Hindawi
Journal of Chemistry
Volume 2022, Article ID 7160782, 10 pages
https://doi.org/10.1155/2022/7160782

*Research Article*

# Characteristics of Pyrolysis and Copyrolysis Products Sewage Sludge in Different Temperature Ranges

**Yunbing Li,[1] Hongli Li,[1] Qihang Zhang,[1] Xinyi Wang,[1] Xin Wang,[1,2,3] and Pen Jin[1,2,3,4]**

[1]*College of Chemical Engineering and Technology, Northwest Minzu University, Lanzhou 730000, China*
[2]*Key Laboratory of Environment-Friendly Composite Materials of the State Ethnic Affairs Commission, Lanzhou, China*
[3]*Gansu Provincial Biomass Function Composites Engineering Research Center, Lanzhou, China*
[4]*Key Laboratory for Utility of Environment-Friendly Composite Materials and Biomass in University of Gansu Province, Lanzhou, China*

Correspondence should be addressed to Pen Jin; 186132287@xbmu.edu.cn

Received 9 June 2022; Revised 2 August 2022; Accepted 17 August 2022; Published 8 September 2022

Academic Editor: Shoufeng Tang

Rapid modernization, population growth, and improvement in people's quality of life have resulted in an increase in urban sewage sludge as the main solid waste. At present, pyrolysis is the main treatment method for sludge due to carbon-free effects and less air pollution compared with incineration. To enhance the energy utilization value of sludge, copyrolysis of sludge and biomass with varying effects has been reported. Herein, biomass and sludge were pyrolyzed and copyrolyzed using self-designed fixed-bed pyrolysis and condensation collection system. The pre-fixed-bed process parameters were optimized by orthogonal test, and it was found that the carrier gas flow rate (a) > bed thickness (b) > constant temperature time (c). The optimum process combinations were 250 mL/min carrier gas, 10 mm bed thickness, and 10 min constant temperature. Experiments show that the ultimate pyrolysis temperature affects the oil production of fixed-bed pyrolysis by up to 15%. Copyrolyzing *Sargassum thunbergii* and sludge boost oil output at first and then drops; the maximum value is at 20% sludge. When pine sawdust and sludge were copyrolyzed, oil output climbed marginally and subsequently fell fast; the highest value was at 20% sludge. Peanut shell and sludge copyrolysis yield the most oil at 40% sludge content, and the experimental value is smaller than the linear value at 80% sludge content.

## 1. Introduction

The rapid development of the urban economy, population growth, and improvement of people's quality of life have resulted in an increase in urban sewage sludge (sludge for short) as the main solid waste. Long-term accumulation of waste biomass, especially waste agricultural and forestry biomass, leads to environmental pollution and causes a huge waste of biomass resources. The treatment of such huge sludge emissions has become an urgent environmental problem at present in most countries. Nearly all countries around the globe have clear requirements for sludge disposal and nearly follow the disposal principles, stabilization, and recycling. Compared with developed countries, sludge disposal technology started in China recently. In July 2003, the State Environmental Protection Administration issued the "Pollutant Discharge Standard for Urban Sewage Treatment Plants" (GB18918-2002), which specially added the content of sludge control standard and greatly improved the level of sludge disposal [1, 2]. The rapid increase in population also has negative consequences in the form of energy shortage and has increasingly become the focus of researchers' attention [3, 4]. The greenhouse effect, environmental pollution, and continuous use of energy reserves caused by the wanton utilization of fossil also have become the main obstacles to human development. Developing environment-friendly renewable new energy resources have become an urgent need of global human development in the 21st century.

Biomass charcoal is generally an alkaline substance, which can be used as a soil additive to reduce the acidity of soil and the toxicity of toxic elements such as aluminum and heavy metals to plants. Biochar, a solid product of biomass pyrolysis, also has great value as it contains more essential nutrients for plants and promotes soil nutrient circulation and plant growth. Biomass energy, as one of the renewable energy resources with wide distribution, huge reserves, easy utilization, and zero carbon dioxide emission in nature, has a very low utilization rate at present. According to statistics, the output of agricultural waste in 2010 was about 730 million tons, which could produce $1.2 \times 10^{18}$ J of energy, equivalent to $4 \times 10^{10}$ tons of standard coal. In 2010, the sludge output of urban sewage treatment plants in China was about 30 million tons [5]. Effective development and utilization are of great strategic significance to alleviate the energy crisis, promote the development of emerging energy industries, prevent global warming, and promote the establishment of a circular society. Transforming agricultural and forestry biomass into energy in an environment-friendly manner has become a hot field of discussion and research in the scientific community in recent years [6, 7].

Pyrolysis technology refers to the process of using heat energy to transform macromolecular substances into small molecular substances, producing coke, condensable pyrolysis oil, and noncondensable gas in an oxygen-free or oxygen-deficient atmosphere. The research shows that both sludge and biomass have high volatile content and good pyrolysis characteristics. Using pyrolysis technology can not only achieve safe, economic, and reasonable disposal of sludge to obtain energy products such as pyrolysis oil and fuel gas but also transform many agricultural and forestry biomass into biomass energy. At present, there are two main ways, i.e., analyze the weight loss process of pyrolysis and study its basic kinetics through thermal analysis methods such as TG, DTA, and DSC. The other is to use the fixed-bed, fluidized-bed, and other reaction bed devices to carry out pyrolysis reactions at different heating rates and obtain relevant information such as product distribution. The effects of component distribution detection and pyrolysis process on biomass pyrolysis have been reported [8, 9]. However, the specific reaction mechanism of biomass pyrolysis is not exactly described because of the complex composition of biomass-, region-, and environment-specific variations in biomass, and the greater influence of experimental and equipment conditions on the process.

The industrial application of pyrolysis needs suitable reactors that can jointly treat irregular and heterogeneous substances. The fixed-bed reactor is the simplest reactor having widespread applicability with low operating cost [10]. However, the feeding of raw materials may not be continuous due to the limitation of fixed beds. The rotary kiln bed can accommodate large variations in fuel shape, size, and composition, calorific value, and need minimal pretreatment. It is less sensitive to the fuel nature [11]. However, the heat transfer mechanism in rotary reactors is complex and dependent on kiln configurations. The conical spouted beds possess vigorous cyclic characteristics that allow larger-sized and irregular shape particle handling. It can pyrolyze fine materials as well as sticky solids without segregation and agglomeration problems compared with other common fluidized beds [12]. However, when fine substances are processed, instability problems often arise in the scaling-up of the process [13] and lack commercial high-temperature applicability. Contrary to fixed-bed pyrolysis, fluidized-bed pyrolysis (FBP) is a continuous process and has been extensively applied especially in commercial plants [14]. However, not very common for industrial applications, the fixed-bed reactor is widely used in research and development.

At present, pyrolysis is the main treatment method for sludge due to carbon-free effects and less air pollution compared with incineration [15]. In addition, its products including biochar, biogas, and biooil may be refined to chemicals with good economic values [10]. However, higher energy consumption for high-efficiency pyrolysis of individual sludge due to relatively high moisture and ash contents is the main limitation [16]. To enhance the energy utilization value of sludge, many studies have been performed on the copyrolysis of sludge and biomass with both synergistic and antisynergistic effects of copyrolysis.

Although there are many reports on pyrolysis research technology at present, it mainly focuses on separate thermal thermogravimetric research of different biomass, kinetic speculation and investigation of pyrolysis process products, and the separate pyrolysis resource utilization of sludge. However, there are few literature reports on the combination of biomass and sludge that promote pyrolysis mutually during the copyrolysis of this topic. This study was designed to investigate the mutual synergy and basic copyrolysis reaction process when sludge and biomass are copyrolyzed. The product components were analyzed, and the influence of the copyrolysis process on the composition and distribution of solid, liquid, and gas three-phase products were discussed to provide useful basic data for the research work of complementary advantages and organic combination of biomass renewable energy and sludge recycling.

## 2. Materials and Methods

*2.1. Materials.* The biomass used in this research was composed of reed leaves, bagasse, foxtail algae, and banyan tree roots. The biomass was collected from the surrounding areas of the campus. Pine sawdust and peanut shells were purchased from processing plant waste. The urban sewage sludge was collected from the sewage sludge precipitated after the urban domestic sewage treatment at a sewage treatment plant in Lanzhou. The biomass was fully dried at 105°C and then pulverized to 90 mesh for use.

Pine sawdust has the highest cellulose content and contains more lignin; reed leaves and bagasse both contain more cellulose and hemicellulose, but the lignin content is very low. Foxtail algae contain the most hemicellulose; peanut shells contain mainly hemicellulose, lignin, and other relatively small components. The root of the banyan tree has more lignin and hemicellulose, but the content of cellulose is very low. In addition, there are significant differences between biomass and sludge in terms of moisture, ash, volatile matter, and fixed carbon content, which is manifested in the fact that the sludge contains a lot of ash and the volatile content is very low, while the biomass generally contains more of volatiles. The content of fixed carbon in sludge was relatively low, while the content of fixed carbon in biomass varied significantly with different species.

The raw material composition and its industrial analysis were determined by Van Soest cellulose analysis and industrial analysis GB/T 212-2001. Different kinetic models were used to fit the thermogravimetric data of sludge and biomass by single or coheating. To determine a suitable kinetic model, the kinetic parameters were calculated, and the variation law of kinetic properties with the investigated factors was obtained. The change in the law of basic properties and kinetic parameters of pyrolysis were correlated with investigation factors such as sludge mixing, the synergistic mechanism of the pyrolysis process, and agricultural and forestry biomass to improve or promote sludge pyrolysis.

### *2.2. Experimental Set-Up and Procedure*

*2.2.1. Experimental Set-Up.* In this research, a self-designed fixed-bed reactor and a condensing device were used for investigation. See the schematic diagram of the pyrolysis process in Figure 1 for the main components and assembly methods. The device is composed of a Nitrogen bottle, gas flow rate regulating valve, rotameter, quartz tube, tube furnace, serpentine condenser tube, and three-port valve; gas collection bag; accumulative gas flowmeter; and liquid collection bottle. The sample is placed gently into the quartz tube of the furnace and slowly pushed to the center of the quartz tube in the tube furnace with a push rod. The furnace is heated according to prespecified conditions. The sample is heated in a nitrogen environment to generate pyrolysis gas and residual solids. The pyrolysis gas flows out with the carrier gas and condenses in the condensing device to form condensable liquid products and noncondensable gas under this condition, and the noncondensable gas is collected by the gas-collecting bag. The liquid components are collected in a liquid collecting vessel. The solid product in the tube furnace is naturally cooled to 50°C in the continuous nitrogen atmosphere.

### *2.3. Experimental Procedure*

*2.3.1. Loading and Sampling.* Samples were accurately weighed (45 ± 1 g each) and they were termed m1. The samples were evenly spread in the Shi Ying sample dish by natural stacking and covered to prevent them from blowing away. The cover was removed when moving to the tube furnace and gently put into the quartz tube. The sample was slowly pushed to the center of the quartz tube to the tube furnace with a push rod.

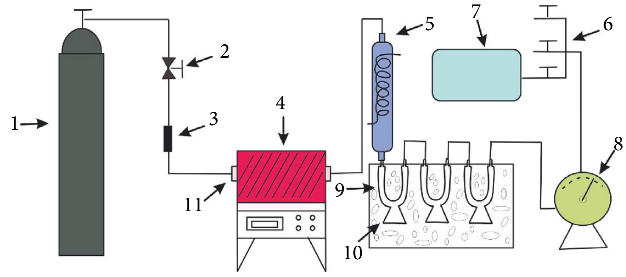

Figure 1: Schematic diagram of fixed-bed pyrolysis device. 1—Nitrogen bottle; 2—gas flow rate regulating valve; 3—rotameter; 4—tube furnace; 5—serpentine condenser tube; 6—three-port valve; 7—gas collection bag; 8—accumulative gas flowmeter; 10—liquid collection bottle; 11—quartz tube.

*2.3.2. Pyrolysis Experiments.* After placing the sample in the furnace, the nitrogen valve was slowly opened to let nitrogen enter the reaction system. Then, the nitrogen flow rate was adjusted with a gas-regulating valve for 10 min. According to the needs of the experiment, set the temperature-raising program. The heating power was switched on and the tube furnace starts to heat up according to the set heating program. In order to study the effect of heating rate on fixed-bed pyrolysis, we performed five experiments on biomass pyrolysis at different heating rates, 10°C/min, 20°C/min, 30°C/min, 40°C/min, and 50°C/min. The instrument was connected to the evacuated gas-collecting bag and the initial volume reading V1 of the cumulative gas flowmeter was recorded. The reactant sample was heated in a nitrogen environment to generate pyrolysis gas and residual solids. The pyrolysis gas is flown with the carrier gas and condensed in the condensing device to form condensable liquid products. The noncondensable gas was collected in the gas-collecting bag.

After the reaction was completed, the condensed water and heating power supply were turned off and the gas collection bag was removed. The end volume reading ($V_2$) of the cumulative gas flowmeter was recorded. The condensing device was removed, and all liquid products in the conical flask were collected. The condenser and the liquid products from the pipe to the tail were cleaned with chloroform, poured into the conical flask together, and evaporated the chloroform till dry to obtain the constant mass ($m_2$) of the liquid product biooil (containing water). The solid product in the tube furnace was cooled to 50°C in the continuous nitrogen atmosphere. The nitrogen supply was turned off, and the solid product-cracked carbon was removed, weighed, and recorded as ($m_3$). Finally, calculate the yield of the three-phase product (yield), and the yield is calculated by the mass percentage of the product to the raw material (wt %). The main components of the gas in the gas-collecting bag were analyzed by gas chromatography (Europeanized GC-9160). The volume fraction of each component was calculated by the external standard method, and the total mass of gas products was obtained by calculations.

## 3. Results and Discussion

*3.1. Optimization of Process Parameters in the Early Stage of Fixed Bed.* In the fixed-bed pyrolysis experiment, the preliminary pyrolysis process parameters, such as carrier gas flow rate, bed thickness, and constant temperature time after the final temperature, also have a certain influence on the experiment, which needs to be optimized. Because of its orthogonality, representativeness, and comprehensive comparability in the process optimization experiment, the orthogonal experimental method has become an efficient experimental method to optimize the process. In this research, the sludge was selected as the representative, and the three factors and three levels (L934) orthogonal test was carried out with the carrier gas flow rate, bed thickness, and constant temperature time after the final temperature as the investigation factors to optimize the process [17, 18]. See Table 1 for investigation factors and levels:

The results of the orthogonal experiment were analyzed with the yield of water-bearing biooil (hereinafter referred to as the oil yield) as the measurement standard, as shown in Table 2.

For the orthogonal experiment, detailed experimental information cannot be obtained directly from the original experimental results, which needs further processing. To better analyze the significance of each factor, it is necessary to analyze the variance of the results, compare the F value, and judge the significance of the factors (See Table 3 for specific analysis). It can be seen from the table that factor A (carrier gas flow rate) is a significant influencing factor at the level of $\alpha = 0.05$, and its $F$ ratio is higher than the critical value of $F$, while the other factors are insignificant.

From (Figure 2) orthogonal experiment effect curve of pyrolysis, it can be seen intuitively that the carrier gas flow rate has the greatest influence on the oil yield when the optimal carrier gas flow rate is 250 mL/min. Too low-flow rate or too high-flow rate will reduce the oil yield, and too low a flow rate will not take the volatile matter out of the reaction zone, resulting in the secondary decomposition of volatile matter in the high-temperature zone. This will result in more noncondensable gases, which will reduce the oil yield [18]. Wang et al. designed a high-pressure reaction system and found that the temperature and residence time were the most effective factors in the conversion of sewage sludge to biooil [19]. Wang et al. conducted a study to assess the combustion characteristics of pyrolytic oil from sewage sludge. They found that the yield of sludge pyrolytic oil was affected by the nitrogen flow rate, pyrolytic temperature, heating rate, and residence time [19].

### *3.2. Effect of Pyrolysis Final Temperature on Fixed-Bed Pyrolysis.*

The final pyrolysis temperature refers to the temperature at the end of the pyrolysis process and is one of the important technological parameters for a pyrolysis reaction. As can be seen from Figure 3, the final temperature of pyrolysis has an obvious influence on the oil yield of fixed-bed pyrolysis. With the continuous increase in the final temperature, the overall trend of oil yield increased first and then decreased, and there was a maximum oil yield final temperature point. The oil yield of sludge increased obviously before reaching 650°C and started decreasing after 650°C. However, the oil yield of pine sawdust increased rapidly before 550°C, slightly increased at 650°C, and then decreased after 650°C. For the copyrolysis process of East sawdust and sludge, the influence of the final pyrolysis temperature was the linear sum of the effects of the final temperature on the two raw materials alone, and no other effect was observed. The changing trend of oil yield occurs because when the final pyrolysis temperature is too low, the pyrolysis process is not sufficient, and the yield is low. However, if the final pyrolysis temperature is too high, the pyrolysis oil will be cracked again, resulting in a decrease in oil yield and an increase in gas yield. Therefore, there is an optimal final pyrolysis temperature to maximize the oil yield [20]. Beis and coworkers obtained the maximum oil yield (44%) at the final pyrolysis temperature of 500°C, with a heating rate of 5°C/min and a nitrogen gas flow rate of 100 mL/min in a fixed-bed lab-scale reactor [17].

### *3.3. Effect of Heating Rate on Fixed-Bed Pyrolysis.*

The heating rate is one of the important technological parameters of pyrolysis reactions. The control of the heating rate affects the residence time and reaction mechanism of pyrolysis volatile matter in the high-temperature reaction zone to a certain extent [17]. Figure 4 is a trend diagram of the influence of heating rate on the individual and copyrolysis process of sludge and biomass in a fixed-bed experiment. It can be seen from the figure that with the increase in heating rate, the oil yield of the three types of pyrolysis reactions all showed a trend of first increasing and then decreasing, and the optimal pyrolysis rate was about 30°C/min [17]. The results of this study are consistent with previous literature. In a study on the pyrolysis of rapeseed (*Brassica* napus L.), the maximum oil yield (51.7%) was obtained in the Heinze reactor at 550°C, at a heating rate of 30°C/min [18].

### *3.4. Effect of Mixing Ratio on Copyrolysis of Biomass and Sludge.*

The mixing ratio is another key issue in the study of copyrolysis of biomass and sludge. Under different mixing ratios, both the characteristic temperature of thermogravimetric analysis and the reaction parameters of kinetics will change in the copyrolysis process, which also shows that the mixing ratio has a great influence on the copyrolysis of biomass and sludge, and the interaction mechanism of the influence is not very clear at present [21].

#### *3.4.1. Copyrolysis of Myriophyllum and Sludge.*

As can be seen from Figure 5, the oil yield of *Myriophyllum fortunei* and sludge during copyrolysis shows a trend of slightly increasing at first and then decreasing, and the highest oil yield value is 20 wt% sludge content [22]. In a previous study, accelerative interactions between sludge and sawdust copyrolysis were observed. The strongest effect was found at 20 wt% sludge addition [23].

Figure 6 is a graph showing the change in the yield of gas and solid products generated during the pyrolysis of *Myriophyllum fortunei* and sludge with the mixing ratio of sludge. It can be seen from the graph that with the continuous addition of sludge, the gas production rate of mixed copyrolysis is opposite to that of pyrolysis carbon, and the

Table 1: Process optimization factors in pyrolysis process.

| Experimental level | Experimental factors | | |
|---|---|---|---|
| | Carrier gas flow rate *a* (mL/min) | Bed thickness *b* (mm) | Constant temperature time *c* (min) |
| 1 | 100 | 6 | 5 |
| 2 | 200 | 10 | 10 |
| 3 | 300 | 14 | 20 |

Table 2: Results of orthogonal pyrolysis experiment (L934).

| Test number | 1 | 2 | 3 | Experimental result (oil yield %) |
|---|---|---|---|---|
| | *A* | *B* | *C* | |
| 1 | 1 (100) | 1 (6) | 1 (5) | 39.3 |
| 2 | 1 | 2 (10) | 2 (10) | 43.7 |
| 3 | 1 | 3 (14) | 3 (20) | 42.6 |
| 4 | 2 (250) | 1 | 2 | 45.8 |
| 5 | 2 | 2 | 3 | 43.9 |
| 6 | 2 | 3 | 1 | 43.2 |
| 7 | 3 (400) | 1 | 3 | 42.1 |
| 8 | 3 | 2 | 1 | 39.9 |
| 9 | 3 | 3 | 2 | 41.4 |
| 1 (mean) | 41.867 | 42.400 | 41.533 | |
| 2 (mean) | 44.300 | 43.633 | 43.000 | |
| Mean value | 41.133 | 43.167 | 42.767 | |
| Extreme difference | 3.167 | 2.833 | 1.467 | |

Table 3: Variance analysis results of pyrolysis orthogonal test (L934) ($\alpha = 0.05$).

| Factor | Sum of square of deviations | Freedom | *F* ratio | *F* critical value | Significance |
|---|---|---|---|---|---|
| Carrier gas flow rate *a* | 16.487 | 2 | 8.800 | 6.940 | * |
| Bed thickness *b* | 0.020 | 2 | 0.011 | 6.940 | |
| Constant temperature time *c* | 12.887 | 2 | 6.879 | 6.940 | |

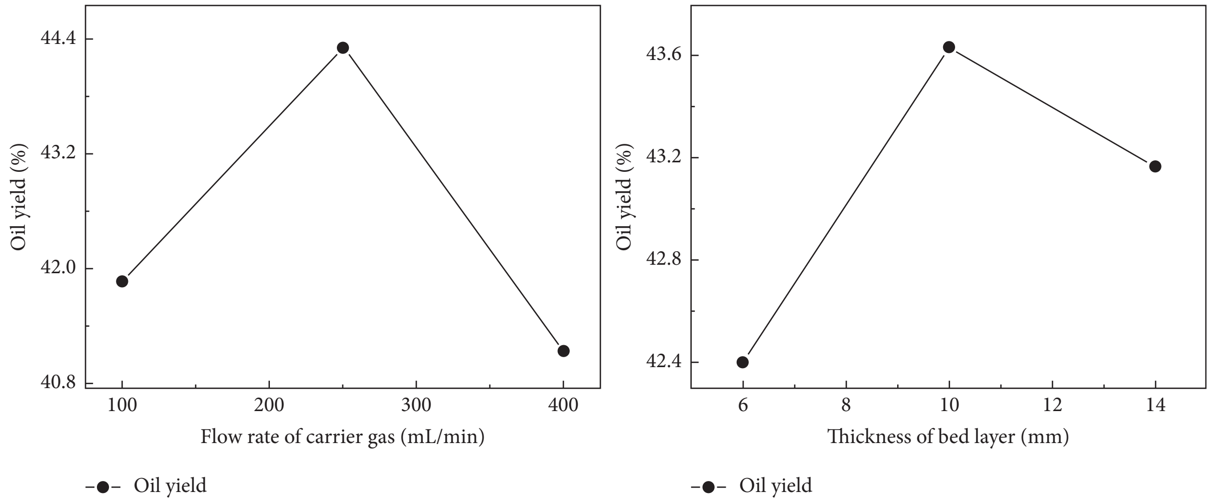

Figure 2: Pyrolysis orthogonal experiment ($L_{934}$) effect curves of various factors.

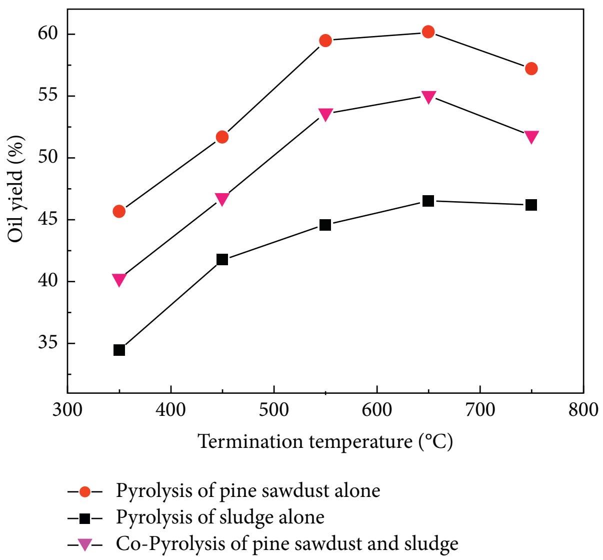

Figure 3: Influence of pyrolysis termination temperature on fixed-bed pyrolysis process.

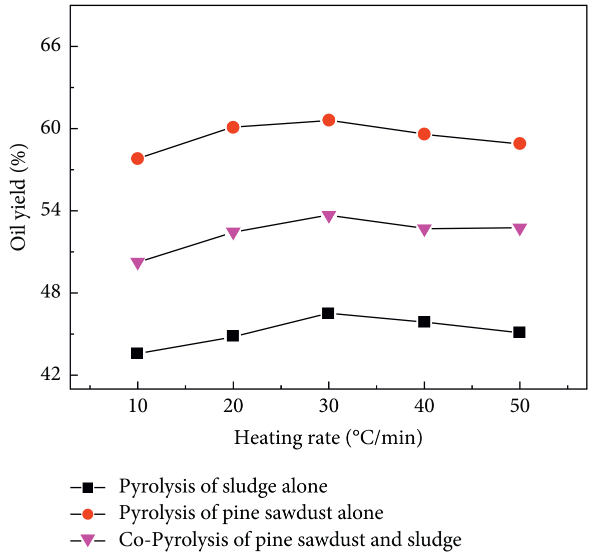

Figure 4: Influence of heating rate on fixed-bed pyrolysis process.

gas yield is decreasing continuously, while the solid pyrolysis carbon is increasing. Combined with the oil yield curve (Figure 5), the copyrolysis process of sludge and *Myriophyllum verrucosum* is more advantageous to obtain a higher yield of liquid product biooil at a lower amount of sludge.

*3.4.2. Copyrolysis of Pine Sawdust and Sludge.* Figure 7 shows the change in oil yield with mixing ratio and the comparison with the calculated value of linear addition of oil yield when pine sawdust and sludge are copyrolyzed. With increasing the sludge content, the oil yield of copyrolysis shows a trend of slowly increasing first and then rapidly decreasing to a certain level, and the maximum oil yield was at 20 wt% of sludge. Among them, only when the sludge content is 20 wt%, the experimental value of oil yield is greater than the linear additive value.

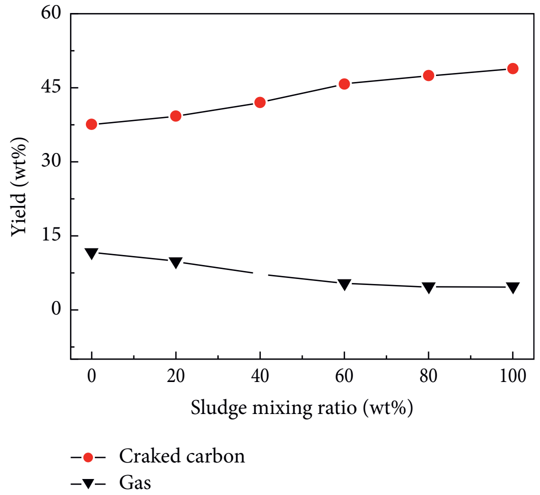

Figure 5: Copyrolysis oil yield curve of lexus algae and sludge as a function of mixing ratio.

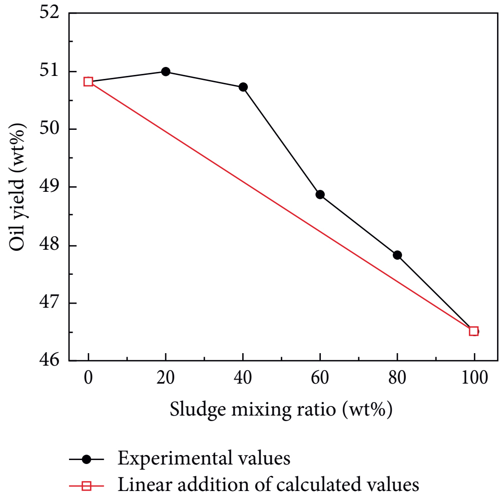

Figure 6: Changes in gas and solid two-phase products of copyrolysis of foxtail algae and sludge with the mixing ratio.

The change in the yield of gas and solid products generated during the pyrolysis of pine sawdust and sludge with the mixing ratio of sludge is shown in Figure 8. It shows that upon continuous addition of sludge, the gas production rate of copyrolysis was opposite to the yield of cracked carbon, and the gas yield decreased in a stepwise manner, while the solid cracked carbon increased. Combined with the oil yield curve 7, the copyrolysis process of sludge and pine sawdust is more advantageous to obtain a higher yield of liquid product biooil when the amount of sludge is 20 wt%, and the yields of pyrolysis carbon and pyrolysis gas are both at a lower level.

*3.4.3. Copyrolysis of Peanut Shell and Sludge.* The curve of peanut shells and sludge copyrolysis is shown in Figure 9. It

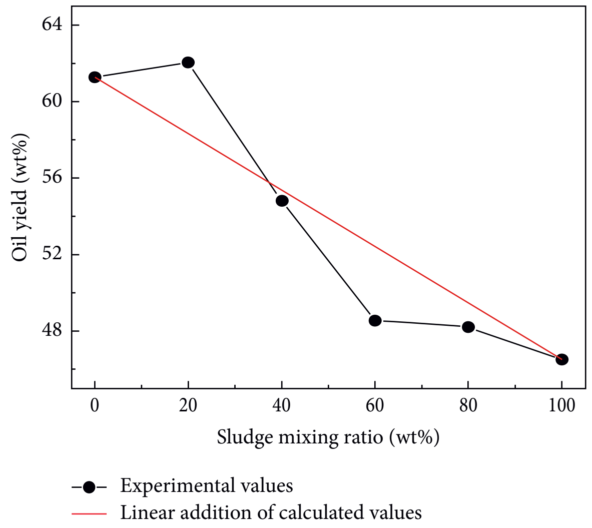

FIGURE 7: Variation curve of the oil production rate of pine sawdust and sludge copyrolysis with mixing ratio.

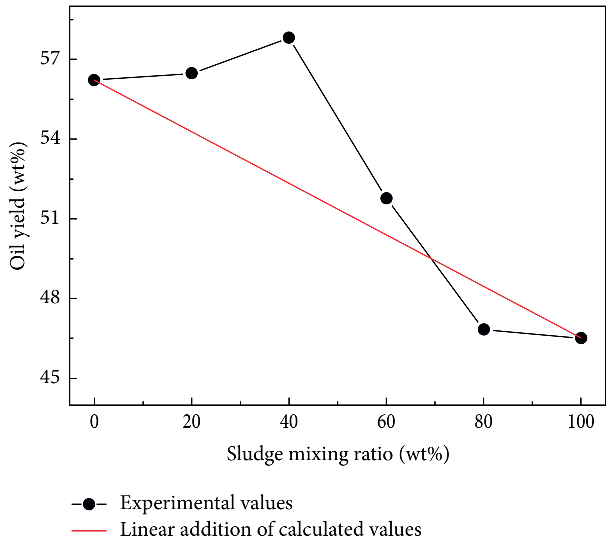

FIGURE 8: Copyrolysis of pine sawdust and sludge with gas and solid two-phase products as a function of mixing ratio.

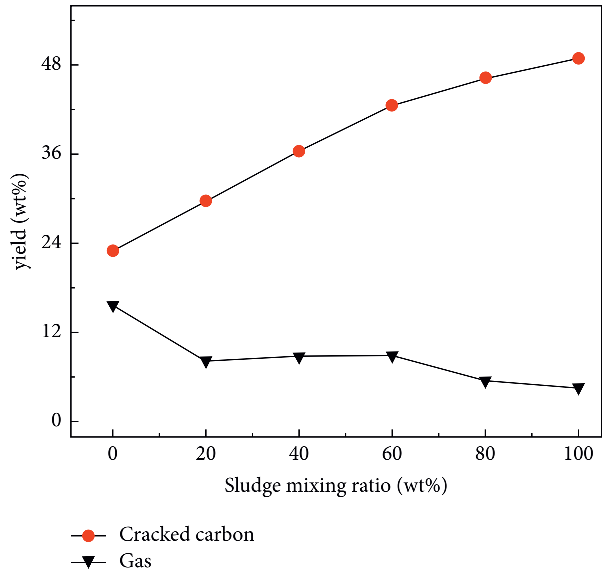

FIGURE 9: Copyrolysis curve of peanut shell and sludge oil yield with the blending ratio.

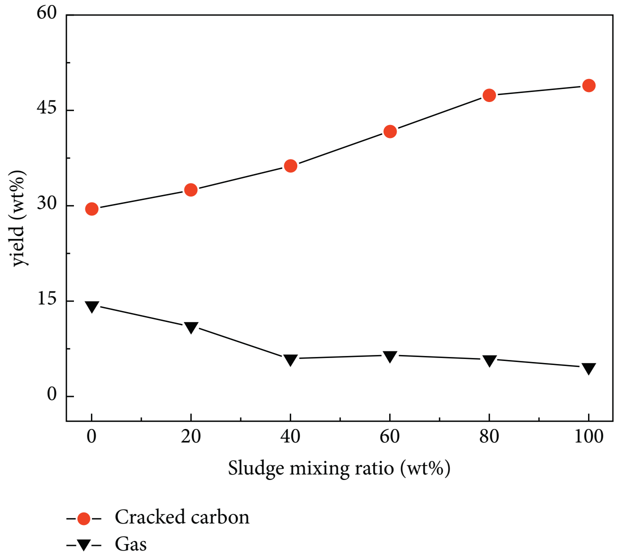

FIGURE 10: Copyrolysis gas and solid two-phase products of peanut shells and sludge vary with the mixing ratio.

shows that with increasing sludge content, a changing trend of oil yield is observed, i.e., it first slowly increases and then rapidly decreases. The highest oil yield is about 58 wt% when the sludge content is 40 wt%.

The changing trend of pyrolysis gas and solid products with sludge content when peanut shells and sludge are copyrolyzed is shown in Figure 10. It can be seen that by increasing the sludge content, the gas yield first decreases and then tends to be stable. Solid cracked carbon is increasing with the increase in sludge content. Combined with the change in oil yield in Figure 9, it is not difficult to find that peanut shell and sludge have good oil yield by c-pyrolysis when the sludge content is 20 wt% and 40 wt%. Wang et al. [10] reported that copyrolysis of sludge and wheat straw reduces pyrolysis process heat demand and produces a strong synergistic effect when the optimum amount of wheat straw is added. Ding and Jiang [24] reported the sludge decomposition using copyrolysis of sludge with biomass without an external heat supply. However, Guo et al. [25] reported $CO_2$ as the main product for copyrolysis of sludge and corn stalk (biomass) and observed an antisynergestic effect on NOx emission at low heating temperatures. Ruiz-Gómez et al. [26] observed no significant synergistic effect for mixed sludge and manure thermal decomposition by thermogravimetry (TG) analysis.

Generally, it is believed that biomass pyrolysis results from the combined action of cellulose, hemicellulose, and lignin [27]. However, the pyrolysis of its main components does not happen at the same time. Literature shows that the pyrolysis of hemicellulose, cellulose, and lignin mainly occurs at 200–260°C, 240–350°C, and 250–500°C, respectively [28]. Hemicellulose being composed of saccharides (including glucose, mannose, xylose, etc.) has a branched structure and amorphous nature and is easily transformed into volatile substances at a lower temperature. In contrast, cellulose is mainly composed of D-glucopyranose connected by $\beta$-(1,4)-glycosidic bonds, with little branching and linear molecular structure that owe high thermal stability. On the other hand, lignin contains aromatic rings and many branched chains rendering it thermolabile and decomposing at lower temperatures. However, abundant hydrogen bonding in lignin affects its thermal degradation requiring higher energy to achieve rapid cracking. Therefore, the pyrolysis of lignin starts at a lower temperature and lasts almost until the end of the whole pyrolysis process [29–33].

Bradbury et al. [34] modified and improved the model parameters based on the Broido–Nelson model and got the widely accepted Broido–Shafizadeh model (B-S model) for cellulose pyrolysis. The pyrolysis of cellulose at low pressure (1.5 Torr) was described by a three-reaction model. It was assumed that an “initiation reaction” led to the formation of an “active cellulose” which was subsequently decomposed by two competitive first-order reactions, one yielding volatiles, and the other char and a gaseous fraction. Sharma and Rao [28] studied the pyrolysis behavior of rice hulls in the state of particles and powder and determined its kinetic parameters. The experimental results showed that the reaction order was 1.5 at low temperature and 2.0 at high temperature, and the kinetic parameters obtained with the isothermal experiment were consistent with those obtained through the non-isothermal experiment.

Sludge pyrolysis can be traced back to a French patent in 1939 [35], where they proposed the treatment process of sludge pyrolysis. Later in the 1970s, German researchers developed sludge pyrolysis technology at a lower temperature. At the end of the 1990s, Australian scientists set up a sludge refinery in China to treat sludge by using low-temperature sludge pyrolysis technology [36]. The composition of sludge is complex, the reaction and equipment conditions are different during pyrolysis, and the properties of different sludge are quite different, so the detailed pyrolysis mechanism is still unclear. Generally, it is considered that different temperature ranges correspond to different reactions: the first stage is 100°C~120°C, which is the removal stage of adsorbed water on the sludge surface. From the study of the differential thermal curve, there are obvious endothermic peaks, and most of the water is evaporated in this stage. The second stage (200–450°C) is the melting, cracking, and volatilization stage of aliphatic compounds. Above 300°C is the transformation stage of protein-containing substances such as bacterial residues and microorganisms, and the chain-breaking process of amino acids, while above 390°C is the pyrolysis reaction of sugar polymers [37]. Few researchers [38] investigated the kinetics of fresh sludge and composted sludge and established a “five-component kinetic model.” The five components are low-stability organic compounds, hemicellulose, cellulose, lignin-plastic mixture, and inorganic compounds. Coats–Redfern integral method was used to fit the kinetics of pyrolysis of the five components.

Young et al. [39] reported a pyrolysis gasification process, where the conversion of sludge into activated carbon and fuel gas was studied in the furnace, and the process route and product composition distribution were determined. The results showed that the best gasification conditions were as follows: steam injection rate of 10 ml/min, gasifier temperature of 820°C, and moisture concentration of 11% for 1 hour. Under this condition, the composition and relative volume concentration of the main gas products were as: $H_2$ (34.1%), CO (18.6%), $CH_4$ (8.5%), and $CO_2$ (8%), and the gas calorific value was 10.107 kJ/Nm$^3$.

Li et al. [40] prepared sludge-activated carbon by chemical activation method with municipal sewage sludge as raw material and zinc chloride as the activator, and its quality was characterized by BET analysis and testing method. They found that the activated carbon with the best quality was obtained when the concentration of 3 mol/L zinc chloride was used as an activator, the activation time was 30 min, the activation temperature was 450°C, and the average BET value was 299.59 m$^2$/g; macroporous volume 0.53–0.58 cm$^3$/g, mesopore 0.1365–0.1986 cm$^3$/g, and micropore 0.2991–0.5623 cm$^3$/g; and the proportion of carbon was increased, the content of heavy metals was extremely low, and it had good adsorption performance. In another study, sludge-activated carbon was prepared using sludge obtained from chemical sewage treatment as raw material, after drying, activating with an activator, drying, grinding, and carbonizing under nitrogen protection, and achieved 585.3–2007 maximum allowable concentration [41].

## 4. Conclusion

To solve the common problems of environmental pollution and energy shortage faced by human society at present, research has been focused on the utilization of waste raw materials to generate energy. Combined with the previous research results, the basic idea of this study was to develop biomass energy from waste biomass and sludge resource utilization. The biomass used in this research was composed of reed leaves, bagasse, foxtail algae, and banyan tree roots. Pine sawdust and peanut shells were purchased from processing plant waste. The urban sewage sludge was collected from the sewage sludge precipitated after the urban domestic sewage treatment at a sewage treatment plant in Lanzhou. The biomass and sludge samples were pyrolyzed and copyrolyzed in different experimental conditions to study the effects of reaction parameters on the production of oil content and gas content. The pre-fixed-bed process parameters were optimized by an orthogonal test, and it was found that the carrier gas flow rate (a) > bed thickness (b) > constant temperature time (c). The optimum process combinations were 250 mL/min carrier gas, 10 mm bed thickness, and 10°C/min constant temperature rate. Our experiments showed that the ultimate pyrolysis temperature affects the oil production of fixed-bed pyrolysis by up to 15%. Copyrolyzing *Sargassum thunbergii* and sludge boost oil output at first, then drops; the maximum value obtained was 20% sludge. When pine sawdust and sludge were copyrolyzed, oil output climbed marginally and subsequently fell fast; the highest value was at 20% sludge. Peanut shell and sludge copyrolysis yields maximum oil at 40% sludge content, and the experimental value is smaller than the linear value at 80% sludge content. The results of this study can aid in the available information for further improvement in process parameters and the successful conversion of waste materials to useful energy.

## Data Availability

Data generated in this study are included in this manuscript.

## Conflicts of Interest

The authors declare that there are no conflicts of interest.

## Acknowledgments

The research was supported by the Fundamental Research Funds for the Central Universities (Grant no. 31920210068), the University Innovation Capacity Improvement Project of Gansu Province (No. 2019B-26), the Project of Innovation and Entrepreneurship Training Plan for University-Level College Students in 2022 (Nos. X202210742271 and X202210742285), a novel core-shell structure Cr-Zn@$SiO_2$@SAPO-34 catalyst for confinement catalysis of biomass pyrolysis oil to prepare light olefins, Key Laboratory of Environment-Friendly Composite Materials of the State Ethnic Affairs Commission, Gansu Provincial Biomass Function Composites Engineering Research Center, and Key Laboratory for Utility of Environment-Friendly Composite Materials and Biomass in University of Gansu Province.

## References

[1] Q. Zhang, W. Yang, H. Ngo et al., “Current status of urban wastewater treatment plants in China,” *Environment International*, vol. 92-93, pp. 11–22, 2016.

[2] L. Jin, G. Zhang, and H. Tian, “Current state of sewage treatment in China,” *Water Research*, vol. 66, pp. 85–98, 2014.

[3] L. Jianping, L. Minrong, W. Jinnan, L. Jianjian, S. Hongwen, and H. Maoxing, “Global environmental issues and human wellbeing,” in *Report on Global Environmental Competitiveness (2013)*, pp. 3–21, Springer, Berlin, Germany, 2014.

[4] X. Yuan, R. Mu, J. Zuo, and Q. Wang, “Economic development, energy consumption, and air pollution: a critical assessment in China,” *Human and Ecological Risk Assessment: An International Journal*, vol. 21, no. 3, pp. 781–798, 2015.

[5] P. Commission, “Twelfth five year plan (2012–2017),” *Faster, More Inclusive and Sustainable Growth*, vol. 1, 2012.

[6] X. Yang, Y. Song, G. Wang, and W. Wang, “A comprehensive review on the development of sustainable energy strategy and implementation in China,” *IEEE Transactions on Sustainable Energy*, vol. 1, no. 2, pp. 57–65, 2010.

[7] Z. Yuan, C. Wu, H. Huang, and G. Lin, “Research and development on biomass energy in China,” *International Journal of Energy Technology and Policy*, vol. 1, no. 1/2, pp. 108–144, 2002.

[8] C. J. Gómez Díaz, *Understanding Biomass Pyrolysis Kinetics: Improved Modeling-based on-Comprehensive-Thermokinetic Analysis*, Universitat Politècnica de Catalunya, Barcelona, Spain, 2007.

[9] A. L. Brown, *A Chemical and Kinetic Study of Cellulose and Biomass Pyrolysis at High Heating Rates*, University of Colorado at Boulder, Boulder, CO, USA, 2001.

[10] X. Wang, S. Deng, H. Tan et al., “Synergetic effect of sewage sludge and biomass co-pyrolysis: a combined study in thermogravimetric analyzer and a fixed bed reactor,” *Energy Conversion and Management*, vol. 118, pp. 399–405, 2016.

[11] Y. Liu, C. Ran, A. R. Siddiqui et al., “Pyrolysis of sewage sludge in a benchtop fluidized bed reactor: characteristics of condensates and non-condensable gases,” *Renewable Energy*, vol. 160, pp. 707–720, 2020.

[12] R. Aguado, R. Prieto, M. J. José, S. Alvarez, M. . n. Olazar, and J. Bilbao, “Defluidization modelling of pyrolysis of plastics in a conical spouted bed reactor,” *Chemical Engineering and Processing: Process Intensification*, vol. 44, no. 2, pp. 231–235, 2005.

[13] J. Makibar, A. Fernandez-Akarregi, I. Alava, F. Cueva, G. Lopez, and M. Olazar, “Investigations on heat transfer and hydrodynamics under pyrolysis conditions of a pilot-plant draft tube conical spouted bed reactor,” *Chemical Engineering and Processing: Process Intensification*, vol. 50, no. 8, pp. 790–798, 2011.

[14] M. Saidi, H. Basirat Tabrizi, and J. R. Grace, “A review on pulsed flow in gas-solid fluidized beds and spouted beds: recent work and future outlook,” *Advanced Powder Technology*, vol. 30, no. 6, pp. 1121–1130, 2019.

[15] M. Haghighat, N. Majidian, A. Hallajisani, and M. samipourgiri, “Production of bio-oil from sewage sludge: a review on the thermal and catalytic conversion by pyrolysis,” *Sustainable Energy Technologies and Assessments*, vol. 42, Article ID 100870, 2020.

[16] S. S. A. Syed-Hassan, Y. Wang, S. Hu, S. Su, and J. Xiang, “Thermochemical processing of sewage sludge to energy and fuel: fundamentals, challenges and considerations,” *Renewable and Sustainable Energy Reviews*, vol. 80, pp. 888–913, 2017.

[17] S. H. Beis, Ö. Onay, and Ö. M. Koçkar, “Fixed-bed pyrolysis of safflower seed: influence of pyrolysis parameters on product yields and compositions,” *Renewable Energy*, vol. 26, no. 1, pp. 21–32, 2002.

[18] O. Onay and O. Mete Koçkar, “Fixed-bed pyrolysis of rapeseed (brassica napus L.),” *Biomass and Bioenergy*, vol. 26, no. 3, pp. 289–299, 2004.

[19] Y. Wang, G. Chen, Y. Li, B. Yan, and D. Pan, “Experimental study of the bio-oil production from sewage sludge by supercritical conversion process,” *Waste Management*, vol. 33, no. 11, pp. 2408–2415, 2013.

[20] Z. Wang, Q. Guo, X. Liu, and C. Cao, “Low temperature pyrolysis characteristics of oil sludge under various heating conditions,” *Energy & Fuels*, vol. 21, no. 2, pp. 957–962, 2007.

[21] Z. Wang, L. Xie, K. Liu et al., “Co-pyrolysis of sewage sludge and cotton stalks,” *Waste Management*, vol. 89, pp. 430–438, 2019.

[22] B. Singh and P. Kumar, “Physicochemical characteristics of hazardous sludge from effluent treatment plant of petroleum refinery as feedstock for thermochemical processes,” *Journal of Environmental Chemical Engineering*, vol. 8, no. 4, Article ID 103817, 2020.

[23] J. Zhu, L. Zhu, D. Guo, Y. Chen, X. Wang, and Y. Zhu, “Co-pyrolysis of petrochemical sludge and sawdust for syngas production by TG-MS and fixed bed reactor,” *International Journal of Hydrogen Energy*, vol. 45, no. 55, pp. 30232–30243, 2020.

[24] H.-S. Ding and H. Jiang, “Self-heating co-pyrolysis of excessive activated sludge with waste biomass: energy balance and sludge reduction,” *Bioresource Technology*, vol. 133, pp. 16–22, 2013.

[25] S. Guo, Y. Han, L. Wang, D. Che, H. Liu, and B. Sun, “Synergistic effects of co-combustion of sewage sludge and corn stalk and the resulting gas emission characteristics,” *IET Renewable Power Generation*, vol. 14, no. 9, pp. 1596–1605, 2020.

[26] N. Ruiz-Gómez, V. Quispe, J. Ábrego, M. Atienza-Martínez, M. B. Murillo, and G. Gea, “Co-pyrolysis of sewage sludge and manure,” *Waste Management*, vol. 59, pp. 211–221, 2017.

[27] D. Vamvuka, E. Kakaras, E. Kastanaki, and P. Grammelis, “Pyrolysis characteristics and kinetics of biomass residuals mixtures with lignite,” *Fuel*, vol. 82, no. 15-17, pp. 1949–1960, 2003.

[28] A. Sharma and T. R. Rao, “Kinetics of pyrolysis of rice husk,” *Bioresource Technology*, vol. 67, no. 1, pp. 53–59, 1999.

[29] D. Y. Leung, X. Yin, and C. Wu, “A review on the development and commercialization of biomass gasification technologies in China,” *Renewable and Sustainable Energy Reviews*, vol. 8, no. 6, pp. 565–580, 2004.

[30] J. J. Orfão, F. J. Antunes, and J. L. Figueiredo, “Pyrolysis kinetics of lignocellulosic materials—three independent reactions model,” *Fuel*, vol. 78, no. 3, pp. 349–358, 1999.

[31] H. Chen, N. Liu, and W. Fan, “Two-step consecutive reaction model and kinetic parameters relevant to the decomposition of Chinese forest fuels,” *Journal of Applied Polymer Science*, vol. 102, no. 1, pp. 571–576, 2006.

[32] K. Raveendran, A. Ganesh, and K. C. Khilar, “Pyrolysis characteristics of biomass and biomass components,” *Fuel*, vol. 75, no. 8, pp. 987–998, 1996.

[33] H. Yang, R. Yan, H. Chen, D. H. Lee, and C. Zheng, “Characteristics of hemicellulose, cellulose and lignin pyrolysis,” *Fuel*, vol. 86, no. 12-13, pp. 1781–1788, 2007.

[34] A. G. W. Bradbury, Y. Sakai, and F. Shafizadeh, “A kinetic model for pyrolysis of cellulose,” *Journal of Applied Polymer Science*, vol. 23, no. 11, pp. 3271–3280, 1979.

[35] S. Shibata, “Procede de fabrication d’une huile combustible a partir de bone digeree,” *French patent*, vol. 838, no. 2, 1939.

[36] H. Campbell, “Sewage sludge treatment and use: new development,” *London: Elsevier Applied Science*, vol. 28, pp. l–290, 1989.

[37] V. Frišták, M. Pipíška, and G. Soja, “Pyrolysis treatment of sewage sludge: a promising way to produce phosphorus fertilizer,” *Journal of Cleaner Production*, vol. 172, pp. 1772–1778, 2018.

[38] A. G. Barneto, J. A. Carmona, J. E. M. Alfonso, and J. D. Blanco, “Kinetic models based in biomass components for the combustion and pyrolysis of sewage sludge and its compost,” *Journal of Analytical and Applied Pyrolysis*, vol. 86, no. 1, pp. 108–114, 2009.

[39] N. C. Young, S. C. Kim, and K. Yoshikawa, “Pyrolysis gasification of dried sewage sludge in a combined screw and rotary kiln gasifier,” *Applied Energy*, vol. 88, no. 4, pp. 1105–1112, 2011.

[40] Y. Li, J. Tian, W. Qian, W. Liang, H. He, and Y. Jin, “Preparation and characterization of activated carbon from sewage sludge,” in *Proceedings of the Conference on Environmental Pollution and Public Health*, Wuhan, China, October 2010.

[41] N. Almahbashi, S. Kutty, M. Ayoub et al., “Optimization of preparation conditions of sewage sludge based activated carbon,” *Ain Shams Engineering Journal*, vol. 12, no. 2, pp. 1175–1182, 2021.