelling Studies

The swelling behavior of lignite (LIG-F) which was obtained from demineralization step in hydrogen bonding solvents as DMSO, THF and Pyridine, was performed by using the volumetric swelling technique. Glass tube with 6.0 mm diameter was used and the fraction < 0.1 mm size was taken for the experiments. At the end of swelling part, these samples were subjected to thermogravimetric analysis to investigate the kinetic parameters during pyrolysis.

TGA (Thermogravimetric Analysis)

Pyrolysis experiments were carried out by non-isothermal thermogravimetry using TGA analyzer. The experimental procedure involved placing the sample (app. 10 mg) into a platinum crucible and heating from room temperature to approx. 1000 °C at a linear heating rate of 5, 10 and 20 °C.min⁻¹ under the nitrogen flow.

The weight losses occurring in correspondence to the temperature rise were continuously recorded with a computer working in coordination with the furnace and the control unit of the analyzer. Thus, the data required to determine the pyrolysis characteristics and kinetics of the samples were collected.

Kinetic Study of Samples

The rate of conversion, dx/dt for TG experiment at constant rate of temperature change, β = dT/dt may be expressed by

$$\frac{dx}{dt} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (1)$$

where f(x) is the function of conversion, such as (1-x) for first order reaction, E is the activation energy, A is the Arrhenius factor, R is the gas constant and x is the degree of advance defined by

$$x = \frac{w_0 - w}{w_0 - w_f} \quad (2)$$

where, w is the weight of the sample at a given time t, w₀ and w_f, refer to values at the beginning and the end of the weight loss. Equation (1) can be written as;

$$\frac{dx}{dT} \frac{dT}{dt} = A \cdot \exp\left(-\frac{E}{RT}\right) f(x) \quad (3)$$

or

$$\frac{dx}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(x) \quad (4)$$

where β is dT/dt. Integration of Equation (4) gives the Coats-Redfern Equation;

$$\ln\left[\frac{g(x)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\right] - \frac{E}{RT} \quad (5)$$

where g(x) is the integrated form of f(x). According to Eqn.(5), a plot of ln(g(x)/T²) versus (1/T) gives a straight line of slope (-E/R). In the kinetic parameter calculations, it is assumed that the second order reaction mechanism can describe the decomposition

of lignite samples. Activation energies and Arrhenius factor were calculated according to this mechanism and shown in Table 2 and 3.

III. RESULTS

In this research, the first step is coal demineralization. HCl, HNO₃ and HF was employed successively for this purpose, than carbonate minerals, pyrite and silicate minerals were isolated from organic matter, respectively. To ensure removal of these mineral, IR spectrum analysis results were used based on changes in the functional groups resulting because of demineralization of the raw lignite sample. IR spectrums of the samples were given in Figure 1. Absorption bands due to the carbonates near 1450-1410, 880-860, and 1600-1640 cm⁻¹ were identified in the spectrum of the raw sample. Absorption bands of silicate minerals near 1100-900 cm⁻¹, bands of kaolinite near 3700-3600 cm⁻¹, and bands of pyrites near 415 and 440 cm⁻¹ are identifiable in the spectrum of the raw coal. With HCl, HNO₃, and HF, the carbonate, silicate, and pyritic bonds largely disappeared [2]. It is known that, certain minerals have catalytic effect on pyrolysis process. In the study of Öztaş and Yürüm, calcium and magnesium ions were removed from coal by using HCl. They pointed out that, removal of illite, kaolinite, chlorite and quartz minerals caused an increase in conversion of coal pyrolysis [12]. Chen et. al., studied the effect of mineral matter and sulfur distribution in hydrolysis. To remove mineral and pyrite from coal HCl/HF or HCl/HF and CrCl₂ solution were used in their study. They reported that, demineralized lignite showed lower yields of tar and water than raw lignite [13].

Coal has complex macromolecular structure which affects product evolution during conversion processes. The effect of cross-linking in the complex coal structure was investigated by Öztaş and Yürüm [12]. Pyridine was used to identify the effect of cross-linking. They resulted that, pyrolysis temperature increased with increasing cross-linking, especially, at higher temperature above 400° C. In the study of Tekeşet. al., various kind of solvent was used as swelling agents to understand the effect on the extraction yield. Solvent molecules penetrate into a coal structure and make it expand. So, small molecules formed by pyrolysis can escape easily from coal matrix with this expansion. They reported that, swelling and acid washing increased the extraction yields [14].

Thermogravimetric curves (TG) of lignite samples (raw and swollen samples) for 5, 10 and 20° C/min heating rates were performed, respectively. The TGA curves for raw (LIG-F-R) and treated lignite samples with DMSO (LIG-F-D), THF (LIG-F-T) and pyridine (LIG-F-P) at 5, 10 and 20° C/min heating rates were given in Figure 2-4, respectively.

As seen from these figures, when the heating rate was increased, maximum decomposition temperature increased. The maximum decomposition temperatures are 410° C, 420° C and 430° C for 5, 10 and 20° C/min heating rates, respectively. TGA curves of lignite samples were decomposed in a single stage, between approximately 340-560° C. So, kinetic calculations according to Coats-Redfern equation were performed in this temperature range.

A pyrolysis reaction of lignite was assumed as second order model. The activation energy and R² values were calculated according to second order model in this study and determined using the Coats Redfern equation and given in Table 2 and 3.

According to determination of kinetic parameters and as given in Table 2 and 3, TGA data of all lignite samples, second order reaction mechanism assumption is valid. Regression coefficients of all samples are close to 1 then these values support the second order model assumption. We can say that, the activation energy is decreased after solvent swelling study of demineralized lignite samples when comparing the activation energy of raw lignite sample (LIG-F-R). The activation energy of LIG-F-D has the least value in all samples as 10.62, 11.20 and 14.69 kJ.mol⁻¹ for 10, 20 and 5° C/min heating rates, respectively. The activation energies of samples can be ordered of LIG-F-D < LIG-F-P < LIG-F-T < LIG-F-R. If we compare the solubility parameters of these solvents they are in order of 13.0, 10.7 and 9.5(cal/cm³)^{1/2} for DMSO, Pyridine and THF, respectively [15, 16]. Decrease in activation energies of lignite samples showed that the relation between solubility parameters. Similar trend was obtained by Tekeşet. al. Extraction yield of pre-swollen samples are higher than raw lignite and in the order of DMSO > Pyridine > THF. [14]. In the study of Xie et. al., they reported the increase in the formation of volatile matter from 10.5 to 19.7% when compared to raw and swollen coal sample. And because of re-arrangement of coal structure, activation energies were decreased [17]. It can be said that solvent swelling procedure catalyzed the thermal decomposition reaction of lignite due to decrease in activation energies.

IV. CONCLUSION

The effect of demineralized and solvent swelling on pyrolysis kinetic was studied in this research. First, the organic structure has been isolated from mineral matter. As given in the IR spectrum, carbonates, pyrite and silicates were removed from organic structure by using HCl, HNO₃ and HF, respectively. In the second step, solvent swelling lignite samples were performed with hydrogen bonding solvents (DMSO, Pyridine and THF). Final step was to perform TGA analysis of treated and swollen lignite samples. TGA analyses were

performed at a rate of 5, 10 and 20°C/min heating rates. As expected, the maximum decomposition temperatures were shifted to the right in temperature axis and found to be 410° C, 420° C and 430° C for 5, 10 and 20° C/min heating rates, respectively. Second order reaction mechanism was assumed in the pyrolysis of lignite then kinetic parameters were calculated by Coast-Redfern equation. Activation energies of raw and swollen samples were compared. It was found that, all swollen samples have less activation energies than raw sample for all heating rates. DMSO has the least activation energy values in other samples as 10.62, 11.20 and 14.69 kJ/mol for 10, 20 and 5°C/min heating rates, respectively. It can be concluded that solvent swelling has positive kinetic effect on pyrolysis due to formation of lower energy conformation after swelling.

V. ACKNOWLEDGMENT

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TABLES

Table 1 Proximate and ultimate analysis of raw lignite [6].

Ultimate analysis (wt % db)	Soma-Lignite
C (total)	60.4
C (organic)	58.7
C (inorganic)	1.7
H	5.6
N	0.9
S (total)	1.2
Proximate analysis (wt. % as received)	
Moisture	13.7
Ash	14.6
Volatile Matter	37.3
Fixed Carbon	34.4

Table 2 Activation Energy of lignite samples for all heating rates

Heating Rate	ActivationEnergy (kJ/mole)		
	5° C/min	10° C/min	20° C/min
LIG-F-R	30.45	25.15	30.39
LIG-F-D	14.69	10.62	11.20
LIG-F-T	27.78	25.76	26.14
LIG-F-P	23.26	17.83	23.13

Table 3 Regression coefficient of lignite samples for all heating rates

Heating Rate	R ²		
	5° C/min	10° C/min	20° C/min
LIG-F-R	1.00	0.98	0.99
LIG-F-D	0.96	0.95	0.96
LIG-F-T	0.99	0.99	0.99
LIG-F-P	0.98	0.99	0.99

FIGURES

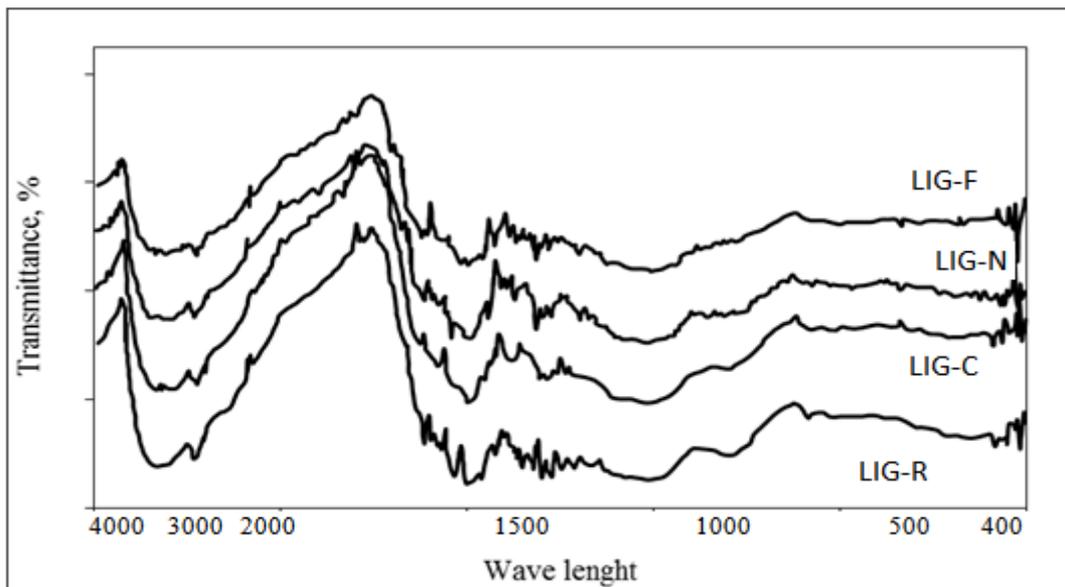


Figure 1 The IR spectrum of raw and demineralized lignite [2].

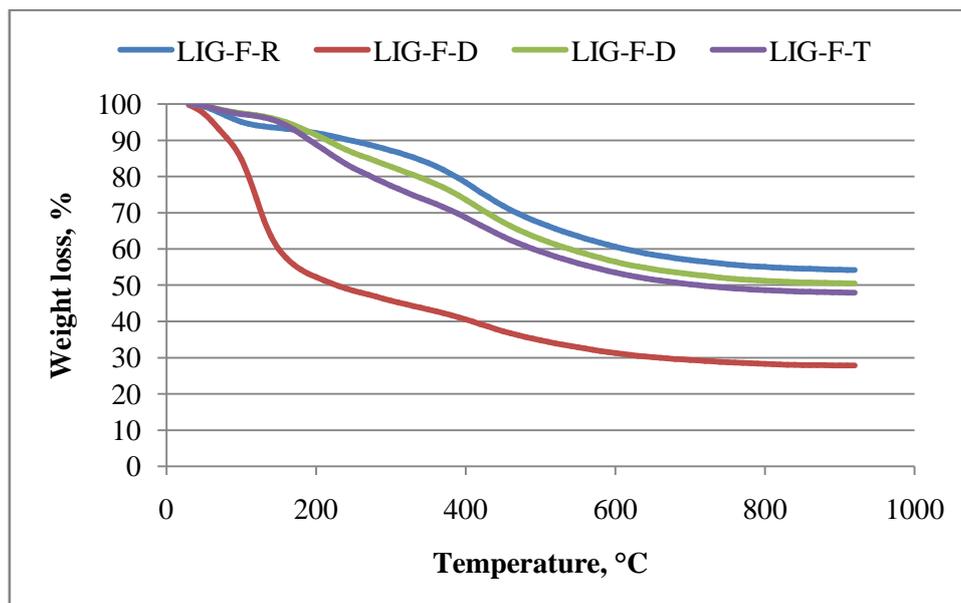


Figure1TGA curves of lignite samples for 5° C/min heating rates

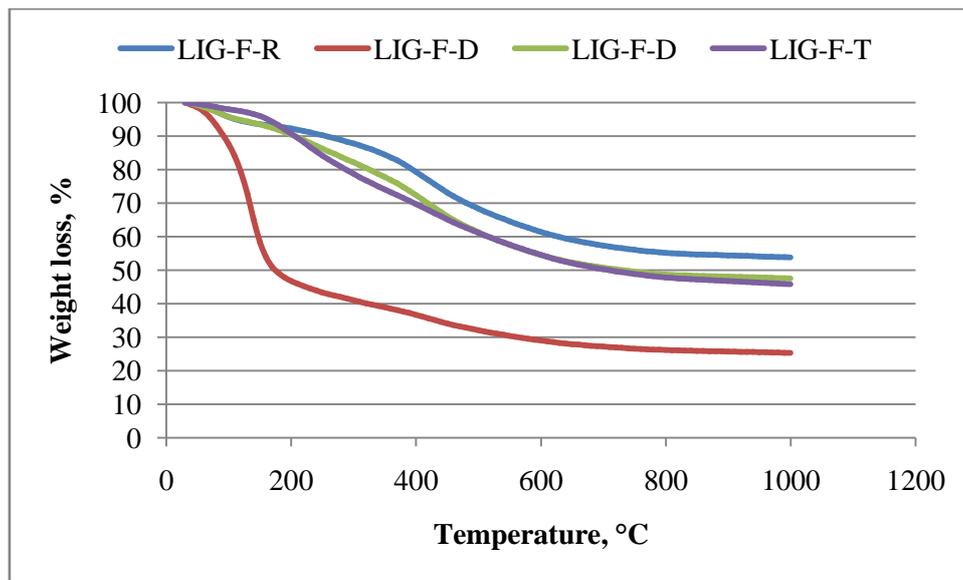


Figure 2 TGA curves of lignite samples for 10° C/min heating rates

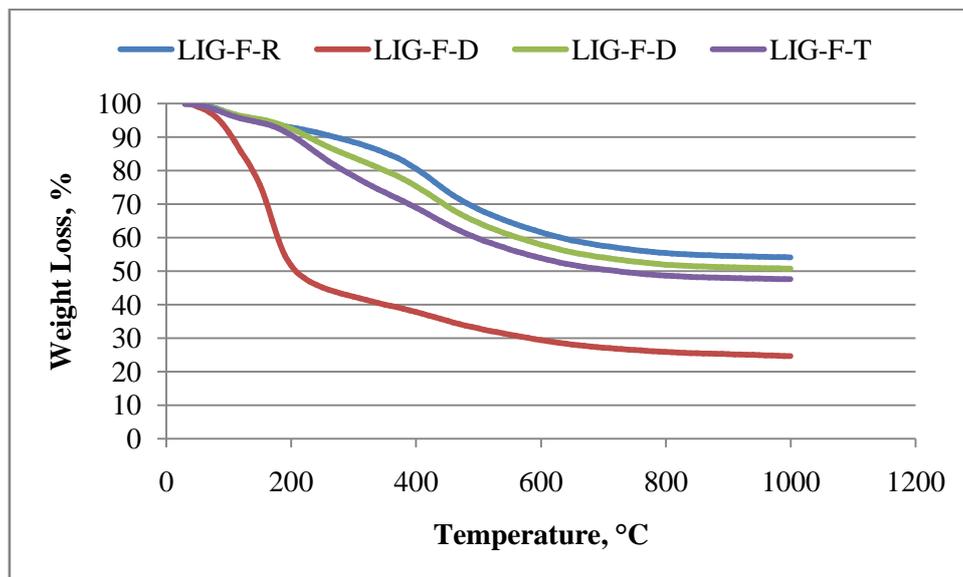


Figure 3 TGA curves of lignite samples for 20° C/min heating rates