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Thermal performance analysis of optimized biomass conversion in developing organic waste biorefinery to achieve sustainable development goals

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ABSTRACT

To make energy sector sustainable, waste to energy system should be used, as statistics of the International Energy Agency (IEA) shows that the lack of renewable energy and environmental degradation are the major pressing problems confronting the global community. However, in south Asian regions, the situation escalates as a result of severe dependency on conventional energy sources, coupled with the limitations and challenges involved in maintaining a green environment and Waste-to-Energy (WtE) strategies. In this region, energy majorly relies on imported conventional fuel. In addition to harming the environment, imported fossil fuel has also increased the risk of geopolitical unrest. In the current research, rice husk is used as a bio-organic waste that is produced in large volumes and a significant byproduct of agro-based biomass sector. In this research, sample composition of rice husk is demineralized in 5% hydro-chloric acid for different burning ratios and the modified thermo-chemical methodology was used to the acidified rice husk at three different heating rates (20 °C min^{-1}, 30 °C min^{-1} and 40 °C min^{-1}) respectively in thermogravimetric analyzer (TGA). Proximate, thermal and kinetic analysis was used for observing the degradation patterns of demineralized rice husk. Proximate analysis revealed that the leaching of rice husk has successfully infused HCl, resulting in substantial rise in fixed carbon (FC) and calorific value (CV) by 10.53 % and 10.82 % respectively, along with decrease in the carbon footprint of about 60.55%. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves have shown decreasing behavior of conversion efficiency to the increase in flow rate, with the maximum drop of 12.7 % observed at 40 °C. With the use of the TGA equipment, the conversion efficiency was evaluated based on the sample's peak weight loss. The current study has reported synergistic effect of flow and heating rate on the degradation temperatures, activation energy and reactivity of acidified rice husk. Lowest activation energy 180.46 kJ permole with highest reactivity of 0.01192345 %*min °C was observed at 40 ml and 20 °C combination. Accordingly, degradation temperatures of burning profiles increased due to lower convective cooling and higher temperature gradient within the particle of rice husk sample. In addition, pre-exponential data and slopes of TG curves have validated the results of activation energy ob-

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tained from TGA experimentation. The sustainable biomass conversion approach is envisioned to significantly refine the waste bio refinery system to achieve SDGs.

1. Introduction

Circular economy emphasizes on countries to utilize resources that have been previously discarded or wasted as a means of achieving sustainable development [1]. Using traditional solid fuels depletes the environment and substantially impacts global problems (e.g., greenhouse effect and global warming) [2]. To maintain energy security, it is crucial to invent and use unconventional or alternative energy sources [3]. Different economic factors and population expansion in different parts of the world significantly impact the biomass production rate [4]. Twofold expansion in population has been experienced since 1960; previous Figures suggest that the Earth's population will increase thrice by 2050 [5]. However, this tendency is not uniformly distributed, with urban regions having larger population increases due to rural-urban migration, which contributes to agricultural residue buildup [6]. Asia, which includes established and developing countries, is the world's biggest continent, producing around 4.4 billion metric tons of crop leftover annually [7].

To thoroughly understand solid waste production and management in every nation, elements such as economy and climate must be considered [8]. Solid waste is the fourth-largest contributor to global methane emissions with an annual output of 550 Tg of methane [9]. Effective management of solid waste is critical for limiting the negative environmental consequences of hazardous solid waste [10]. To manage bio waste and its emissions, an integrated waste management strategy is needed to be developed, and there is an emerging demand for viable and varied solutions to address waste growth sustainably [11]. Improper solid waste management can harm the environment, ecosystem, and human health, and can result in the scarcity of natural resources [12].

Due to the shortage of resources in emerging nations, this problem is growing more rapidly. South Asian countries use a solid waste management system consisting of primary and secondary waste collection and open dumping [13]. However, these developing countries are facing substantial environmental difficulties due to poor solid waste management [14]. These third world countries produce large amounts of bio waste from homes and agriculture through organics and biomass [14,15]. Unfortunately, only 65% of solid trash is collected and disposed of through proper channels, while the remaining dumped publicly [15]. Dumping happens often in public places such as parks, streets, highways, and railway sectors in many major cities [16]. Open dumping of garbage can result in serious health and environmental issues due to soil, water, and air pollution [17]. It can also leads to increase in contamination and economic losses [18]. To solve these issues, developing nations must enhance their solid waste management systems by expanding the coverage and effectiveness of their main and secondary collection systems, encouraging trash recycling and reuse, and ultimately reducing the volume of garbage delivered to open landfills [19]. Furthermore, educating the public on the need for effective waste management and encouraging their participation in trash reduction activities will help to build a cleaner, healthier, and more sustainable environment for inhabitants [20]. According to studies, up to 75% of the waste in third world countries landfills and waste management sites is organic waste [21]. Due to industrialization, the developing countries' energy demand is rising rapidly [22]. In such a scenario, one way to address both the waste and energy issues simultaneously is by employing WtE techniques [23,24]. By adopting this approach, we can transform our problems into opportunities and solutions.

Based on literature, it has been found that a majority of the waste is made up of organic materials. This supports the usage of waste to energy (WtE) culture to achieve an appropriate waste management approach in the current circumstances [25,26]. It involves biological decomposition of organic waste into oxygen, carbon dioxide, moisture, and water forms ash [27]. This approach is considered natural, sustainable, safe, and inexpensive [28]. WtE may also help with soil enrichment and agricultural growth while minimizing landfill dependency [29]. It has been reported that thermal degradation temperatures, such as Maximum weight Loss temperature (T_M), ignition temperature (T_I), and Burn-out temperature (T_B), play a crucial role in energy generation and production when considering WtE technologies [30]. Furthermore, these temperatures considerably influence biomass environmental behavior [31]. T_I is an important metric for constructing and running WtE equipment and processes respectively [32]. Meanwhile, T_M and T_B temperature are important indications of the thermal stability and performance of biomass materials, especially in high-temperature applications [33]. Enhancing the efficiency of conversion processes is the primary objective of technical advancements in utilizing biomass to meet commercial energy demands [34]. This involves optimizing operating parameters through kinetic modeling, particularly in large-scale pyrolysis and gasification systems. Kinetic modeling quantitatively represents various reactions, enabling predictions of reactor performance, process design, pollutant evolution, and improved control strategies [35]. Pollutant evolution, in our investigation delves into the intricate changes that various pollutants, such as chemical compounds or emissions, undergo [36]. These alterations encompass the potential shifts in their harmfulness or their capacity to influence the environment, particularly in relation to their interactions within the ecosystem during biomass demineralization processes [37].

However, the complex absolute reaction mechanism of lignocellulose pyrolysis, which generates hundreds of intermediate-phase reactions, necessitates the use of apparent kinetics in simulations. Waste biomass contributes large percentage of the energy produced by renewable sources, about 10% of all renewable energy was produced globally in 2019 from biomass [38]. Conversion efficiency in the processing of lignocellulose biomass typically varies between 25% and 40% [39,40]. Lignocellulosic biomass has the capacity to yield a substantial amount of biofuels [41,42]. It was projected that around 196 million gallons of cellulosic ethanol will be produced worldwide in 2020 [43]. An ideal thermal kinetic model should consider both primary and secondary disintegration reactions [44,45]. Although there have been significant contributions to kinetic modeling, literature lacks sufficient estimation and evaluation of optimum values for key kinetic parameters affecting the pyrolysis and combustion process across various lignocellulose materials [46,47]. To evaluate the kinetics Flynn-Wall model in materials science and kinetics, the Flynn-Wall-Ozawa model—also known as the Flynn-Wall model or the Ozawa model—is used to examine the processes underlying chemical reactions, particularly in the context of solid-state kinetics [48–50]. This model is specifically utilized to clarify intricate reaction pathways and evaluate the kinetic parameters associated with a range of thermal phenomena, including phase transitions, decomposition reactions, and solid-state reactions [51,52].

Recent studies collectively examine the effect of demineralization on raw biomass reactions, using thermogravimetric analysis (TGA) to investigate the multiple weight loss transitions [53]. In addition, the effect of inorganic substance removal from biomass was observed on the basis of thermal degradation, pyrolysis and gasification characteristics [54]. Detailed analyses revealed that all the transformations were occurred due to the development of thermolysis behavior after post-demineralization [55]. Advance thermal research was done in order to understand the changes in kinetics, thermal stability, and consequent potential of thermochemical based modifcations in biomass materials for understanding the viability of multiple WtE conversion processes [56,57].

The present study evaluates thermal and kinetic properties for co-combustion of lignocellulose biomass, such as rice husk for developing sustainable WtE applications in the context of biomass cracking**.** Fig. 1 depicts main theme and the parameters that were determined in this research. Investigation of kinetics will provide practical grounds for understanding the reaction matrix and mechanisms, which contributes to cracking. These examinations aids in controlling and designing the process to facilitate the formation of desired products. Degradation temperatures were observed under different burning schemes to predict real-time burning scenarios in WtE conversion machinery. Optimizing the design and performance of conversion machinery requires a thorough understanding of the biomass breakdown temperature. It aids in determining the best operational parameters for biomass conversion processes like pyrolysis and gasification, such as temperature ranges, residence periods, and heating rates. In addition reactivity and activation energy have been compared for different flow rates and heating rates for effective biomass decomposition and for efficient resource utilization. By examining the relationship between reactivity, activation energy, flow rate, and heating rate, a precise kinetic mechanism can be developed for biorefinery setup.

2. Materials & methodology

Fig. 2 provides an illustration of the current research methodology. Raw biomass was taken and sieved into a powder form using a mesh size of 0.0093 mm. To ensure the absence of dust or other contaminants adhered to the biomass, it was cleaned with deionized water before undergoing the demineralization process. After dehumidification, powdered biomass was chemically treated with 5% hydrochloric acid (HCl) to improve fuel-burning efficiency. An orbital shaker was used to circulate and shake the samples at 250 rpm for 2 h for effective and efficient treatment of rice husk and to establish the best possible contact between the biomass sample and the leaching agent. Using a filtering funnel, the sample was rinsed with distilled water after 2 h to remove any remaining contaminants. In order to lessen the possibility of biased analysis, this step was crucial.

This method facilitates the continuous measurement of sample weight loss considering temperature and time. This study's temperature range selected for experimentation was from 25 to 950 °C. Burning was carried out using three heating rates: 20 °C/min, 30 °C/min, and 40 °C/min, and three different flow rates: 20 mil/min, 30 mil/min, and 40 mil/min. Each TGA experimentation scheme selected a nitrogen environment from 25 to 500 °C, while an oxygen environment was chosen from 500 to 950 °C.

Fig. 3 represents the Schematic Diagram of Thermogravimetric Analyzer. All the latter mentioned procedures were accomplished and controlled by furnace temperature controller and gas flow controller. Temperature Sensor and balance recorder was used to monitor and record the change in temperature and weight of the sample simultaneously. Additionally, a weight Loss recorder was used to capture the change in weight on y-axis with respect to change in temperature on x-axis in order to produce the required thermo gram on the monitor screen.

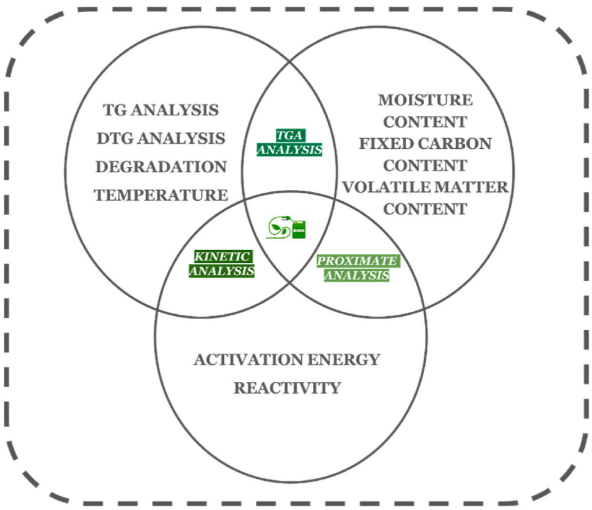

Fig. 1. Graphical summary of current research.

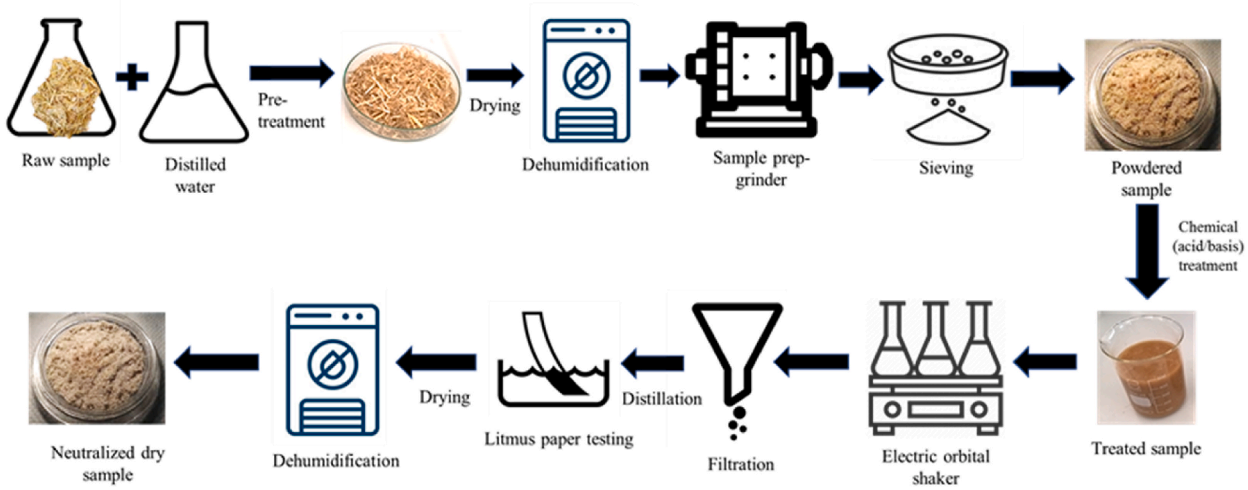

Fig. 2. Process flow diagram for sample preparation of demineralized rice husk.

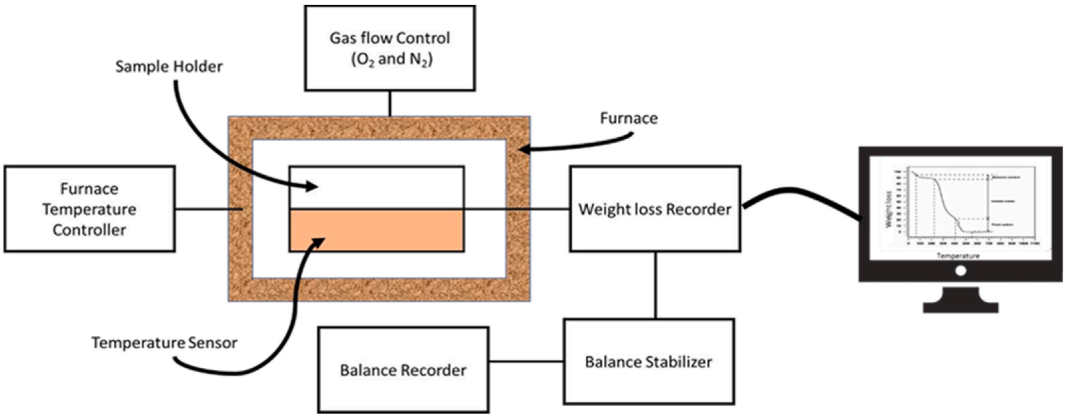

Fig. 3. Schematic diagram of TGA.

In order to do a kinetic analysis based on heating rate and flow rate, TG points from the experiment was gathered and analyzed. The activation energy was calculated using the Arrhenius equation. Exponential factor was calculated using the Flynn-Wall-Ozawa Model. Furthermore, reactivity was ascertained by the utilization of TGA data to assess the sustainability concerning to structural composition. When studying diverse organic materials such as coal, biomass, food, and more, proximate analysis is the term used to describe a series of processes executed to identify the distinct components or proximate elements contained in an item. It entails moisture content, volatile matter, fixed carbon content and ash.

The already established methodologies shows that the thermogravimetric burning strategy solely in purely air or in inert gas zone, applying it to raw biomass samples. However, in this research, a unique approach was adopted. The biomass properties were modified by the acid based leaching, followed by a distinct thermogravimetric burning mechanism. Specifically, demineralized rice husk was degraded under nitrogen environment ranging from 0 ˚C to 500 ˚C, followed by oxidation from 500 ˚C to 900 ˚C [57].

3. Results and discussion

3.1. Comparative proximate analysis of raw and treated rice husk sample

To determine how demineralization has affected the characteristics and content of biomass, proximate analysis was used. Determining the qualities connected to organic matter is aided by these analyses. Table .1 validates the proximate analysis results of rice husk sample used in this study is well aligned with the previous Literature. From Table .2 it can be depicted that the energy content of the treated rice husk sample is greater than that of the raw sample. HCl usage has improved the quality by removing some of its contaminants, increased its fixed carbon (F C) content by 55.41 % and accelerated the volatilization rate. The treated biomass sample contained less ash than the raw sample, which is attributed to the HCl's demineralization effect. Demineralization facilitates the removal of inorganic components by 60.55 % from the biomass, resulting in lower ash content in the treated sample. The biomass sample underwent 2-h treatment process to produce efficient and sustainable results for practical usage. However, literature suggests that treating the biomass longer than this may harm its structural composition. Excessive treatment by HCl can cause severe degradation of the

Table 1
Validation of current study data with literature.

Components (%)	Current Study	[58]	[59]	[53,60]	[61]	[62]
Moisture	9.7	7.75	6.33	9.15	6	8.20
Volatile Matter	55.8	63.25	70.33	78.25	63.3	62.16
Fixed Carbon	15.7	22.35	6.03	4.78	14.26	13.80
Ash	18.8	13.65	17.33	16.98	10.62	24.04
Calorific Value (kcal/kg)	3892	4092	4290.5	2970.7	3343	3322.1
Sulfur	0.18	0.19	nd	0.03	0.43	0.87

Table 2
Percentage change due to demineralization.

Components (%)	Raw rice husk	Treated rice husk	% Change
Moisture	9.7	7.8	24 % -
Volatile Matter	55.8	59.9	29.39 % +
Fixed Carbon	15.7	24.4	55.41 % -
Ash	18.8	7.9	60.55 % -
Calorific Value (kcal/kg)	3892	4302	10.53 % +
Sulfur	0.18	0.11	10.82 % -

rice husk's matrix. This decomposition may negatively impact its physical formation and reduce its effectiveness for numerous applications. In addition over exposure to HCl can shear off favorable components present in biomass, hence decreasing its suitability in terms of mechanical and chemical properties. In addition, proximate analysis has also shown that the treatment has increased the endothermicity of the biomass, it could improve the heat transmission to the sample's center. It is noteworthy that the observed increase in endothermicity can be attributed to both the chemical treatment and the enhanced porosity of the rice husk. The leaching effect has also reduced the concentration of Sulfur in rice husk by 10.82 % due to the chemical conversion of Sulfur into soluble sulfur, which was removed during the neutralization process of the sample. Due to the removal of unwanted Sulfur content, higher heating value of rice husk has been improved which may increase the life of biomass conversion machinery (see Table 2).

3.2. Thermogravimetric analysis of treated rice husk under different burning conditions

TGA specifically assisted in understanding the material's thermal deterioration behavior based on demineralization in this publication. Thermogravimetric (TG) curves of demineralized biomass sample are displayed in Fig. 4, illustrating change with respect to heating and flow rates. The majority of the sample exhibit a three-stage reaction which involves removal of moisture, releasing of volatiles and energy generation from F.C. Fig. 4 also indicates that the increasing heating rate influences the TG curves of biomass. An increase in heating rate affects the degradation rate and the location of the maximum temperature shoulders. Additionally, the reactivity of biomass was affected by changes in the heating rate, with the curves shifting to the right and weight loss occurrence increasing with temperature. As a result, volatile matter (V.M) release was not favored. Conversely, slower heating rates necessitate more immediate thermal energy and a longer heating period to bring the inner gas's temperature down to that of the furnace or sample. In contrast, greater heating rates cause a sample to decompose at a higher temperature because they shorten the reaction time within the same temperature range [63]. Moreover, due to its lower density & thermal diffusivity high flame propagation speed may be achieved. Rice husk, like many organic materials, can be prone to oxidation at high temperatures. Nitrogen provides the shielding af-

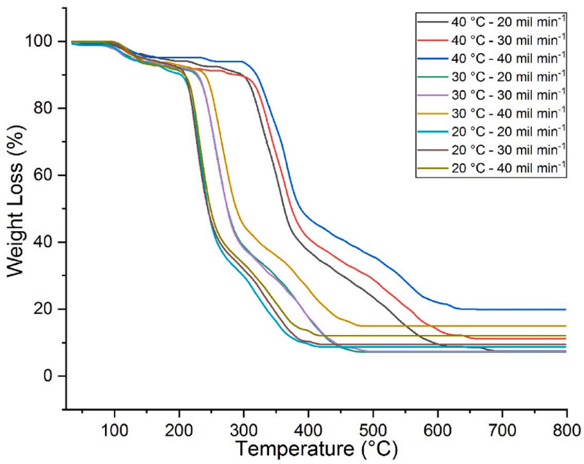

Fig. 4. Process flow diagram for sample preparation of demineralized rice husk.

fect to prevent this oxidation, in order to maintain the structural integrity of the sample and ensuring that the observed fuel degradation is entirely based on thermal activity [64]. By applying the nitrogen atmosphere in all the experiments, mature comparability between different samples or trials can be achieved [65]. This consistency is important for estimating reliable conclusions about the thermal nature of the rice husk under controlled environment. The usage of HCl as a treating agent has reduced the inorganic content of carbon present in biowaste for efficient production of energy and other valuable products during biorefinery WtE operations. By focusing on the influence of flow rate in Fig. 4, it can be observed that increasing the flow rate leads to a decrease in the residence time of the sample. Increased flow rate promotes organic carbon formation and increases heat liberation during volatilization and combustion stages, which leads to higher combustion activity. Furthermore, as the flow rate increases, there is a slight increment in the gradient of the TG curves. This is because a higher flow rate can cause increased turbulence and mixing, resulting in the fluid surface interaction of the object more frequently at different angles. Consequently, producing larger effective surface area.

From Fig. 4, it can also be deduced that with constant heating rate and increased flow rate, a drop in conversion efficiency of the sample was observed, which was 12.7 % for 40 °C, 9.85 % for 30 °C and 9.4 % for 20 °C.

3.3. Differential thermogravimetric examination of rice husk under various heating rate and flow rate

Overall, DTG (Differential thermogravimetric) analysis is a powerful tool for studying the thermal properties of biomass and can provide important information for developing efficient and sustainable biomass-based energy systems and different chemical processes. Fig. 5 represents the DTG curves of the different biomass samples on the basis of flow rate and heating rate. It can be witnessed that during DTG analysis, pronounced regions were detected through the DTG curves of all samples, supporting the overall pattern of biomass burning. In the initial stages, an increase in mass before actual degradation was observed, which may be due to the chemisorption of oxygen. Atoms or molecules cling to a surface by this process of creating chemical bonds, a phenomenon [66]. Stronger bonds are formed during chemisorption as opposed to weaker forces such as van der Waals interactions in physical adsorp-

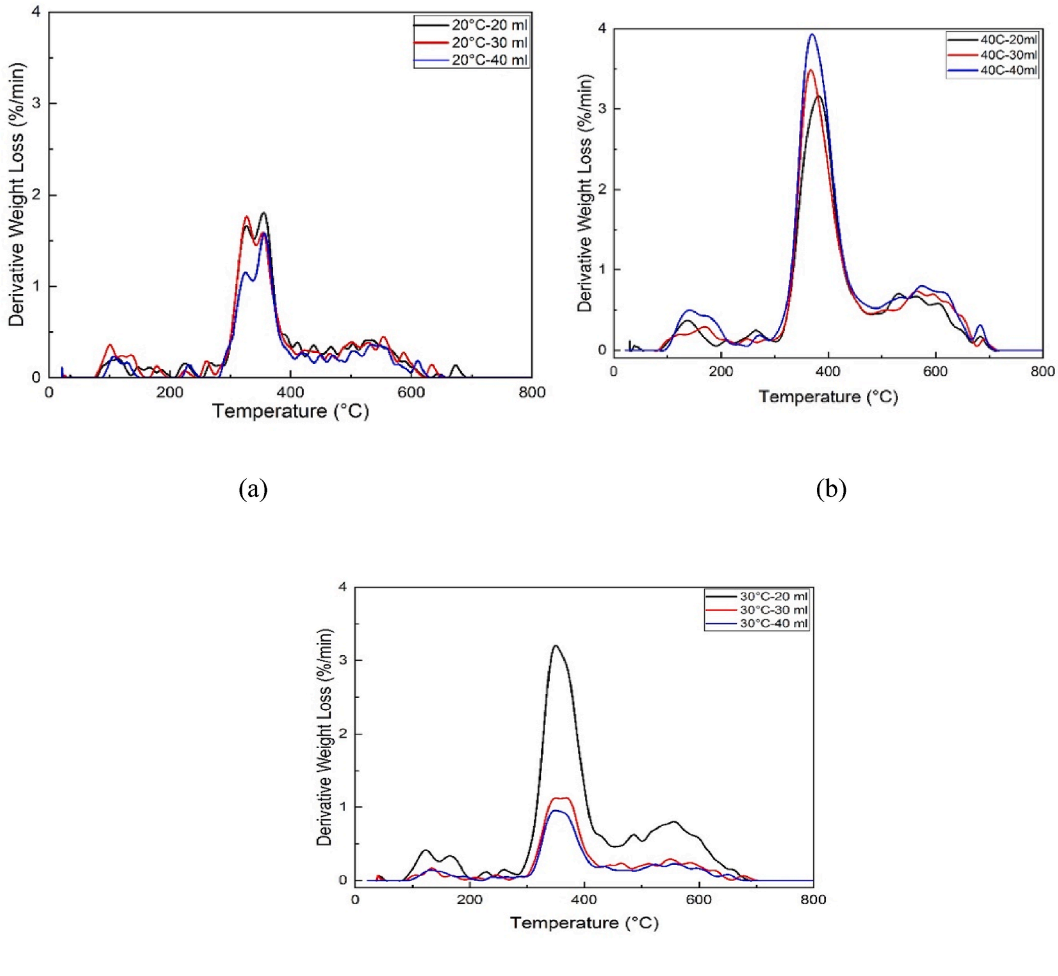

Fig. 5. DTG curves of treated rice husk at different heating and flow rates (a) 20 °C heating rate profile (b) 30 ^{0}Cheating rate profile (c) 40 °C heating rate profile.

tion, which frequently leads in the creation of a separate chemical layer on the surface. For all combustion environments, moisture evaporation occurred within the temperature range of 30 °C and 160 °C.

The observed uncertainty, which is a feature of the TGA apparatus, significantly increased the amount of time needed for the samples to burn out. This difference in burnout durations demonstrates unequivocally how the measured uncertainty directly affects the thermal behavior and breakdown kinetics of the samples under analysis.

High volatization was observed in all the DTG curves. Higher reactivity was reported due to the presence of macromolecular constituents in biomass, which are connected together with weak ether bonds. Thus, oxygen-rich polymers in demineralized biomass e.g., cellulose and hemicelluloses have pronounced inclination towards decomposition even at low temperatures. The second stage of mass reduction occurred between 460 and 800 °C at a slower rate and is linked with lignin degradation and char combustion. The DTG graphs indicated that the atmospheric reaction is reduced with an increase in heating rate, resulting in smoother and more stable burning. However, an increase in flow rate leads to unnecessary conversion of multi-stage cracking into unresolved multi-stage cracking. The progressive disintegration of complex organic compounds into smaller molecules at various temperature ranges is referred to as "multistage cracking" in biomass. Different phases of thermal degradation are involved in this process, which produces smaller hydrocarbons, gases, and biochar, all of which are essential for the generation of biofuel and biochemicals during the conversion of biomass.

3.4. Degradation profiles of treated rice husk under multiple decomposition scenarios

Optimizing the peak temperatures during biomass conversion operations in a biorefinery setup is critical for maximising product yields, regulating reaction pathways, and descent consumption of biomass feedstock parameters. Data obtained from TG and DTG curves were utilized to characterize the thermal degradation of biomass samples at various operating conditions. These parameters include: T_I which represents the ignition occurring point on the TG curve,T_B indicates the completion point of reaction, T_M is a point where maxium drop of mass take place. The investigation revealed that, with the increase in heating rate, the reaction zones for all stages shifted to longer temperature peaks. From Fig. 6 it can be observed that with the increase in heating rate, there is a minor increase in the T_I. The highest T_I was reported at 40 °C and 40 ml combination while the lowest T_I was reported at 20 °C and 20 ml combination. The observed trend revealed that at higher flow rates, degree of heat dissipation increases due to which threshold temperature required for ignition also increases. Moreover, as the flow rate increases the exposure time of rice husk to high-temperature region decreases, which leads to improvement in dilution of oxygen concentration for sustainable ignition. With the increase in the heating rate there was an instaneous increase in temperature, promoting productive combustion and gas volatization. Favorable combustion can improve flame stability and reduce turbulence. Achieving the optimal balance between biomass and air is vital for complete combustion. If there's an irregularity, it can produce incomplete combustion, causing the instability of the flame. The heat generation rate during burning affects stability of the flame. Turbulence in heat release can affect the steadiness state of flame temperature. Flames operate under defined temperature ranges. Extreme change in temperature values can affect the flame stability.

Fig. 7 represents the T_M profiles under various heating and flow rate combinations. It can be observed that as the flow rate and heating rate increases T_M increases. T_M reported from 20 to 40 °C were 352.7 °C, 368.5 °C & 392.4 °C respectively. When the heating rate was increased, the fuel undergoes a faster proportion of heating. Rapid heating leads to instantaneous release of energy during the burning process. As a result, the combustion process becomes more reactive and the temperatures within the combustion space rise to higher states. It should be noted that the higher heating rate has produced faster chemical reactions within the rice husk, causing a rapid conversion of biomass into combustion products. Intensified energy release amplifies the overall

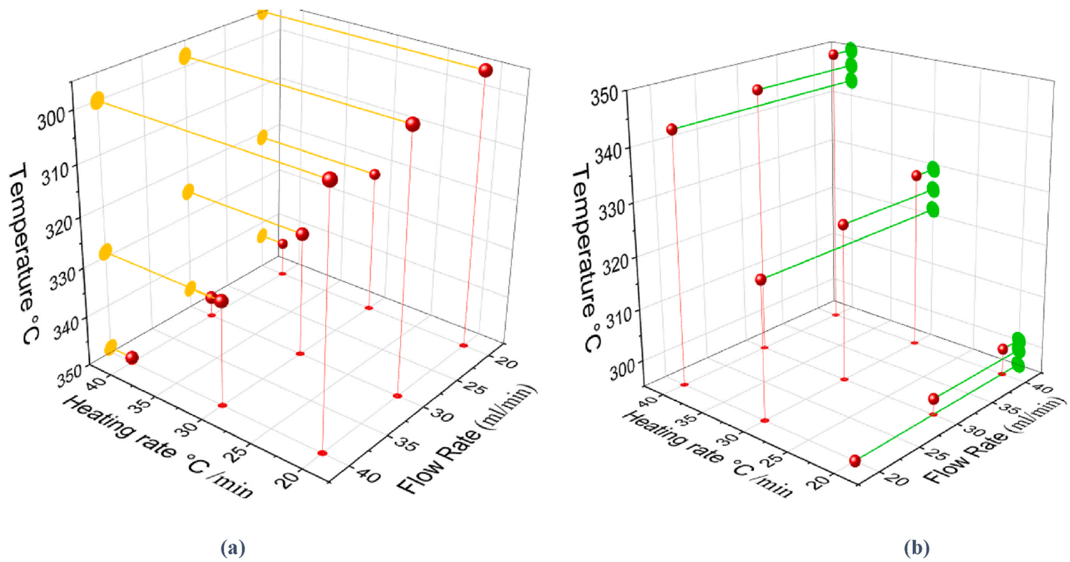

Fig. 6. Ignition temperature (T_I) profiles of Rice husk (a) Heating Rate profile (b) Flow rate profile.

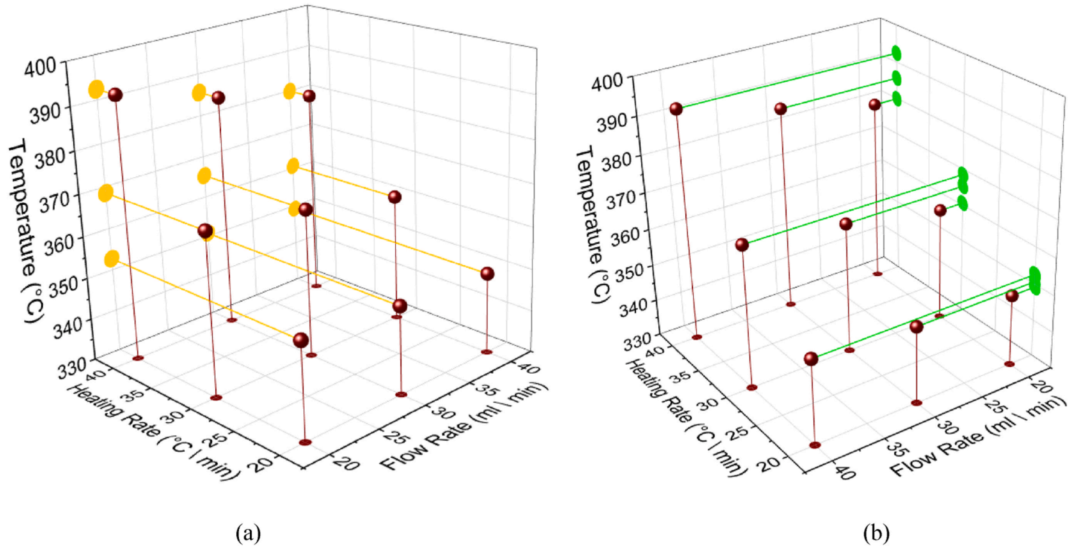

Fig. 7. Maximum weight loss Temperature (T_m) profiles of Rice husk (a) Heating Rate profile (b) Flow rate profile.

burning process, resulting into elevated temperatures within the combustion region. Moreover Fig. 6 also depicted that T_M is influenced by the flow rate rise. Higher T_M values were observed with the increase in flow rate, e.g., when the flow rate is rising, there is an enhancement in mixing between the fuel and air within the combustion chamber. This improved mixing will develop a highly reactive reaction mechanism, leading to efficient and sustainable burning. The reported rise based on heating rate and flow rate may be due to the adiabatic nature achieved during burning. Higher flow rates and heating rates can lead to improved heat transfer processes in the system and produce maximum weight loss.

Fig. 8 represents T_B profile based on heating rate and flow rate. In case of $T_{B,}$ Incremental behavior has been observed on the basis of heating and flow rates. Increasing the flow rate enhances oxygen availability for the combustion and pyrolysis zone. This improved oxygen supply promotes more efficient and complete combustion of the biomass. As a result, a higher proportion of the fuel is burnt. When the heating rate is increased, biomass burning occurs more rapidly, which promotes faster release of energy during combustion and pyrolysis. The release of energy at higher rate promotes fast combustion, generating high-temperature gradients within the combustion chamber. High temperatures in chamber give rise to T_B.

3.5. Reactivity examination of acidified rice husk for observing different burning patterns

Rice husk is a renewable and abundant source of green energy. It can be degraded to produce heat and electricity. Its reactivity as a fuel is satisfactory as it has high C V, low moisture and low ash content. In the current work, the leaching technique has improved fuel quality in terms of reactivity. It can be seen in Fig. 7, that the leaching has improved the reactivity of every component of the bio-

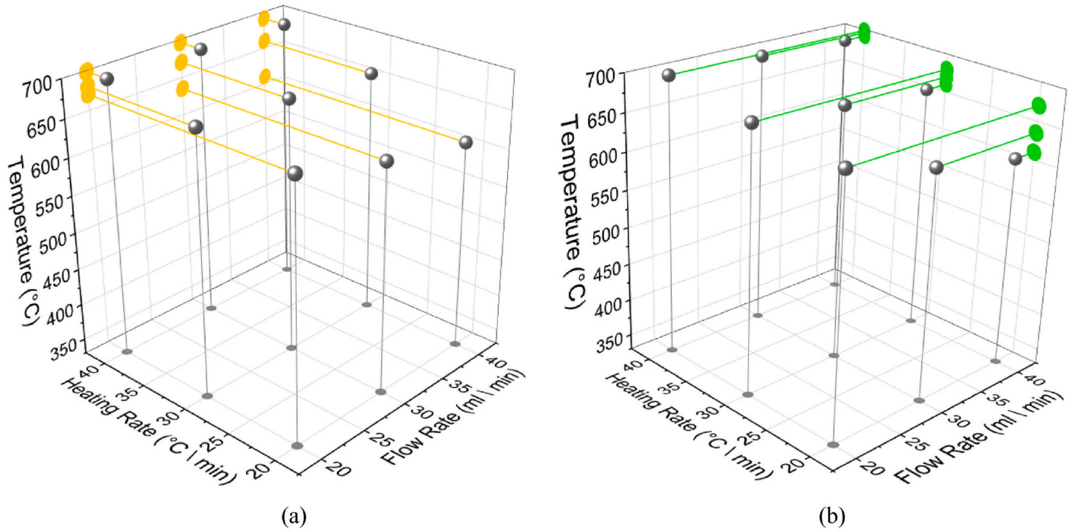

Fig. 8. Burn-out temperature (T_B) Profiles of Rice husk (a) Heating Rate profile (b) Flow rate profile.

mass sample with a major increase in the hemicellulose region. Different values of reactivity illustrated different reactivity patterns based on heating and flow rate.

Considering 20 °C, 30 °C and 40 °C series in, in which rate of heating was constant while rate of flow was varied from 20 to 40 ml min^{-1}, it can be witnessed that as the flow rate rises, the reactivity of rice husk has been droped. Which indicates that the flow rate influences the residence time of the biomass within the reactor, and a reduced residence time can produce incomplete reactions and lower reactivity.

From Fig. 9 it can been seen that the flow rate and heating rate affected reactivity. It can be observed that when heating rate was high and flow rate was low then the reactivity value was higher as compared to the reactivity values which were observed on higher flow rates. The availability of additional reactive species to react with oxygen as a result may raise the biomass's reactivity. Furthermore, convective movement of oxygen from the surrounding air to the biomass might result in an increase in oxygen availability to the biomass at greater heating rates. This may accelerate the pace at which the biomass and oxygen react, raising the reactivity of the mixture. In the case of 40 °C and 40 ml, both the heating rate and flow rate is high, which is quite an unfavorable situation.

The gasification or combustion phases can be recognized in all DTG profiles under oxygen and nitrogen: clearly, the peaks differ in position and height. Therefore, evidence of the reactivity of samples can be Reactive characteristics, however, were identified for every peak [67], including the area in the burning profile occupied by somewhat inferior peaks or shoulders. This led to the computation of a mean reactivity (RM) value together with the corresponding peak temperature; the results are shown in Table 3. The temperature ranges that the reactivity parameters were concentrated in were 105–699 °C. Additional reactions were generated by char gasification, combustion, and devolatilization. For proportional analysis based on the values of RM, the fuel samples may be graded as 20 °C - 20 ml > 20 °C–30 ml > 20 °C–40 ml, 30 °C - 20 ml > 30 °C - 30 ml > 40 °C - 40 ml > 40 °C - 30 ml > 40 °C - 20 ml > 40 °C - 40 ml under control conditions, the RM values were slightly higher at 40 °C heating rate due to the fact that at higher heating rate, the rate of reactivity is higher. Different patterns were observed under the conditions mentioned above.

3.6. Investigation of minimum energy requirements for activating optimal decomposition

TGA profiles were used to derive the kinetic parameters of all types of fuels using a linear variant of the Arrhenius equation. Under varied atmospheric circumstances, the treated rice husk sample's activation energy, order of reaction, and correlation coefficient were

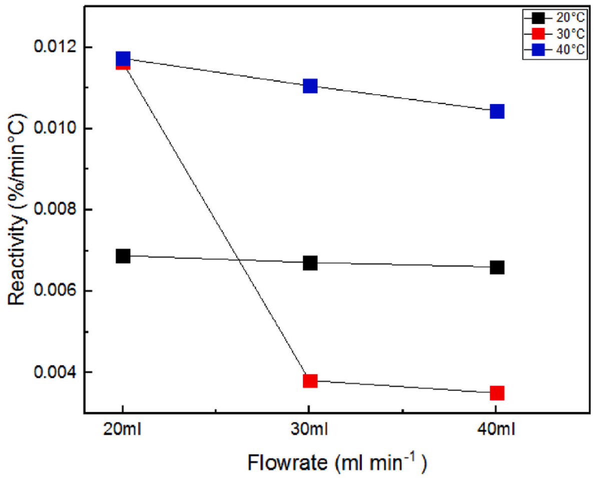

Fig. 9. Reactivity of treated sample of rice husk with respect to different heating rate and flow rate.

Table 3
Mean Reactivity at different heating and flow rate.

Burning Conditions	Ignition Temperature	Peak Temperature			Mean Reactivity
	Ti	Tp1	Tp2	Tp3	RM
	° C	° C	° C	° C	%/min° C
20 °C –20 ml	295	107.3	352.7	670.1	0.00687897
20 °C –30 ml	298	113.6	350.7	635	0.00671037
20 °C –40 ml	300	105.7	349.2	610.1	0.00660273
30 °C –20 ml	321	124.6	368.5	680.2	0.01163195
30 °C –30 ml	325	111.5	365.3	670.1	0.00381258
30 °C –40 ml	329	135.6	360.6	660.1	0.00355394
40 °C –20 ml	343	124.8	392.4	698.7	0.01192345
40 °C –30 ml	346	115.6	385.6	695.8	0.01005505
40 °C –40 ml	349	114.8	379.9	690.8	0.01022862

investigated at different heating and flow rates. At n = 0.67, n = 1, n = 0.3, and n = 0.5, the reaction kinetics were modelled, and the values of activation energy series at different flow rates and heating rates depicts an increasing trend. Regarding reaction order, there was no consensus in the literature, with some research supporting these findings and others asserting that pyrolysis is finely defined as a worldwide first-order reaction [67].

Fig. 10 depicts the values of activation energy based on flow rate and heating rate. As, the heating rate increases and flow rate decreases, lower activation energy was observed. Considering 30 °C and 40 °C series, it can be seen that with the increase in the flow rate, higher activation energy was observed, due to the reason that at higher flow rates, heat transfer will decrease which results in a decline in the required energy to initiate the reaction. In contrast at higher heating rates, reaction occurs more rapidly, requiring less activation energy.

The Freeman-Carroll method was used to get a complete overview of the kinetic values to estimate the consequence of the changing in the heating and flow rates on the combustion and pyrolysis characteristics. To remain concerned about the drop in weight of biomass, Arrhenius kinetic parameters of the degradation method were considered, as shown in Table .4. Table .4 characterizes the activation energy values consistent with the weight reduction phases of volatile and char combustion, respectively. For pyrolysis leading to burning, the weight removal happens in two zones, i.e., for volatile and char combustion activation energy points were observed.

Generally, the kinetic studies were agreed with the isothermal and non-isothermal conditions. However, non-isothermal conditions can be mportant if distinct situations were fabricated for observing the kinetics. Such settings can be achieved by heating the sample constantly and through well-organized operational conditions in a TG analyzer [57].

Table .4 demonstrates the finding of kinetic parameters based on heating rate and flow rate. Fig. 10 demonstrates the relation between the conversion and mass loss rates. This association can be used for all zones in the same way. As the mass curve decreases to the small value, the conversion rate reduce to a minimum value. The mass drop and conversion rate increase until the maximum value decreases. Table .4 also validates the above-mentioned statement that with increased heating rate and decreased flow rate, activation energy decreases. This is because a higher flow rate promotes limitations in heat transfer efficiency. In addition, higher flow rate causes higher reaction rate. Table 4 Shows that the pre-exponential component rises with decreasing activation energy. This supports the idea that the higher reaction rate and faster collisions throughout the reaction are what caused the lower activation energy.

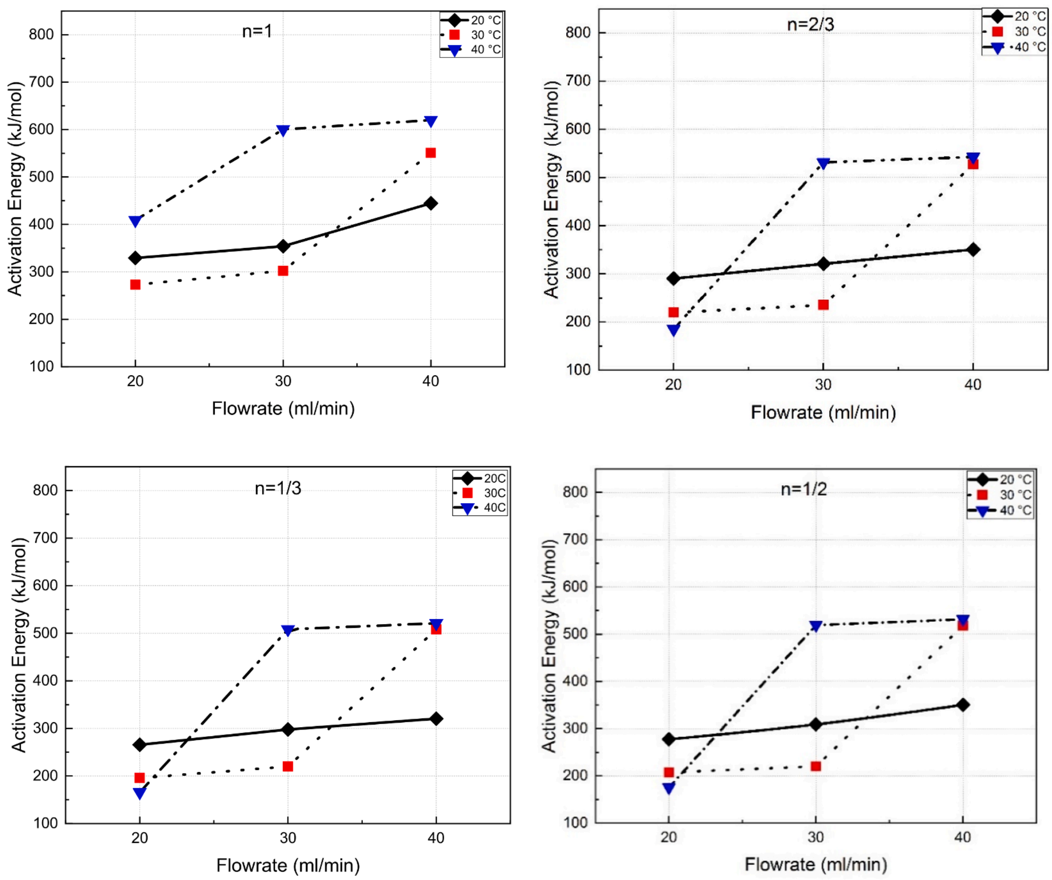

Fig. 10. Different values of activation energy on the basis of reaction order.

Table 4
Kinetic parameters of treated rice husk at different heating rate and flow rate.

Sr.#	Samples	Slope				Activation Energy kJ/mol				Pre-exponential factor s-1			
	Reaction Order	n = 1/3	n = 1/2	n = 2/3	n = 1	n = 1/3	n = 1/2	n = 2/3	n = 1	n = 1/3	n = 1/2	n = 2/3	n = 1
1	20 °C-20 ml	3193.70	3337.30	3489.00	3962.44	265.52439	277.46329	290.07546	329.44	4.22 E+48	4.36 E+49	9.095 E+25	6.81 E+29
2	20 °C-30 ml	3582.2	3718.1	3858.8	4257.9	297.8308	309.12814	320.82593	353.9764	2.41 E+47	2.82 E+48	1.004 E+19	1.879 E+24
3	20 °C-40 ml	3855.0	4215.3	4216.4	5348.1	320.51193	350.46438	350.55469	444.64302	2.32 E+47	5.2 E+24	3.893 E+15	8.747 E+17
4	30 °C-20 ml	2354.0	2491.0	2641.3	3283.3	195.71236	207.10429	219.60222	272.98161	5.28 E+26	2.07 E+48	4.31 E+49	2.477 E+56
5	30 °C-30 ml	2646.2	2646.4	2828.3	3635.7	220.00845	220.02519	235.14557	302.27386	3.46 E+23	6.84 E+27	9.69 E+28	1.76 E+32
6	30 °C-40 ml	6112.2	6245.40	6390.88	6623.5	508.1697	517.87403	527.28526	550.67825	4.32 E+16	5.81 E+17	1.84 E+18	1.395 E+21
7	40 °C-20 ml	2038.87	2170.61	2227.3	4918.1	169.51	180.46	185.18374	408.89652	1.17 E+16	4.364 E+49	5.685 E+50	2.262 E+56
8	40 °C-30 ml	6112.22	6228.94	6390.8	7222.0	508.17	517.87	531.33789	600.44138	1.08 E+14	1.45 E+17	1.727 E+49	3.362 E+51
9	40 °C-40 ml	6266.96	6391.60	6528.63	7457.7	521.04	531.40	542.790	620.03803	4.39 E+13	1.32 E+15	2.098 E+16	3.243 E+18

Additionally, there is a direct proportionality between slope and activation energy. Slope is decreasing together with the decline in activation energy.

3.7. Uncertainty analysis of TGA equipment with the perspective of current study

It is noteworthy to note that during every test, a significant uncertainty error was continuously recorded in the Thermal Gravimetric Analysis (TGA) equipment, ranging from 4 to 5°. The burnout times in each sample showed this disparity clearly. For the samples, the observed uncertainty significantly extended the burnout length.

4. Conclusion

. The findings suggests that demineralization has improved organic properties of the rice husk, indicating complete combustion trends and higher energy output. Furthermore, the possibility of combustion at lower temperatures without the need for external heating was implied by the finding of the lowest activation energy under particular conditions. The results suggested that certain combinations of heating and flow rates have a significant impact on degradation profiles, with lower activation energy and higher reactivity under some circumstances. Furthermore, the thermogravimetric analysis validation of the data matches the patterns that have been observed, indicating the importance of these parameters in the biomass conversion process. All the experimentation and analyses has revealed the following findings:

Demineralization of rice husk has reported an increase in fixed carbon and calorific value by 10.53 % and 10.82 % respectively.

Minimum activation energy of 180.46 kJ/mol was observed at 40 ml and 20 °C. Low activation energy allows the combustion to occur at low temperatures, thus eliminating the need of external source for heating.

0.01192345 %/min ^{0}C was the highest reactivity observed due to the degradation of acidified rice husk. Fuel having good reactive properties can be considered efficient in terms of conversion to other forms of energy.

A substantial improvement in waste biorefinery systems and alignment with Sustainable Development Goals 7 and 13 was shown by the sustainable biomass conversion strategy. This study opened the door to a more environmentally friendly and cleaner energy landscape by demonstrating encouraging developments in using rice husk as a competitive substitute to lessen reliance on fossil fuels. The results underlined the intricacy of biomass conversion by highlighting the notable improvements in characteristics following demineralization as well as the complicated degradation patterns found by thermochemical investigation. This investigation not only highlighted the cooperative effects of many parameters on the degradation process, but it also carefully examined the data to corroborate the findings and provide insightful information for projects using sustainable energy.

An integrated strategy to fuel production that relies on regional energy sources and a variety of WtE techniques is required in order to advance sustainable environmental practices. The current study will offer the fundamental groundwork for the creation of biomass burning technologies that are optimum. The purpose of this study was to improve the fuel quality in order to maximize the use of rice husk and protect thermo-mechanical equipment. Furthermore, combining demineralized biomass with readily available solid fossil fuels, such as coal, will lessen the country's reliance on significant fossil fuels and assist to provide a continuous energy supply network.

CRediT authorship contribution statement

Tayyab Qureshi: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Muhammad Farooq:** Writing – review & editing, Writing – original draft, Visualization, Validation, Supervision, Resources, Project administration, Investigation, Funding acquisition, Formal analysis, Data curation. **Shahid Imran:** Writing – review & editing, Visualization, Supervision, Resources, Project administration, Methodology. **Fahid Riaz:** Writing – review & editing, Visualization, Software, Funding acquisition. **Muhammad Farhan:** Writing – review & editing, Validation, Supervision, Software, Formal analysis. **Muhammad Asim:** Writing – review & editing, Supervision.

Declaration of competing interest

No conflict of interest.

Data availability

Data will be made available on request.

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