## **EFFECT OF DIFFERENT BINDERS ON THE COMBUSTION PROPERTIES OF LIGNITE Part I. Effect on thermal properties**

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#### Abstract

Coal briquettes and the binders were tested from the view of resistivity to transportation, loading and storage by measuring the abrasion index and strength to crushing. The binders used in coal briquetting also affect the combustion properties of the coal. Combustion properties of the Tuncbilek lignite and different binders were analysed by thermogravimetric (TG/DTG) methods. Molasses, carboxyl methylcellulose (CMC), sulphide liquor, heavy crude oil, sodium silicate, cornstarch, lime, peridur, and bentonite, cement poly(vinyl acetate) were used as binders. It was observed that molasses and CMC decreased the residue content at the end of the combustion period, whereas, heavy crude oil, sulphide liquor and corn starch increased the calorific values of the samples.

Keywords: binder, coal, combustion, thermogravimetry

#### Introduction

Coal is physically heterogeneous and chemically a complex mixture of organic and inorganic species, which undergoes appreciable physico-chemical changes when heat treated. The main studies of coal using thermal analysis techniques include characterisation, catalytic effects due to inorganic substances, combustion, pyrolysis, kinetic analysis and briquetting techniques. Briquetting is the best solution to minimise the energy loss and pollution as well as to supply a standard quality household fuel. In general, Turkish lignites are not suitable for briquetting without using a binder. Typical binders used for coal briquetting are: starch, poly(vinyl acetate), molasses, sulphide liquors, carboxyl methylcellulose, tar, pitch, crude oil, clay, cement and sodium silicate. Saracogullari and Gencer [1] briquette Soma and Tuncbilek lignites with various binders and additives. It was observed that a compound binder consisting of plant stalks, molasses and lime did not cause air pollution. The strength of the briquettes produced, combustion properties in stoves and boiler furnaces were also examined. It was concluded that the briquettes are strong enough to be used as a do-

1418–2874/2001/ \$ 5.00 © 2001 Akadémiai Kiadó, Budapest Akadémiai Kiadó, Budapest Kluwer Academic Publishers, Dordrecht mestic fuel, but they are not resistant to water. Ozden [2] tested the coked briquettes for abrasion and crushing strength in three dimensions to determine the best carbonisation temperature and the blend composition. Briquettes were found suitable for domestic heating purposes after stove combustion tests. Yildirim and Ozbayoglu [3] investigated the conversion of Elbistan lignite into nitrogen-rich, alkali-soluble humic acid and determined the optimum conditions for nitric acid oxidation and ammoniation. As a result, a humic acid solution containing 10.75 mass% nitrogen was obtained with 88.2 mass% recoveries from the lignite. Beker et al. [4] determined the optimum conditions for briquetting blends of an Afsin-Elbistan lignite and Siberian bituminous coal. Haykiri-Acma et al. [5] investigated the combustion characteristics of blends of an Afsin-Elbistan lignite and Siberian bituminous coal with and without binder agents. The combustion curves of the coal and binder agent samples and of the blends were obtained using differential thermal analysis. Rosenvold et al. [6] analyzed twenty-one bituminous coal samples from by differential scanning calorimetry and non-isothermal thermogravimetry. Three regions of endothermic activity were distinguished where the first peak corresponds to devolatilization of the organic matter and a partially resolved probably corresponds to cracking and coking processes subsequent to the pyrolysis step. Morgan et al. [7] determined coal-burning profiles by thermogravimetric analysis. They have claimed that kinetic parameters from Arrhenius plots of profiles cannot readily be related to any specific stage of combustion. It was suggested that burning profiles could provide a valuable, rapid laboratory method of ranking coals in terms of their burnout performance. They also pointed out that coal-burning profiles obtained from thermogravimetric analysis depends on coal properties and particle size. Kök et al. [8, 9] determined the effect of particle size on combustion characteristics of coal. For this purpose, non-isothermal thermogravimetry (TG/DTG) experiments were carried out on twelve different size fractions, and the thermogravimetric data were analyzed by Arrhenius type kinetic model. The results indicated that activation energies were increased as the particle size decreased. It was also pointed out that as the particle size decreased, peak temperatures and burn-out temperatures of the samples decreased slightly and decrease in particle size caused more residue left at the end of the combustion process. Durusov et al. [10] reported pyrolytic behaviour of raw and microbiologically treated lignite. Their experiments were carried out in a thermo-balance apparatus at atmospheric pressure from 25 to 900°C at a heating rate of 20°C min<sup>-1</sup>. The results indicated good behaviour of the microbiologically treated lignite compared with raw lignite. They observed an increase in the activation energy after microbial removal of sulfur from coal.

#### Experimental

In this research, TG/DTG experiments were conducted with a Polymer Laboratory 1500 thermal analysis unit. TG/DTG experimental procedure involves placing the sample (~25 mg), setting the heating rate ( $10^{\circ}$ C min<sup>-1</sup>) and air flow rate ( $15 \text{ cm}^3 \text{ min}^{-1}$ ), then commencing the experiments. All the experiments were per-

 Table 1 Proximate and ultimate analysis of Tuncbilek lignite sample

Basis	Moist./ %	Ash/ %	Volatile/ %	Fixed car./%	Carbon/ %	Hydrogen/ %	Nitrogen/ %	Sulphur/ %	Oxygen/ %	Cal. value/ kcal kg <sup>-1</sup>
Air dry	2.33	53.3	25.1	19.2	29.8	2.4	1.27	0.70	10.1	2876
Dry	-	54.5	25.7	19.7	30.6	30.6	1.30	0.72	10.4	_
Ash free	_	_	56.7	43.3	67.3	67.3	2.86	1.58	22.8	_

formed in a temperature range of 25–900°C. Approximate layer thickness was 2 mm, whereas the diameter of the sample pan was around 5.7 mm. Prior to experiments the equipment was calibrated for temperature readings and the balance was calibrated for buoyancy effect, allowing qualitative estimation of mass changes. Calorific values of the samples were measured using a bomb calorimeter according to the ASTM standards.

In this research Tuncbilek lignite sample was used. R.O.M lignite sample was crushed to a particle size of -212 micron to obtain homogeneous mixing with different binders. There was only a loose, surface contact between the particles. Proximate and ultimate analysis of the Tuncbilek lignite is given in Table 1. Molasses, sulphide liquor, CMC, crude oil, cornstarch (caustisized with NaOH), lime, bentonite, cement, peridur (mostly organic but contains traces of silica like materials) and their mixtures in different ratios were used.

#### **Results and discussion**

In general, all types of coals start to lose volatile matter from the decomposition of phenolic structures and oxidation of carbon from carboxylic and carbonyl groups in the temperature interval of 200–350°C. At around 350°C, primary carbonisation starts initially with the release of carbon dioxide and hydrogen. Methane and other lower aliphatic compounds are evolved together with hydrogen, carbon monoxide and alkyl aromatic compounds with increasing temperature [11].

Three different reaction regions were observed in the TG/DTG curves of Tuncbilek raw sample (Fig. 5). Evaporation of moisture from the coal was observed



Fig. 1 TG and DTG curves of molasses added samples

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in the temperature range of 25–110°C. Second stage corresponded to the combustion of the sample (250–600°C). The third region was due to the decomposition of mineral constituents in the coal sample and was observed between 630–750°C. Figure 1 rep-



Fig. 2 TG and DTG curves of lime added samples



Fig. 3 TG and DTG curves of peridur C10 and peridur XC3 added samples

Type of binder	Burnout temperature/°C	Residue at max. peak/%	Max. peak temperature/°C	Residue at the end of combustion/%	Remaining comb. mat. at max. peak temperature/%	Calorific value/ kcal kg <sup>-1</sup>
-	787	73	443	48.5	25	2876
Molasses 10%	766	66	474	44.2	22	2842
Molasses 15%	777	68	441	42.9	26	2992
Molasses 20%	787	67	435	40.9	27	2982
CMC	775	66	451	44.6	22	2875
S. liquor	763	72	445	46.4	26	3035
Heavy oil	786	67	458	41.6	26	3843
S. silicate	799	64	596	47.4	17	2763
Corn starch	794	69	453	45.6	24	2958
Lime 10%	781	78	424	50.6	28	2772
Lime 15%	786	76	440	51.0	26	2575
Lime 20%	828	67	562	52.1	15	2310
Peridur C10	760	62	498	45.4	17	3285
Peridur XC3	749	60	504	45.8	14	3155
Bentonite	780	73	478	50.9	23	2593
Cement	760	73	492	51.3	23	2339
Lime 5%+ Molasses 10%	771	61	549	45.7	17	2812
P. acetate	761	67	471	43.5	24	4431

### Table 2 Thermogravimetric results of the raw and binder added coal samples

resents the TG/DTG curves of Tuncbilek lignite mixed with 10, 15, 20% of molasses. Another mass loss is observed at around 200°C that represents the decomposition of a molasses and intensity of the exotherm is increased with the increasing amount of



Fig. 4 TG and DTG curves of bentonite, cement and 5% lime+10% molasses added samples



Fig. 5 TG and DTG curves of raw and s. silicate, poly(vinyl acetate) added samples

molasses. This is due to the combustion of molasses, which can be seen in the calorific values of the samples. Residue at the end of the combustion in all the samples (10-20% mixtures) decreased with the Tuncbilek lignite content (Table 2). Figure 2 represents the TG/DTG curves of Tuncbilek lignite mixed with 10, 15, 20% of lime.



Fig. 6 TG and DTG curves of CMC and c. starch added samples



Fig. 7 TG and DTG curves of S. liquor and heavy crude oil added samples

Further mass loss is observed at around 700-750°C and the intensity of the endotherm is increased with the increasing amount of molasses. This is due to the combustion of lime in the high temperature oxidation region. The residue at the end of the combustion in all the samples (10-20% mixtures) is increased in proportion with the amount of lime added (Table 2). Figure 3 shows the TG/DTG curves of Tuncbilek lignite mixed with peridur C10 and CX3. No additional effect is observed on the TG/DTG curve of the Tuncbilek lignite. The residue at the end of the combustion decreased with the Tuncbilek lignite content (Table 2). Figure 4 shows the TG/DTG curves of Tuncbilek lignite mixed with bentonite, cement and lime+molasses. Additional mass loss is observed at around 200°C due to the combustion of molasses. Figure 5 represents the TG/DTG curves of Tuncbilek lignite mixed with silicate and acetate. No additional effect was observed on the TG/DTG curve of the Tuncbilek lignite. The highest calorific value is obtained with the mixture of lignite and acetate. Effect of CMC and cornstarch on the Tuncbilek lignite is given in Fig. 6. An additional peak is observed at around 280°C due to the combustion of binders. These binders also decreased the residue at the end of the combustion (Table 2). Figure 7 represents the TG/DTG curves of Tuncbilek lignite mixed with liquor and heavy crude oil. Sulphide liquor has no additional effect on the combustion curve of Tuncbilek lignite. Additional peak is observed at around 180°C due to the phenolic structure of heavy crude oil.

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