

EVALUATION OF KINETIC BEHAVIOUR OF REFUSED DERIVED FUEL SAMPLES BY USING THERMOGRAVIMETRIC ANALYSIS

by

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Original scientific paper

<https://doi.org/10.2298/TSCI220621198A>

The intensification of municipal-solid-waste (MSW) production, energy usage, and the curb of the landfill have developed the need for our society to use MSW under the vision of a waste-to-energy (WTE) approach to eradicating MSW as well as to address the energy issues across the world. The WTE alteration is an environment-friendly way of disposing of MSW. This study examines the usage of plastic, wood, and paper for refuse-derived fuel (RDF) production. The RDF is solitary of MSW energy yields, whose dependability and superiority are analysed in the current work. Two different RDF have been obtained from diverse waste streams at the plant site to find the finest RDF based on energy efficiency. Plastics, wood, and paper are the principal constituents in the method of occupied RDF. The results exhibited that the RDF-PA holds a high amount of carbon as-well-as hydrogen content and a decent calorific value, which leads to better fuel quality. The retention time under combustion and pyrolysis, the volatile matter portion of RDF, has increased accordingly. As per obtained results, RDF-PA is a good option for energy applications and fuel for combustion and pyrolysis reactions.

Key words: kinetics, MSW, RDF, combustion, pyrolysis, activation energy, thermogravimetric analyser

Introduction

Environmental issues emerging from fast industrialisation and economic development include MSW management. Products like tires and furniture are included in MSW (e.g., yard waste and food). Industrial, hazardous, and construction waste are not included in this category. A massive amount of MSW is continuously produced differently because of daily activities. Open spilling and landfilling are the most common forms of MSW management. These strategies have dire effects like contamination of the environment, methane gas production,

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which contributes to global warming, and labour aspects [1]. The MSW can generate energy, while chemical bonds between C-H-O are broken due to the presence of such bonds, according to [2]. The globe is anticipated to generate 3.40 billionns of waste yearly by 2050, up from 2.01 billionns. A Global Snapshot of Solid Waste Management through 2050 compiles significant national and urban solid waste data [3]. However, daily waste production in Europe approaches 1.4 kilograms per capita [4]. Then, waste is separated and segregated based on size, quantity, and quality. The waste composition varies by country due to different collection methods and lifestyles. The MSW, in general, is made of plastic and has a high ash content [5].

The MSW generation per capita is a measure of waste-generating intensity that can be used to monitor progress in waste prevention (reduction and reuse) and adjust consumption pat-

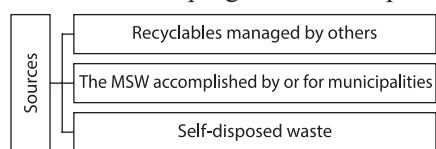


Figure 1. Waste torrents and MSW generation

terns toward resource efficiency. It can also be used to construct future estimates of total MSW generation. Most countries that are not very developed still use the informal sector for recycling. Another option is for people to dispose of their garbage at the source, as shown in fig. 1.

The WTE function is reported gradually, such as the remedy of problems caused by increasing trash quantity in developing cities and rapidly growing energy needs. The WTE plants are an excellent way to reduce the environmental impact of landfill. In Singapore, which has minimal land, incinerating waste is a perfect way to keep the only landfill open for a long time [6]. In the context of escalating energy prices, energy recovery using WTE plants is a good alternative. The RDF is a significant calorific value fuel generated after extracting non-flammable components such as ferric material, glassware, sediment, *etc.* While WTE is still a sustainable process producing reusable fuel, eliminating the dependency on fossil fuels, and reducing greenhouse gas emissions, hazardous gases are produced while burning fuels [7]. The following are some financial benefits of the WTE business.

Fuel created from municipal solid trash, called *refuse-derived fuel*, has the potential to replace fossil fuels in power generation. Recycled content (RDF) includes paper plastics and textiles with a higher calorific value. International Energy Agency (IEA) and International Solid Waste Association (ISWA) member countries are increasingly using RDF as fuel in WTE plants, and this trend is expected to continue soon [8]. Because of current restrictions, most combustion systems can easily take RDF as a substitute fuel without considerable adjustments [9]. Because of this, they are manufacturing high calorific value RDF is complicated because it requires a more significant number of separation processes, which increases manufacturing costs [8-10].

The RDF's primary component is the pyrolysis behaviour of various paper samples, including writing and coating paper. Polysaccharides, such as cellulose and hemicellulose, are polymeric carbohydrate structures [11]. Serious efforts have also been made to investigate the thermal degradation of RDF as a single fuel [12]. For the SRF production, pre or post shredding operation must be needed, and refined process consume more time. So due to the abundance of waste, RDF can be considered a fuel of choice for SRF production which will be efficient for the energy production on industrial scale. From further research, RDF de-volatilisation was described as the sum of its lignocellulosic, semi-lignocellulosic, and char production. As a result, an extensive study was conducted on RDF energy recovery, which included considerations of environmental, economic, and energy factors [12].

The RDF is fabricated from a method to treat MSW to create a gas that may be burnt effortlessly in a combustion boiler. To supply RDF, waste needs to be shredded and carefully

sorted to eliminate all non-combustible fabric consisting of glass, metal, and stone. Shredding and separating have performed the use of a sequence of mechanical procedures which might be energy intensive. The World Bank has predicted that it requires 80-100 kW h to process 1 t of MSW and a similarly 110-130 kW h to dry the waste [13]. After the waste has been shredded and separated, the combustible component is formed into pellets which can be sold as fuel. The authentic goal of this method was to generate a fuel suitable for mixing with coal in coal-fired power plants, fig. 2. This, however, caused system issues and the current approach is to burn the fuel in specifically designed power plants [14]. An alternative is to combine the RDF with biomass waste after which burn the mixture in a power plant. Since RDF production should be preceded through careful sorting, this sort of technique is satisfactorily suitable to situations where extensive recycling is planned. Furthermore, this has been explored that the availability of AAEM (alkali and alkaline earth metals) can significantly affect the thermally degrading performance of RDF and their kinematic characteristics [14, 15]. There are many plants installed in different capacities worldwide like Asia, the Middle East, *etc.*

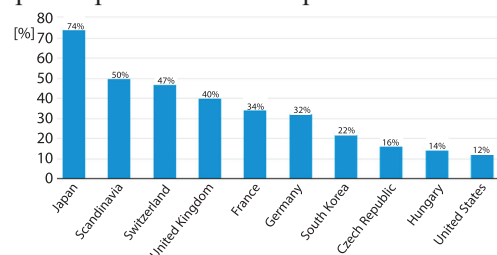


Figure 2. The MSW burned with energy recovery worldwide

This study aims to determine the qualitative, ecological, and thermal behaviour of a diversity of RDF premised on a configured volume using a thermogravimetric analyser (TGA). Analyser estimate to energy perspective of discarded material. Therefore, multiple samples were burned and pyrolyzed to classify the premium reconfiguration under the given conditions. All data were analysed to determine kinetic results via several approaches, also, the RDF samples' energy component is determined by their calorific values. Multiple kinds of RDF were nominated based on accessibility trends.

Material and methods

Method of waste-to-energy

By converting garbage into biogas, syngas, or heat, energy from waste products can be consistently beneficial. Physical, thermal, and biological techniques are three technological methods for adapting energy from waste materials [6, 16].

Sample materialization

The RDF samples were chosen from the Pakistani different cities like Lahore, Faisalabad, and surroundings. The RDF-PA and RDF-PL are the sample designations, and MSW was handled on three lines at the plant. Through transitory over trammel, the gathered MSW remains unglued based on organic and inorganic components at first. The organic garbage was composted, while the inorganic waste was sent to a recovery centre where recyclables and non-recyclables were separated. The source of the waste is Lahore Waste Management (LWM) Company, which deals with maximum chunk of waste in Lahore, Faisalabad and surrounded cities. The working of the company is to collect the whole chunk of waste from the different sites and gather it to one place.

Non-recyclable garbage is still more thoroughly processed into RDF. Following the fraternisation zone, non-recyclable garbage is crumpled into little pieces. Several sorts of trash are blended to varying degrees to get the desired properties according to the requirements. Finally, the pellet of RDF is moulded by accumulation treacle to achieve the pellets' lasting obligato-

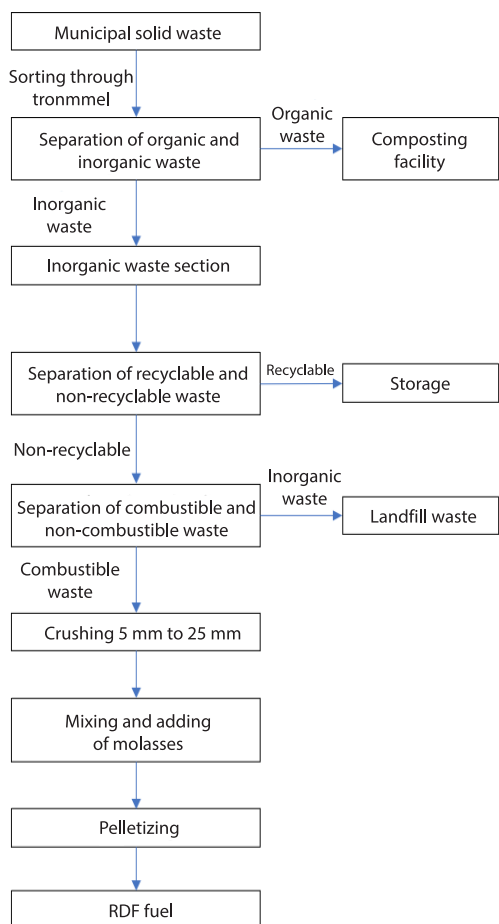


Figure 3. Representation of sample development

the ASTM E711-87 standard. The sample was placed in a steel bath and adjusted accordingly in an isentropic-shielded combustible cavity. The calorimeter was validated with benzoic acid projectiles before conducting the research.

The current investigation's C, N, O, S, and H contents were determined using an ASTM D-3176-compliant LECO 628 CHN-X analyser (Germany). To simultaneously determine C, H, and N, the samples were placed in a combustion chamber set to approximately 950 °C. As an add-on, this analyser might still be used to determine the sulphur content. The chamber temperature was increased to 1350 °C to identify the presence of sulphur. The substances of oxygen have been calculated by subtracting the contents of C, H, N, and ash using:

$$C\% + H\% + N\% + O\% = 100\% \quad (1)$$

The TGA was performed using the SDT q600 TGA instrument under ISO 11358-1 (America). A clay crucible was used to hold samples weighing roughly 15 mg. The temperature was first raised to 25 °C and held for 1 minute. Following that, the samples have heated up evenly to 950 °C using the rate of heat 10 °C per minute and a dry-air stream of 40 ml per minute.

ry. Figure 3 depicts a sample-making schematic diagram, and the percentage of each sample is RDF-PA: 50% plastic, 30% paper, 20% wood, RDF-PL: 30% plastic, 40% paper, 30% wood.

The RDF covering waste from plastics and paper were nominated for this study, which looked at their combustion and pyrolysis performances. The material selection was based on their high availability and was most likely chosen for RDF production. Waste Busters recognised two samples, RDF-PA and RDF-PL, in the shape of bits with a diameter of 38 mm.

Apparatus and procedure

From the detailed observation of proximate analysis, it was believed that the fuel would be free of fixed-carbon and volatile materials. The moisture content of the RDF samples was evaluated using an oven, the EYELA NDO 450-ND (Tokyo), under ASTM typical E790-08. The sample was then oxidised through Lenton (South Korea) muffle furnace for two hours at 550-950 °C to separately estimate the explosive and ash content. The aforementioned analysis was carried out under ASTM standards E897-88 and E830-87, respectively. Finally, the fixed carbon remained as anticipated by deducting the extent of moistness, ash content, and volatility from the overall sum of samples. The bomb calorimeter, LECO AC 500, was used to determine the calorific values of the samples (Germany). This study's technique is based on

Results and discussions

– Decisive and proximate analysis

As shown in fig. 4, the TGA and DTG arches demonstrated the behaviour of samples with substantial portions for humidity content released, de-volatilisation, and char degradation. The temperature increased to 760-960 °C for all RDF samples, with inclusive de-volatilisation. Firstly, the moisture content deteriorated, where a continuous weight remained reached, and then the temperature increased up to 760-960 °C for all RDF samples, with de-volatilisation ensuing. Quantity of moisture contents, fixed carbon, volatile matters, and slag contents all have been covered in this study. Table 1 shows the results of the ultimate and proximate analyses with volatile matters (VM) and ash as a significant constituent of RDF.

The VM in RDF-PA and RDF-PL has been calculated as 67.9% and 76.7%, respectively, with ash contents of 14.4% and 19.6%. Lower ash content in RDF-PL compared to RDF-PA could be due to more plastics than other constituents [19]. In its arrangement, RDF-PL established the lowest amount of gripping constituent (*e.g.*, paper). Because RDF-PA contains a high concentration of fixed carbon and has a low moisture content, it has a lower ignition temperature than RDF-PL, allowing ignition occur at a lower temperature [17, 18].

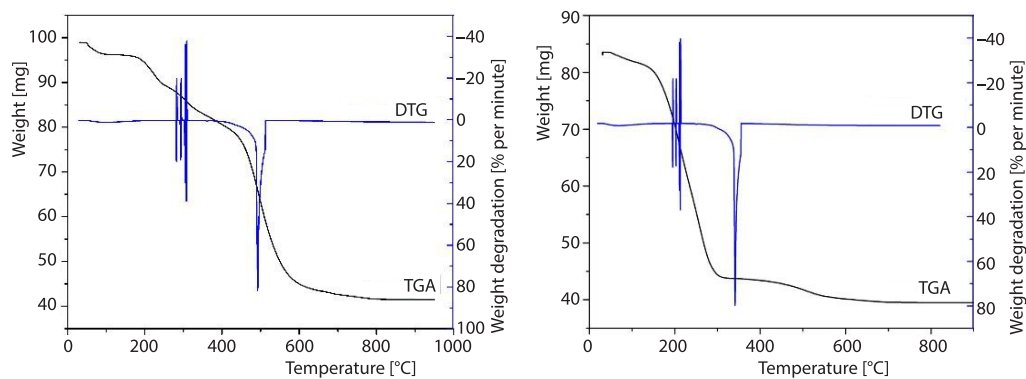


Figure 4. The TGA and DTG profile of combustion of RDF-PA and RDF-PL separately

As shown in tab. 1, hydrogen contents in RDF-PA are lower than in RDF-PL. However, the volume of hydrogen in RDF-PL was somewhat advanced. Hydrogen produces water through spontaneous ignition, like a furnace [9]. The principal cradle of trash, acid rain, and the production of delicate PM in the atmosphere is a NO_x . The RDF-PA, on the other hand, has a lower nitrogen content and is less likely to produce NO_x after ignition than former RDF. The sulphur is integral to RDF and is accountable for scrabbling and catching. Due to the fabric mills and natural timber wastage with various structures of such RDF, the sulphur concentration in RDF-PA and RDF-PL may also be present [19].

The RDF-PA and RDF-PL have calorie values of 5348 and 5278 kcal/kg, respectively. Plastic, on the other hand, has a higher ignition heat due to its consistent biochemical affection and lower oxygen concentration [20]. The heightened calorific assessment of RDF-PA is conceivably the cause of the existence of plastics [20]. Table 1 shows that both RDF samples are made up of high quality waste and have a calorific value that is acceptable. The maximum calorific value of RDF-PA facilitates complete ignition, resulting in additional beneficial heat output. As a result, it was shown to be well-organised extra energy compared to the RDF-PL.

Table 1. Ultimate and proximate analysis of given samples

Samples	Unit	RDF-PA	RDF-PL
Carbon	[%]	55.34	53.44
Oxygen	[%]	34.6	19.5
Hydrogen	[%]	3.51	4.4
Sulphur	[%]	0.01	0.12
Nitrogen	[%]	0.64	1.8
Moisture contents	[%]	4.3	1.6
Volatile matters	[%]	67.9	76.7
Ash contents	[%]	14.4	19.6
Fixed carbon	[%]	9.1	7.5
Net calorific value	[kcalkg ⁻¹]	5348	5278

– Combination characteristics

The TGA is used to detect mass changes, thermal stability, and degradation of samples. Figure 4 depicts the ignition of RDF products. The DTG curves of RDF feature spikes and tails for mass loss in various regions. The dehydration step began at 10 °C and continued until 170 °C, during which all moisture and minimal volatile materials were eliminated. The humidity content was vaporised, followed by the de-volatilisation of RDF at an approximate temperature (380 °C) in the first control region. The carbon deterioration occurs in the following zone because of char-ignition. The TGA curve shows that RDF-PA has the lowest humidity content and could withstand extra time and use enormous warmth to become explosive as the intensity of the curl has substantially slighter than that of the RDF-PL.

These impacts boosted the full results of the proximate analysis. The primary fragmentation for RDF stayed within 200 °C and 700 °C during its firing. Initially, constituents of RDF with substantially lower sublimation points, such as viscose, were heated and evaluated as equal to lignin through complex organics [18, 21]. Because of the probable rise in polymeric materials as in RDF, it could be noticed through DTG analysis of RDF that crest and its duration grows. The RDF-PA has a significantly more dramatic DTG gradient than other RDF-PL, possibly due to hemicellulose's overall exclusion [19]. Moreover, although RDF-PA was persistently enabled, RDF-PL has revealed piercing peaks at exact temperatures. In addition, compared to previously described RDF, the number of peaks was less [2, 18, 21]. A peak in RDF samples indicates the presence of distinct volatile matter parts during decay and ignite. When the temperature and level of detonation of distorted aspects of combustible matter in the RDF have closely existed, relatively littler peaks form, which could be true for all the RDF used in this work [22, 23].

On the other hand, the diluting gases of plastic had no impact on ignition. The assumed sample ignition proficiency results fall within the range of published fuel combustion performance. Basic ignition outlines often demonstrate a similar pattern by a tiny difference because of a change in the arrangement of such available specimens; the weighed destitution pattern appeared earlier than projected, creating the impression of unification.

– Pyrolysis characteristics

At a heating rate of 10 °C per minute, fig. 5, TGA and DTG outline the thermal degradation properties of various blends. The RDF pyrolysis procedure can be alienated into the following distinct steps: humidity and minor volatile matter removal (100 °C). The RDF-PA hemicellulose degradation (170-330 °C). Lignin and cellulose decomposition (340-440 °C)

and lignin degradation (>400 °C) [24, 25]. The final strength of the second region was significantly more significant than the first region, according to the TG curve. Because of the delayed degradation in the RDF sample creation, the weight loss rate decreased from 310-920 °C. Over an inclusive temperature of 180-900 °C, the loss of carbon atoms typically occurs at a slower pace. Because of the oxygen level of both RDF samples, carbon dioxide generation may be measured [26]. The CO₂ was a primary contributor to uncontrolled gases with high absorbance intensity in the nitrogen environment. The first region of weight loss, as shown in fig. 5, monitors moisture loss and eliminates very light volatile components. Because of the heat contravention of weak links in the polymeric edifice of the fundamental elements of biomass and the synthesis of sturdier, extra steady bonds to yield their place, de-volatilisation occurred in the first region of weight loss. The temperatures at which the most significant weight loss occurred were labelled on DTG curves by the location of the curve's peaks.

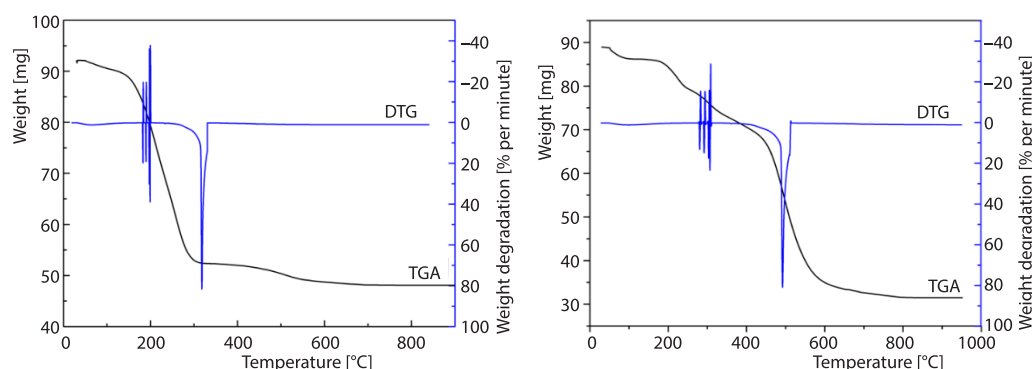


Figure 5. The TGA and DTG profile of pyrolysis of RDF-PA and RDF-PL, respectively

Roughage is crystal-like and durable, whereas hemicellulose is amorphous and has a weak structure. Lignin is a cross-linked amorphous mastic with no unique erection that confounds fibrous cellulosic components. The peak point of the RDF-PA and RDF-PL DTG curves was estimated to have migrated to a low temperature as the amount of paper in the sample increased [27]. The main contribution the discharge of gases such as SO₂, CH₄, and carbon sulphide was the generation of carbon dioxide in the nitrogen atmosphere (COS). Sulphur may be responsible for producing SO₂ [1], whereas methane formation may be shaped by de-volatilisation [28].

– Kinetics characteristics

Two combustion or gasification phases can be recognised in all DTG profiles under O₂: obviously, the peaks differ in position and height. As a result, info on the reactivity of RDF samples can be derived. As a result, reactivity parameters for each peak were determined, including the proportion of ancillary spikes or shoulders in the smouldering characteristics [29]. In this approach, a number indicating the mean reactivity (MR) was determined for both RDF samples and the accompanying peak temperature, *T_p*. the findings are shown in tabs. 2 and 3. In the N₂ condition, the reactivity parameters centred between 160 °C and 410 °C and 420 °C and 900 °C, and the most significant reactivity value was observed under these ranges. Additional reactions like de-volatilisation, char gasification, and combustion occur when O₂ is present. Under O₂, volatile and char combustion zones were related with temperature ranges of 150-390 °C and 390-900 °C, respectively. In comparison RDF-PL, RDF-PA has a lower lignin content, which explains why the RDF-PA sample is more reactive.

The kinetic parameters of all categories of fuels have been estimated utilising TGA profiles applying a linear variant of the Arrhenius equation. The activation energy, E , order of reaction, n , and correlation coefficient, R^2 of the examined RDF Samples were computed under various atmospheric conditions. At $n = (0.3, 0.5, 0.67)$, and $n = 1$, the reaction kinetics were modelled, and the values of E_a increased by a factor of two. For one order of reaction, the best line of fit has been provided for the apparent energy of activation values, shown in tabs. 2 and 3.

For the comparison study, the fuel samples could be ranked as RDF-PA and RDF-PL under N_2 , but the MR values were slightly higher under N_2 than under O_2 . Accordingly, all these values were more significant than N_2 and showed an RDFPL > RDFPA trend. Different trends have been observed under the conditions mentioned previously, but there is a slight and comparable discrepancy in their MR values. As with N_2 , RDF-PL had a high MR value of 0.67, while RDF-PA had a low MR of 0.18, as shown in fig. 6. These blend fuels had low MR under O_2 combustion reactivity analysis. The MR values in the O_2 atmosphere were slightly lower than those in the N_2 atmosphere; this phenomenon is also supported by this research [29, 30]. Under N_2 to O_2 internal combustion, distinct types of reactions have been identified.

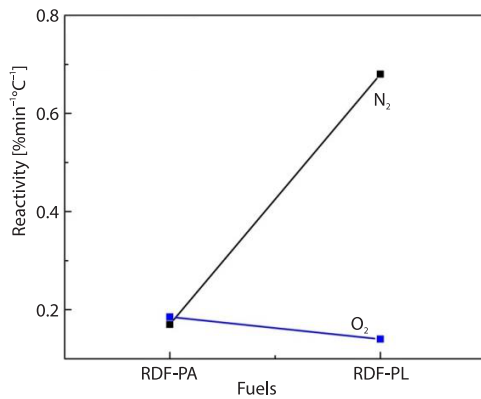


Figure 6. Reactivity flow of given fuels under combustion and pyrolysis

Table 2. Reactivity chart for combustion and pyrolysis analysis

Feedstock	Results							
	Under nitrogen atmosphere				Under oxygen atmosphere			
	Ignition temperature	Peak temperature		Mean reactivity	Ignition temperature	Peak temperature		Mean reactivity
	T_i	T_{p1}	T_{p2}	MR	T_i	T_{p1}	T_{p2}	MR
	[°C]	[°C]	[°C]	[%min ⁻¹ °C ⁻¹]	[°C]	[°C]	[°C]	[%min ⁻¹ °C ⁻¹]
RDF-PA	277	97	494	0.18	281	102	493	0.175
RDF-PL	171.61	138	322	0.67	280	109	348	0.14

Table 3. Kinetic analysis for combustion analysis

Items	Symbol	Units	Combustion Analysis							
			RDF-PA				RDF-PL			
			$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$
Activation energy	E	[KJmol ⁻¹]	99.24	108.7	117.7	137.9	92.23	105.97	119.67	155.96
Frequency factor	A	[s ⁻¹]	9.90·10 ⁶	8.59·10 ⁷	7.22·10 ⁸	7.62·10 ¹⁰	1.94·10 ⁶	4.73·10 ⁷	1.13·10 ⁹	4.82·10 ¹²
Co-relation Co-efficient	R^2		0.97582	0.97654	0.97776	0.9778	0.97582	0.9781	0.9783	0.97845

By using the Freeman-Carroll method, mapping the chart between $\ln(1/T^2)$ and $1/T$, E can be determined by the alteration or conversion degree mechanism. The Freema-Carroll procedure continued to develop a complete understanding of the kinetic factors because of the mixture of constituents on the combustion infrastructures. The conclusion of the kinetic attributes and the identical correlation factor, R^2 , suggested via the Freeman-Carroll technique are validated in tabs. 3 and 4. The consequences show that weight decay may be complete through E in the interest of sample ignition [31], which are 98.86 kJ/mol, 108.06 kJ/mol, 117.109 kJ/mol, and 137.29 kJ/mol for $n = 1/3, 1/2, 3/4,$ and 1 in nitrogen condition, and 99.24 kJ/mol, 108.7 kJ/mol, 117.7 kJ/mol, and 137.9 kJ/mol for $n = 1/3, 1/2, 3/4,$ and 1 in oxygen atmosphere, respectively for the RDF-A. While for RDF-PL, 121.558 kJ/mol, 135.324 kJ/mol, 149.054 kJ/mol, and 185.844 kJ/mol in nitrogen and 92.23 kJ/mol, 105.97 kJ/mol, 119.67 kJ/mol, and 155.96 kJ/mol in oxygen condition for $n = 1/3, 1/2, 3/4,$ and 1 , correspondingly. As shown in the results, RDF can decrease the E rate during the initial combustion stage while increasing its value during the critical ignition phase. These findings bolstered the case for enhanced combustion structures and the delayed ignition technique (as publicised in tabs. 3 and 4). Additionally, a high proportion of volatiles in the sample was associated with a high level of consistent E .

Table 4. Kinetic analysis for pyrolysis analysis

Items	Symbol	Units	Pyrolysis Analysis							
			RDF-PA				RDF-PL			
			$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$	$n = 1/3$	$n = 1/2$	$n = 2/3$	$n = 1$
Activation energy	E	[KJmol ⁻¹]	98.6	108.09	117.109	137.29	121.558	135.324	149.054	185.844
Frequency factor	A	[s ⁻¹]	8.60·10 ⁶	7.75·10 ⁷	6.29·10 ⁸	6.59·10 ¹⁰	1.75·10 ⁹	4.19·10 ¹⁰	9.87·10 ¹¹	4.53·10 ¹⁵
Co-relation Co-efficient	R^2		0.97568	0.97654	0.97786	0.9778	0.97568	0.9781	0.9783	0.97845

Conclusions

Due to a large amount of volatile matter attributed to the fixed-carbon inclusions, all RDF decayed in the initial phases (gas phase). Non-etheless, RDF-PA had the highest volatile fraction and the lowest ash content compared to the other samples. Because of the progressive summation of hydrogen and carbon, RDF-PA potential for energy application was boosted. Furthermore, low sulphur content has been perceived in RDF-PA, which is satisfactory from an environmental standpoint and had the highest calorific value because it contains more carbon than the further trials. The fattening value of full RDF examined in the modern investigation was appropriate for industrial ignition. For the persistence of incineration and mass loss, RDF-PA had the most extended retaining duration under identical pre-determined conditions.

Consistent with the current study, the thermal consistency of the RDF was found to be increasing with the increase in carbon content. As a result, the sample's lowest carbon concentration causes low stability and is unsuitable for an energy proposal. The CO₂ and CO were the significant gases emitted, with methane and hydrogen making up a tiny portion of the total. The TGA analysis revealed that the ignition of RDF, including plastic and paper sawdust, occurs in two-stages. The first phase involves igniting volatile elements, followed by the ignition of residuals and char formation at high temperatures. By including materials such as plastic and paper in sludge fuels, researchers improved the RDF's ignition profile and burnout characteris-

tics while also reducing SO₂ generation, which was accompanied by an increase in NO_x output. Interfaces between discrete elements promote the ignition of volatiles, resulting in increased SO₂ and NO_x emissions.

On the other hand, these connections remained in place to prevent the interaction of residual and produced char, as well as the creation of NO₂. The kinetic process demonstrates that when paper accumulates, the activation energy rises compared to plastic, indicating an increase in the energy obstruction for RDF combustion. The iso-thermal investigation also revealed that RDF combustion approaches could be divided into three groups based on their ignition kinetics, which was organised by diffusion, interfacial reaction, and nucleation methods, which could be used together or independently. It's the first time that iso-thermal analysis of micro-reactions originating during the igniting operation has revealed entire kinetics triplets for RDF.

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