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Combustion characteristics of Turkish hazelnut shell biomass, lignite coal and their respective blends via thermogravimetric analysis

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Abstract: Thermal behavior and combustion kinetic of coal, hazelnut shell, and coal/hazelnut shell blends at the proper ratio were investigated with thermogravimetric analysis (TG). Four mass ratios (20, 30, 40, 50 mass %) of coal/biomass blends were prepared and oxidized under dynamic conditions from temperature 298 to 1173 K at different heating rates. TG analysis indicated that the combustion of blended samples divided into two stages namely devolatilization and char oxidation combined with coal combustion step. The influence of biomass blends on thermal and kinetic behavior of coal was studied under non-isothermal conditions. It was found that the thermal degradation temperature of coal was higher than that of blended samples due to the molecular structure strength. Ozawa–Flynn–Wall model was applied to deal with non-isothermal TG data for the evaluation of the activation energy corresponding to the combustions of coal, hazelnut shell, and coal/hazelnut shell blends. The average activation energy changed in the range of 90.9–215.3 kJ mol^{-1}, respectively, depending on blending ratio.

Keywords: Biomass. Coal blend. Combustion. Thermogravimetric analysis. Non-isothermal kinetics. Activation energies.

Introduction

Energy concerns arising from the diminution of fossil fuel supplies have increased the attentions to find economically feasible energy supply to substitute the fossil energy. Biomass offers significant advantages as a feedstock not only representing the least costly renewable energy options in most cases but also decreasing the dependency on limited fossil fuels [1]. Biomass fuels include wood, agricultural residues, forest residues, and energy crops [2]. Combustion is one of the most simple and direct technology utilizing of biomass to displace some amount of fossil fuel for commercial or industrial uses: hot air, hot water, steam, and electricity. Recently, thermal analysis provides a quick quantitative technique for the assessment of combustion processes under non-isothermal conditions and the effective kinetic parameters for the various decomposition reactions can be predicted [3–8].

The combustion of biomass alone reduces the releases of carbon dioxides and sulfur oxides, however it should be noticed that in comparison with solid fossil fuels, biomass contains much less carbon and more oxygen and has a low heating value [9]. Co-firing biomass with coal, in comparison with single coal or biomass firing, helps to improve combustion performance, meet pollutant emission limits, and decrease concurrently fossil fuels consumption and the fuel cost [10]. Additionally, previous research indicated that combustion of biomass, without fossil fuels led to technical problems such as corrosion and fouling on the hot surfaces [11]. Therefore, biomass as blended with coal during combustion is more advantageous to solve the problems encountered when it is burned alone. A number of studies on coal and biomass [2, 3, 8, 12–14] combustion with thermogravimetric analysis (TG) have been reported including some TG studies on co-combustion coal and biomass [10, 12]. However, there is a still need to study TG analysis of a different waste biomass blended with coal to develop our understanding of the impact of a different waste biomass on combustion parameters.

Hazelnut shell as an agricultural waste product has great potential to be used for energy source since it is renewable, sustainable and cheap energy sources. Turkey is the world's leading hazelnut producer and approximately $3x10^5$ tons of hazelnut shells have been produced per year [15]. Such a residue has no usage area and disposal of these large volumes is problematic. Therefore research on the combustion process of a hazelnut shell waste would be beneficial for providing application as a biomass fuel. Furthermore information about biomass combustion kinetics is important to evaluate biomass as a feedstock for fuel and control of thermochemical processes.

The present research work focused on the kinetic assessments of the combustion of hazelnut shell, Beypazari lignite and their blending under non-isothermal conditions. Heating rate on the combustion characteristics and kinetic parameters were investigated. The thermal properties and activation energy of the hazelnut shell blended coal samples were systematically analyzed by the Ozawa–Flynn–Wall model. Furthermore, the non-isothermal data was utilized to determine reaction order of hazelnut shell blended coal samples considering Avrami theory. The data obtained will be useful to understand the behavior of coal/hazelnut shell blends during combustion, and to investigate extensive studies for their possible application in bigger scales.

Experimental

Materials and characterization

The coal came from Beypazari, a region central Anatolia. The hazelnut shell used in this study was obtained from various areas of Turkey. Prior to analysis, the coal samples were ground to 80 mesh ASTM under a nitrogen atmosphere and dried at 383 K under a vacuum. For hazelnut shell samples, 80 mesh size was used for this study. The proximate analyses of the Beypazarı lignite and hazelnut shell were done at the Instrumental Analysis Laboratory of the Scientific and Technical Research Council of Turkey, Ankara. Morphology of the hazelnut shell was examined by scanning electron microscopy. Leo Supra 35VP Field emission scanning electron microscope (SEM), Leo 32 was used for images. Imaging was generally done at 2–5 keV accelerating voltage, using the secondary electron imaging technique.

Thermogravimetric analysis

TG measurements were performed on a Netzsch STA 449 C Jupiter differential thermogravimetric analyzer (precision of temperature measurement ±2 °C, microbalance sensitivity <5 μg) under air atmosphere with a flow rate 60 mL min^{-1}, with heating rates of 5, 10, 20, and 30 K min^{-1} over 298 to 1173 K temperature range. In order to obtain TG curves, each sample (coal and hazelnut shell) as well as each of the blends (Coal–hazelnut shell 20 mass %, Coal–hazelnut shell 40 mass %, and Coal–hazelnut shell 50 mass %) was approximately 25 mg in order to prevent heat transfer limitations. To assure reproducibility of satisfactory results, TG experiments were replicated at least twice.

Kinetic Theory

The rate of degradation or conversion, $d\alpha/dt$, is the linear function of a temperature-dependent constant, $k(T)$, and the temperature-independent function of conversion, $f(\alpha)$ for heterogeneous solid-state reactions. It can be defined as follows:

$$\frac{d\alpha}{dt} = k(T)\,f(\alpha) \qquad (1)$$

Temperature dependence of the rate constant is usually described by the Arrhenius equation. The mathematical description of the data is defined in terms of three kinetic parameters, as preexponential factor, *A*, the activation energy, *E*, and an algebraic expression of the kinetic model in function of the conversion α, $f(\alpha)$.

$$\frac{d\alpha}{dt} = Ae^{-\frac{E}{RT}} f(\alpha) \qquad (2)$$

At the same time,

$$\beta = \frac{dT}{dt} = \text{constant} \qquad (3)$$

where β is the heating rate. By inserting this term into Eq. 2, the above rate expression can be converted into non-isothermal rate expressions describing reaction rates as a function of temperature at a constant β. Eq. 2 can be transferred as follows:

$$\frac{d\alpha}{dT} = \frac{1}{\beta} Ae^{-\frac{E}{RT}} f(\alpha) \qquad (4)$$

The integration of the Eq. 4 up to conversion α gives directly:

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^{T} e^{-\frac{E}{RT}} dT \qquad (5)$$

According to non-isothermal isoconversional methods applied by Ozawa [16], Wall and Flynn [17] using the Doyle's approximation of *p(x)* [18], the activation energy can be determined by assessing the temperatures corresponding to fixed values of a from experiments at different heating rates:

$$\ln(\beta) = \ln\left[\frac{AE}{Rg(\alpha)}\right] - 5331 - 1052\frac{E}{RT} \qquad (6)$$

The activation energy *E* can be calculated by plotting lnβ versus 1/*T*.

In order to obtain reaction order, Avrami theory [19–21] studied and the non-isothermal data where the variation of the degree of conversion with temperature and heating rate can be explained as:

$$\alpha(T) = 1 - \mathrm{e}\left[\frac{k(T)}{\beta^{n}}\right] \qquad (7)$$

Taking double logarithm of both sides of Eq. 7 with substituting Arrhenius equation gives

$$\ln\left[-\ln(1-\alpha(T)\right] = \ln A - \frac{E}{RT} - n\ln\beta \qquad (8)$$

A plot of ln[-ln(1-$\alpha(T)$] versus lnβ, which is obtained at the same temperature from a number of isotherms taken at different heating rates, should give in straight lines. The slope will have the value of the reaction order or the Flynn–Wall–Ozawa exponent n [16, 23]. Extra aspects of the technique apply to examine the process that is explained by Ozawa [24].

Results and Discussion

Characterization of Materials

The proximate analysis of Beypazarı lignite and hazelnut shell was demonstrated in Table 1. The samples contained different percentages of fixed carbon, volatile matter, moisture and ash content. The Beypazarı lignite indicated higher amount of ash yield as compared to hazelnut shell, while a higher percentage of moisture content was detected in hazelnut shell sample. Biomass typically has a high volatile matter content up to 80-90% [25]. Similar situation was observed and the hazelnut shell sample had much more volatile matter and much lower fixed carbon in contrast to the lignite sample. Higher volatile matter content of the biomass provides an improved combustion with a better burn out and lower unburned carbon in the ash [26].

Table 1. Proximate Analysis of the Beypazarı lignite and hazelnut shell

Proximate analysis /%	**Beypazarı lignite**	**Hazelnut shell**
Volatile matter	34.9	86.2
Fixed Carbon	22.5	12.6
Ash	36.4	1.2
Moisture content	6.2	7.8

Morphology of the hazelnut shell and the residue of fired hazelnut shell obtained at 1173 K were investigated by SEM, Fig. 1. Physical appearances of hazelnut shells and its ashes were quite different. The hazelnut shell had lumpy granular structure before heat treatment. After heat treatment, some voids in a micron scale were appeared and the morphology of burned hazelnut shell resembled a sponge.

-Figure 1-

Effect of heating rate

The thermal degradation behavior of coal, hazelnut, and coal–hazelnut shell blended samples were determined by TG at four heating rates (β) 5, 10, 20, and 30 K min^{-1}. TG results for coal, hazelnut, coal–hazelnut shell 20 mass %, coal–hazelnut shell 40 mass %, and coal–hazelnut shell 50 mass % were presented in Fig. 2. As it might be examined, the mass loss characteristics under oxidative atmosphere for coal and hazelnut shell showed different combustion profiles. One sequential zone was observed in coal case, while hazelnut shell and blended samples have two. For those samples, devolatilization stage was followed by char oxidation combined with coal combustion step [12]. As shown in Fig 2, the thermal degradation temperature of coal is higher than that of blended coal samples. This was explained by the difference between molecular structure strength of coal and hazelnut shell. According to structural analysis study of Demirbaş [27], hazelnut is mainly consisting of 30.4%

hemicellulose, 26.8% cellulose, and 42.9% lignin polymer that are connected with very weak ester bonds. However, high aromatic content in the coal structure requires high temperature to decompose [13].

The solid residue yields were about 36.1% for coal and 29.3% for coal–hazelnut shell 20 mass %. The residual mass decreased with an increasing amount of hazelnut shell content in the blend and it reached to 0.1% for hazelnut shell. This indicated the high combustion potential of the hazelnut shell sample. Since the hazelnut shell contained less fixed carbon and high volatile matter that volatilized more easily under the combustive conditions. Furthermore, with the increase of heating rate, the samples were experienced a short exposure time to the particular temperature which in turn affects combustion kinetics. When heating rate increased, TG curves were very close to each other, and mass loss observed at higher temperatures. This trend was attributed to changes in the heat transfer.

-Figure 2-

Analysis of kinetic parameters

The isoconversional method is mostly studied for the investigation of combustion kinetics of carbonaceous material. Using this method, at least three dynamic curves with different heating rates were required. For this study, different percentages of conversion (α) 20, 30, 40, and 50 % were considered. The plots of $\ln\beta$ versus $1/T$ with respect to several conversion degrees were depicted in Fig. 3. The correlation between conversion and activation energy is essential to explore the mechanism and kinetics of decomposition process. It is noted that, there were mostly linear relations for the four different percentages of conversion. Therefore, the activation energies were calculated from the corresponding slopes according to the Ozawa–Flynn–Wall kinetic model. Tables 2 and 3 indicated the activation energies at given conversion and average activation energies of the coal, hazelnut shell and blended samples. It was observed that the calculated activation energies for hazelnut shell blended samples were found consistently higher than those of coal. Similar behavior has been previously reported by Siti et al. [28] where they used Malaysian oil palm biomass, sub-bituminous coal in their experiment. According to Gil et al. [29], a high temperature or a longer reaction time is obligatory for the reactions with high activation energy. This could be attributed to the higher activation energy in combustion of biomass as compared to coal. On the other hand, the 20 mass % blend was reasonably similar to activation energy of the coal sample. Resembling the activation energy corresponding to coal was consistent with the activation energies that were reported for low rank coal [12]. Activation energies corresponding to the hazelnut shell here used are higher than those found for low rank coals but lower than E values for materials such as residues from composting [30] and sugarcane bagasse [31]. Furthermore, increasing the temperature, combustion of the sample followed with mass losses largely attributing to decrease in activation energies.

-Figure 3-

Fig. 4 showed ln[-ln(1-$\alpha(T)$)] versus lnβ plot for the comparison of reaction orders. It was assumed that n values depend on temperature and type of carbonaceous material. Temperature dependence of n values for coal, and hazelnut shell blended coal samples were represented in Table 4. It could be seen that the reaction order values were close to zero and the reaction order in the range of 0.17–0.40. There was not any linear relationship between the reaction order and activation energy values. Coal and coal–hazelnut shell 20 mass % had comparable n values and greater than 50 mass % blended and hazelnut shell samples. It was obvious that the reaction orders were dependent on the extent of the reaction and they were not constant during the reaction proceeded. This behavior was attributed to presence of multiple reaction steps as devolatilization and combustion. The n value for hazelnut shell was in agreement with those found in the literature in the combustion of biowastes [32].

-Figure 4-

Table 2. Values of activation energy, slopes and correlation coefficients (R^2) corresponding to linear fittings in Fig. 3.

Sample	**Conversion**	**Slope**	***E*/ kJmol^{-1}**	R^2
Coal	20	-17.3	135.9	0.99
	30	-12.6	99.5	0.99
	40	-9.1	71.9	0.99
	50	-7.1	56.1	0.98
Coal–hazelnut shell 20 mass %	20	-19.3	152.5	0.95
	30	-14.2	112.2	0.96
	40	-8.6	67.9	0.97
	50	-6.0	47.4	0.95
Coal–hazelnut shell 40 mass %	20	-20.4	161.2	0.96
	30	-10.0	104.3	0.96
	40	-10.4	82.2	0.92
	50	-8.5	67.2	0.98
Coal–hazelnut shell 50 mass %	20	-25.7	202.9	0.99
	30	-23.3	184.2	0.99
	40	-19.7	155.6	0.93
	50	-15.9	125.6	0.96
Hazelnut shell	20	-27.4	216.5	0.98
	30	-27.3	215.7	0.98
	40	-26.4	208.6	0.98
	50	-27.9	220.5	0.98

Table 3. Values of activation energy estimated by the Ozawa–Flynn–Wall isoconversional method

Sample	Average activation energy/ $kJmol^{-1}$
Coal	90.9
Coal-20% hazelnut shell	95.0
Coal-40% hazelnut shell	103.7
Coal-50% hazelnut shell	167.1
Hazelnut shell	215.3

Table 4. Reaction order (*n*) as a function of temperature

Temperature/K	Coal	Coal-20% hazelnut shell	Coal-40% hazelnut shell	Coal-50% hazelnut shell	Hazelnut shell
673	0.21	0.25	0.31	0.10	0.20
723	0.31	0.36	0.34	0.16	0.18
773	0.38	0.39	0.39	0.24	0.40
Average *n*	0.30	0.33	0.35	0.17	0.17

Conclusions

Hazelnut shell and Beypazari lignite are significant energy sources in Turkey, and blending of these two samples may provide a way to compensate negative effects of each other. The addition of hazelnut shell into coal affected the combustion system in such a way that more mass loss was clearly observed compared to the combustion of coal alone. Furthermore, comprehensible thermal decomposition differences were observed during the combustion of coal and coal/hazelnut shell blends. In general: (1) the thermal degradation temperature of coal is higher than that of blended coal samples due to molecular structure strength; (2) increasing the heating rate resulted in more pronounced heat transfer limitations that caused the combustion to complete at higher temperatures; (3) as blending ratio increases, residual mass decreases. The kinetic analyses demonstrated that the activation energy and reaction order changes in the range of 90.9–215.3 kJ mol^{-1} and 0.17–0.40, respectively, depending on blending ratio. Among the tested blends, the 20 mass % blend indicated the lowest activation energy (95.0 kJ mol^{-1}). TG analysis allowed ascertaining that differences between coal and hazelnut shell combustion were significant and the feasible combustion could be achieved with the lower hazelnut shell mass % blends. The present study showed the combustion kinetics of coal/hazelnut shell blends that might be very useful before planning their large-scale incineration. However, the kinetic parameters achieved in this work obtained from reaction rates only by considering temperature, regardless of mass transfer, therefore specific combustion operation parameters should be further studied for a combustion reactor.

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Figure Captions:

Fig. 1. SEM micrographs of **(a)** hazelnut shells **(b)** residue of fired hazelnut shell at 1173 K.

Fig. 2. TG curves of the combustion of coal, hazelnut shell, and hazelnut shell blended coal samples at different heating rates (β).

Fig. 3. Curves indicating the kinetic model proposed by Ozawa-Flynn-Wall to various conversion percentages corresponding to the combustion of coal, hazelnut shell, and hazelnut shell blended coal.

Fig. 4. Curves indicating the reaction order n for 673 K, 723 K, and 773 K along the combustion of coal, hazelnut shell, and hazelnut shell blended coal at different heating rates.

Figure 1.a
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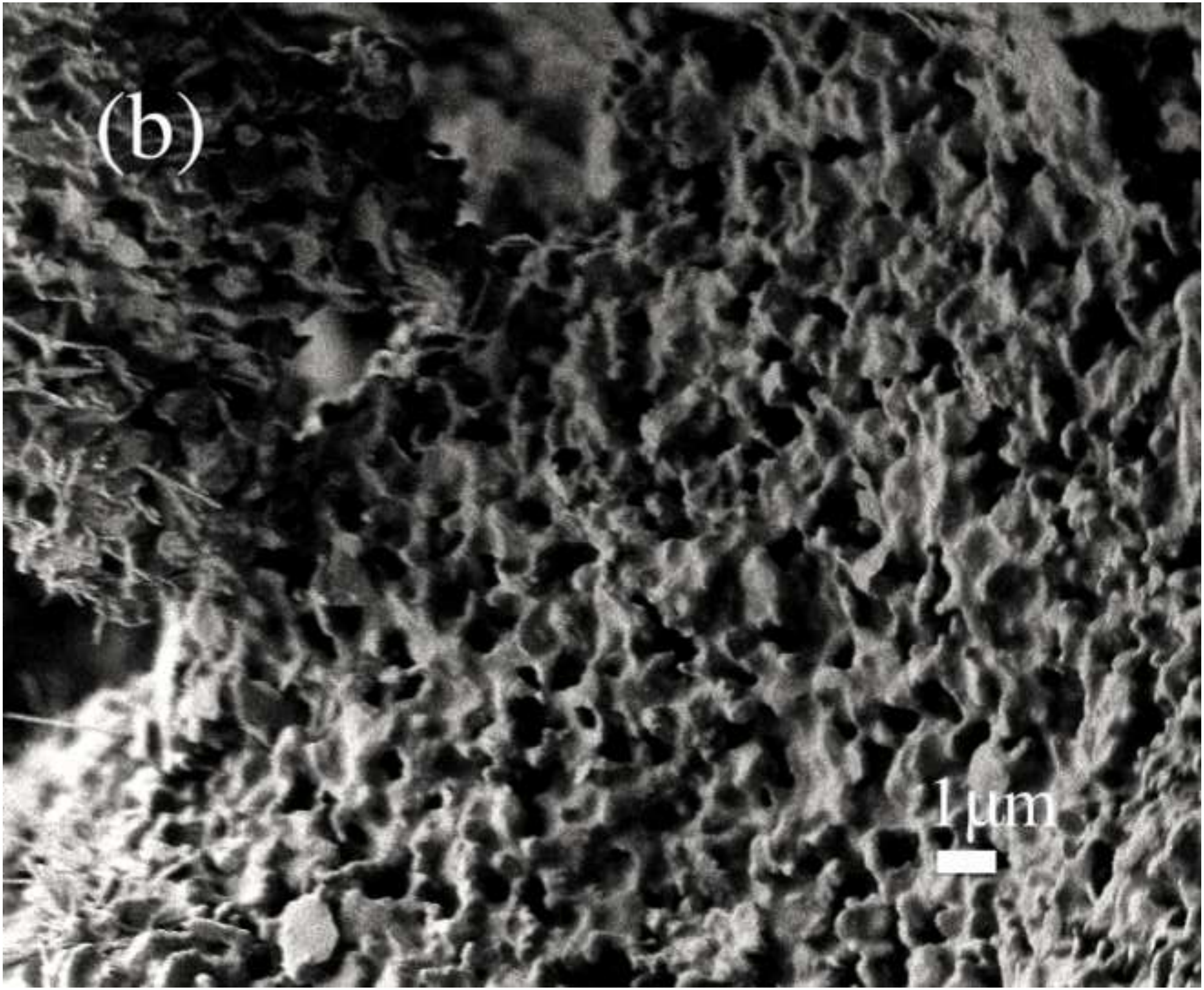

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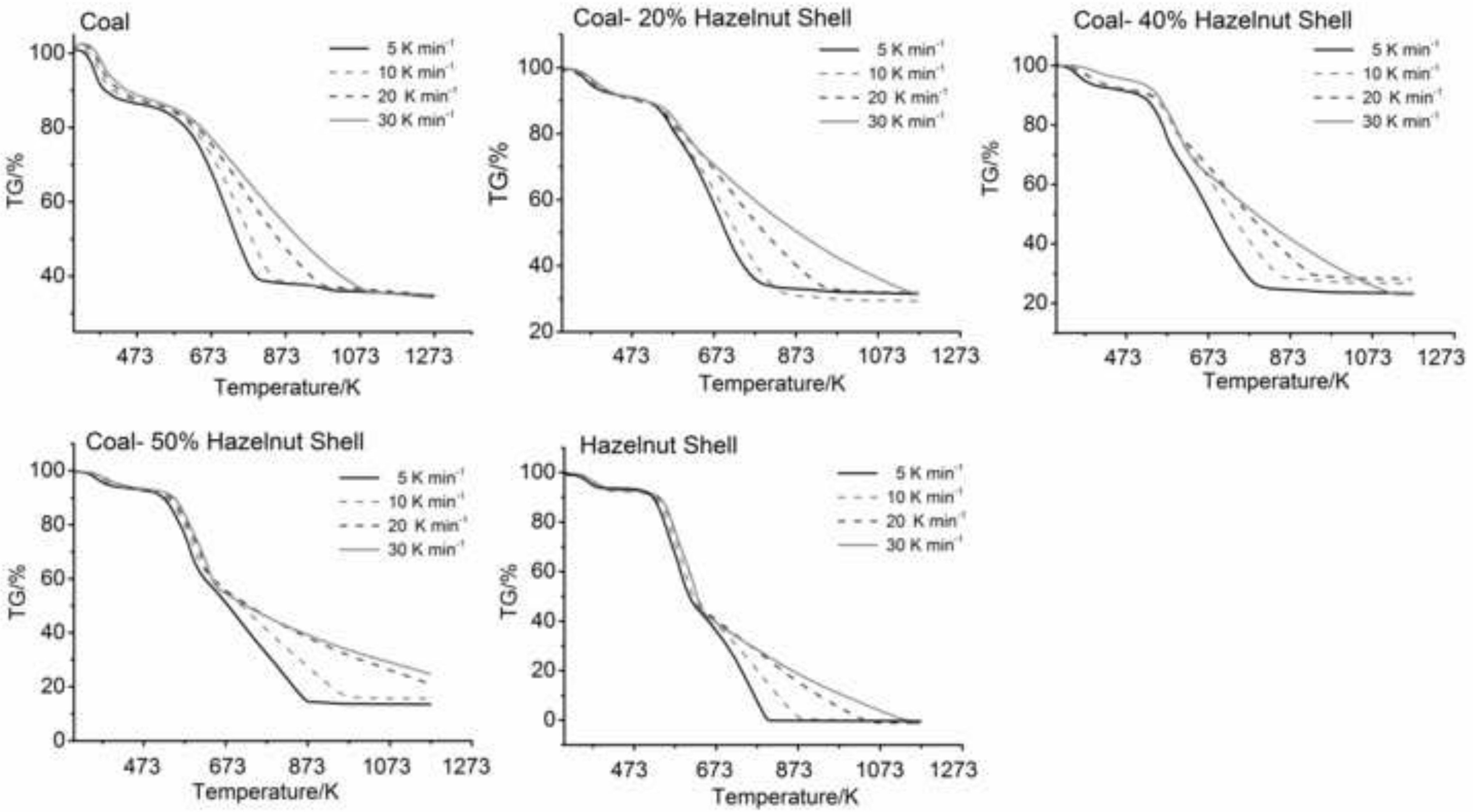

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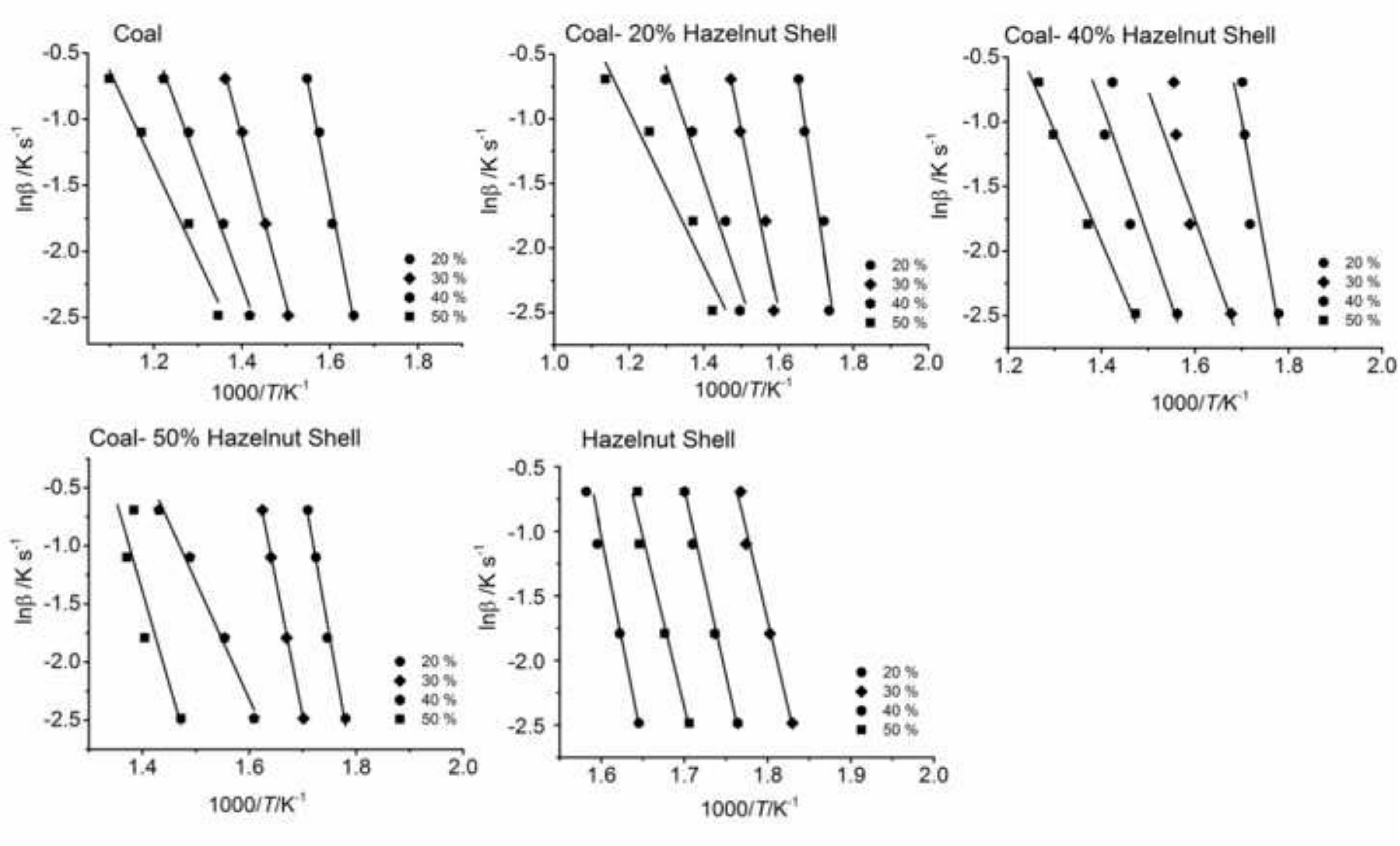

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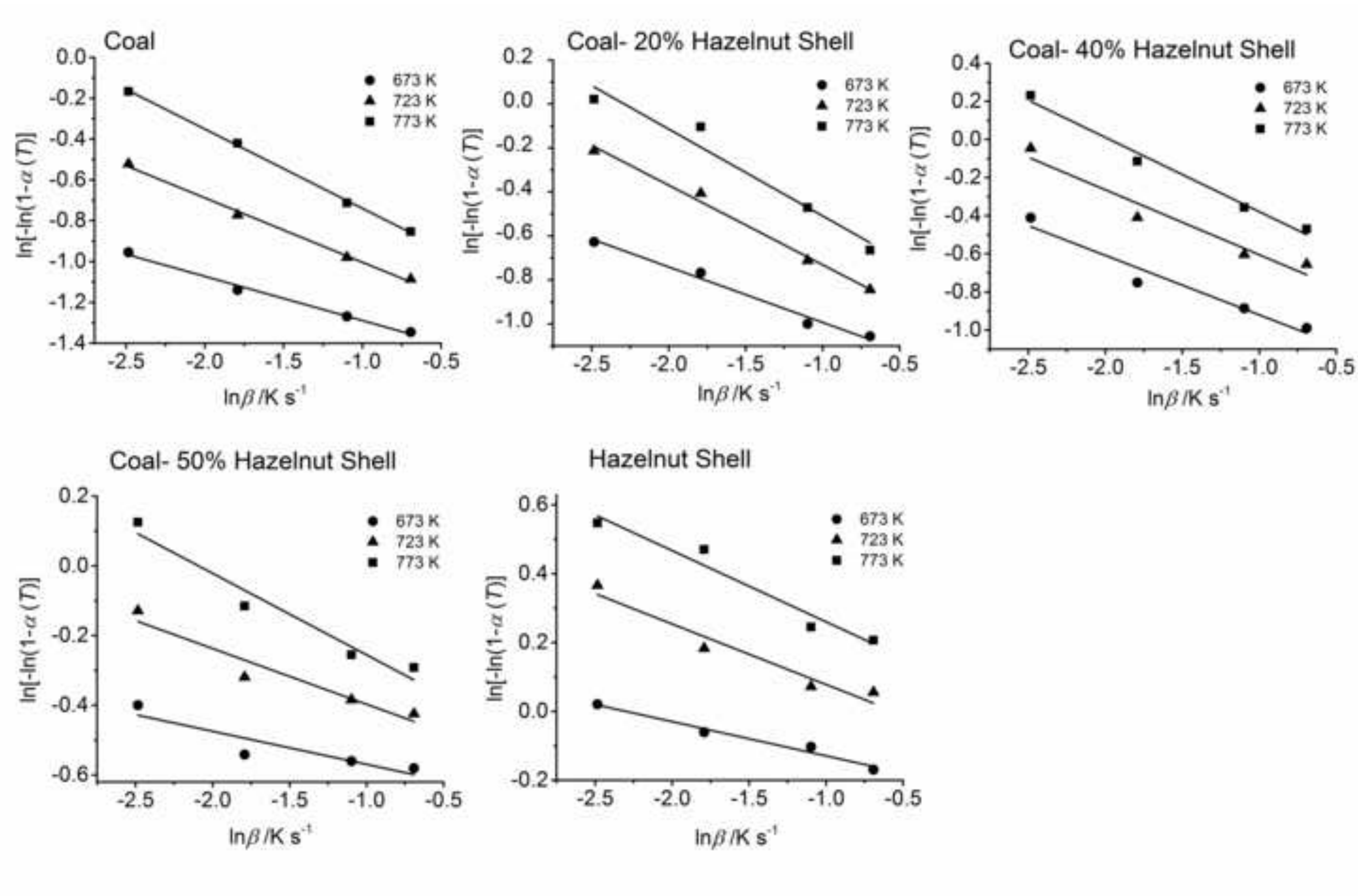

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Yuda Yürüm		30.07.2014, Turkey
Author	Signature	Date and Place