CHAPTER III

EXPERIMENTAL

3.1 Materials and Chemical Reagents

3.1.1 Preparation of polymer containing sulfonic acid group by oxidation method

1. Crumb rubber (Thai Union Commercial Development Company Limited)
2. Hydrogen peroxide solution (H_2O_2, 30%) (AR grade, Fisher Chemical)
3. Formic acid (HCOOH, 98%) (AR grade, MERCK)
4. Nitric acid (HNO_3, 65%) (AR grade, QREC)
5. *n*-Hexane (n-C_6H_{14}, 65%) (AR grade, QREC)
6. Deionized water

3.1.2 Catalyst Characterization

1. Sodium chloride (NaCl, 99.8%) (AR grade, QREC)
2. Sodium hydroxide (NaOH, 99%) (AR grade, QREC)
3. Tetrahydrofuran (C_4H_8O, 99%) (AR grade, QREC)
4. Barium nitrate ($Ba(NO_3)_2$, 99.5%) (AR grade, Ajax Finechem)
5. Phenolphthalein indicator ($C_{20}H_{14}O_4$)
6. Methyl orange ($C_{14}H_{14}N_3NaO_3S$, Dye content 85%) (ACS reagent, SIGMA Aldrich)
7. Sodium carbonate (Na_2CO_3, 99.5%) (ReagentPlus®, SIGMA Aldrich)
8. Ammonium hydroxide solution (NH_4OH, 28-30% w/w) (ACS reagent, Fisher Chemical)
9. Hydrochloric acid (HCl, 37%) (AR grade, SIGMA Aldrich)

10. Barium chloride dihydrate ($BaCl_2$, 99%) (ACS reagent, SIGMA Aldrich)
11. Silver nitrate ($AgNO_3$) (ACS reagent, SIGMA Aldrich)
12. Toluene (C_7H_8, 99.5%) (AR grade, QREC)
13. Ethanol (C_2H_5OH, 96%) (ACS reagent, MERCK)
14. Acetic acid glacial (CH_3COOH, >99.8%) (AR grade, SIGMA Aldrich)
15. Sodium carbonate (Na_2CO_3, 99.5%) (ACS reagent, SIGMA Aldrich)

3.1.3 Catalytic esterification

1. Octanoic acid ($C_8H_{16}O_2$, >99%) (AR grade, SIGMA Aldrich)
2. Octanol ($C_8H_{18}O$, 99%) (GC grade, PANREAC)
3. 2-Ethyl-1-hexanol ($C_8H_{18}O$, 99%) (GC grade, Fluka)
4. Pyridine (C_5H_5N, 99.5%) (AR grade, QREC)
5. *n*-Heptane (n-C_7H_{16}, 99%) (GC grade, RCL Labscan Limited)
6. *n*-Hexane (n-C_6H_{14}, 99%) (AR grade, QREC)
7. Methyl undecanoate ($CH_3(CH_2)_9CO_2CH_3$, 99%) (GC grade, SIGMA Aldrich)
8. *N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide ($CF_3CON(CH_3)Si(CH_3)_3$) (Synthesis grade, SIGMA Aldrich)
9. Sodium sulfate (Na_2SO_4, >99%) (ACS reagent, SIGMA Aldrich)

3.2 Equipments and Apparatus

1. pH meter
2. Hot plate and stirrer
3. Hood
4. Paraffin oil bath
5. Reflux condenser

6. Vaccuum oven
7. Hot air oven
8. Shaker
9. Volumetric flask
10. Three-necked round bottom flask
11. Burette
12. Universal indicator paper
13. Beaker
14. Filter paper No.1 and 42
15. Syringe filter (0.2 micron)
16. Glass funnel
17. Stirring rod
18. Petri dish

3.3 Oxidation of Crumb Rubber to Prepare Rubbers Containing Sulfonic Acid Group

Crumb rubber with particle size of 2.5-5.0 mm was obtained from the Thai Union Commercial Development Company Limited. Composition and physical properties of the rubber as reported by the company are shown in Table 3.1. The oxidation of crumb rubber was carried out in a 100-mL three-necked round bottom flask equipped with a reflux condenser and a magnetic stirrer. Different concentrations of HNO_3 (2 M, 4 M, 6 M and 8 M) or H_2O_2 (10, 20 and 30 wt.%) were used as oxidizing agents. Typically, 10 g of crumb rubber was mixed with a solution of oxidizing agent (100 mL) in the flask. Oxidation temperature was controlled by an oil bath at 50 °C in case of using H_2O_2 and at 80 °C for HNO_3. After the reaction course, 5 h for H_2O_2 and 3 h for HNO_3, the oxidized crumb rubber was separated from the reaction mixture by filtration and washed thoroughly with deionized water until the filtrate became neutral. Then, the recovered crumb rubber was dried in a vacuum oven at 80 °C for 2 h. In addition to the typical method, the extraction of the oxidized rubber was used to remove non-functionalized and functionalized rubber by using the different solvents, *n*-hexane and ethanol. Typically, 3 g of the oxidized rubber was refluxed with 25 mL of solvent at 60 °C for 5 h. Then, the refluxed rubber was dried in a vacuum oven at 60 °C for 3 h. The oxidized crumb rubber prepared under different conditions are summarized in Table 3.2.

Table 3.1 Properties of crumb rubber from the Thai Union Commercial Development Co.,Ltd.

GRADE	UCD – 103
COLOR	BLACK
REFINATION	FINELY STRAINED AND REFINED
RAW MATERIAL	WHOLE TYRE
CHEMICAL ANALYTICAL DATA	
ACETONE EXTRACT (%)	15±3
ASH (%)	6±3
CARBON BLACK (%)	25±3
MOISTURE : LESS THAN (%)	1
RUBBER HYDROCARBON (%)	50±3
PHYSICAL PROPERTIES OF THE VULCANIZED RECLAIM	
SPECIFIC GRAVITY (AT 25°C)	1.14±0.02
MOONEY VISCOSITY (ML 1' +4' AT 100 °C)	60±15
HARDNESS (SHORE A)	55±3
TENSILE STRENGTH (PSI)	920MIN
ELONGAYION (%)	250 MIN

Table 3.2 The oxidized crumb rubbers prepared in this study

Sample name[1]	Oxidizing agent	Concentration	Reflux condition	
			Temp. (°C)	Time (h)
CR-H_2O_2(10%)	H_2O_2 with HCOOH[2]	10%	50	5
CR-H_2O_2 (20%)	H_2O_2 with HCOOH[2]	20%	50	5
CR-H_2O_2 (30%)	H_2O_2 with HCOOH[2]	30%	50	5
CR-H_2O_2 (20%NoF)	H_2O_2	20%	50	5
CR-H_2O_2 (30%NoF)	H_2O_2	30%	50	5
CR-HNO_3 (2M)	HNO_3	2 M	80	3
CR-HNO_3 (4M)	HNO_3	4 M	80	3
CR-HNO_3 (6M)	HNO_3	6 M	80	3
CR-HNO_3 (8M)	HNO_3	8 M	80	3

[1] The oxidized rubber was designed as CR-*X* (*Y*) where *X* represents the type of oxidizing agent, and *Y* indicates the concentration of oxidizing agent.

[2] The mole ratio of H_2O_2 with HCOOH was 1:1

3.4 Catalyst Characterization

Physicochemical properties of crumb rubber before and after the oxidation under different conditions were characterized by following techniques;

3.4.1 X-ray fluorescence spectrometry

X-ray fluorescence spectrometry (XRF) [3] was used to analyze the chemical composition in crumb rubber by using Philips PW2400 wavelength dispersive X–ray fluorescence spectrometer at the Scientific and Technological Research Equipment Centre of Chulalongkorn University.

Figure 3.1 shows the X-ray photon absorption of atom which performed the electron ejecting from the orbital. Normally, the X-ray photon energy is greater than the binding energy between an electron and the nucleus of atom. When the atom adsorb the X-ray photon energy enough, the inner electron (K-shell) within the lower energy level orbital becomes unstable and ejects to the outside while the outer electron (L or M-shell) within the higher energy level orbital transfers to replace the inner electron. This process emitted the photon which equal to the difference in energies between the level occupied by the inner and outer electron. The emitted photon is specific as the characteristic X-ray of the each element. Moreover, all observable elements within sample are usually determined by numbering in a set amount of time and the number of photons in the characteristic X-ray energy lines. The resulting are possible to identify the elemental composition in the samples and to measure quantity of each elements.

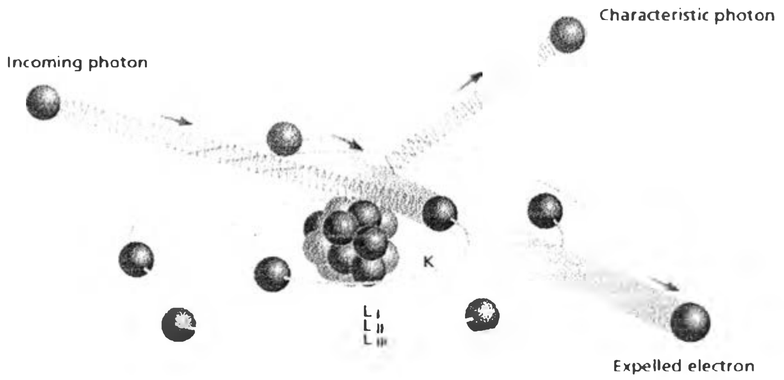


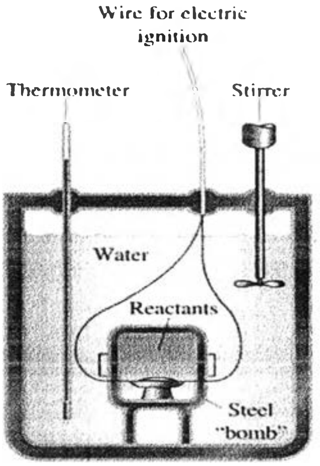
Figure 3.1 Production of characteristic radiation [3].

3.4.2 Bomb calorimetry

Bomb calorimetry was used to measure the sulfur content in crumb rubber before and after the oxidation. The procedure followed the standard method ASTM D3177 by using a PARR 6200 calorimeter.

Bomb calorimeter is the equipment used to determine the changing internal energy of sample. The energy was measured by the exothermic reaction from the combustion of organic substance with oxygen in the bomb calorimeter. This energy is the heating value of the combusted sample. The general reaction working in high pressure and constant volume shows in Figure 3.2. Furthermore, Bomb calorimetry can used to determine the amount of sulfur in a coal by precipitating the dissolved sulfur in the washing solution as $BaSO_4$ after cleaning the bomb with methyl orange. This method is continued the combustion by collecting the washing solution. It is controlled pH balance with sodium carbonate and ammonium hydroxide. After pH value reached to 7.0, the solution is boiled and filtered with the filter paper No.1.

Then, the filtrate is continuously stirred which was adding HCl and $BaCl_2$. This solution is continuously boiled overnight at the room temperature. Filter by the filter paper No.42 is used to collect the precipitate as $BaSO_4$. It is washed by hot water until 1 drop of $AgNO_3$ solution produces no more the presence of precipitate. Finally, the precipitate is combusted in the furnace at 850 °C for 3 h. The ash from combustion is weighted to determine the sulfur content in a coal.



$$C_xH_y + zO_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$

Figure 3.2 Schematic of the internal part of the bomb calorimeter.

3.4.3 Thermogravimetric/differential thermal analysis

Thermogravimetric/differential thermal analysis (TG/DTA) was applied to study the thermal degradation behavior of crumb rubber before and after the oxidation using a Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer. The platinum pan with 8-15 mg of sample was loaded on the sample holder in the analyzer. The temperature was heated from 40 to 1000 °C with a heating rate of 10 °C/min and a dried nitrogen flow (50 mL/min).

TG/DTA was used to examine the mass change of sample in a controlled atmosphere as a function of temperature or time. This technique is able to characterize the decomposition patterns, the degradation mechanisms, the thermal stability of sample, the organic and inorganic content in a sample which has useful for the simple chemical analysis. The analysis was performed by continuous weighting of sample in a controlled atmosphere as the temperature was increased at the constant heating rate. The applications of TG/DTA in the polymer field were determination of the thermal stability of polymers, compositional analysis and identification of polymers from their decomposition pattern. The TG/DTA data are normally plotted with the mass change on the vertical axis and the temperature on the horizontal axis.

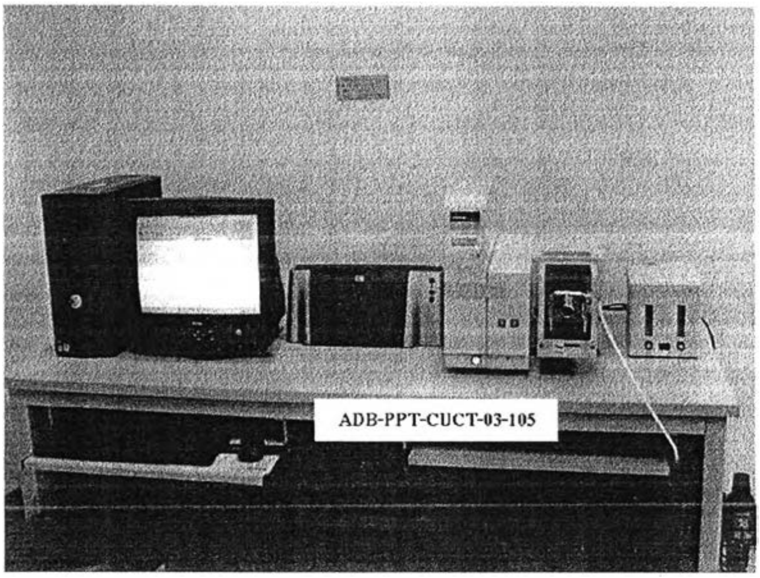


Figure 3.3 Perkin Elmer Pyris Diamond thermogravimetric/differential thermal analyzer.

3.4.4 Fourier transform infrared spectroscopy

Functional groups of the original and the oxidized crumb rubber were characterized by Fourier transform infrared spectroscopy (FTIR) using a Perkin Elmer (Spectrum One) infrared spectrometer at the Scientific and Technological Research Equipment Centre of Chulalongkorn University. The sample preparation followed the KBr method. The infrared spectra was recorded at room temperature for 64 scans over 4000-400 cm^{-1} at a resolution of 4 cm^{-1}.

FTIR was the simple and reliable method widely used in research and industry which covered both of organic and inorganic chemistry. This technique is used to analyze and examine the presence of certain functional groups in a molecule or the basic chemical compound of the sample in solid, liquid and gas phase. The result from this method was shown in the relation of wave number and transmittance called "Infrared spectrum" or "IR". The infrared spectrum was the part of electromagnetic radiation and had wave number at 12,800-10 cm^{-1} featured from far IR (200-10 cm^{-1}), mid IR (4000-200 cm^{-1}) and near IR (12800-4000 cm^{-1}). Typically, the spectrum at 4000-

400 cm^{-1} was useful for chemical structure identification. The examination was analyzed by the vibration or rotation of the infrared adsorbed molecule. The infrared spectrum adsorption of molecule, the frequency of the infrared had to equal with the frequency of molecule. Because of the specific vibration from the molecule adsorption, the organic compound gave the specific data to analyze their own chemical structure.

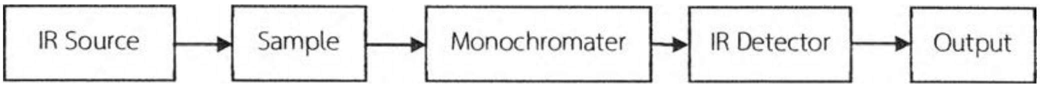


Figure 3.4 Instrument setup in a Fourier transform infrared spectrometer.

3.4.5 Scanning electron microscopy

Scanning electron microscopy (SEM) was used to study the morphology of crumb rubber before and after the oxidation. The SEM images were recorded on a JEOL JSM-5410 LV scanning electron microscope using a 15 kV electron beam with a magnification of 15-35,000. The SEM images of the samples were observed at 200X, 1,000X and 5,000X after coating the sample with gold.

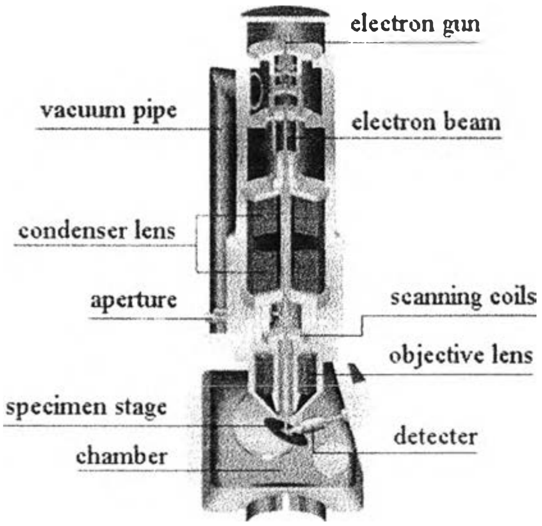


Figure 3.5 Schematic of scanning electron microscope [2].

Typically, SEM was used to analyze the surface of materials by measuring and evaluating surface pitting, failure analysis, characterization of dust, deposits, contaminants, particles, filter residues, and other applications. The SEM technique was performed by rastering the generated electrons cloud over the condenser lens. After passing the condenser, the electron was compressed to the electron beam and transferred to the objective lens. Then, the beam was scattered over the surface of specimen and emitted the secondary electrons. The secondary electrons were detected by the detector and translated the signal to the image on the display.

3.4.6 Swelling method

The swelling degree of samples was measured by swelling test following ASTM D471. Typically, 0.2 g of rubber was immersed in 5 mL of toluene at ambient temperature for 24 h. Then, the rubber was separated from the solvent by filtration. The solvent remaining on the rubber was carefully absorbed by tissue paper, and the weight of swollen rubber was measured. The swelling ratio (Q) was calculated according to the equation below;

$$Q = \frac{(M - M_0)}{M_0} \tag{3.1}$$

where Q is the swelling ratio, M is the mass of swollen rubber and M_0 is the dry mass of initial rubber. The swelling degree of polymer in organic and other solvents was important to investigate the swelling behavior of polymer for the ion-exchange application.

3.4.7 Sol/gel method

The sol and gel fraction of samples were measured by determination of gel fraction following ASTM D3616. The gel fraction was measured by immersing 0.2 g of sample in 25 mL of a solvent in a volumetric flask. Then, the flask was shaked on a shaker at 200 round per minute for 18 h to ensure that the sample was thoroughly dispersed in the solvent. After the end of period, the sample was separated from the solvent by filtration. Then, the sample was dried in hot air oven at 60 °C for 18 h. The sol fraction was calculated by the equation below;

$$Sol\ (\%) = \frac{W_0 - W_d}{W_0} \times 100 \quad (2)$$

$$Gel(\%) = 100 - Sol\ (\%) \quad (3)$$

where *Sol* (%) is the content of dissolved fraction in the sample, *Gel* (%) is the content of fraction remaining in the sample after equilibrating with the solvent, W_0 is the initial mass of sample and W_d is the total dried mass of sample after the process. The sol and gel fraction of polymer in organic compounds were important to explain the dissolution behavior of polymer for application as catalyst.

3.4.8 Acid-base titration for cation-exchange capacity

The ion-exchange capacity of the oxidized crumb rubbers was measured by an acid-base titration method. The data attained was reported in mmol/g of the oxidized crumb rubber which corresponded to the ion-exchange capacity or the acid content (H+). In this work, the acid content was analyzed by two titration techniques, the direct titration and the back titration. Figure 3.6 shows the flow diagram of two titration techniques. The direct titration was initiated by immersing the original crumb rubber or the oxidized crumb rubber in the solvent, DI water (deionized water) or DI water mixed with tetrahydrofuran (THF) 10/10 volume by volume, under stirring for the ion exchanging. After 18 h, the solution was titrated by sodium hydroxide (NaOH). On the other hand, the back titration was performed by immersing the original crumb rubber or the oxidized crumb rubber in 1 M sodium chloride (NaCl) under stirring. After 18 h, the solution was titrated by NaOH to calculate the ion-exchange capacity. These two techniques used phenopthalene as indicator in the titration step.

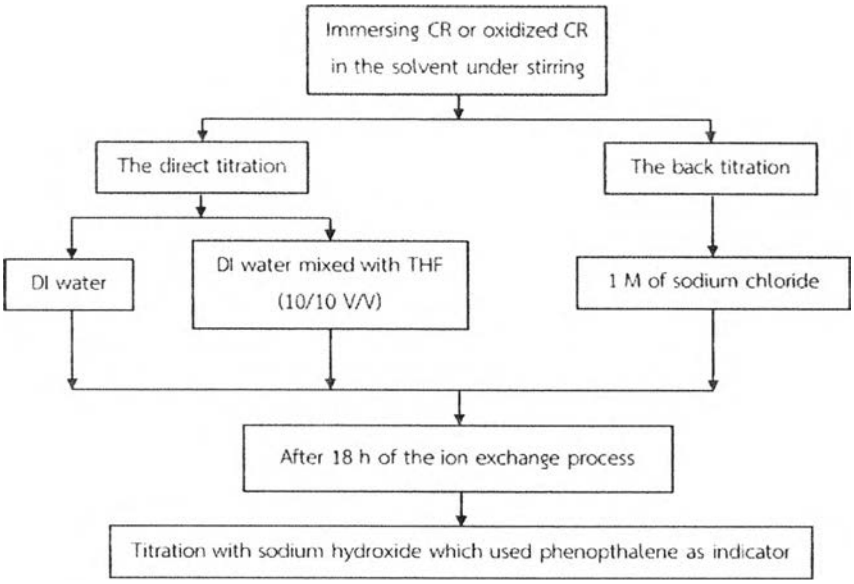


Figure 3.6 Flow diagram of two titration techniques.

3.5 Esterification of Octanoic Acid with Long Chain Alcohols

The oxidized crumb rubbers were studied for their catalytic activity in the esterification of octanoic acid with long chain alcohols. Figure 3.7 shows the equipment set up for esterification. The reaction was performed in a 100-mL three-necked round bottom flask connected with a reflux condenser and a magnetic stirrer. The reaction temperature was controlled at 120 °C by a paraffin oil bath for 8 h. Typically, the total batch size of reaction mixture was 20 g in which the molar ratio of alcohol/carboxylic acid was 2:1. Figure 3.8 shows flow diagram of the esterification. After the reaction, the acid conversion of the solution was analyzed by gas chromatography (GC) using an Agilent Technology 7890A GC system equipped with 15 m x 0.320 mm DB-5 HT column.

To prepare the sample for GC analysis, 3 mL of solution mixture from the reaction was filtered by syringe filter (pore diameter = 0.2 micron). The filtrate was dried by the suspension of anhydrous sodium sulfate (Na_2SO_4) for removing of water. Then, 0.1 g of filtrate was pipetted to completely mix with 2 g of pyridine. The 100 microliter of mixture was pipetted into a vial. After that, 100 microliter of *N*-Methyl-*N*-(trimethylsilyl)trifluoroacetamide ($CF_3CON(CH_3)Si(CH_3)_3$) or MSTFA was added to derivatize the mixture. For the complete derivatization, the sample had to continuously shake for 2-3 min and let the sample stand at room temperature for 15-

30 min. Then, 100 microliter of the internal standard which prepared from 0.6 g of methyl undecanoate ($CH_3(CH_2)_9CO_2CH_3$) or C-11 mixed with 25 mL of pyridine was added into the mixture. Finally, *n*-heptane was added for adjusting the volume of the mixture in a vial to reach 1 milliliter. The step for sample preparation for the GC analysis is shown in Figure 3.9.

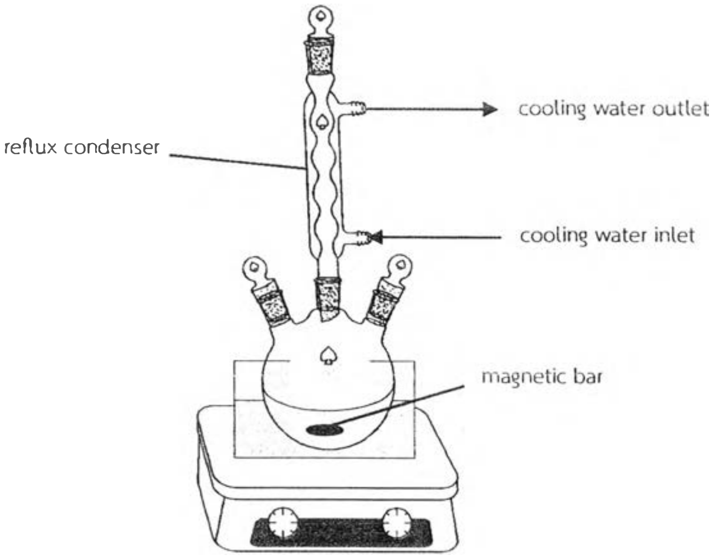


Figure 3.7 The equipment set up for the esterification.

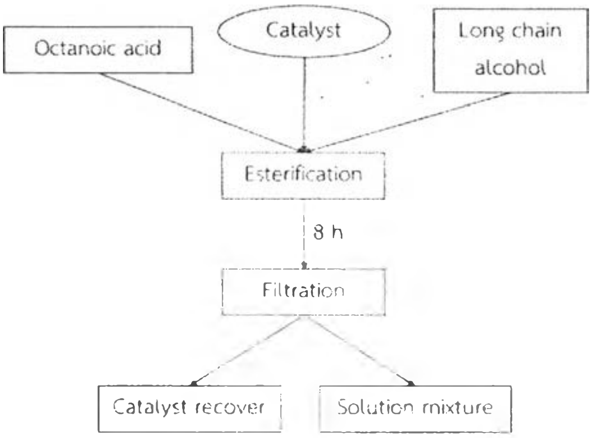


Figure 3.8 Flow diagram of the esterification.

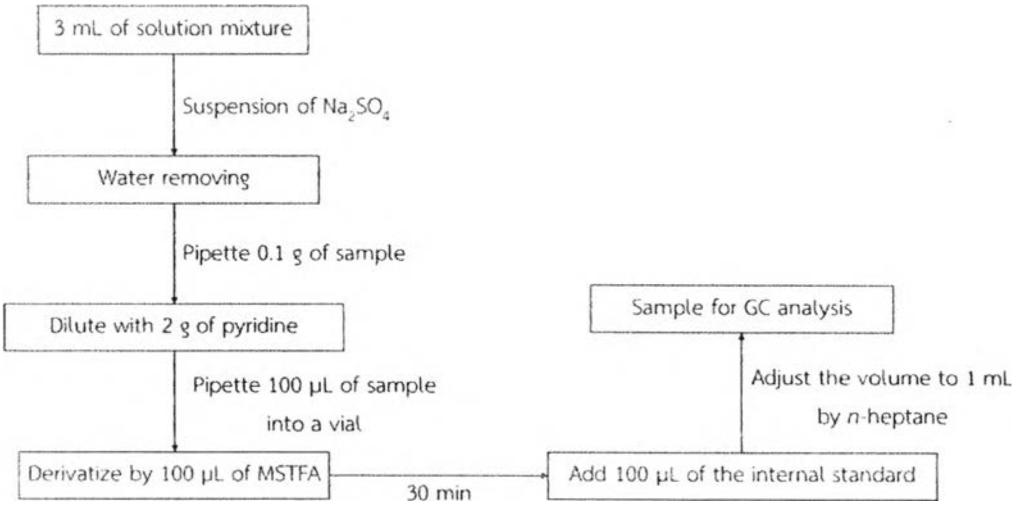


Figure 3.9 Flow diagram of the sample preparation for GC analysis.

For the catalyst recovery, the leftover solution mixture was filtered by the filter paper No.42. The complete filtration was performed overnight. Then, the recovered catalyst was washed with 150 mL of *n*-hexane to remove the reaction mixture remaining on the catalyst. Finally, the catalyst was dried in a hot-air oven at 60 °C for 5 h.

The analysis conditions for analyzing the acid conversion are summarized in Table 3.3. The column temperature program started at 50 °C and held at this temperature for 2 min to allow the solvent developed. Then, the temperature was increased to 170 °C at the constant heating rate of 15 °C/min. After that, the heating rate was changed to 25 °C/min for heating the column from 170 °C to 260 °C and maintained the final temperature for one min. The overall program took about 15 min for one sample. The schematic of column temperature program is shown in Figure 3.11.

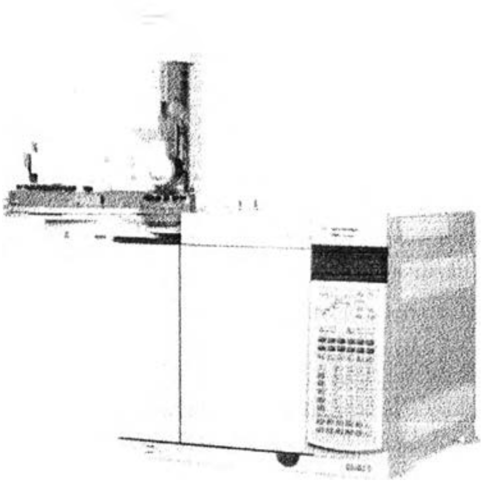


Figure 3.10 GC Agilent Technology 7890A GC system equipped with DB-5 HT column.

Table 3.3 The analysis conditions for analyzing the acid conversion

Condition	Value
Carrier (He) flow rate	3 milliliter
Hydrogen flow rate (for FID)	30 milliliter per minute
Air flow rate (for FID)	20 milliliter per minute
Detector temperature (for FID)	280 °C
Injection mode	Cool on column (COC)
Injection port temperature	200 °C
Injection volume	0.1 microliter
Initial column temperature	50 °C
Final column temperature	250 °C

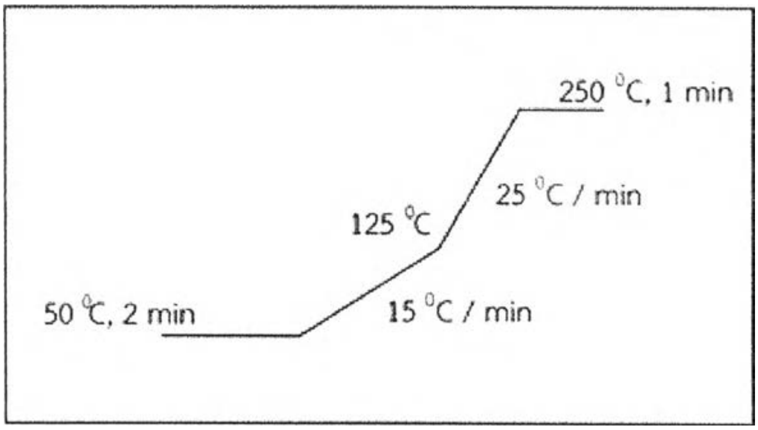


Figure 3.11 The temperature program of GC column for analyzing the acid conversion from the esterification of octanoic acid with long chain alcohols.