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INVESTIGATION OF THE THERMAL DEGRADATION BEHAVIOR OF COAL/BIOMASS BLENDS FOR KINETICS ANALYSIS WITH SEQUENTIAL METHOD IMPLICATION

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Abstract

Pakistan currently has a problem in the energy supply and demand. There is a large gap between supply and demand for electricity. The depletion of fossil fuels and environmental pollution factors also exist. These factors convert the intention to implement co-firing of coal and biomass. Being agricultural land and producing a significant amount of agricultural waste and have a little valuable use of this waste. Keeping in mind for effective use of this agro-waste the pyrolysis behavior of Pakistani local coal (LC), rice husk (RH), and their blends 75LC/25RH wt.%, 50LC/50RH wt.%, 25LC/75RH wt.% were studied using a thermogravimetric analyzer in a nitrogen environment with 10K/min heating rate. A sequential method approach is used to calculate kinetics parameters quickly and accurately. With the assumption of first-order reaction, calculation is performed. The research findings revealed that the addition of rice husk to the blends led to an increase in the activation energy for devolatilization, rising from 22.9 kJ/mol to 45.2 kJ/mol. However, the activation energy for char degradation decreased from 60.4 kJ/mol (100%LC) to 14.2 kJ/mol (100%RH) as the proportion of rice husk in the blends increased. Moreover, the rate of mass degradation also increased with higher amounts of rice husk in the blends. These results suggest that the decrease in char degradation activation energy allows for a reduction in operational temperature, thereby facilitating a reliable co-pyrolysis process. Such a process holds the potential to design a low-cost and effective gasification process, aiding in overcoming the energy challenges.

Keywords: **Activation energy, Biomass degradation, Kinetics, Pyrolysis, Sequential Method.**

1. INTRODUCTION

Energy serves as the foundation for a nation's economic stability. Fossil fuels, including natural gas, crude oil, and coal, are pivotal to sustaining the economy, providing essential resources for heat production and electricity generation [1]. From a setting purpose of regard well as money, man has tried to extend the potency of energy production from initial raw materials. Considering the environmental aspect of reading, coal's poor conversion to energy indicates that a lot of earth's resources are wasted as well as a lot of waste is produced [2]. The combustion of coal has great alarm on the environment due to CO, NOx and SOx emissions that can cause global warming and acid rain phenomena [3]. The alternative proposal implies reducing emissions by minimizing coal combustion and incorporating the co-firing of coal and biomass materials [4]. Coal reserves eventually expand compared with biomass fuels that may be reproduced often.

The primary use of biomass in utilities is either as a standalone fuel in boilers or co-fired with coal. In this context, coal/biomass blends are considered a viable alternative for co-pyrolysis [5]. Additionally, cofiring presents a viable approach to address specific limitations found in individual samples. For instance, it can help mitigate challenges arising from high volatile matter in biomass, significant sulfur fractions, and undesirable ash content found in coal [6]. In addition to this, there may be a synergistic effect in the mixture because of the presence of ash in both samples. Despite the simplicity of the coal/biomass co-firing concept, further study is needed for the emissions, combustion efficiency, and impact on current co-firing equipment's performance [7]. Hence, a critical matter that demands complete comprehension is the data related to the chemical composition, thermal behavior, and reactivity of biomass fuels, along with their co-pyrolysis with coal [4]. Unlike fossil fuel, biomass reduces CO_2 emission and provides a less costly, non-depleting, reliable, and sustainable source of renewable energy. The RH is an abundantly available biomass from agricultural waste that can be cofired with coal. It is produced as a byproduct while the rice milling process is carried out. Some quantity is used to feed animals, a little amount for energy generation, and the rest is dumped to waste [8]. Globally, it is produced in millions of tons according to literature [9]. The commercial development of thermochemical devices for the conversion of carbonaceous materials requires a comprehensive understanding of the control of combustion constraints and their impact on the process parameters of kinetics. In this case, thermal analysis methods i.e., thermogravimetry analysis (TGA), and differential thermogravimetry analysis (DTGA), techniques have been increasingly used in the assessment and characterization of coal/biomass sources as a resource for defining the combustion characteristics and kinetic parameters [10, 11, 12]. Thermogravimetric Analysis (TGA) is an analytical technique that analyzes mass changes in a substance under regulated temperature circumstances, yielding significant information on reaction kinetics and combustion parameters. In terms of kinetics, TGA data on mass loss rates at various temperatures may be used to calculate reaction rates and activation energy, allowing researchers to better understand the rate of thermal degradation and other events. In combustion investigations, TGA exposes the temperature and rate at which a material decomposes or burns, giving valuable information regarding combustion efficiency, ignition temperature, and material stability. Thus, TGA is useful in assessing the thermal and combustion behaviors of diverse materials, which has applications in material science, chemistry, and environmental research. Thermogravimetric Analysis (TGA) was combined with CHNS (carbon, hydrogen, nitrogen, and sulfur) analysis to offer a thorough knowledge of material attributes by integrating thermal degradation data with elemental composition insights. While TGA examines mass changes at regulated temperatures to assess reaction kinetics and combustion properties, CHNS analysis quantifies the material's elemental makeup. This combination technique enables researchers to conduct extensive assessments of thermal stability, reaction rates, and combustion efficiency, providing a more complete view of the material's behavior under thermal and combustion-like circumstances. The primary objective of this research was to investigate the combustion characteristics and kinetics of coal/biomass (Rice Husk) mixtures. A model-free approach Kissinger–Akahira–Sunose (KAS) method [13] and Flynn–Wall–Ozawa (FWO) method [14], or a model-fitting approach sequential method [15] can be used to derive the kinetic parameters. A sequential method was introduced to efficiently and precisely determine the kinetic parameters of biomass pyrolysis. Additionally, the investigation generated valuable data on the combustion of these coal/biomass blends. Moreover, these findings contribute to a deeper comprehension of the coal/biomass combustion behavior, aiming to fulfill system level requirements.

2. MATERIAL AND METHOD

2.1. Material

The samples used in this study were low-rank local coal (LC) from Potohar region (32°33'19.3"N 72°18'54.4"E) and rice husk (RH) from the District Sheikhupura region (31°39'40.6"N 74°06'25.0"E) of Pakistan. The samples were ground with ball mill to less than 1000 µm and 200 µm to 700 µm particle size limits were selected for maximum inter particle heat transfer [13]. The sample mass was measured on balance to make the blends with composition by weight percent (wt.%) of 100LC/0RH wt.%, 75LC/25RH wt.%, 50LC/50RH wt.%, 25LC/75RH wt.%, and 0LC/1000RH wt.%, presented in Table 1. A thorough mixing process was used to achieve homogeneity. It was important to select blends that represented a reasonable range of blends for the study.

Table 1.
Sample Proportions

Sample	Designation	Proportions
1	Coal	100%
2	Coal: Rice Husk	75%: 25%
3	Coal: Rice Husk	50%:50%
4	Coal: Rice Husk	25%: 75%
5	Coal: Rice Husk	100%

2.2. Experimental setups

Bomb calorimeter was used to calculate the calorific value of coal, rice husk and their blend samples. Calorific values were obtained by following ASTM E711-87 with the help of LECO AC 500 bomb calorimeter.

The CHNS analyzer was used to calculate the elemental composition of Carbon, Hydrogen, Nitrogen, and Sulfur in the prepared samples. This test, performed with the ASTM D-3176 and LECO628 CHN-X analyzer, was used to measure the percentage of elements.

The thermal degradation behavior of coal, rice husk, and their mixtures was evaluated using a Thermogravimetric Analyzer. The ISO 11358-1 standard method was followed, and the SDT Q600 apparatus was employed for conducting the Thermogravimetric analysis (TGA) measurements. ISO 11358-1:2014 – Plastics – Thermogravimetry (TG) of polymers, Part 1: General principles provide the general principles for doing thermogravimetric analysis (TGA) on polymers. This ISO standard specifies a uniform methodology for measuring the mass change of a polymer sample under controlled heating, which provides information on thermal stability, composition, and decomposition behavior. It covers important topics such sample preparation, equipment calibration, and data interpretation, ensuring that TG values for polymers are accurate and comparable across laboratories. ISO 11358-1, which is widely used in materials research and industrial quality control, contributes to the standardization of processes for measuring polymer thermal characteristics.

For the tests being conducted, temperature, time, particle size, and sample composition are measured as independent variables, while weight and heat flow are dependent variables. Non-isothermal conditions apply, and other likely variables include initial temperature (room temperature), final temperature (1073.15 K), heating rate (10 K/min), N_2 gas flow rate (10 ml/min), and sample size (mg), which were detained static during testing. These parameters affect the shape of the weight vs. temperature/time trace obtained from the TGA. They were selected to minimize the error between actual and calculated thermograms.

In analysis, a detailed weight loss curve can be obtained in the thermal decomposition of rice husk. Non-isothermal techniques are often used because maintaining a constant heating rate is more difficult than maintaining the environment at a constant temperature, primarily regarding exothermic reactions [16].

2.3. Kinetic Model

The kinetic parameters determined in most studies depends on many factors including atmosphere, flow rate, heating rate, sample shape, sample quality, etc. The mathematical model used to estimate the data has a significant impact on the estimation of results. The derivation of kinetic parameters was evaluated in most of the scientific literature, including activation energy.and pre-exponential factors in chemical reaction data [17]. The reaction rate equation (1) is applied where the thermal decomposition of solids occurs:

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{1}$$

The conversion factor can be represented by:

$$f(\alpha) = (1-\alpha)^n \tag{2}$$

where “n” represents the order of reaction and (1-α) represents the unreacted portion of the sample.

The material’s degree of conversion (α) is characterized by the following definition:

$$\alpha = \frac{m_o - m}{m_o - m_f} \tag{3}$$

Where m_0, m_f, and m_t represent the initial mass, final mass, and time-dependent mass, respectively.

$$k = Aexp\left(-\frac{E_a}{RT}\right) \tag{4}$$

Where "A" is pre-exponential constant, R is the ideal gas constant, T is the temperature in kelvin, and E_a is the activation energy.

Using equation (2) to equation (4), equation (1) becomes

$$\frac{d\alpha}{dt} = k(1-\alpha)^n = Aexp\left(-\frac{E_a}{RT}\right)(1-\alpha)^n \tag{5}$$

Where "k" represents the reaction rate constant obtained through the Arrhenius equation explain.

After arrangement and integration of equation (5),

$$\int_0^{\alpha} \frac{d\alpha}{(1-\alpha)^n} = \frac{1}{n-1}\left[\frac{1}{(1-\alpha)^{n-1}} - 1\right] = \\ = \frac{A}{\beta}\int_0^{T} \exp(-\frac{E_a}{RT})\, dT \tag{6}$$

Where β is the heating rate $(\beta = \frac{dT}{dt})$.

The integral term is solved as $(RT^2/E_a)\exp(-E_a/RT)$ [18]. Equation (6) becomes

$$\frac{1}{n-1}\left[\frac{1}{(1-\alpha)^{n-1}} - 1\right] = \frac{ART^2}{\beta E_a} exp\,(-\frac{Ea}{RT}) \;= K\frac{RT^2}{\beta E_a} \tag{7}$$

According to the study, during the reaction when the temperature rises, the reaction rate. dα /dt reaches to a maximum, and then the reaction rate will reach zero when the reactants are exhausted. When the maximum value of the reaction rate occurs, the differentiation of equation (5) with respect to time or temperature is equal to zero [13]

$$\frac{d}{dt}\left(\frac{d\alpha}{dt}\right) = \frac{d\alpha}{dt}\,\left[\frac{\beta Ea}{RT^2} - An(1-\alpha)^{n-1}\,exp\left(-\frac{Ea}{RT}\right)\right] = 0 \tag{8}$$

At maximum temperature (T_m)

$$\frac{\beta Ea}{RT_m^2} = An(1-\alpha_m)^{n-1}\exp(-\frac{Ea}{RT_m}) = k_m\, n(1-\alpha_m)^{n-1} \tag{9}$$

After arranging and combining equation (7) and (9) it gives

$$(1-\alpha_m) = (1-\alpha)_m = n^{\frac{1}{1-n}} \tag{10}$$

By substituting equation (10) into equation (7) and equation (9) lead to

$$Ea = K_m\frac{RT_m^2}{\beta} \tag{11}$$

From equation (5) and equation (10), Equation (11) will become.

$$Ea = RT^2(1-\alpha)_m^{-n}\left(\frac{d\alpha}{dT}\right)_m = n^{\frac{n}{n-1}}RT_m^2\left(\frac{d\alpha}{dT}\right)_m \tag{12}$$

The determination of the pre-exponential factor is possible by

$$A = n^{\frac{n}{n-1}}\,\beta\left(\frac{d\alpha}{dT}\right)_m \exp\,[n^{\frac{n}{n-1}}\,T_m\left(\frac{d\alpha}{dT}\right)_m] \tag{13}$$

Through thermogravimetric data at maximum reaction rate $((1-\alpha)_m$ and $\left(\frac{d\alpha}{dT}\right)_m)$ both pre-exponential factor and activation energy can be obtained without the complicated calculations.

2.4. First-order reaction kinetics

For first-order reaction considerations, after arranging and integration, Equation (5) leads to

$$-\ln(1-\alpha) = \frac{ART^2}{\beta Ea}\exp(--\frac{Ea}{RT}) = \frac{kRT^2}{\beta Ea} \tag{14}$$

Also, from equation (5)

$$K = \frac{1}{1-\alpha}\frac{da}{dt}$$

Substituting k value in equation (14) and after arrangement it gives

$$Ea = \frac{-RT^2}{(1-\alpha)\ln(1-\alpha)}\left(\frac{d\alpha}{dT}\right)_m = eRT^2\left(\frac{d\alpha}{dT}\right)_m \tag{15}$$

And determination of the pre-exponential factor by

$$A = e\beta\,\left(\frac{d\alpha}{dT}\right)_m \exp\,[\,eT_m\left(\frac{d\alpha}{dT}\right)_m] \tag{16}$$

Similarly, when it comes to nth-order reactions, the kinetic parameters can be determined using first-order reaction data from thermogravimetric analyses, provided that the maximum reaction rate is known, along with the essential information of temperature and reaction rate. In these instances, it is more suitable to assume that biomass pyrolysis adheres to the first-order reaction law, especially when cellulose content is significantly high and cellulose pyrolysis is linked to the pyrolysis of other components [15].

3. RESULTS & DISCUSSION

Experimental results in Figure 1 show that increasing the rice husk content in the blend decreases the calorific value. Pure coal has a higher heating value (HHV) than pure rice husk. A 50:50 blend of coal and rice husk is optimal for commercial use due to balanced reactivity and compliance with emission protocols. This blend also mitigates slagging issues in thermo-mechanical machinery caused by excess rice husk. Utilizing rice husk as a fuel source is more sustainable, repurposing agricultural waste that would otherwise be discarded.

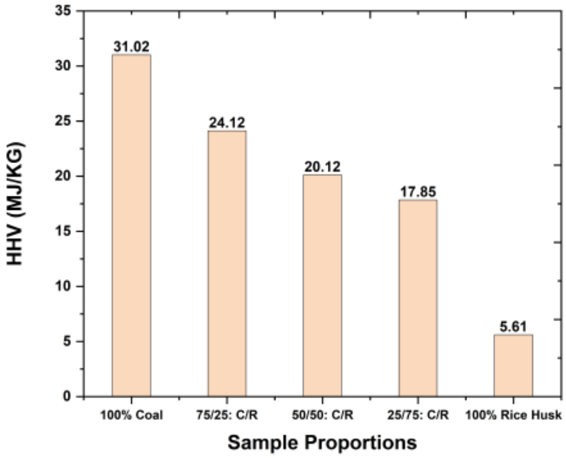

Figure 1.
Higher Heating Value

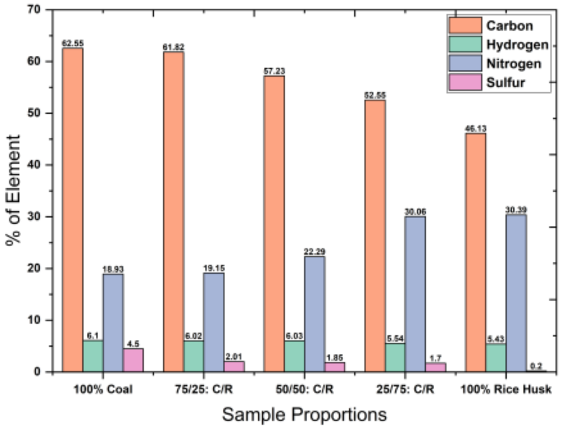

Figure 2.
Elemental Analysis

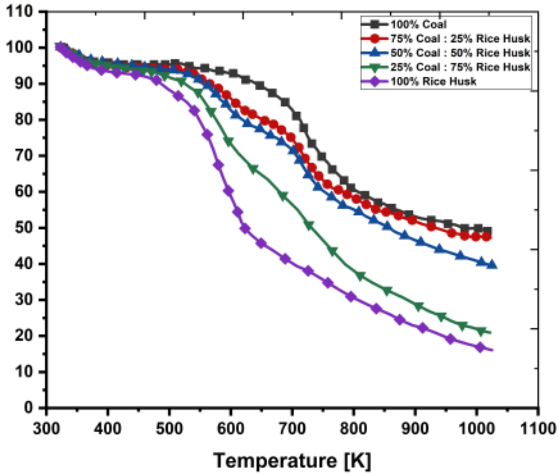

Figure 3.
Mass Degradation of coal, rice husk and their blends

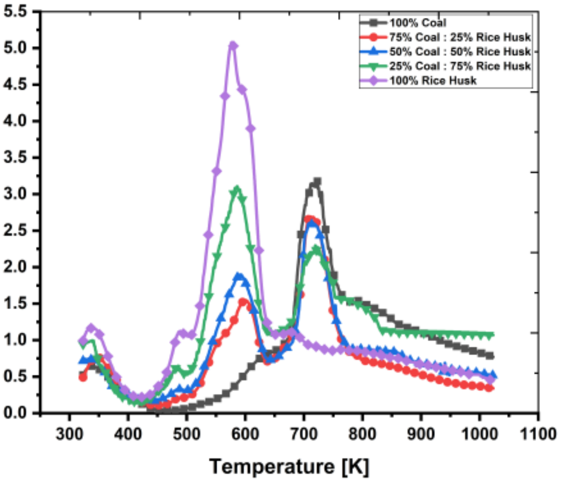

Figure 4.
DTGA Data Evaluationblends

Elemental analysis (Figure 2) shows that coal has high sulfur content, leading to SOx emissions, which are environmentally harmful. Using rice husk can reduce SOx emissions. Rice husk also has more nitrogen, but NOx formation occurs at elevated temperatures. Increasing rice husk reduces char degradation temperature, lowering NOx formation. Agricultural waste like rice husk contains minimal unreacted carbon and sulfur [19], making it ideal for heat treatment due to its high organic material content. Blending rice husk with coal addresses the issue of nitrogen in rice husk, which can lead to the generation of thermal NO (nitrogen oxides) at elevated temperatures. Rice husk contains a substantial quantity of nitrogen, which, when burned at elevated temperatures, can combine with oxygen to produce thermal NO. However, combining rice husk with coal, which has a lower nitrogen content, can lessen the total nitrogen concentration in the fuel combination. This diluting effect reduces the possibility for nitrogen oxide production during burning. Additionally, coal burns at greater temperatures than rice husk, thus mixing may help regulate combustion temperatures and limit NO generation. Additionally, the use of coal can help reduce nitrogen oxide emissions by enabling the use of low-NOx combustion technologies such staged combustion or flue gas recirculation.

Figure 3 shows the weight loss curves of coal, rice husk, and their blends at a heating rate of 10 K/min under non-isothermal conditions. The curves for the blends lie between those of coal and rice husk. Rice husk exhibits higher reactivity during pyrolysis due to its thermally stable components like silica, as established in previous studies [20].

The main concern is to discuss the rate of pyrolysis in mass degradation. Temperature range 323K to 1023K is selected from TGA data. Figure 4 shows three

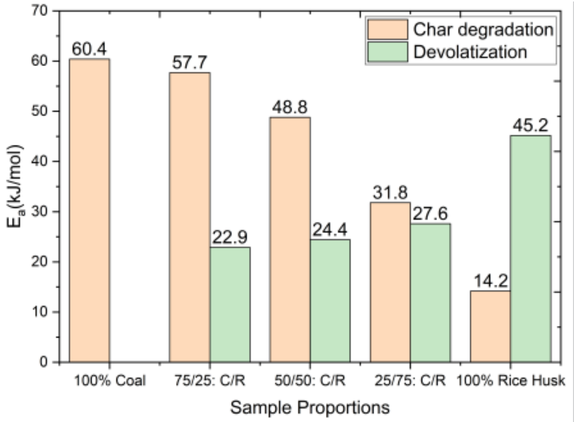

Figure 5.
Activation Energy

pyrolysis stages according to weight loss. The initial weight loss rate is due to moisture removal [21] . It is reported that this stage lies up to almost 450K [22], after this temperature second stage starts, which is so-called active pyrolysis. This stage has a maximum area from 410K to almost 850K. The maximum degradation rate or mass loss rate can be observed in this section. In this stage, most of the volatile gases like CO_2, CO, CH_4, remaining H_2O and other volatile hydrocarbons are released in this area. The third stage starts at above 850K the remaining portion of the volatile evolved in this section is up to 1100K.

In Figure 4 DTG reaction rate profile is slightly mounted before the peak, at temperature 450K to 500K near, exhaustion of hemicellulose should be observed. The main peak in between temperatures of 530K to 620K, where the pyrolysis of biomass occurred, weight loss came from the disintegration of cellulose. In this temperature range, hemicellulose and cellulose react entirely, and the lignin content continues to decompose slowly. In comparison with cellulose and hemicellulose, lignin is a highly crosslinked aromatic polymer with a broad range of chemical bond activity [23] its pyrolysis occurred at an extensive temperature range [24] of 430K to 1200K. The highest weight loss occurs during the active pyrolysis, to this end, the third peak is considered in all cases for kinetic studies. At this stage, the biomass is completely dry, and its key components (hemicellulose, cellulose, lignin) decompose with an increase in temperature. Coal consists of a complex polymer network such as the aromatic cluster of an aliphatic bridge [25]. Meanwhile, biomass consists of light hydrocarbons with weak intermolecular bonds, which evolved at low temperature. Coal, and rice husk blends with the ratio 25:75 C:R showing some deviation above 800K. It may be due to instrument error, human error, not properly mixed, and data evaluation error.

The TG-DTG data is essential for thermal and kinetics assessments, and it comprises key parameters such as initial temperature, final temperature, reaction region, peak temperature, and resultant mass loss. These parameters play a crucial role in defining the combustion characteristics and thermal behavior of coal, biomass, and their combinations. In terms of thermal stability two main factors are: reactivity and degradation. In the case of coal, degradation is more, while in case of rice husk, reactivity is high. Coal: rice husk 50:50, will be the right choice for the commercial feasibility, as higher reactivity leads to incomplete combustion, while higher degradation leads to ineffective and inefficient burning.

The activation energy and pre-exponential factor for coal, biomass, and their blends were determined using the sequential method. Assuming a first-order reaction for solid fuel pyrolysis, the steps involved plotting temperature against DTGA data to evaluate (Ea) and the pre-exponential factor (A).

Step 1: order of reaction finalized which assumed for biomass is n=1. Step 2, unreacted fraction $(1\text{-}\alpha)_m$ of the sample at the maximum reaction rate is determined. Step 3, corresponding temperature T_m is determined at this peak point. Step 4, reaction rate ($d\alpha/dT$) is determined through the equation $d\alpha/dT = 1/\beta^* \, d\alpha/dt$, where β is the heating rate (set by 10 K/min). Step 5, activation energy and pre-exponential factors are determined by using Eq. (15) and Eq. (16) respectively. The above-mentioned procedure is implemented for each sample and corresponding results are compiled in Table 2. In Figure 5

Table 2.
Kinetics Data

Samples	Devolatilization				Char Degradation			
	T_{m1} (K)	E_{a1} (kJ/mol)	K (min^{-1})	A (min^{-1})	T_{m2} (K)	E_{a2} (kJ/mol)	K (min^{-1})	A (min^{-1})
100% Coal	---	---	---	---	722.8	60.4	0.1391	3241.1
75/25: C/R	594	22.9	0.0776	7.854	710.6	57.7	0.1375	2413.7
50/50: C/R	584	24.4	0.0845	11.88	707.5	48.8	0.1173	471.5
25/75: C/R	582	27.6	0.0981	29.48	719.6	31.8	0.0739	15.18
100%Rice Husk	574	45.2	0.1645	2111.4	674.3	14.2	0.0373	0.4603

it can be observed that thermal activation energy of sample decreases with the increase of the rice husk composition in 2nd thermal evaluation profile for char degradation. In the 1st thermal evaluation profile devolatilization range activation energy increases with the increase of rice husk in blends due to high volatile present in rice husk. An increase in the activation energy leads to a decrease in pre-exponential factor for char degradation, so for an optimal solution, it is required that the blend should have low activation energy, to accomplish required reaction with minimal amount of external energy usage.

The sequential method enables the detailed examination of pyrolysis kinetics for biomass, coal, and their blends by determining kinetic parameters such as reaction sequence, pre-exponential factors, and activation energy. This approach is applicable to various biomass pyrolysis reactions, capturing data at the peak reaction rate and temperature, ensuring representative and reliable measurements.

4. CONCLUSION

This method quickly and accurately calculates kinetic parameters using thermogravimetric analysis of coal, rice husk, and their blends. Assuming a first-order reaction, a sequential method was used for simulation, yielding reliable data for co-pyrolysis process design.

- The DTG evaluation profiles for coal and rice husk blends shows three thermal evaluation profiles related to moisture removal, volatile emission, and char degradation.
- The two fuels do not have a synergistic effect on one another.
- The Coal stability is high as compared to rice husk. Through blending with rice husk, the thermal stability of coal can be reduced. This can be an easy approach for the design of the co-pyrolysis process.
- The activation energy in the devolatilization process increased from 22.9 kJ/mol to 45.2 kJ/mol with the increase in the composition of rice husk in blends, a rise in volatile components is responsible for the increase. In char degradation, the activation energy decreases with the increase of rice husk composition in blends. The char degradation temperature also decreased which is favorable for the designing of gasification process environment friendly and cheap.

Co-pyrolysis compared to coal alone, enables thermochemical energy recovery at lower temperatures, reducing construction costs and pollutant emissions, thus proving the reliability of co-pyrolysis for coal/biomass blends. Using AI to improve the co-pyrolysis of coal and rice husk blends can revolutionize process sustainability and efficiency. Without the need for repeated tests, machine learning models can improve process design by predicting kinetic parameters and optimizing blending ratios. Adaptive modifications to optimize reaction conditions for higher energy yields are made possible by real-time AI monitoring. While automated quality control and predictive maintenance guarantee operational stability and reliable biofuel production at scale, sophisticated models can reduce emissions. Furthermore, a digital twin model offers a virtual representation of the co-pyrolysis procedure, facilitating ongoing parameter improvement and feedback. Coal and biomass co-pyrolysis is now a feasible, environmentally benign energy production method thanks to these AI-driven techniques that simplify process efficiency, cut emissions, minimize operating costs, and promote sustainable thermochemical energy recovery.

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