Pyrolysis Conversion Reaction Mechanism of Sewage Sludge to Biofuel

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Abstract: The conversion reactions to produce biofuel include many possible paths and routes leads to chemical changes due to each bath. For example, biofuel produced from solid wastes mainly consists of methane gas (CH4) and carbon dioxide (CO2), in addition to traces of chemicals as impurities. To determine the optimum reactants quantities, and to help engineers in designing the pyrolysis plants we made this research. In this research we will suggest the mechanisms of the internal (sub) reactions that occurs during the conversion of sewage sludge to biofuel via pyrolysis operation according to the results of the analysis of samples taken from different stages of the pyrolysis depending on the products of the research of (Pyrolysis of Sewage Sludge), and its analysis before and after the reaction.

We used and will use many techniques as shown below:
1- Fourier-Transform Infrared (FTIR) analysis in order to know the chromophores to the reactants and products.
2- X-Ray Fluorescence (XRF) analysis for the reactant to determine the metals in the sludge.
3- Carbon-Hydrogen-Nitrogen analysis (C.H.N.) for the samples before and after and within the pyrolysis.
4- Differential Scanning Calorimetry (DSC) analysis to determine the stages of pyrolysis operation and the rate determining step (slow step) that affect the velocity of the reaction.

Key words: Mechanism, slow step, chemical conversion.

1. Introduction:
The noticeable amounts of sewage sludge are produced during the industrial and domestic wastes of water treatment by biological and chemical processes and it increases rapidly.
Many improvements have been made on the treatment processes of sewage sludge including; thermal treatment, direct treatment (composted as fertilizer), landfill, and dumping to the sea.
On the other hand, all these methods are conventional and cause many problems throughout the process; e.g. the thermal treatment (by combustion or incineration) causes ash resulted from the operation, a land pollution is caused by toxic metals and organic compounds due to the use of direct process (as a fertilizer) [1].
An alternative method called pyrolysis supplies a solution to most of the problems mentioned above except the poisoning by (cadmium and mercury), also it gives a new source of power and new valuable chemicals by utilizing the stored energy [2].
Analysis of the gas phase must be done; these qualitative and semi quantitative analysis show that the pyrolysis process undergoes formation of new compounds.

In order to understand the intrinsic of the pyrolysis of the sewage sludge, study of the kinetics of the pyrolysis is the important part, kinetic data for fuels (fossil and alternative) and solid wastes were reported [3-11].

Few researches deal with the produced gas quantitatively.

The design of the pyrolysis reactor differs from company to another one, it may be designed as continues, batch, or mixes wastes [12-13].

1.1 Aim of the research:
1-Determination of the optimum quantities of the reaction.
2-Having a comparison leads to the best path according to the available conditions.
3- Help the engineers in their calculations about designing the pyrolysis plants.
4- Treatment and purification of the produced gas by releasing the impurities at the proper step.

2. Materials and Methods:

2.1 Sample preparation:
Our samples were provided from (Al-Rustumiya site for treating the sewage water). First the sample was dried in vacuum oven with temperature about 1000°C for 24 hour, and then it was grinded into molecular size within (0.2-2) mm, finally it was sieved out to have different molecular sizes. By using the pyrolysis unit shown in below we did our experiments at different temperatures and molecular size of 0.8 mm.

2.2 Tests and analysis:
In order to determine the chemical properties of the sewage sludge many quantitative and qualitative analysis was applied for the reactant and the products of the pyrolysis: Tables (1-4) show these properties.

2.2.1 FTIR Analysis: Figures (1-5) illustrates the FTIR spectra for the row sewage sludge and for the sample before and after pyrolysis at different temperatures, whereas table (5) summarizes the values of the wavelengths of the whole operation at different temperatures.

2.2.2 Differential Scanning Calorimetry (DSC): In order to complete the results of the pyrolysis of sewage sludge and suggesting the mechanism of the operation, a (DSC) analysis was held to samples of sewage sludge.

To determine the sludge properties, differential scanning calorimetry (DSC); it is a technique measures the difference between the heat needed to increase the temperature (of decomposition and reformation) of the sample relative to a reference, where the sample and the reference exposed almost to the same temperature in a linear relationship as a function of time [14].

The DSC analysis was studied by (Schimadzu DSC-60), at a range of temperature from (0 – 300) °C, and we got the curves (6 and 7).

3. Results and discussion:
The mechanism of pyrolysis of the sewage sludge has been studied via many techniques as mentioned above. By studying these curves, we suggest a mechanism for the sewage sludge pyrolysis and the steps of this reaction, where the reaction occurs in three steps and the second step was the slow step (rate determining step) at a temperature between (141 – 148) °C. By comparing these results with the (FTIR) curves we found that:

- Appearance of a peak at the wavelength range (3600 – 3200) Cm⁻¹ refers to (O-H) bonding of water, also we have a peak at (100) °C in the (DSC) curve (fig. 6) shows that the sample undergoes a dehydration (even the water came from the moisture or within the chemical composition of the
sample) at the first step of pyrolysis. The evidence was when we dried a sample of sludge and analyze it by (DSC), the peak at (100)$^\circ$ C disappeared, (fig. 7).

- The peak at (1100 – 1000) Cm$^{-1}$ refers to (C=O) bonding, and the peak at (1520 – 1400) Cm$^{-1}$ refers to (C-H) bonding show formation of CO, CO$_2$, and some aliphatic compounds from simplest one (CH$_4$) to bigger. In addition, the (DSC) curve shows a peak at (141 – 148) $^\circ$C leads to a change in the phase from solid to liquid and gaseous. By noticing the high loss in mass of the reactant at this temperature (at this step) because of the conversion of most of the mass into gases (this result agree with the peak intensity in DSC curve (fig. 8), it shows that the second step is the rate determining step of the pyrolysis reaction, which also shows a highest conversion to (mainly CO, CO$_2$) according to FTIR peak intensity, then (CH$_4$), and little quantity of unstable (R-C-NH$_2$) which broken into (NH$_3$ + R-CH or R-C-R) [14,15].

- By comparing the second step with the first one we found that it is higher energy than the first step because of the high reactivity compounds resulting from the degradation of oligomers that the sludge consists of, these compounds undergo other reactions to form new stable compounds.
  a. At the range of (220 – 260)$^\circ$ C the curve goes to stability because of these reasons:
  b. The pyrolysis reaction was complete.
  c. Reactions of the unstable transition compounds resulting from the second step, and formation of the final products [16, 17].

According to all the results above, we suggested the mechanism shown in figure (8)

4. Conclusions:

- According to (C,H,N) and (XRF) analysis we found that there are heavy metals in the sample because there is no industrial source near the treatment station.
- FTIR spectra show increasing in the intensity of the peak at the wavelength 1674Å caused by formation of carbonyl group in form of CO$_2$.
- Appearing of new peaks approved breaking and formations of new bonds in forms of new aliphatic short chain compounds contain (C-H) bonds like CH$_4$.
- The (DSC) curves shows that the general reaction takes place according to a mechanism with three steps, and the second step was the rate determining step.

5. Figures

Figure 1. FTIR analysis for the raw sewage sludge
Figure 2. FTIR analysis for dried sewage sludge

Figure 3. FTIR analysis for the produced bio-oil after Pyrolysis at 290°C

Figure 4. FTIR analysis for the produced bio-oil after Pyrolysis at 275°C
Figure 5. FTIR analysis for the produced bio-oil after Pyrolysis at 250°C

Figure 6. DSC curve of the raw sewage sludge

Figure 7. DSC curve of the dried sewage sludge
6. Tables

**Table 1.** Basic tests for sewage sludge

| analysis             | value |
|----------------------|-------|
| moisture             | 3.7   |
| Volatile compound    | 57.3  |
| Ash content          | 34.6  |
| Carbon               | 4.4   |

**Table 2.** Carbon, Hydrogen, Nitrogen (C.H.N) Analysis for sewage sludge

| C    | H    | N    | O    | S    | H/C  | H/N  |
|------|------|------|------|------|------|------|
| 41.13| 5.66 | 4.18 | 48.02| 1.01 | 1.67 | 18.89|

**Table 3.** X-Ray Fluorescence for the sample before drying

| Sample No. 1 | Element | Content | Limit | Value |
|--------------|---------|---------|-------|-------|
|              | Fe      | ND      | 0     | 1.395 |
|              | Kr      | ND      | 0     | 0.0208|
|              | Sn      | ND      | 0     | 0.2851|
|              | Ga      | ND      | 0     | 0     |
|              | Ti      | ND      | 0     | 0.3636|

**Table 4.** X-Ray Fluorescence for the sample after drying
Table 5. Summarizes the values of the wavelengths of the whole operation at different temperatures

| Bonding                                | Wavelength Cm⁻¹ |
|----------------------------------------|-----------------|
| O-H vibration of carboxylic and alcoholic groups | 3600 – 3150     |
| H-bonding N-H group                    |                 |
| Aliphatic C-H stretching CH₃, CH₂, and C-H 2 or 3 bonded | 3010 – 2850     |
| S-H thiols                             | 2515 – 2510     |
| C=O stretching                         | 1794 – 1784     |
| C=O, aromatic C=C                      | 1680 - 1645     |
| Aliphatic C-H deformation              | 1520-1385       |
| C=O, O-H within carbonyl group         | 1419 – 1398     |
| C-O stretching, C-N                   | 1100 – 1000     |
| =C-H & =CH₂                            | 910 – 450       |

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