

## Study of kinetic characteristics of pyrolysis of sewage sludge and waste biomass using thermogravimetry

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The present study reports the utilization of municipal sewage sludge mixed with bagasse undergoes thermal decomposition for pyrolysis experiments and thermogravimetric analysis (TGA). The characterization tests established that bagasse contained higher levels of carbon and volatile matter than sewage sludge. Coats and Redfern method has been applied to TGA and differential thermogravimetric (DTG) data to extract kinetic parameters. The research showed that adding bagasse to sewage sludge during pyrolysis produced a shorter temperature window which scientists linked to quicker volatile component release. Bagasse's high volatile matter content enabled a combustion-like decomposition reaction of sludge to occur at reduced temperatures. A 50–50% sludge and bagasse mixture has lower activation energy than pure sewage sludge, suggesting that the presence of bagasse reduces the amount of reaction energy needed. This research uses Coats and Redfern method to calculate activation energy based on TG–DTG analysis of sewage sludge with bagasse in pyrolysis experiments.

**Keywords:** Bagasse, Co-pyrolysis, Municipal Sewage Sludge, Waste biomass

### Introduction

The stricter environmental regulations regarding waste discharge have caused the worldwide increase in construction of wastewater treatment facilities. The surge in facilities handling wastewater sludge has become a major ongoing problem. The vast amounts of municipal sewage sludge that treatment facilities generate have become a profound environmental challenge<sup>1</sup>. The accumulated sludge material creates a dual danger to environmental and human well-being specifically targeting underdeveloped countries. Each year China generates 20 million tons of wet sewage sludge while maintaining 80% water in the sludge yet remains unable to treat properly 80% of this sewage waste. Municipal waste water treatment facilities produce sewage sludge which functions as their waste by-product. The sludge material contains solid components hidden within a high proportion of water content containing complicated organic and inorganic mixtures. Organic compounds present in sludge are proteins, carbohydrates and fat. Inorganic compound present in sludge are metals and a wide variety of living and non-living microorganisms<sup>2-4</sup>.

India holds the position of the second largest sugarcane producer globally, following Brazil, with

an output of 26 million metric tons in the period 2010-2011. Sugarcane cultivation in India spans approximately 4 million hectares of land, achieving an average yield of 70 tons per hectare. The primary waste materials generated from sugar manufacturing and alcohol production include field residue (left after harvesting), bagasse, filter press cake (or press mud), and spent wash. Bagasse stands out as a significant cellulosic by-product from agro-industries. It is the fibrous substance that remains after the juice is extracted from sugarcane stalks. For every 1000 tons of sugarcane processed, around 280 tons of bagasse are produced. The composition of bagasse typically ranges from 25% to 50% cellulose, 20% to 30% hemicellulose, and 15% to 25% lignin<sup>5</sup>.

Faced with increasingly strict environmental protection standards, traditional disposal methods like landfilling and using sludge on land are becoming less and less viable. In response, thermochemical conversion has gained renewed interest as a promising approach to simultaneously treat and stabilize this problematic waste<sup>6</sup>. Pyrolysis, a key thermochemical process, is particularly important. It not only holds the potential for commercial production of valuable fuel gas and bio-oil but also forms the initial step in other

thermochemical technologies like gasification, combustion, and liquefaction. To effectively develop and implement sewage sludge thermochemical conversion technologies, a deep understanding of how this sludge behaves during pyrolysis is essential<sup>7</sup>. Sludge pyrolysis is a contemporary handling technique that generates fuels. One by-product of pyrolyzing sludge is bio-oil. High oxygen and nitrogen content, high water content, and a low calorific value in comparison to traditional fuels are the characteristics of bio-oil. The yield of bio-oil produced by pyrolyzing the sludge is poor as it contains a lot of ash. Enhancing the production and quality of sludge pyrolysis oil is essential. Co-pyrolysis, a modification of the pyrolysis process, can enhance these. Increased bio-oil yield is observed in experiment of co-pyrolysis of municipal sewage sludge and waste biomass<sup>8</sup>.

Co-pyrolysis is a simple and effective process to rectify the quality and quantity of pyrolysis products<sup>9</sup>. Several studies have been conducted to see the co-pyrolysis characteristic of sludge with different biomass like rice straw, sawdust, rice husk, manure etc. to improve bio-oil yield. Products of pyrolysis can be controlled by changing the pyrolysis conditions. There are different parameters that affect the decomposition of raw material like inert gas flow rate, raw material size, heating rate etc.<sup>10</sup>. Gas obtained from pyrolysis contains CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>. Bio-char, which contains heavy metals, is used as adsorbent in waste water treatment to remove colour and COD in pulp and paper industry. There is improvement in BET surface area and pore volume is observed in biochar generated in co-pyrolysis compared to biochar of pyrolysis of sewage sludge<sup>8,11</sup>. To determine and develop the biomass conversion through pyrolysis, physical and chemical characteristics and pyrolysis kinetics of biomass is necessary.

Thermogravimetric analysis is used to quantify how a component's weight changes in response to temperature changes. This method of thermal analysis calculates how much and how quickly a material's weight changes in response to temperature<sup>12</sup>. To evaluate the potential of sewage sludge and bagasse as a viable biomass feedstock for co-pyrolysis, an understanding of its fundamental physicochemical characteristics and pyrolysis kinetics is essential. Physicochemical characterization, encompassing analyses such as proximate and ultimate analysis,

provides critical insights into its suitability for thermochemical conversion processes. Thermogravimetric analysis (TGA) is a technique employed to examine the changes in the mass of a biomass sample upon heating. This method is considered reliable, straightforward, and rapid for investigating the kinetics of the pyrolysis process. TGA provides valuable data regarding the amount of mass lost by the biomass as a function of both temperature and time<sup>13</sup>. The Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa (OFW), Arrhenius method and Coats-Redfern techniques, are frequently applied to estimate the kinetic parameters governing the pyrolysis of various biomass types and other materials.

The massive quantity of sewage sludge and sugarcane bagasse is available in India. In view of the vast availability; the objective was to find the effect addition of bagasse with sewage sludge in co-pyrolysis. In this work, TGA was performed to investigate the pyrolysis properties of bagasse and municipal sewage sludge and kinetic parameters are determined.

## Experimental Section

### Materials and sample preparation

Sludge from the municipal wastewater treatment plant at Atladra, Vadodara, was used in the experiment. Water made up most of it. This sludge was collected after further treatment at a municipal wastewater treatment plant. To eliminate moisture, secondary sludge was dried for three days in the sun. However, oven drying results in effective and fast drying, Sun drying was considered on basis of large-scale practice and considering economic aspects. Every day for 3 days, 8 h of sun drying was done. Reduction in moisture was assumed considering the loss of weight of feedstocks. The final moisture content was calculated by proximate analysis<sup>14</sup>. Activated sludge is another name for secondary sludge. Protein, carbohydrates, lipids, bacteria, medications, hormones, and other organic and inorganic substances are all mixed together in sludge. The amount of ash in the sludge is high.

Sugarcane bagasse is a one type of biomass. Biomass is most valuable, since it is available worldwide and can be transformed into useful products. Main types of biomasses are forest, wood and agricultural residue, manures, aquatic biomass etc. Bagasse is the residue left over after sugarcane juice is extracted. Bagasse was collected from juice shop, Ahmedabad. A significant amount of moisture was present. To eliminate moisture, bagasse was dried for

three days in the sun. Fig. 1 shows the images of crushed sludge and bagasse used in pyrolysis experiment. Sludge was crushed into roll crusher and measured average particle size by using sieve analysis. Bagasse is crushed by using grinder. Medium sized blade is used in grinder. Then average particle size of bagasse is measured with sieve analysis.

#### Method of experiment

To quantify the moisture content (MC), volatile matter (VM), Ash (A), and fixed carbon (FC) within the sugarcane bagasse sample, standard ASTM methods were followed. ASTM E872-82 for volatile matter, ASTM E871-82 for moisture, and ASTM D1102-84 for ash. The percentages of C, H, N, S in the SB sample were identified as its elemental composition. Subtracting the total percentages of C, H, N, S and A from 100% was the next step in determining the oxygen concentration.

#### Kinetic study

Thermogravimetric analysis is used to measure the change in weight of components with relation to change in temperature. This method of thermal analysis calculates how much and how quickly a material's weight changes in response to temperature. It is employed to choose the pyrolysis temperature range and ascertain the material's composition. TGA was performed using the Mettler Toledo Thermogravimetry Analyzer. In an alumina crucible, roughly  $10 \pm 0.2$  mg of the sample was kept and inert environment was maintained using a continuous flow of high purity argon at a flow rate of 50 mL/min. Thermogravimetry is also one type of pyrolysis in which reaction occurs in inert atmosphere. Sample is heated up to  $800^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ . The weight loss of sample is measured with respect to time and temperature. Kinetic parameters are computed from thermogravimetric analysis using the Coats and Redfern method. The mathematical model for this method is:

$$\ln \left[ \frac{-\ln(1-x)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \right] - \frac{E}{RT}$$

$\ln[-\ln(1-X)/T^2]$  was plotted against  $1/T$ . A straight line may be obtained if the process can be assumed as first order reaction. The slope can be used to get the activation energy  $E$ , and the intercept can be used to determine the pre-exponential factor  $A$ . Correlation is good if value of linear correlation coefficient ( $R^2$ ) is near to one<sup>15</sup>.

## Results and Discussion

#### Characterization of sewage sludge and sugarcane bagasse

Table 1 provides a comparative analysis of the physicochemical characteristics of municipal sewage sludge and sugarcane bagasse. The ultimate analysis reveals that bagasse has significantly higher carbon (45.75%) and hydrogen (4.20%) content compared to sludge (29.15% and 3.40%, respectively), suggesting greater potential energy content. Conversely, sludge exhibits considerably higher nitrogen (2.75%) and oxygen (64.7%) content compared to bagasse (0.6% and 49.45%, respectively). The proximate analysis further

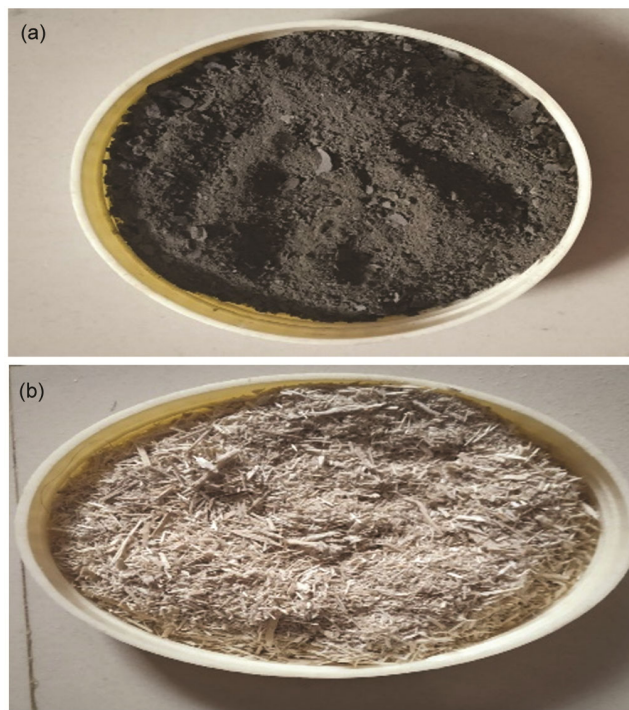


Fig. 1 — Photographs of (a) crushed municipal sewage sludge and (b) powdered bagasse

Table 1 — Typical characterization of municipal sewage sludge and bagasse

Sample	Ultimate analysis (mass%)					Proximate analysis (mass%)				Calorific value (MJ/kg)	
	C	H	N	S	O <sup>a</sup>	M	VM	FC	A	HHV	LHV
Bagasse	45.75	4.20	0.6	0.3	44.1	0.6	85.80	8.55	5.05	16.36	14.53
Sludge	29.15	3.40	2.75	0.6	20.15	0.5	51	4.55	43.95	9.21	8.01

<sup>a</sup>Calculated by difference (100 – sum of C, H, N, S, A)

highlights key differences: bagasse is characterized by a very high volatile matter content (85.80%) and low ash content (5.05%), indicating its propensity for releasing volatile compounds upon heating and leaving minimal inorganic residue. In contrast, sludge shows a much lower volatile matter (VM) content (51%) and a drastically higher ash (A) content (43.95%). These characteristics suggest that bagasse is a more favorable feedstock for pyrolysis due to its higher volatile yield potential and lower ash-related operational challenges. The high ash content in sludge could impede the efficiency of thermal conversion processes. Furthermore, the nitrogen content in sludge indicates greater potential for NO<sub>x</sub> emissions during thermal treatment compared to bagasse<sup>16</sup>. During pyrolysis, nitrogen converts into volatile nitrogen compounds. Upon further heating, the intermediates get converted into NO<sub>x</sub> emissions. However, lower nitrogen content in bagasse reduces the overall NO<sub>x</sub> generation. Overall, the compositional differences highlighted in Table 1 underscore the distinct behaviours of these materials during thermal processing and suggest that co-pyrolysis of sludge with a high volatile matter and low ash biomass like bagasse could potentially enhance the process, although the inherent challenges posed by the high ash content of sludge would still need to be addressed. The high heating values (HHV) are calculated using the correlation<sup>17</sup>.

$$\text{HHV} = 0.3536\text{FC} + 0.1559\text{VM} - 0.0078\text{A} \text{ (MJ/kg)}$$

After finding HHV, LHV is found by correlation<sup>18</sup>.

$$\text{LHV} = \text{HHV} - 0.212\text{H} - 0.0245(\text{M} + 9\text{H})$$

#### Kinetic study

The pyrolysis summaries of sugacane bagasse, municipal sewage sludge, and their 50/50 blend at a heating rate of 10°C/min are shown in Fig. 2. The graph presents the TGA of sludge, bagasse, and their mixture, showing the percentage of weight loss as a function of temperature. Initially, all three materials exhibit a minor weight loss of about 5–10% between 0°C and 150°C, which can be attributed to the evaporation of moisture. As the temperature rises beyond 150°C, distinct differences in thermal decomposition behaviour become evident. Bagasse undergoes rapid weight loss between approximately 200°C and 350°C, indicating a low thermal stability and the presence of easily decomposable organic components like cellulose and hemicellulose. In contrast, sludge shows a more gradual decomposition pattern, with significant weight loss extending from around 200°C up to 650°C. This slower degradation

suggests that sludge contains more thermally stable components or inorganic matter. The mixture of sludge and bagasse exhibits an intermediate decomposition profile, suggesting a synergistic effect where the combination of the two materials enhances thermal stability compared to bagasse alone. By the end of the analysis, sludge retains the highest residual mass, followed by the mixture, while bagasse shows the least residue, emphasizing the stability imparted by sludge in the blend. Overall, the mixture's thermal behaviour implies potential advantages in thermal treatment processes such as pyrolysis or combustion, where improved stability and controlled degradation are beneficial<sup>19</sup>.

The derivative thermogravimetric (DTG) analysis provides further insight into the thermal decomposition behaviour of sludge, bagasse, and their mixture by illustrating the rate of mass loss as a function of temperature (Fig. 3). In the lower temperature range (below 150°C), all three samples

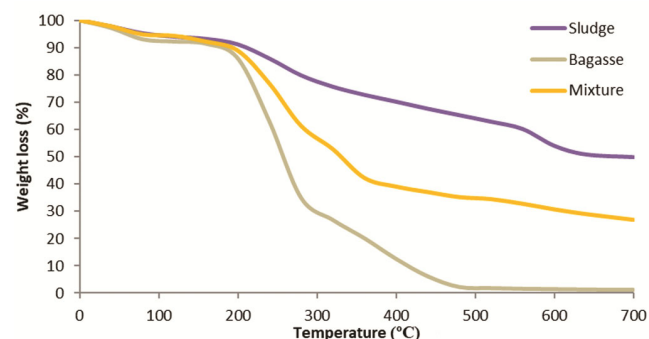


Fig. 2 — TG curves of sludge, bagasse and their 50:50 blend at heating rate of 10°C/min

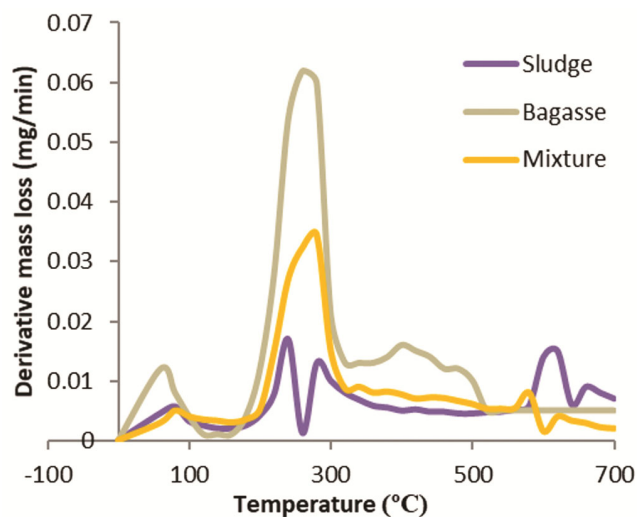


Fig. 3 — DTG curves of sludge, bagasse and their 50:50 blend at heating rate of 10°C/min

exhibit minor peaks corresponding to moisture evaporation and the release of physically bound water. Bagasse demonstrates a prominent and sharp peak centered around 300°C, indicating a rapid degradation phase likely associated with the thermal decomposition of hemicellulose and cellulose, which are major constituents of lignocellulosic biomass. In contrast, sludge presents a broader and less intense peak over a wider temperature range, reflecting a more complex and gradual degradation process that may involve proteinaceous and mineral-bound organic matter<sup>20</sup>.

The mixture exhibits a DTG curve that lies between the two individual components, with a moderately intense peak occurring around the same temperature as bagasse but with reduced magnitude, suggesting a dampening effect due to the presence of sludge. Additionally, a secondary degradation event is observed in sludge and, to a lesser extent, in the mixture at temperatures above 500°C, potentially attributable to the decomposition of more thermally stable components such as fixed carbon or inorganic-organic complexes. These findings confirm that the mixture exhibits synergistic thermal behaviour, with improved stability and a more controlled decomposition profile compared to bagasse alone. This characteristic is advantageous for thermochemical applications such as pyrolysis or combustion, where a steady release of volatiles and char formation can enhance process efficiency and operational control<sup>19</sup>.

### Kinetic analysis

#### Calculation of kinetic parameters

Determining the activation energy is the goal of kinetic research. The smallest amount of energy needed to initiate a reaction is known as activation energy. It is denoted by  $E_a$  and it is expressed in kJ/mol. Thermogravimetric data is used to calculate activation energy. There are various methods used for kinetic study such as Friedman method, Coats and Redfern method, Flynn-Wall-Ozawa method, Arrhenius equation, etc. in literature. Since this

methods require multiple heating rates and the present study uses single heating rate, application of such methods were not feasible.

#### Coats and Redfern method

Coats and Redfern method was used in this study to calculate activation energy of sludge, bagasse and their blend.  $-\ln[-\ln(1-X)/T^2]$  was plotted against  $1000/T$ . Activation energy was calculated based on slope of the graph (Fig. 4). Equation for the graph is  $Y = mX + C$ . is called as correlation coefficient. The  $R^2$  values obtained are 0.8486 for sludge, 0.9491 for bagasse, and 0.9484 for a mixture of 50% bagasse and 50% sludge.

Table 2 shows value of activation energy in different temperature range. Up to 200°C, activation energy required for evaporates moisture content present in material. In temperature range of 200-500°C activation energy is 12.738 kJ/mol for sludge, 25.41 kJ/mol for bagasse and 24.57 kJ/mol for mixture which is pyrolysis zone. Major organic matters decompose in this temperature range, so energy requirement is high. This could be described from thermogravimetric analysis of sludge. In temperature range of 450-700°C activation energy is

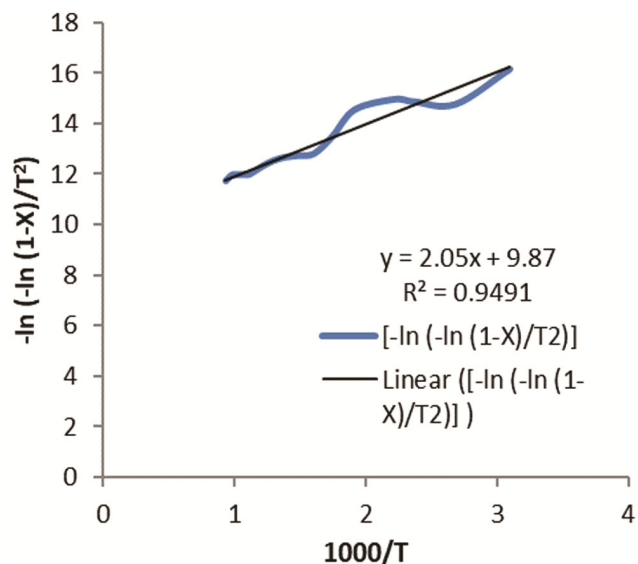


Fig. 4 — Graph of  $[-\ln(-\ln(1-X)/T^2)]$  v/s  $1000/T$  for bagasse

Table 2 — Activation energy calculated by Coats and Redfern method

Temperature range (°C)	Activation energy (kJ/mol)				
	Sludge	Values in literature	Bagasse	Values in literature	Mixture
0-200 (1 <sup>st</sup> zone)	15.06	-	10.94	3.29 [21]	25.94
200-450 (2 <sup>st</sup> zone)	12.73	33.1 [22]	25.41	24.1 [21]	24.57
450-700 (3 <sup>st</sup> zone)	39.10	-	14.17	37.1 [21]	20.28
0-700 (Entire range of temperature)	11.65	19.66[23]	17.04	-	21.14

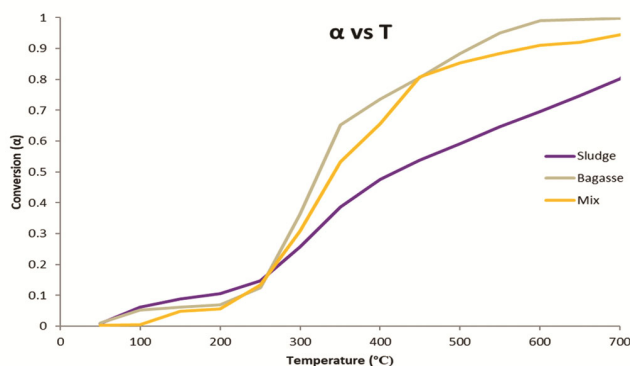


Fig. 5 — Graph of conversion v/s temperature

Table 3 — Fitting results of pyrolysis kinetic equation by Coats and Redfern method

Sample	Fitting equation	Correlation coefficient
Sludge	$Y = 1.4014X + 11.47$	0.84
Bagasse	$Y = 2.05X + 9.87$	0.94
Mixture	$Y = 2.5439X + 9.5698$	0.94

very high, because heavy inorganic matters decomposed in this zone and it requires high amount of activation energy to decompose. Sludge has a lower average activation energy than bagasse.

The fitting results of the Coats and Redfern method's pyrolysis kinetic equation are shown in Table 3. The coefficients of linear correlation are close to unity. This indicates that there is a strong association.

Fig. 5 shows the graph of conversion versus temperature for sludge, bagasse and their blends. For bagasse, conversion rate increase in temperature range of 250–400°C as in this temperature range majority of organic degradable volatile stuff breaks down. Because the majority of organic compounds breakdown at temperatures between 200 and 550°C, bagasse conversion rates are high in this range. Bagasse contains a lot of volatile substances. The conversion rate rises gradually as there are not many organic materials in sludge. When sludge and bagasse are combined, the conversion rate rises.

## Conclusion

According to the current study, sugarcane bagasse is an excellent renewable energy source that may be combined with municipal sewage sludge in co-pyrolysis. The proximate analysis further highlights key differences: bagasse is characterized by a very high volatile matter content (85.80%) and low ash content (5.05%), indicating its propensity for releasing volatile

compounds upon heating and leaving minimal inorganic residue. In contrast, sludge shows much lower volatile matter content (51%) and drastically higher ash content (43.95%). The combination of enhanced volatile yield potential and diminished ash-related operational issues transforms bagasse into an outstanding feedstock for pyrolysis operations. Analysis of material-specific transformations during pyrolysis occurred through thermogravimetric analysis studies. Activation energy measurements resulted from analyzing data obtained from TGA instrumentation. All experimental feedstocks showed their main devolatilization step took place within temperature ranges of 250–500°C for sludge, 200–450°C for bagasse and 250–450°C for both materials during pyrolysis reactions. Research works through different methodologies to evaluate activation energy values. This investigation utilized Coats & Redfern method for all data collection. The activation energies are found to be in the range of 15–39 kJ/mol during Coats & Redfern method investigations. The Coats & Redfern method shows that activation energy of deprived bagasse falls between 10–25 kJ/mol. The sludge and bagasse (50:50) blended fuel demonstrates activation energy levels from 20–25 kJ/mol. Highest activation energy required in sludge pyrolysis is 39 kJ/mol and for mixture pyrolysis 25 kJ/mol which shows the 35% reduction in activation energy was observed upon addition of bagasse in sewage sludge for pyrolysis. However, it is acknowledged that a more comprehensive study with a wider range of mixing ratios, heating rates and different kinetic model would provide more data for synergistic behaviour. The study is limited and does not address the metal analysis. The metal analysis requires advanced instrumentation which was not available for this study. Nevertheless, metal analysis provides useful insights into catalytic effects. These aspects are beyond the scope of current study but they are identified as important for future research work.

## Conflict of interest

The authors declare that they have no conflict of interest.

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