Study of Hydrothermally Lignite and Rice Husk blend: Thermogravimetric Analysis

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Abstract. The increased realization in greenhouse emission has encouraged to grow new technologies to accommodate the confinement and seizure of CO₂. Keeping this situation, the thermal behaviour of lignite, Rice husk, besides their mergers throughout pyrolysis and combustion procedures, was examined in the study for their possible usage as a sustainable and substitute energy resource. The experiments were done in a thermo-gravimetric analyser at a heating rate of 40 °C/min and range from standard room-temp up to 950°C. These blends presented diverse ignition as well as combustion actions dependent on the proportion of rice husk and atmosphere (Oxy-fuel or Nitrogen). These investigational outcomes support to describe as well as expect the performance of lignite and rice husk blends in real applications.

1. Introduction
Consistent, useful, as well as the clean energy resource, remains one of the elementary requirements of humanity. Air pollution is a major global environmental problem, with various adverse effects on health and the environment. International and regional agreements bound nations to reduce emissions of air pollutants. Several conventions regulate atmospheric and related issues, yet there is still no coherent legal framework addressing the protection of the atmosphere. Durable confirmation proposes that the mutually average global temperature and CO₂ absorption have expressively improved the beginning of industrial advancement. Also, they remain sound connected [1]. Anxieties above environmental variation have directed to growing energies, going on emerging technologies near to condense carbon dioxide productions as of humanoid actions [2-3].

Coal has been and will endure some of the key energy resources in the long-term as of its abundant reserves in addition to comparably low-price, particularly intended for the usage of base-load power generation. Intended for illustration, the coal percentage in the world energy feeding remained 29.4% in 2009, as compared to the oil as 34.8% as well as 23.8% natural gas [3]. In the tenure of power generation, in the USA, coal endures the leading fuel, causal around 43.3% of the entire power generation in 2011 [4], and approximately 79% in China.

As shown in Fig 1, the largest producer of power from coal is in China, as compared to the other countries, which has coal and biomass reserves. The new principle intended to condense the GHG emissions by emerging new technologies [4]. The combustion of fossil fuels is the donor to the emissions of carbon dioxide and Green House consequence [5]. The left-over to energy perception is one of the most suitable solutions to handle by the agro-waste as well as to diminish the GHG emissions by cultivating the adeptness of fossil fuels [6].
Pakistani coal has 97% lignite, and residual are sub-bituminous and bituminous coal [7]. Nevertheless, the direct use of lignite has the numeral of Limitations related to the environment adulteration, maximum cost, and minimum energy [8].

Numerous biomass resources, for instance, agricultural, forestry, municipal as well as industrial wastes be able to use as fuel for the generation [9–11]. As described by authors, [12] huge distinctions of biomass features are typically owing to alterations in the methods, heating rate, atmosphere, in addition to the alterations in the chemical configurations.

This work is based on the study of thermal properties of blends using the TG apparatus under isothermal and non-isothermal situations and, similarly, discover out the conduct of the blend linked to the emission-related to the environment as well as energy production. The combustion and pyrolysis study of numerous blends were conceded out to classify the finest configuration of the blend to accomplish the objective.

2. Material and Methods

TG study of given samples was conceded out by the rate of heating 40 °C/min in the Oxy-Fuel and nitrogen environment. The temperature range was ambient to 950 °C; the sample quantity was 10 mg max in gross weight. Oxygen for combustion and nitrogen for pyrolysis in the thermo-gravimetric analyser, the rate of flow was fixed on 20 ml/min, with the rate of heating 40 °C/min, in addition to staying additional 60 mins at 950 °C in pyrolysis. The experiments were completed through SDT q600 America Thermo-Gravimetric Analyzer, according to the ISO 11358-1 standard.

The calorific values of blends were taken through subsequent the ASTM D5865-13 by LECO AC 500 bomb calorimeter (Germany).

Proximate analysis was conceded out in the muffle furnace to measure the moisture, volatile matter, and ash content, according to ASTM standards D3302/D3173, D3175-11, D3174-12, respectively. LECO628 CHN-X analyzer (Germany) remained to amount the sulfur and carbon substances in the samples (ASTM D4239-14, D3172-13, respectively).

2.1. Sample Formation

Pakistani lignite was found from Baluchistan, and the rice husk was collected from the local village to form blends. Three number of diverse arrangements were prepared by variable the attentiveness of the local rice husk (L_{RH}) and lignite of Pakistan (P_{L}). The first composition 30% by weight, lignite, and 50% by weight rice husk was mixed to make P_{L}30-L_{RH}50 blend. Similarly, P_{L}40-L_{RH}60 and P_{L}50-L_{RH}50 found through resolving the P_{L} and L_{RH} in given relations. The ultimate analysis stood accomplished with CHNOS elemental analyzer to analyze carbon, fixed carbon as well as sulfur contents. By using the bomb calorimeter, the calorific value can be found. The Calorific values and ultimate & proximately analysis of all blends are shown in Table 1.
3. Result and Discussion
All samples are predominantly confined Carbon & Oxygen. In PL50/LRH50, the number of carbon contents was in large quantity as compared to the others, which is relatively virtuous in terms of thermal perspective. In PL50/LRH50, low Sulphur contents found as compared to the parent fuels and environment-friendly and no special treatment required for flue gases.

Table 1: Ultimate & Proximate Analysis of parent’s fuels and their blends

|                | Local Rice Husk | Pakistani Lignite | PL30%-%LRH70% | PL40%-%LRH60% | PL50%-%LRH50% |
|----------------|-----------------|-------------------|----------------|----------------|----------------|
| 1 Gross Calorific Value K.cal/Kg | 4082 | 5998 | 4458 | 4980 | 4990 |
| 2 Fixed Carbon % | 22.35 | 43.9 | 28.12 | 32.57 | 33.29 |
| 3 Volatile matters % | 63.25 | 40.09 | 56.07 | 50.05 | 49.56 |
| 4 Ash Contents % | 13.65 | 15.56 | 15.34 | 16.35 | 16.65 |
| 5 Total Moisture % | 7.75 | 6.65 | 5.42 | 7.04 | 5.11 |
| 6 Inherent Moisture % | 0.78 | 0.65 | 0.38 | 1.02 | 0.42 |
| 7 Sulphur Contents % | 0.19 | 4.05 | 1.272 | 1.696 | 2.12 |

Significances of the ultimate and proximate analysis presented that the PL50/LRH50 is the finest sample combination because of its supreme calorific value (4990 Kcal/Kg), which means PL50/LRH50 is the appropriate combination of combustion and energy production at the level of industrial production.

3.1. Pyrolysis
The lingo-cellulosic compounds study is related to pyrolysis because the components decay happens on multiple temperatures between the ranges. Cellulose, as well as hemicellulose, remain polymeric carbohydrate configurations, named polysaccharides. Fig 2 (A, B, C), are combined TG, as well as DTG outlines, show the thermal degradation features of different blends at a 40 °C/min heating rate. Coal-biomass blends can be separated into three main regions in the process of pyrolysis: Firstly, moisture as well as slightly removal of volatile matters (<100 °C); secondly, hemicellulose the degradation of LRH (180-320 °C) as well as lignin and cellulose decomposition of lignite (320-420 °C) and thirdly, lignin degradation of lignite (>420 °C) [13, 14]. From the TG curve, it was detected that the ultimate strength of the second zone was considerably greater than the first zone. From 330 °C toward 950 °C, the weight degradation rate minimized because of the slow decay of lignite in blends. The loss of carbon atoms characteristically happens at a slower rate over a considerable temperature variation of 180-950 °C. CO₂ production is detected because of the oxygen contents of lignite and rice husk [15]. The creation of CO₂ in the nitrogen environment was found chief-contributor to un-restricted gases through the high absorbance-intensity. Correspondingly, methane is produced as a result of de-volatilization. As shown in Fig 2, the moisture degradation and very small amount of volatile constituent’s production is monitored in the first region of weight degradation. Abundant, the de-volatilization happened in the first region of weight degradation, the breakage of thermal bounds of fragile in the polymeric structure of biomass, and the creation of stronger as well as additional steady bonds to take their place [16].

DTG curves show the temperature range upon which the maximum amount of weight degradation happened stay labelled through the peak location in the curve. DTG peaks can be allocated as follow: The first peak of DTG at 80°C, 60°C and 90°C for PL50-LRH50, PL40-LRH60, and PL30-LRH70 respectively, is possibly due to removal of moisture and slight volatile matters and the second because of maximum degradation of weight, 315°C, 320°C and 335°C respectively. The peaks of DTG are considerable nearer of all blends. The third region saw a considerable lower-rate of weight degradation as compared to the second stage.

An evaluation of DTG curves of lignite and rice husk blends established that the peak position moved to low-temperature through the increase of rice husk in the blend [15]. Sulphur dioxide production may be accredited to sulphur in the lignite, whereas methane creation might be produced because of de-volatilization [16].
3.2. Combustion
Thermal stability and thermal decomposition of blends are resolute with thermogravimetric analysis to observe the alteration in mass. Combustion of lignite and rice husk blends P_L50-L_RH50, P_L40-L_RH60, and P_L30-L_RH70 are shown in Fig 3. The first zone can be weight degradation as an outcome exclusion of the moisture contents. The thermal degradation of local rice husks can be done in two different steps. First, the de-volatilization of cellulose and hemicellulose components and second, degradation can be done because of char combustion.

Fig 3 (A, B, C), demonstrate the weight degradation because of moisture contents between 25-100 °C and show a low peak at 100 °C, 80 °C and 60 °C of P_L50-L_RH50, P_L40-L_RH60, and P_L30-L_RH70 respectively, which determine the material stability [17]. About 100 °C of all samples, volatile production is on the go. In the oxy-fuel situation, water production happened for all samples in the range of 100-200 °C. The crucial influence to develop carbon dioxide gas is due to its greater intensity of absorbance. The DTG curve of blends reveals, a high peak at 320 °C, 305 °C and 275 °C for P_L50-L_RH50, P_L40-L_RH60 and P_L30-L_RH70 respectively and the extreme weight loss at 250 °C to 340 °C was perceived in TG curves because of weak internal bonding in rice husk. From 320-375 °C for P_L50-L_RH50, 305-350 °C for P_L40-L_RH60, and 275-305 °C for P_L30-L_RH70, decomposition of lignite is occurring. The degradation of lignite was moderately sluggish than rice husk due to strong bonding between carbon-carbon atoms [17, 18].

4. Conclusion
Co-firing of coal and biomass might deliver an attractive choice for the dumping of rice husk, permitting for energy retrieval, along with economical and eco-friendly supports. Combustion analysis indicated that the thermal stability of the lignite was found to be reduced with the increase of rice husk. The increase in the decay rate through the increase of rice husk amount caused the reactivity of rice husk. P_L50%-L_RH50% was originated to be practicable for the energy creation point of view like power plant
& boilers because of high calorific value and low volatile matters, low ash contents and low ignition temperature as associated for other blends and profitable than the imported coal.

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