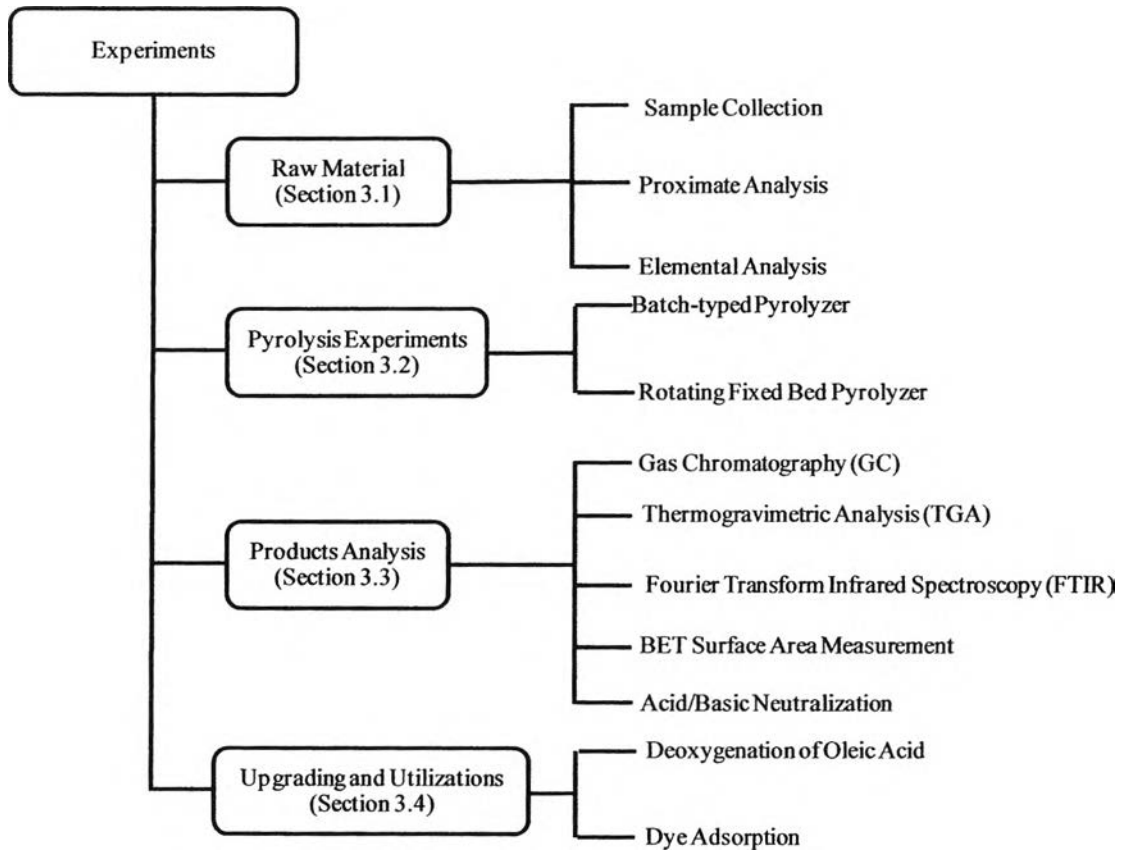




### **CHAPTER III**

### **EXPERIMENTAL**

Chapter III describing the experimental procedures related to the sewage sludge pyrolysis is divided into 4 sections; namely, raw material, pyrolysis experiments, products analysis as well as upgrading and utilizations sections. The raw material section (Section 3.1) contains sample collection, proximate analysis and elemental analysis. The results of this section are presented in Chapters IV, V and VII. The pyrolysis experiment section (Section 3.2) is divided into 2 categories according to the pyrolyzer, i.e., batch-typed and rotating fixed bed pyrolyzer. The obtained pyrolysis products were analyzed according to various techniques including gas chromatography (GC), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), BET surface area measurement and acid/basic neutralization (Section 3.3). The results of products analysis presented in parts of Chapters IV to VIII. The upgrading of pyrolytic liquid by using oleic acid as a model feedstock is described in Section 3.4.1. The utilization of solid product as a dye adsorbent is explained in Section 3.4.2. The results of the upgrading and utilization of pyrolysis products are presented in Chapters V and VIII, respectively. Figure 3.1 depicts the summary of the experiments carried out in this work. The detailed information of each section is presented as followed:



**Figure 3.1** A diagram for the summary of experiments

## 3.1 Raw Material

### 3.1.1 Sample Collection

The sewage sludges from different sources were collected and pretreated as follows:

- 1) Collecting the sewage sludge according to ASTM D346-90
- 2) Naturally drying for 2-3 days
- 3) Grinding the samples by ball milling
- 4) Keeping the sample in a dessicator

### 3.1.2 Proximate and Elemental Analysis

- *Proximate Analysis*

Proximate analysis was undertaken in accordance with the ASTM D3172-89 to evaluate moisture content, volatile mater, fixed carbon and ash.

- *Elemental Analysis*

Elemental composition was analyzed according to ASTM D-3176.

## 3.2 Pyrolysis Experiments

### 3.2.1 Batch-typed Pyrolysis

The thermal decomposition of the sewage sludge under either N<sub>2</sub> or CO<sub>2</sub> atmosphere was carried out in a horizontal stainless-steel tubular reactor (OD. = 0.75 in.) placed in an electrical furnace. Approximately 5 g of the sample were placed in the reactor between the two layers of quartz wool. The reactor temperature was set at the desired temperatures between 350 and 650°C. The pyrolysis products were swept out off the reactor and passed through a condenser immersed in a mixture of ice and acetone. The uncondensable gas was collected by a Tedlar<sup>®</sup> gas sampling bag. At the end of each experiment, the solid residue and condensable liquid were weighed for the evaluation of the product yields. The gas yield was obtained by difference. The products from the pyrolysis were named using *AX* codes, where *A* represents the pyrolysis atmosphere, which is either N for N<sub>2</sub> or C for CO<sub>2</sub>, and *X* represents the pyrolysis temperature.

### 3.2.2 Rotating Fixed Bed Pyrolysis

The experiments were performed in a gas-distributed fixed-bed pyrolyzer. About 50 g of a sample was placed in a wired-mesh basket hung over a gas-distributor installed in a 2.5 L stainless steel reactor heated by an electric furnace. The reactor was purged prior to the experiment by flowing N<sub>2</sub> to eliminate air originally contained in the reactor. The N<sub>2</sub> flow rate was then increased to 100 ml min<sup>-1</sup> while the reactor temperature was increased from room temperature to 550°C with a heating rate of 20°C min<sup>-1</sup>. The swept-out volatile containing products were condensed in a series of cold traps maintained at below 0°C with the aid of an ice/acetone mixture.

## 3.3 Products Analysis

### 3.3.1 Gas Chromatography (GC)

#### 3.3.1.1 *Gaseous Product Analysis*

The uncondensable vapor was chromatographically analyzed using a Shimadzu GC 8A fitted with a TCD. A CTR I (Alltech) packed column was used to separate the gas product under isothermal condition at 50°C. The injection and a detector temperature was 120°C.

#### 3.3.1.2 *Liquid Product Analysis*

The condensable liquid was analyzed using a ThermoFinnigan Trace GC 2000 gas chromatograph coupled with a PolarizQ mass spectrometer. The separation was carried out with a 30 m×0.25 mm capillary column coated with a 0.25 μm thick film of 5% phenylmethylpolysiloxane (ZB-5 MS). Helium was employed as a carrier gas at a flow of 1.0 ml min<sup>-1</sup>. The initial oven temperature of 40°C was held for 5 min and then programmed from 40 to 300°C at 5°C min<sup>-1</sup> when isothermally held for 30 min. Splitless injection was carried out at 300°C and the purge valve was on for 1 min. The ion source and mass transfer line temperatures were 230 and 325°C, respectively. Data were collected in a full-scan mode with the *m/z* ratios between 10 and 300, and with a 5-min solvent delay. The identification of compounds was performed by comparing the mass spectrum of the sample with the NIST mass spectra library. The

percentage of compounds was calculated from the peak area of the total ion chromatogram (TIC).

### 3.3.2 Thermogravimetric Analysis (TGA)

#### *3.3.2.1 Thermal Decomposition Experiments*

Thermal decomposition of sewage sludge was carried out using a TG7 Perkin-Elmer Thermogravimetric analyzer under either N<sub>2</sub> or CO<sub>2</sub> atmosphere. Typically, ca. 5 mg of sample were used for each run under non-isothermal conditions. The sample was heated up from ambient temperature to 105°C and held at this temperature for approximately 10 min to ensure that free-water was completely removed. Then, the sample was further heated to 800°C with a heating rate between 5 and 20°C min<sup>-1</sup>. Three repeated experiments were done for data confirmation. The thermogravimetric and differential thermogravimetric (TG-DTG) data were used to differentiate the pyrolysis behavior as well as to provide the estimation of the kinetic parameters.

#### *3.3.2.2 Temperature Programmed Combustion of Char*

Preparation of sewage sludge char is carried out following by the method as shown in section 3.2.1. For subsequence combustion, non-isothermal reactivity (up to 800°C) toward air (20 ml min<sup>-1</sup>) of sewage sludge chars (~10 mg), particle size of 20/50 mesh, were investigated in a TG7 Perkin-Elmer thermogravimetric analyzer. The heating rate was 20°C min<sup>-1</sup> in all cases. Three repeated experiments were accomplished for data confirmation. The thermogravimetric (TG) and differential thermogravimetric (DTG) data were used to differentiate the reactivity behavior as well as to provide the following parameters. From DTG curves;  $T_v$ , temperature at the beginning of the reaction (°C);  $T_m$ , temperature at the maximum (°C);  $T_e$ , temperature at the end of the reaction (°C);  $t_b$ , burn-out time (s); and  $R_{max}$ , maximum reactivity at  $T_m$  (wt.% s<sup>-1</sup>).

### 3.3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FT-IR) spectra of the char samples were scanned in the range 400-4000 cm<sup>-1</sup> using Thermo Nicolet FT-IR spectroscope modeled Nexus 670 using potassium bromide (KBr) disks at the ratio of

1:50 (char sample/KBr). The total surface acidity/basicity was determined by the conventional back titration methods.

#### 3.3.4 BET Surface Area Measurement

The BET surface area and pore structure of char were obtained from N<sub>2</sub> adsorption isotherms at 77 K using a QUANTACHROME AutoSorb-1 analyzer. The specific surface area was calculated by the Bruanauer-Emmet-Teller (BET) equation. The micropore surface area and volume were calculated by the *t*-method. Prior to the analysis, the samples were outgassed at 250°C for 4 hrs. The surface morphology of the char samples was examined using a scanning electron microscope modeled JOEL 631.

#### 3.3.5 Acid/Basic Neutralization

To determine the total acidity (basicity) of sample, about 0.200 g of sewage sludge char was soaked into 25 mL of 0.025 N NaOH (0.025 N HCl) solution in a closed flask and agitated for 48 hrs at room temperature. While the suspension was decanted, the supernatant was titrated with 0.025 N HCl (0.025 N NaOH) solution to determine the remaining of NaOH (HCl) in the solution.

### **3.4 Upgrading and Utilizations of Pyrolysis Products**

#### 3.4.1 Deoxygenation of Oleic Acid

##### *3.4.1.1 Catalysts Preparation*

Ceria-zirconia mixed metal oxide catalysts were prepared via urea hydrolysis technique. The metal salt solutions (0.1 M) were prepared from cerium nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.0%), Fluka), and zirconium oxychloride (ZrOCl<sub>2</sub>·8H<sub>2</sub>O (99.0%), Fluka) using as sources of Ce and Zr, respectively. The ratio of Ce/Zr metal was altered by varying the volume of the metal salt solution depending on the desire composition of the mixed metal oxide catalysts. After that the 0.4 M of urea (99.0%, Fluka) solution was added to the salt solution with the ratio of 2:1 (v/v). The mixture was aging at 100°C for 50 h. The obtained gel was filtered and left to dry at 110°C overnight. The dried gel was then calcined at 500°C for 4 h in air. Then, the sample was kept in the desiccators prior to further using. For metal supported catalyst, the powder was impregnated with the nitrate salt solution of selected metals, Fe, Ni, Cu and Rh, by

the incipient wetness impregnation method. Then, the obtained slurry was left to dry at 100°C overnight and then calcined in air at 500°C for 4 hr.

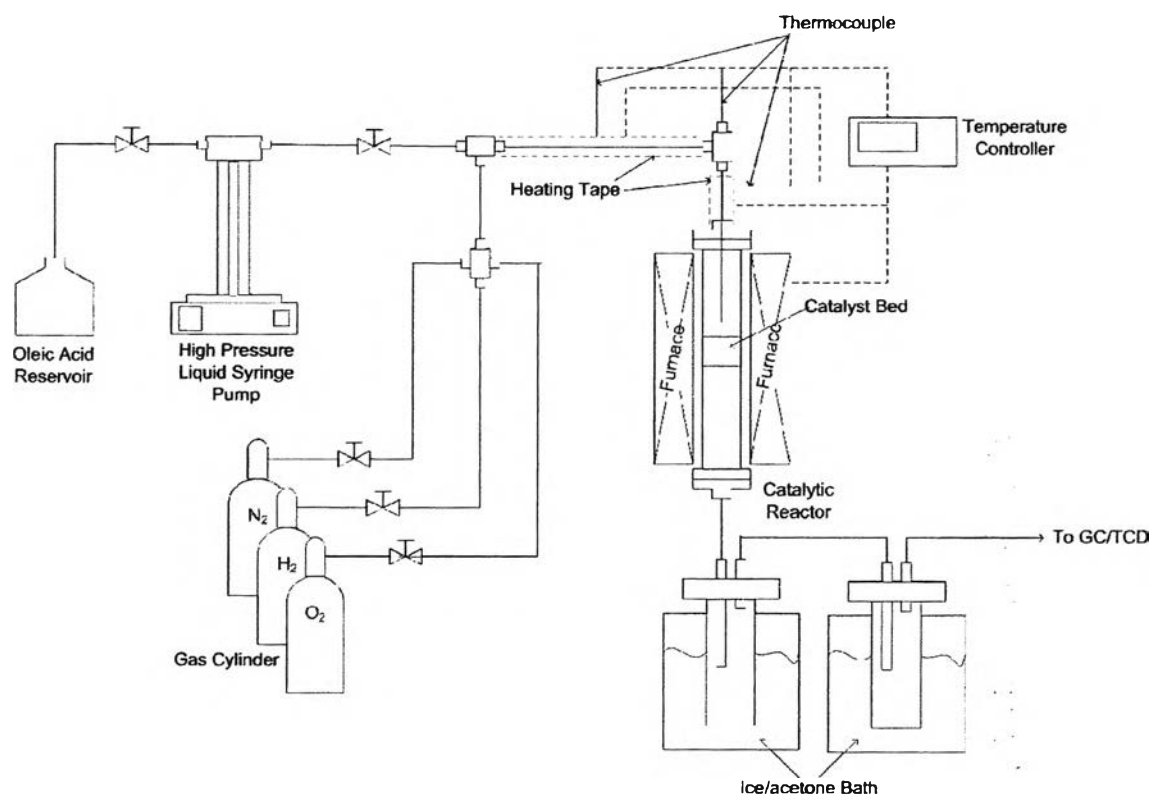
#### 3.4.1.2 Catalysts Characterization

Crystallographic structure of prepared catalysts was examined by X-ray diffraction (XRD) on a Rigaku X-ray diffractometer system equipped with a RINT 2000 wide-angle goniometer using Cu K $\alpha$  radiation and a power of 40 kV $\times$ 30 mA. The intensity data were collected at 25°C over a  $2\theta$  range of 20-80°.

Specific surface areas were determined by N<sub>2</sub> adsorption at 77 K (five point Brunauer-Emmett-Teller (BET)) method using a Quantachrome Corporation Autosorb. Prior to the analysis, the samples were outgassed at 250°C for 4 h.

#### 3.4.1.3 Activity Test

Catalytic activity tests for the decarboxylation of oleic acid (C<sub>17</sub>H<sub>33</sub>COOH) were carried out in a stainless steel packed bed reactor (I.D. 3/8 in.) as shown in the schematic diagram in Figure. 3.2. Typically, 0.30 g of catalyst was packed between the two layers of the glass wool. The reactor was placed in an electrical furnace equipped with K-type thermocouples. The temperature of the catalyst bed was monitored and controlled by Shinko temperature controllers. The reaction temperature was carried out in the range of 325-425°C. Oleic acid was fed 1.0-5.0 ml h<sup>-1</sup> by the ISCO model 260D high pressure liquid syringe pump with the dilute of nitrogen gas. The flow rate of nitrogen was kept at 50 ml min<sup>-1</sup> by the use of Brooks mass flow controllers. The products stream at the reactor outlet was condensed by two condensing traps that kept at room temperature and immersed in the ice/water bath.



**Figure 3.2** Schematic diagram of fixed-bed continuous flow deoxygenation system

### 3.4.2 Dye Adsorption Experiments

Three dyes from different classes namely, acid yellow 41, basic blue 49, and reactive red 198, were selected for evaluating the adsorptive capacities of sewage sludge derived char. Dye structures and their characteristics presented as in Figure 3.3 and Table 3.1, respectively. For adsorption experiments, ca. 0.150 g of each char sample was mixed with a 50 cm<sup>3</sup> dye solution of a concentration range between 10–750 mg l<sup>-1</sup> in a closed Erlenmeyer flask without further pH adjustment. The flask containing suspension was then shaken for 48 hrs using a horizontal shaker operated at 150 rpm. Preliminary adsorption tests indicated that the holding time of 48 hrs is enough for the suspension to reach its equilibrium. For each set of experiments, a blank test (without adsorbent) was always carried out.

After 48 hrs, the suspension was filtered and the remaining dye in the supernatant was analyzed using a Shimadzu UV-Vis spectrophotometer Model UV-2550 at its maximum absorption wavelength as indicated in Table 3.1.



**Table 3.1** Dye characteristics

Class <sup>a</sup>	Commercial name	Generic name	$\lambda_{\max}$ <sup>b</sup>
Acid	Telon light yellow FG	C.I. acid yellow 49	402
Basic	Astrazon blue FGGL	C.I. basic blue 41	606
Reactive	Remazol red RB	C.I. reactive red 198	518

<sup>a</sup> monoazo in chemical class

<sup>b</sup> maximum adsorption wavelength