Co-thermal degradation characteristics of rice straw and sewage sludge

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ABSTRACT

This study investigates the kinetic behaviors and gas evolution of rice straw, sewage sludge, and their blends under co-thermal decomposition processes using Thermogravimetric analysis combined with Fourier-Transform Infrared Spectroscopy (TGA-FTIR). The experimental results indicate that sewage sludge could be enhanced the volatile matter decomposition in rice straw co-thermal process at lower temperatures. Activation energy decreases from 53.07 kJ/mol to 48.62 kJ/mol with an increase in sewage sludge addition from 50% to 80% under pyrolysis conditions. The major volatile components were aliphatic chains with double bonds, as well as carbonyl, hydroxyl, and C–H groups in organic compounds by FTIR identification. The tested materials characteristics in terms of volatile matter-to-fixed carbon (VM/FC) ratio was significantly affected the thermal degradation performance. Activation energy was decreased with increasing the VM/FC ratio. It implied that co-thermal reaction could be accelerated. In summary, the results could provide the important information for co-thermal treatment of sewage sludge and rice straw in commercial-scale plant.

Keywords: Rice straw; Sewage sludge; kinetic analysis; TGA-FTIR; pyrolysis; gasification.

Highlights

- Kinetic characteristics in co-thermal treatment of rice straw and sewage sludge was investigated.
- Biomass containing higher volatile matter content has a higher activation energy.
- Blending 40% rice straw and 60% sewage sludge was optimum ratio for co-pyrolysis.
- Kinetic results provide the information for the design and operation work in thermal process.
1. **Introduction**

Approximately 130 thousand tons (based on 80% moisture content) of sewage sludge (SS) derived from municipal wastewater treatment plants (WWTPs) are generated in Taiwan per year. The amount of sewage sludge is expected to dramatically increase due to the rapid increase in sewer system establishment and stringent requirements for water resources protection. Sanitary landfills are currently a major solution for sewage sludge final disposal. Rice production is one of the most important agricultural activities in Taiwan. The average rice straw (RS) generation is nearly 1.5 million tons per year [1]. The common traditional habits of farmers include open firing rice straw treatment. However, this option will not be sustainable at current or projected levels due to increasing competition for landfill space, higher costs, more stringent environmental standards, and the implementation of policies to promote recycling. Energy recovery from rice straw and/or sewage sludge has become an attractive solution using thermal chemical conversion processes including combustion, torrefaction, pyrolysis, and gasification. One of the issues of public concern for energy conversion is sewage sludge containing high moisture content resulting in relatively low energy yield. Sewage sludge and other kinds of organic wastes could be an alternatives technology for solving the obstacles and improving the energy yield. To cope with the increasingly stringent regulations, constantly rising treatment, and final disposal costs of sewage sludge and rice straw, the Taiwan government planned to establish strategies and develop innovative technologies for treating the above wastes and achieving the circular economy target. Among the thermal conversion technologies, gasification is an innovative technology because it has several potential advantages associated with high carbon conversion, high calorific value synthesis gas, and flexible biomass utilization and/or agricultural waste-to-energy [2-5]. On the other hand, sewage sludge and biomass (pine sawdust) co-gasification were also investigated in previous literature [6]. The literature results indicated that co-gasification could improve volatile matter thermal behavior and enhance energy conversion efficiency.
Thermogravimetric analysis (TGA) has become a common analysis technique to investigate thermal behaviour and kinetics. This involves the weight loss characterization of tested materials as a function of the reaction temperature controlled in simulated thermal reaction atmospheres. Typical TGA advantages are accurate real-time sample mass measurements, high reproducibility, and well-defined temperature and gas-phase conditions [7-9]. TGA has been applied in recent years to the study of sewage sludge, rice straw, woody biomass, plastics, and other organic waste thermal characteristics using simulated pyrolysis conditions [6, 10-13]. TGA is coupled with spectrometers, such as Fourier transform infrared spectroscopy (FTIR), to analyze the temporal resolution of specific gas-phase fragments. This contributes to the analysis and understanding of thermal degradation mechanisms before waste and/or biomass treatment [14-17].

However, little information has been collected on the relationships between waste and/or biomass characteristics, reaction kinetics, and gaseous speciation during the thermal degradation process. Moreover, biomass properties play important roles in thermal degradation process determination. Some parameters such as volatile matter (VM), fixed carbon (FC), moisture (H₂O), or elemental contents (C, H, N, S) are key factors that affect the energy conversion process. The volatile and fixed carbon contents in biomass are practical parameters for evaluating the volatility and ignitability [18]. Practically, the different characteristics of biomass fuels from coal to plastic, include their higher volatile matter and lower carbon content. Pyrolysis and gasification system modifications need to consider these characteristics along with other factors carefully. Therefore, the objectives of this research were: (1) to determine the kinetic triplets in co-thermal degradation of rice straw, sewage sludge, and their blends; (2) to understand the characteristics of gas evolution and possible speciation during the co-thermal degradation process; (3) to investigate the relationship between the tested materials characteristics and kinetic triplets during the co-thermal degradation process.
2. Materials and methods

2.1 Materials

The feedstocks used for the co-thermal process in this research were sewage sludge and rice straw, respectively. Sewage sludge was sampled from Dihua urban WWTP, which was established in July 1980 with a capacity of 500,000 m³/day in Taipei City, Taiwan. Sewage sludge was treated using gravity thickening, anaerobic digestion, and dewatering. To reduce the sludge volume and save transportation cost, sewage sludge dewatered by drying prior to the final disposal. Rice straw was collected from Chung-Li District, Tao-Yuan city located in the northern part of Taiwan. Rice straw and sewage sludge were first dried, shredded, and sieved to extract a particle size between 150 µm and 210 µm. In order to precisely analyze the thermal reaction, rice straw was pelletized using a mini-pellet press due to its light and bulky properties. Proximate analysis indicated the percentage by weight of moisture, ash content, volatile matter, and fixed carbon. The tested samples were determined in triplicate using regulation testing procedures announced by the Taiwan Environmental Protection Administration (EPA) and the Chinese National Standard (CNS) which are similar to the American Standard for Testing Materials (ASTM). The ultimate analysis of the combustibles in the sewage sludge and rice straw was also analyzed in triplicate using an elemental analyzer (Elementar Analyzer Vario MICRO cube). The sewage sludge and rice straw energy contents were determined using a bomb calorimeter (Parr 1341 calorimeter).

2.2 Experimental conditions

Thermogravimetric (TG) analysis is a common technique used to understand thermal behavior and investigate the reaction kinetics in rice straw and sewage sludge co-pyrolysis and/or gasification. The thermogravimetric analyzer (TGA) used in this study is a commercially available laboratory instrument (TGA-STA 7300, Thermal Analysis System, Hitachi). The dried
sewage sludge was prepared by drying and mixing with 20 wt.%, 40 wt.%, and 50 wt.% of rice straw, respectively. The TGA experiments were performed from 40 °C to 1000 °C and operated at heating rates of 5, 10, 20 °C/min in different pyrolysis and/or gasification atmospheres. In the pyrolysis experiments, about 3 mg of the tested samples were pyrolyzed under 100 ml/min with 100% N₂ as the carrier gas. To further simulate the gasification atmosphere air and nitrogen was well-mixed as the carrier gas and controlled between 0.3 vol.% and 1.0 vol.% air mixing ratio under total a flow rate of 100 ml/min.

Rice straw and their blends were evaluated using TGA and TGA-FTIR (Fourier Transformer IR) analysis. To determine the thermal reaction conditions, raw materials were placed in a ceramic crucible 5 mm in inner diameter and 5 mm in height. A precision balance constantly weighed the crucible carrying the samples with a resolution of 0.1 µg. At different reaction rates (5, 10, 20 °C/min), the total time needed for the entire process was calculated. A change in the heating rates brings a corresponding change in air/N₂ ratios of 0.3/99.7, 0.5/99.5, and 1.0/99.0, respectively. Figure 1 illustrates the schematic diagram of an experimental set-up for TGA-FTIR.

![Figure 1. Schematic diagram of TGA-FTIR experiment](image-url)
2.3 Kinetic analysis

The thermal decomposition reaction kinetics of carbonaceous materials is complicated. The kinetic parameters were determined, including activation energy, reaction order, and pre-exponential factor, respectively. The activation energy was determined using the integral method [5, 19] that can be simply expressed as the Arrhenius equation:

\[
\frac{dX}{dT} = -Ae^{\frac{E}{RT}}X^n
\]  

(2)

Where

\[A: \text{pre-exponential or frequency factor (min}^{-1})\;\]
\[E: \text{decomposition reaction activation energy (kJ/mol)}\;\]
\[n: \text{order of reaction}\;\]
\[R: \text{universal gas constant (kJ/mol.K)}\;\]
\[t: \text{time (min); T: absolute temperature (K)}\;\]

The multiple linearized regression form of the Arrhenius equation was used to determine A, E, and n by applying a least-squares (multiple linear regression) techniques. The ideas for calculating reaction order were introduced by previous published literature [20]. Multiple regression analysis can be regarded as an extension of straight-line regression to the situation in which more than one independent variable must be considered. The implied form of the linearized rate equation is

\[y = B + Cx + Dz\]  

(3)

The parameters \(y\), \(x\), \(z\), \(B\), \(C\), and \(D\) in Eq. (3) are defined as follows

\[y = \ln\left\{\frac{1}{(w_i-w_f)}\left(\frac{dw}{dt}\right)\right\}\]  

(4)

\[x = \frac{1}{RT}\]  

(5)
\[ z = \ln \left( \frac{w - w_f}{w_0 - w_f} \right) \]  

(6)

Where \( w \): weight of sample at time \( t \) (min); \( w_f \): weight of residue at the end of the reaction (g); \( w_0 \): initial weight of the sample. The coefficients \( B, C, \) and \( D \) in Eq. (2), which correspond to the logarithm of the pre-exponential factor \( \ln A \); the activation energy \( E \); and the reaction order \( n \), respectively, were determined for each type of rice straw, sewage sludge and their mixture using the multiple linear regression analysis methods using thermo-gravimetric data by Statistica software (Data analysis-software system, version 10).

3. Results and discussion

3.1 Analysis results of thermal kinetic

3.1.1 Comparison between the pyrolysis and gasification of rice straw

The physical-chemical characteristics of rice straw and sewage sludge are shown in Table 1. Elemental analysis shows that tested samples have high carbon content at nearly 40%. The higher heating value of sewage sludge (4,200 kcal/kg) was higher than that of rice straw (3,800 kcal/kg). The higher heating value of these materials has proven that sewage sludge and rice straw have potential as bio-fuel for thermal processes. Nevertheless, volatile matters, which are the key factor in thermal conversion process improvement on average at 59.38% and 64.22% from sewage sludge and rice straw, respectively.

Table 1 Characteristic of tested sewage sludge and rice straw

| Proximate analysis (wt. %)          | Sewage sludge | Rice straw |
|------------------------------------|---------------|------------|
| Moisture                           | 6.71 ± 0.88   | 10.47 ± 0.97|
| Ash                                | 23.02 ± 0.12  | 9.56 ± 0.22 |
| VM                                 | 59.38 ± 0.16  | 64.22 ± 0.47|
| FC                                 | 10.89         | 15.75      |

| Ultimate analysis (wt. %, dry basis) |
|-------------------------------------|
| C                                   | 39.74 ± 0.91 | 39.86 ± 0.59 |
| H                                   | 5.89 ± 0.15  | 6.18 ± 0.18  |
| N                                   | 6.5 ± 0.17   | 0.94 ± 0.05  |
| S                                   | 1.14 ± 0.05  | 0.23 ± 0.05  |
| O                                   | 17.0         | 32.76       |
Energy content (kcal/kg)

|       | HHV    | LHV    |
|-------|--------|--------|
|       | 4,200 ± 20 | 3,800 ± 60 |

Figure 2 shows thermogravimetric analysis TG (in wt.%) and derived thermogravimetric DTG (in wt.%/min) curves obtained during the decomposition of rice straw in pyrolysis and gasification at heating rates of 10 °C/min from 40 °C to 1000 °C. From the DTG curves, it could be illustrated that only one peak is observed in the DTA graph corresponding to the number of degradation stages. Besides, the temperature of the peak in the DTA corresponds to the temperature at which max degradation occurs. As observed in Figure 2, the pyrolysis process can be divided into three main stages. At the first stage (40-178 °C) corresponds to the moisture lost during drying, about 1.71 wt.% of rice straw. The second step (179-500 °C) relates to organic matter decomposition, and about 57.75 wt.% of the biomass was lost during this stage. The final stage (>500 °C) is inorganic matter degradation (residual). The sample weight loss during rice straw pyrolysis was 71.51 wt.%. The weight decreased rapidly, attributed mainly to cellulose, hemicellulose, and partial lignin devolatilization [21-22]. The lignin decomposition continued to give a gradual weight loss beyond 450 °C. Hemicellulose and cellulose pyrolysis occurred rapidly in the range of 250–340 °C and 340–400 °C, respectively, contributing to a sharp drop in the TG profile [23].

In a partial oxidative atmosphere (gasification process), rice straw thermal degradation can be classified into three steps, (i) moisture evaporation, (ii) cellulose, and hemicellulose pyrolytic decomposition and (iii) lignin and char oxidative pyrolytic decomposition. The first step was from room temperature to 175 °C, with about 3.38 wt.% rice straw weight. The second step is the fast decomposition stage, from 176 °C to 530 °C. About 55.9% of the weight is lost during this stage. During the whole gasification process, weight loss is about 70.51%. The rice straw weight loss performance was similar under both pyrolysis and gasification conditions at low temperatures, showing that the presence of an air atmosphere did not contribute to the increasing sample decomposition rate.
3.1.2 Effect of added sewage sludge on thermal performances

As seen in Figure 2, a comparison between the pyrolysis/gasification behavior of sewage sludge and rice straw blends can also be made. According to the results, the weight loss profiles for rice straw, sewage sludge, and additives obtained from pyrolysis slightly differ from that of gasification. Thermal degradation of both RS, SS and their additives during pyrolysis in an inert atmosphere can be classified into three main stages including (i) moisture evaporation, (ii) main devolatilization, and (iii) continuous devolatilization. The beginning and ending temperatures of the decomposition process are important characteristic parameters for feedstocks. In the case of pyrolysis, the beginning sewage sludge and rice straw temperatures were 153 °C and 178 °C, and the corresponding ending temperatures were 517 °C and 500 °C, respectively. Sewage sludge and their blends, the major decomposition temperature at a lower temperature range varies 147-173 °C to 515-535 °C. The final weight loss at the end is close to 500 °C due to ash and fixed carbon, which are not decomposed at this temperature. Rice straw and sewage sludge have narrow decomposition temperature ranges for adding rice straw samples resulting in Ti decreasing by 5-31 °C. This indicates that adding sewage sludge to rice straw results in shifting to lower initial decomposition temperature compared to that of rice straw. Comparing with the pyrolysis process, DTG gasification performance curves also show one prominent reaction zone exists in the heating rate range studied and the SS, RS weight loss and their blends have the same trends (Figure 2b). The weight loss curve results for the tested samples are recognized to have similar trends, meaning that these materials have potentially promising applications in co-pyrolysis/gasification. This proved that biomass and their blends have the same pyrolysis and gasification thermal decomposition behavior and the thermal degradation of all materials occurred in a single stage.
Figure 2. A comparison between TG/DTG curves detected from rice straw, sewage sludge and their additives pyrolysis and air gasification at 10 °C/min heating rate.

Table 2 shows some kinetic parameters (activation energy and pre-exponential factor) and temperature range (TR) of rice straw, sewage sludge, and blends thermal decomposition behavior obtained from pyrolysis and gasification simulations. In rice straw pyrolysis analysis, the activation energy obtained by the Arrhenius plot method was 75.40 kJ/mol for a heating rate of 10 °C/min. Sewage sludge was observed to react faster during pyrolysis compared to rice straw. The lower activation was found at 49.10 kJ/mol, which may be due to the slightly higher amount of ash in sewage sludge. This conclusion is consistent with the previous published literature result that reduced the activation energy from 87.7 kJ/mol to 51.6 kJ/mol by adding oil-palm solid wastes into paper sludge under pyrolysis conditions [23]. The higher activation energies were obtained for gasification 89.56 and 60.12 kJ/mol in rice straw and sewage sludge, respectively. Rice straw was found to be more reactive to gasification compared to sewage sludge. This is due to the relatively higher amount of volatile matter in rice straw compared to sewage sludge. Highly reactive combustible components may account for the high reactivity towards gasification by sewage sludge samples. As shown in Table 2, the activation energy increases with increasing rice straw addition in the 48.62-53.07 kJ/mol range in pyrolysis and 63.73-68.66 kJ/mol under gasification conditions with 20 wt.% to 50 wt.% addition ratio.
In the multiple regression model, the multiple correlation coefficient ($r^2$) value indicates the dependent variable relation (activation energy) and two other predictor variables (pre-exponential and reaction order). Table 2 shows the coefficient of multiple correlations are in the region of 0.7~0.9 and is not a measure of the straight-line model appropriateness. The linear regression establishing the relationship between the fitted line and all of the activation energy and time function data points, respectively. The strong correlation coefficients have partial correlation ($r^2$) in the 0.9~0.99 range and decrease slightly by adding one more variable (reaction order). The calculating reaction order idea was introduced in numerous studies [7, 19, 24]. The biomass reaction order was found at around 0.69-3.57 (as indicated in Table 3) [25-39]. The reaction order values were different from stage to stage and changed with different fuel mixing ratios.

The rice straw and their blends exponential factors were in the $0.71 \times 10^5$-$18.6 \times 10^6$ (s$^{-1}$) pyrolysis condition range. Higher pre-exponential values were found in the gasification simulation, with the higher estimated value in the $1.97 \times 10^5$ - $0.59 \times 10^8$ (s$^{-1}$) range, respectively. That can be explained by oxidation reactions occurring after the gasification process, from reaction by-products that include syngas, char and tar productions, respectively. Tar product is decomposed due to the presence of oxygen, making the thermal decomposition process longer than pyrolysis. The results were also confirmed by previous published literature [26, 27]. Similar phenomena occurred in this research with higher activation energy found under gasification conditions due to highly reactive ash components. Comparison of different atmospheres, it leads to the conclusion that an increasing tendency in the increasing degree of oxidation causes the increases in the degradation rates and shifts the decomposition of non-biodegradable matter to lower temperatures, since a more exothermal balance.
Table 2. Kinetic constants for pyrolysis, sample gasification at 10°C/min heating rate

| Items       | Pyrolysis (N₂ atmosphere) | Gasification (air atmosphere) |
|-------------|---------------------------|-------------------------------|
|             | TR(°C) | Thermal decomposition rate | r²   | TR(°C) | Thermal decomposition rate | r²   |
| SS          | 153-517 | k = 1.37 x 10⁵ e⁴⁹.⁴⁰/RT (X)².⁴¹ | 0.90 | 148-550 | k = 1.97 x 10⁶ e⁶⁰.¹²/RT (X)³.⁵⁷ | 0.84 |
| 20RS:80SS   | 173-535 | k = 0.71 x 10⁵ e⁴⁸.⁶²/RT (X)².⁵² | 0.86 | 154-659 | k = 5.40 x 10⁵ e⁶³.⁷³/RT (X)³.⁵⁰ | 0.81 |
| 40RS:60SS   | 154-515 | k = 0.84 x 10⁴ e⁵⁰.⁶¹/RT (X)⁰.⁹ | 0.84 | 160     | k = 14.4 x 10⁵ e⁶⁴.³¹/RT (X)².⁴⁵ | 0.78 |
| 50RS:50SS   | 147-516 | k = 1.44 x 10⁵ e⁵³.⁰⁷/RT (X)⁰.⁶⁹ | 0.83 | 160-551 | k = 19.1 x 10⁵ e⁶⁵.⁵⁰/RT (X)².⁲⁶ | 0.80 |
| RS          | 178-500 | k = 18.6 x 10⁴ e⁷².⁴⁰/RT (X)².⁴³ | 0.82 | 166-534 | k = 0.59 x 10⁶ e⁸⁹.⁵⁶/RT (X)².¹² | 0.71 |

r² in a multiple regression model

3.2 Thermal decomposition kinetics of different types of biomass

Table 3 summarizes some characteristic parameters obtained from pyrolysis/gasification thermogravimetric data. The followings are initial weight loss (T₁), temperature parameters at the end of the reaction (Tₐ), the corresponding peak temperatures (Tₚ) of thermal decomposition behavior with different types of biomass such as rice straw, rice husk, sugarcane baggage, pinewood, sewage sludge, etc. via Arrhenius law in the literature [28-39]. Biomass kinetic analysis plays an important role in determining the reaction kinetics necessary for mathematical modeling and reactor operational parameter optimization. TGA analysis of raw materials was therefore considered during the pyrolysis/gasification conditions.

The physical characteristic of the wastes influences the thermal digestion process related to the temperature peak (Tₚ). In thermal conditions, when these materials are exposed to high temperatures, their structure, and atomic configuration are changed, which causes some exothermic or endothermic peaks to appear in the thermal diagram [40]. When the DTG curves have a peak, it implies that at this temperature, the molecular relaxation becomes greater and promotes the process to a faster reaction rate. Table 3 illustrates the peak temperature for the decomposition process, which occurs mostly in the 270-350 °C range. Higher peak temperatures 358-491 °C were found, particularly in coal and polypropylene. Volatile matter is highly thermal sensitive. High volatile matter content indicates that a large amount of weight will be lost under high temperatures in the thermal digestion process. Maintaining the pyrolysis/gasification temperature below Tₚₐₙₐₜₜ (maximum temperature) to avoid significant mass and energy loss must
be carefully considered [41]. Furthermore, some wastes are incomplete decomposition conditions in the temperature range near 600 °C. This may suggest that the pyrolysis temperature must be controlled at lower degrees than 600 °C in order to ensure the majority of the material reacts and decomposes.

In general, material that has low activation energy requires more input energy demand. Therefore, the tested sludge has higher fixed carbon content that it required more energy for the thermal decomposition process. To further understand the enhanced syngas yield tendency in gasification-oxidation reaction (C + ½ O₂ → CO), the carbon-to-fixed carbon (C/FC) ratio was used as an index for the gasification reaction. The experimental results indicated that the activation energy of the tested sludge samples were ranged from 50 to 100 kJ/mol with C/FC ratio ranged between 2 and 4. It implied that the tested sludge could easily produce more CO which improves the producer gas lower heating value due to carbon partial oxidation reaction progression. The kinetics of co-pyrolysis/gasification were thoroughly investigated by previous published literature [42-47]. The experimental results indicated that biomass could enhance the degradation of plastics corresponded with an increase in light liquid products [45]. Co-pyrolysis of biomass and plastic could promote as well to obtain high quality chars with higher calorific values as compared bio-chars only generated in biomass pyrolysis [46]. The iso-conversion method was developed by previous published research that could calculate the kinetic parameters in co-pyrolysis of microalgae biomass and low-rank coal [47]. Therefore, TGA results could contribute to enhance the knowledge of tested materials containing high C/FC ratio thermal degradation characterization and to establish the optimum operation conditions for syngas production.
| Feedstocks         | Carrier gas | Flow rate (ml/min) | Ti  | Tp1 | Tp2 | E (kJ/mol) | A (min\(^{-1}\)) | n  | R\(^2\) | Ref. |
|--------------------|-------------|--------------------|-----|-----|-----|------------|------------------|----|--------|------|
| Rice straw         | N\(_2\)     | 100                | 178 | 319 | 500 | 75.40      | 18.6 x 10\(^{6}\) | 1.43 | 0.82   | This study |
|                    | Air         | 100                | 175 | 323 | 530 | 89.56      | 0.59 x 10\(^{8}\) | 2.12 | 0.71   | This study |
| Sewage sludge      | N\(_2\)     | 100                | 153 | 317 | 500 | 49.10      | 1.37 x 10\(^{7}\) | 2.41 | 0.90   | This study |
|                    | Air         | 100                | 148 | 415 | 550 | 60.12      | 1.97 x 10\(^{7}\) | 3.57 | 0.84   | This study |
| 20%RS+80%SS        | N\(_2\)     | 100                | 173 | 324 | 535 | 48.62      | 0.71 x 10\(^{7}\) | 1.52 | 0.86   | This study |
|                    | Air         | 100                | 154 | 329 | 569 | 63.73      | 5.40 x 10\(^{7}\) | 3.3  | 0.81   | This study |
| 40%RS+60%SS        | N\(_2\)     | 100                | 154 | 321 | 515 | 50.61      | 0.84 x 10\(^{7}\) | 0.9  | 0.84   | This study |
|                    | Air         | 100                | 160 | 323 | 551 | 64.31      | 1.44 x 10\(^{7}\) | 2.45 | 0.78   | This study |
| 50%RS+50%SS        | N\(_2\)     | 100                | 147 | 320 | 516 | 53.07      | 1.44 x 10\(^{7}\) | 0.69 | 0.83   | This study |
|                    | Air         | 100                | 166 | 325 | 534 | 68.66      | 1.91 x 10\(^{7}\) | 2.26 | 0.80   | This study |
| Rice straw         | N\(_2\)     | 100                | 266 | 320 | 353 | 59.93      | 2.4 x 10\(^{4}\) | 1.0  | 0.995  | [28] |
| Sewage sludge      | N\(_2\)     | 100                | 248 | 310 | 385 | 19.66      | 13.91            | 1.0  | 0.998  | This study |
| Sewage sludge      | Air         | 50                 | 150 | 299 | 550 | 31.87      | 27.35            | 1.1  | 0.982  | [29] |
| Sewage sludge      | N\(_2\)     | 150                | -   | -   | -   | 65.7       | 3.9 x 10\(^{5}\) | 1.0  | 0.998  | [30] |
| Industrial sludge  | H\(_2\)O−Ar | 150                | 227 | -   | -   | 527        | 68.08            | 1.0  | 0.991  | This study |
| Fluff              | 150         | 227                | -   | -   | -   | 527        | 83.0             | 1.27 | 1.0    | 0.951 |
| Scrap tire powder  | N\(_2\)     | 150                | 227 | -   | -   | 527        | 132.4            | 4.1 x 10\(^{3}\) | 1.0  | 0.994  |
| Rice husk          | N\(_2\)     | 100                | 172 | 348 | 576 | 87.41      | 1.32 x 10\(^{7}\) | -   | 0.984  | [31] |
|                    | Air (1st zone) | -                  | 321 |     | 510 | 20.8       | 3.77 x 10\(^{7}\) | 1.41 | -      | -      |
|                    | Air (2nd zone)| -                  | -   |     | -   | 1.41 x 10\(^{7}\) | 0.47             | -   | -      | -      |
| Sugarcane bagasse  | N\(_2\) (1st zone) | 140              | 325 |     | 535 | 0.28       | 0.4              | 0.995 |
|                    | N\(_2\) (2nd zone) | 325              | -   | 493  | 43.0 | 0.15      | 0.3              | 0.971 |
| Cotton stalks      | N\(_2\) (1st zone) | 150              | 287 |     | 102 | 1.22      | 1.0              | 0.997 |
|                    | N\(_2\) (2nd zone) | 287              | -   | 471  | 98.5 | 0.45      | 0.7              | 0.966 |
| Chlorella vulgaris  | Air         | 25                | 165 | -   | 367 | 41         | 3.9981           | -   | -      | -      |
| Pine wood          | N\(_2\)     | 45                | 245 | -   | 405 | 68.71      | 1.75 x 10\(^{3}\) | -   | -      | -      |
| Activated carbon   | N\(_2\)     | 45                | 80  | -   | 800 | 5.32       | 6.43 x 10\(^{6}\) | -   | -      | -      |
| Coal Char          | N\(_2\)     | 600               | 506.5 | 653.3 | 130.12 - 153.17 | 7.12 x 10\(^{3}\) | 1.0 | >0.96  | [36] |
|                    | CO\(_2\)    | 200-500           | 760 | 820  | 285.46 | 3.9 x 10\(^{11}\) | -   | -      | -      |
| Coal               | Air         | 50                | -   | -   | -   | 52.7       | 3.3 x 10\(^{9}\) | -   | -      | -      |
|                    | O\(_2\)     | 50                | -   | -   | -   | 93.1       | 1.3 x 10\(^{10}\) | -   | -      | -      |
| Coal               | N\(_2\) (1st zone) | 358              | 491 | -   | 128.9 | 5.5 x 10\(^{8}\) | 1.0 | 0.995  |
|                    | N\(_2\) (2nd zone) | 358              | 358 | -   | 36.9  | 3.78      | 0.986            | -   | -      | -      |
|                    | N\(_2\) (3rd zone) | 358              | 491 | -   | 128.9 | 5.5 x 10\(^{8}\) | 1.0 | 0.995  |
| HDPE               | N\(_2\)     | 30                | 439 | -   | 523  | 457.2     | 3.5 x 10\(^{8}\) | 1.0 | 0.998  |
| LDPE               | N\(_2\)     | 30                | 426 | -   | 526  | 300.4     | 2.2 x 10\(^{6}\) | 1.0 | 0.998  |
| Plastic (PP)       | N\(_2\)     | 30                | 399 | 491 | 507  | 319.7     | 5.9 x 10\(^{3}\) | 1.0 | 0.998  |

- : not available

Ti, Tp1, and Tp2 express the initial, peak and final temperature of volatile matter release

R\(^2\): correlation coefficient

### 3.3 Characterization of the gas evolution during the co-thermal degradation of rice straw and sewage sludge

Figure 3(a) shows the 3D FTIR diagram of the rice straw pyrolysis process with a heating rate of 10 °C/min. The results indicated that four pyrolysis stages occur at the temperature ranges...
of 40-178°C, 179-319 °C, 320-500 °C, and above 500 °C. Figure 3 (b) displays the observed change in the FTIR spectra during the rice straw pyrolysis process. The main gas phases that occur in pyrolysis include CO, CO$_2$, CH$_4$, HCl, aldehyde, CH$_3$COOH, phenol, and methanol. Based on the results obtained from TG-DTG curves (as shown in Figure 2), the results showed the chemical reaction occurs to change from one phase to others, either the endothermic reaction (usually for melting) or exothermic reaction (e.g. crystallization, release some energies). The first stage is related to the dewatering process (moisture content evaporation) from the start of run 40 °C to 178 °C. During this stage, the amount of water vapor increases, and the identifiable gaseous product is water. The initial peaks at 1750-1250 cm$^{-1}$ and 4000-3200 cm$^{-1}$ represents of moisture within the biomass and sludge as detailed by the published literature [13, 15, 35, 48, 51]. The second stage corresponds to biomass decarboxylation and oxidation. When the temperature is higher than 151 °C, the rice straw chemical structure starts to change dramatically. Some gaseous products are detected in this stage, such as CO$_2$, CO, CH$_4$, and water vapor. The band at 2920 cm$^{-1}$ represents C-H stretching. The band at 2350, 2250 cm$^{-1}$ is assigned to the carbonyl (C=O) stretching. Carbonyls mainly exist in the side chains of lignin structural units. The band near 3000-2600 cm$^{-1}$ can be described as C-H bending in cellulose and hemicellulose. The peak at 2250-2000 cm$^{-1}$ is indicative of C-O stretching.

The TGA-FTIR spectra for rice straw demonstrate characteristic peaks involved in the representative of SO$_2$. The literature results reported that the aromatic compounds at the absorbance wavenumber of 1342 cm$^{-1}$ and 1600-1450 cm$^{-1}$ [52]. This suggests that the second stage was mainly responsible for the initial decomposition of rice straw contaminants. When the operation temperature was reached to 500 °C, almost all functional groups are eliminated due to organic matter decomposition. Gaseous products are now generated, such as H$_2$O, CH$_4$, and phenol (C$_6$H$_5$OH) that would be further decomposed in the third stage. According to the analysis results of TGA-FTIR, the evolution of gaseous products increases with the temperature, reaching their maximum values between 178 and 500 °C. At the higher temperature range from 500 °C
to 1000 °C, the release of pollutant gases is almost negligible due to the pyrolysis reaction completion.

TG-FTIR is also a good technique for determining the different gaseous species existing during different thermal decomposition processes. Figure 3 (c) showed the gas evolution in the rice straw gasification. Gasification is a partly oxidizing process that converts biomass into useful energy such as syngas, which contributes to developing hydrogen, methanol, and synthetic fuels [53]. In the air, the gasification process air is injected into the TGA-FTIR. The IR spectra results show that more CO, CO₂ products are measured under the operating condition. That can be explained using the following reactions (R₁-R₃):

\[
\begin{align*}
\text{R}_1 & : \quad C + \frac{1}{2} O_2 \rightarrow CO \quad \text{Carbon partial oxidation} \\
\text{R}_2 & : \quad CO + \frac{1}{2} O_2 \rightarrow CO_2 \quad \text{Carbon monoxide oxidation} \\
\text{R}_3 & : \quad C + O_2 \rightarrow CO_2 \quad \text{Carbon oxidation}
\end{align*}
\]

The major producer gases in rice straw gasification, including CO₂, CO, CH₄, HCl, NO, ether, alcohol, and phenol, were a little bit different with that of producer gases in pyrolysis. The two highest peaks were found at 319 °C and 323 °C corresponding with the FTIR spectrum for volatiles in rice straw gasification. Partial air oxidation reaction could promote the reaction rate. However, a benzene skeleton was found in the pyrolysis case. SO₂ gases were found in gasification due to the sulfur contained in the rice straw and formation under the partial oxidation atmosphere. On the other hand, the higher and broader peak related to organic hydrocarbon compounds, such as C-O stretching at wavenumber as 1300-950 cm⁻¹, was found in rice straw pyrolysis. This could explain that some interactions existed such as hydrogen bonding interaction. Therefore, if the peak is broader, it could mean the number of bonds occurs in the gas product must be considered. More tar (oil) is generated by pyrolysis compared with gasification.
Figure 3. FTIR analysis of rice straw pyrolysis/gasification with a heating rate of 10 °C/min
The FTIR spectrum indicated the gases generated during rice straw and sewage sludge mixture pyrolysis (rice straw proportion from 0 to 50% as a function of both wavenumber and temperature. Figure 4 (a) illustrates that the gases evolution of the 3D FTIR diagram in pyrolysis of sewage sludge (0% of rice straw) and mixtures with 20%, 40%, and 50% of rice straw. The main volatile components in organic compounds identified by FTIR were aliphatic chains with double bonds accompanying C=O, OH-, and C–H groups. The major functional groups and gaseous species were measured in the pyrolysis reaction, including C=O stretching (2400-2250 cm⁻¹), C-O stretching (2240-2000 cm⁻¹), C-H stretching (3000-2600 cm⁻¹), O-H (4000-3500 cm⁻¹), SO₂ (1350 cm⁻¹), HCl (2789 cm⁻¹), and NH₃ (850-736 cm⁻¹). During the pyrolysis process, specific chemical compounds, such as syngas, aldehyde, acid gas or polluted air (HCl, SO₂, NH₃), were determined by TGA-FTIR. Figure 4 (b) shows the TGA-FTIR spectrograms representing possess characteristic absorption bands within the 1700-800 cm⁻¹ region, such as acetic acid, toluene, phenol, and formic acid. With the presence of NH₃, HCl and other acid gases were detected by TGA-FTIR revealing a similar trend that it was confirmed by previous pyrolysis works [49, 54]. Figure 4 (c) illustrates clearly the characteristic infrared absorption peaks of the volatile components. That was observed that absorbance increases with higher gas concentration when the rice straw mixing ratio is increased from 0% to 40%. It implied that increasing the rice straw mixing ratio up to 40% increases the concentration of the gaseous product. However, in the case of the rice straw content increasing from 40% to 50%, the gaseous products seem to be decreased due to the corresponding with lower absorbance. This is because the hydrocarbon reformation and/or water-gas shift reactions could be inhibited. Besides, ash agglomeration could be occurred and block oxygen diffusion into the char particles due to the rice straw containing a high potassium and silicon concentration [55]. Table 4 displays the detected gaseous species adsorption bands during pyrolysis and further presents a comparison between the present study and that of other previous researchers using TG-FTIR [14-16, 35, 48-50]. The waste materials (biomass and sludge) pyrolysis process
presents CO₂, CO, CH₄, CH₃COOH, HCOOH, methanol, phenol, and esters as the main gaseous species produced. The rice straw chemical structure was indicated that the abundant chemical bonds were O-H, C-H, C=C and C-O, and aromatic C=C/C-H. It implied that the aromatic compounds formation was probably released by the pyrolysis oils which were determined as aromatic C-H bond bending (wavenumber was between 2000 and 1660 cm⁻¹)[51]. The literature results were also proved that some weak peaks were representing aromatic hydrocarbon in the 1400-1000 cm⁻¹ range [50]. Based on the TG-FTIR analysis results, the main groups in the rice straw were aliphatic chains with double bonds, as well as carbonyl (C=O), hydroxyl (O-H) and alkane (C-H) and alkyl amine. In summary, the experimental results suggested that rice straw controlled at the mixing ratio of 40 wt.% with 60 wt.% sewage sludge could be the optimum conditions in co-thermal treatment. From the kinetic analysis results, rice straw and sewage sludge co-gasification can reduce the required activation energy and enhance the reaction rate. This study discussed how mixing rice straw with sewage sludge could simulate the pyrolysis and gasification process and quantitatively analyze the gaseous components. Further studies are necessary to understand the FTIR that gives reliable quantitative information regarding the functional groups presented.
Figure 4. Gas released from sewage sludge, and their mixtures with rice straw as detected by TGA-FTIR.
Table 4. Gaseous species based on wavenumbers (cm\(^{-1}\)) and functional groups for pyrolysis studies

| Sample                                                                 | Wavenumber range (cm\(^{-1}\)) | Peak (cm\(^{-1}\)) | Species                  | Functional group | Vibration | Ref. |
|------------------------------------------------------------------------|---------------------------------|--------------------|--------------------------|------------------|-----------|------|
| Rice straw, sewage sludge, and their blend                            | 2375 - 2250                     | 2350, 2250         |                          |                  |           |      |
| Wood, plastic, tire, and RDF                                           | 2400 - 2250                     | 2350               |                          |                  |           | [14] |
| Spruce and pine biomass                                               | 2400 - 2240                     | 2359, 2322         |                          |                  |           | [35] |
| Straw with absorbed glycerol                                           | 2400 - 2240                     | 2360               | CO\(_2\)                 | C=O              | Stretching| [48] |
| Solid waste, paper mill sludge, and their blends                       | 2400 - 2240                     |                    |                          |                  |           | [49] |
| Marine sediment                                                        | 2400 - 2240                     |                    |                          |                  |           | [16] |
| Palm kernel shell (PKS) from palm oil                                 | 2400 - 2250                     |                    |                          |                  |           | [50] |
| Rice straw, sewage sludge, and their blend                            | 2167 - 2120                     | 2170               |                          |                  |           |      |
| Wood, plastic, tire, and RDF                                           | 2250 - 2000                     | 2110, 2200         |                          |                  |           | [14] |
| Coals, sawdust, rice straw, and corn stalk                            | 2240 - 2027                     |                    | CO                        | C-O              | Stretching| [50] |
| Palm kernel shell (PKS) from palm oil                                 | 2250 - 2000                     |                    |                          |                  |           |      |
| Solid waste, paper mill sludge, and their blends                       | 2240 - 2200                     | 2178               |                          |                  |           | [49] |
| Marine sediment                                                        | 2240 - 2060                     |                    |                          |                  |           | [16] |
| Rice straw, sewage sludge, and their blend                            | 3964 - 3500                     | 3800, 3600         |                          |                  |           |      |
| Wood, plastic, tire, and RDF                                           | 4000 - 3500                     |                    |                          |                  |           | [14] |
| Coals, sawdust, rice straw, and corn stalk                            | 1750 - 1250                     |                    | H\(_2\)O                  | O-H              | Stretching| [50] |
| Palm kernel shell (PKS) from palm oil                                 | 4000 - 3400                     |                    |                          |                  |           |      |
| Straw with absorbed glycerol                                           | 4000 - 3600                     |                    |                          |                  |           | [48] |
| Solid waste, paper mill sludge, and their blends                       | 4000 - 3500                     |                    |                          |                  |           | [49] |
| Spruce and pine biomass                                               | 3900 - 5200                     | 3853, 3568         |                          |                  |           | [35] |
| Rice straw, sewage sludge, and their blend                            | 1900 - 1600                     | 1750, 1720         | C-O(H)                   |                  |           |      |
| Wood, plastic, tire, and RDF                                           | 1900 - 1600                     |                    |                          |                  |           | [14] |
| Spruce and pine biomass                                               | 1845 - 1500                     | 1768, 1745         | CH\(_3\)COOH              | C=O              | Stretching| [15] |
| Coals, sawdust, rice straw, and corn stalk                            | 1900 - 1603                     |                    |                          |                  |           | [50] |
| Palm kernel shell (PKS) from palm oil                                 | 1900 - 1650                     |                    |                          |                  |           |      |
| Solid waste, paper mill sludge, and their blends                       | 1850 - 1600                     |                    |                          |                  |           |      |
| Rice straw, sewage sludge, and their blend                            | 1200 - 1100                     | 1120               | HCOOH                     | C-O(H)           | Stretching| [14] |
| Wood, plastic, tire, and RDF                                           | 1200 - 1100                     | 1400, 1745         |                          |                  |           | [15] |
| Coals, sawdust, rice straw, and corn stalk                            | 1200 - 1100                     |                    | C\(_6\)H\(_5\)OH          | O-H              | Bending   | [14] |
| Palm kernel shell (PKS) from palm oil                                 | 1400 - 1200                     | 1100, 1300         |                          |                  |           | [35] |
| Straw with absorbed glycerol                                           | 1500 - 1325                     | 1373               | C\(_6\)H\(_5\)OH          | O-H              | Bending   | [15] |
| Rice straw, sewage sludge, and their blend                            | 1300 - 1200                     |                    |                          |                  |           | [50] |
| Wood, plastic, tire, and RDF                                           | 1279 - 1100                     | 1100               | O-H                      |                  | Blending   | [14] |
| Spruce and pine biomass                                               | 1300 - 950                      | 1165, 1120         | CH\(_3\)OH               | C-O              |           | [35] |
| Palm kernel shell (PKS) from palm oil                                 | 1200 - 1000                     |                    |                          |                  |           | [50] |
| Straw with absorbed glycerol                                           | 1100 - 1030                     | 1055               |                          |                  |           | [48] |
| Rice straw, sewage sludge, and their blend                            | 1600 - 1450                     | 1470               | Aromatic                 | C-H              | Bending   | [35] |
| Spruce and pine biomass                                               | 1000 - 650                      | 669, 642           |                          |                  |           | [50] |
| Palm kernel shell (PKS) from palm oil                                 | 1690 - 1450                     |                    |                          |                  |           | [16] |
| Marine sediment                                                        | 1600 - 1420                     |                    |                          |                  |           | [49] |
| Solid waste, paper mill sludge, and their blends                       | 1850 - 1600                     | 1720               | Aldehyde                 | C-O              | Stretching| [48] |
| Straw with absorbed glycerol                                           | 1700 - 1600                     |                    |                          |                  |           | [16] |
| Palm kernel shell (PKS) from palm oil                                 | 1460 - 1365                     |                    | Alkanes                  | C-C, C-H         | Stretching| [50] |
| Marine sediment                                                        | 850 - 736                       |                    | NH\(_3\)                  |                  |           | [16] |

RDF: Refuse-derived fuel
4. Conclusions

The co-pyrolysis/gasification characteristics and kinetic analysis with or without sewage sludge, rice straw, and their blends additives under different heating rates using TG-FTIR were studied. The results obtained in this research were given as follows. From the rice straw (RS), sewage sludge (SS), and their blends TG and DTG analysis, it was found that SS is decomposed at a lower temperature than RS. The temperature range of volatile matter devolatilization is broader when the extra RS amount is gradually added. RS has a significant influence on the volatile matter released in co-pyrolysis/gasification. Activation energy calculated using the Arrhenius equation could approximately increase from 48.62-53.07 kJ/mol in a linearly correlating behavior with increasing RS addition. The rice straw and their blends exponential factors were in the pyrolysis condition range of 0.71*10^5 – 18.6*10^6 (s^-1). TGA-FTIR revealed a series of organic species (the gaseous volatile) containing moisture, CO₂, CO, CH₄, acidic gases, and aromatic compounds. In addition, this study also proved that the RS co-pyrolysis/gasification process imposed a significant impact on gaseous pollutants reduction (CO₂, NO, and SO₂). This is an astounding acknowledgment for the co-thermal treatment of partial oxidation performance for some blends. The main volatile components identified by FTIR were aliphatic chains with double bonds, as well as carbonyl, hydroxyl, and C–H groups in organic compounds. In particular, functional groups and gaseous species contributed to the entire pyrolysis reaction were: C=O stretching (2400-2250 cm⁻¹), C-O stretching (2240-2000 cm⁻¹), C-H stretching (3000-2600 cm⁻¹), O-H (4000-3500 cm⁻¹), and SO₂ (1350-1342 cm⁻¹), HCl (2798-2789 cm⁻¹), NO (1762 cm⁻¹) and NH₃ (850-736 cm⁻¹). The experimental results show that RS controlled at 40 wt.% mixed with 60 wt.% SS was the optimum co-thermal treatment proportion. In summary, by exploiting such information, operators or designers can choose a suitable condition for running pyrolysis/gasification in commercial-scale plant in the future.
Declarations

Availability of data and materials
The datasets supporting the conclusions of this article are included within the article.

Competing interests
The authors declare that they have no significant competing financial, professional, or personal interests.

Funding
The authors would like to express their appreciation and gratitude to the Ministry of Science and Technology (MOST) (Project No. MOST-107-2621-M-008-003) for financially supporting this research.

Author’s contributions
The manuscript draft was interpreted and written by Thi Ngoc Lan Thao Ngo. Prof. Kung-Yuh Chiang provided technical support, revised the manuscript, and also supervised the research. All authors read and approved the final manuscript.

Acknowledgments
The authors would like to thanks the Precision Instrument Support Center of National Central University in providing the analysis facilities.
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