## CHAPTER IX CONCLUSIONS AND RECOMMENDATIONS

## 9.1 Conclusions

The pyrolysis of sewage sludge was investigated. The studies of the thermal decomposition (pyrolysis) behavior and the evaluation of kinetic parameters were achieved by means of thermogravimetric analysis (TGA). The collection of product distribution data as a function of pyrolysis temperature and the analysis of pyrolytic products for their chemical compositions were completed. Moreover, the upgrading and utilization of the pyrolytic products (liquid bio-oil and solid residue) were illustrated.

The pyrolysis of sewage sludge at elevated temperature showed two decomposition steps. The first reaction at 300-350°C was found to be the decomposition of cellulose, hemicellulose and some aliphatic amino acid whereas the second decomposition at higher temperature, 400-500°C, was due to the decomposition of complex and/or aromatic structures. For the decomposition under CO<sub>2</sub> atmosphere, two decomposition steps were also observed. However, the first reaction was significantly accelerated whereas the secondary reaction temperature was shifted to a lower temperature. The kinetics studies showed that the apparent activation energies for the first reaction of both N<sub>2</sub> and CO<sub>2</sub> atmospheres was 72 kJ mol<sup>-1</sup> while that of the second reaction decreased from 154 to 104 kJ mol<sup>-1</sup> under CO<sub>2</sub> atmosphere. The typical reaction order of the decomposition under both N<sub>2</sub> and CO<sub>2</sub> atmospheres was in the range of 1.0-1.5.

For the product yields, the solid yield decreased while the liquid and gas fractions increased with the increase in the temperature. The solid yield slightly reduced while the gas and liquid yields were somewhat improved in the presence of  $CO_2$ . The amount of H<sub>2</sub>, CO and CH<sub>4</sub> formed was higher for the decomposition under CO<sub>2</sub> atmosphere than N<sub>2</sub> atmosphere. Furthermore, CO<sub>2</sub> influenced the liquid product by increasing the oxygenated compounds thus decreasing the aliphatic compounds via the insertion of CO<sub>2</sub> into the unsaturated aliphatic compounds, resulting in carboxylics and ketones formation.

The pyrolysis of several types of materials such as polyethylene (PE), polypropylene (PP), polystyrene (PS), waste tire (WT) and oil sludge (OS) in a fixed-

bed reactor at 550°C was also investigated. It was found that gas, liquid and solid yields were related to volatile, ash and fixed carbon representing in the proximate analysis. The materials containing high volatile matter yielded high gas and liquid fractions while materials containing high fixed carbon and ash yielded high solid fraction. However, there were some variations in each fraction depending on the structure of the materials. The composition of the derived oils was similar in the content but different in the distribution. They consisted of (1) aliphatics (2) single ring aromatics and its alkyl derivatives, (3) oxygenates and (4) nitrogenates. However, there was no direct relationship to the derived oil composition and its feedstock structures. But, each constituent in the derived oil can be speculated from the decomposition of its primer.

Since as received pyrolytic liquid derived from sewage sludge contained significant amount of oxygenated compounds in the form of carboxylic acid (up to 45 wt.%). Therefore, it cannot be readily used as conventional diesel fuels. The further upgrading by deoxygenation was required. The deoxygenation of oleic acid, pyrolytic liquid model compound, over the ceria-zirconia mixed metal oxide (Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>) was investigated. The results showed that the deoxygenation of oleic acid can be achieved via deoxygenation by direct removal of the carboxylic part of oleic acid generating CO and CO<sub>2</sub> as major products in the gas phase with the selectivity toward C<sub>17</sub>-hydrocarbons. Ce<sub>0.75</sub>Zr<sub>0.25</sub>O<sub>2</sub> was found to be the most active and stable catalyst for the oleic acid deoxygenation. A first order kinetic model was found to fit perfectly with experimental data. The calculated activation energy was ca. 23 kcal mol<sup>-1</sup>.

For the solid product, the combustion of sewage sludge char derived from pyrolysis was considered as important advantages due to their energy content. Chars derived from pyrolysis under  $N_2$  and  $CO_2$  atmospheres were investigated for their combustion reactivities. According to the thermogravimetric experiments, the combustion reactivities of chars strongly depended on pyrolysis temperature at which the char prepared regardless of the pyrolysis atmospheres used. The reactivities of all chars sample become less reactive with the increase of the pyrolysis temperature.

Instead of using sewage sludge char for providing heat, sewage sludge char was used as a potential adsorbent for dye removal. The sewage sludge char derived from pyrolysis under  $CO_2$  atmosphere possessed a high surface area and basicity than that of derived from pyrolysis under  $N_2$  atmosphere. Adsorption studies showed that these chars were considerably efficient for the removal of dyes. The adsorption

mechanism was found to rely on the electrostatic interactions and dispersive interactions. The equilibrium data fitted well with the Langmuir model suggesting the monolayer coverage of dye molecules at the outer surface of sewage sludge derived chars. The maximum adsorption capacities of acid yellow 49, basic blue 41 and reactive red 198 dyes were reported at 116, 588 and 25 mg g<sup>-1</sup> of char, respectively.

## 9.2 Recommendations

The preliminary study on the mass and energy balances on the pyrolysis system shows the worth-while possibility of a practical operation for the conversion of sewage sludge to liquid fuels, energy (heat) and valuable chemicals and also this work provides either the principle of pyrolysis of sewage sludge or illustrates some of the upgrading/utilization technique for the pyrolytic product. The upgrading/utilization of sewage sludge char are quite practical. However, a practical implementation needs a better understanding for the upgrading/utilization technique for the liquid product. Depending on specific applications, developments of reliable low cost of upgrading and refining techniques are needed.