

CHAPTER III EXPERIMENTAL AND ANALYTICAL METHOD

3.1 Materials

3.1.1 Chemical for synthesis mesoporous materials and composites

- Tetraethoxysilane (TEOS) ($\text{SiC}_8\text{H}_{20}\text{O}_4$) (AR grade, 98%, Sigma Aldrich)
- 3-mercaptopropyltrimethoxysilane (MPTMS) ($\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$) (AR grade, >96%, TCI)
- Dodecylamine (DDA) ($\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2$) (AR grade, 98%, Sigma Aldrich)
- Natural rubber (NR) (commercial grade, Thai Hua Chumporn Natural Rubber Co., Ltd. (Thailand))
- Tetrahydrofuran (THF) (AR, grade, 99.5%, Wako Pure Chemical Industries, Ltd.)
- H_2O_2 (AR grade, 30%, Wako Pure Chemical Industries, Ltd.)
- Sulfuric acid (H_2SO_4) (AR grade, >95%, Fluka)
- Absolute ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) (AR grade, 99.5%, Wako Pure Chemical Industries, Ltd.)

3.1.2 Commercial catalyst

Nafion[®] SAC-13 is product of Sigma Aldrich. The physicochemical properties are shown in Table 3.1.

Table 3.1 The physicochemical properties of Nafion[®] SAC-13.

Composition	Surface area	Pore diameter	Pore volume	Density	Features and benefits
Fluorosulfonic acid Nafion [®] polymer on amorphous silica, 10-20% (porous nanocomposite)	>200 m^2/g	>10 nm	>0.6 mL/g	2.1 g/mL at 25 °C (lit.)	Stable to 200°C. Catalyst for acylations, alkylations, esterifications and isomerizations. 10x4 times more surface area than Nafion [®] pellets.



3.1.3 Chemical for esterification

- Absolute ethyl alcohol (C_2H_5OH) (AR grade, 99.5%, Wako Pure Chemical Industries, Ltd.)
- Acetic acid (CH_3COOH) (AR grade, 99.9%, Wako Pure Chemical Industries, Ltd.)
- Octanoic acid ($CH_3(CH_2)_6COOH$) (AR grade, >98%, Sigma Aldrich)
- Lauric acid ($CH_3(CH_2)_{10}COOH$) (AR grade, >98%, Sigma Aldrich)

3.1.4 Chemicals for reaction product analysis

- *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) (>98.5%, Aldrich)
- Tetrahydrofuran (THF) (AR, grade, 99.5%, Wako Pure Chemical Industries, Ltd.)
- Pyridine (C_5H_5N) (AR grade, 99.5%, Wako Pure Chemical Industries, Ltd.)
- *n*-Heptane (C_7H_{16}) (AR grade, 99%, Wako Pure Chemical Industries, Ltd.)
- *n*-Octane (C_8H_{18}) (AR grade, 99.%, TCI)
- *n*-Decane ($C_{10}H_{22}$) (AR grade, 99.%, TCI)

3.2 Instruments and equipment

- Three-neck round bottom flask 50 mL
- Duran glass bottle 250 mL
- Beaker, 250, 500 and 1000 mL
- Volumetric flask, 100, 250 and 500 mL
- Magnetic bar
- Hot plate stirrer
- Dropper
- Pipette and micro pipette
- Silicone bath



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- Condenser
- Oven
- Vacuum oven
- Muffle furnace
- Desiccator
- Filter paper, No. 1

3.3 Preparation of mesoporous silica and composites with NR

3.3.1 Hexagonal mesoporous silica (HMS) synthesis

HMS was synthesized using TEOS as the silica source and DDA as the organic template according to the procedure reported by Yin et al. [99]. Generally, DDA was dissolved in a solution of ethanol and deionized water under stirring for 15 min and then TEOS was added dropwise. The molar composition of the synthesis mixture was summarized in Table 3.2. The synthesis mixture was vigorously stirred for 0.5 h at 40 °C and then aged for 18 h at ambient temperature in order to obtain the HMS. Subsequently, the white solid product was recovered by filtration, thoroughly washed with deionized water, and dried at 100 °C overnight. Template was removed by extraction with 0.05 M H₂SO₄/ethanol at 70 °C for 8 h. The HMS synthesized in ethanol was assigned as HMS-E.

The preparation of HMS in THF as the synthesis media was also studied. The molar composition of the synthesis mixture was also summarized in Table 3.2. The synthesis procedure was similar to that of HMS-E. The hexagonal mesoporous material obtained was denoted as HMS-T.

Table 3.2 Synthesis molar composition of HMS-E and HMS-T.

Sample	Molar composition (mol%)				
	TEOS	DDA	H ₂ O	Ethanol	THF
HMS-E	0.1	0.03	2.94	0.08	-
HMS-T	0.1	0.03	2.94	-	0.37



3.3.2 Natural rubber and hexagonal mesoporous silica composites (NR/HMS) synthesis

The NR/HMS composites were synthesized via a sol-gel method adapted from the procedure reported by Chaichua et al. [85]. Firstly, 1 g of NR sheet with thickness of 1 mm was swollen in TEOS at ambient temperature for 16 h and then dissolved in THF under stirring to obtain a homogeneous solution. To this NR solution, DDA were added drop by drop under constant stirring, subsequent additional TEOS. After 1 h, deionized water was slowly added dropwise into the slurry and stirring was maintained at 40 °C for 0.5 h. The molar compositions of the synthesis mixtures are summarized in Table 3.3. The gel attained was aged at 40 °C for 3 days. After that it was precipitated in 100 mL of ethanol. The solid product was then filtered and then vacuum dried at 60 °C for 2 h. Finally, the template in mesoporous silica composite was removed by extraction as in section 3.3.1. The composite was hereafter assigned as NR/HMS-X where X represents the synthesis conditions, in terms of the molar composition of the components, as shown in Table 3.3.

Table 3.3 Synthesis molar composition of NR/HMS composites.

Sample	Molar composition (mol%)				
	TEOS	DDA	H ₂ O	NR	THF
NR/HMS-1	0.1	0.03	2.94	0.01	0.37
NR/HMS-2	0.1	0.03	4.42	0.01	0.37
NR/HMS-3	0.1	0.03	5.89	0.01	0.37
NR/HMS-4	0.1	0.04	2.94	0.01	0.37
NR/HMS-5	0.1	0.05	2.94	0.01	0.37
NR/HMS-6	0.1	0.07	2.94	0.01	0.37
NR/HMS-7	0.1	0.03	2.94	0.02	0.74
NR/HMS-8	0.1	0.04	5.89	0.01	0.37



3.3.3 Propylsulfonic acid-functionalized hexagonal mesoporous silica (HMS-SO₃H) synthesis

Propylsulfonic acid-functionalized hexagonal mesoporous silica (HMS-SO₃H) was prepared via sol-gel process and condensed with 3-mercaptopropyl trimethoxysilane. In a typical procedure, DDA was dissolved in a solution of THF and then deionized water was added under stirring. Subsequently, TEOS was added dropwise into the solution and the synthesis mixture was stirred at 40 °C for 0.5 h. After that MPTMS and H₂O₂ were added dropwise and stirring at 40 °C for 1 h. The molar compositions of synthesis mixture are summarized in Table 3.4. After ageing the resulting gel at ambient temperature for 18 h, the solid HMS-SO₃H was filtered and air dried overnight. The organic template was removed by extraction as in section 3.3.1. The HMS-SO₃H material was assigned as HMS-SO₃H (x) where x represents the MPTMS/TEOS molar ratio in the synthesis mixture.

Table 3.4 Synthesis molar composition of HMS-SO₃H materials.

Samples	Molar compositions					
	TEOS	DDA	H ₂ O	MPTMS	H ₂ O ₂	THF
HMS-SO ₃ H (0.1)	0.1	0.04	5.89	0.01	0.07	0.37
HMS-SO ₃ H (0.2)	0.1	0.04	5.89	0.02	0.14	0.37

3.3.4 Propylsulfonic acid-functionalized natural rubber and hexagonal mesoporous silica composites (NR/HMS-SO₃H) synthesis

The acidic mesoporous composite based on NR and hexagonal mesoporous silica (NR/HMS-SO₃H) was synthesized via the *in situ* sol-gel method using THF as the synthesis media. Typically, 1 g of NR sheet (1 mm thickness) was swollen in TEOS at room temperature for 16 h. The swollen NR sheet was then dissolved in THF to obtain a homogeneous solution. Subsequently, the NR solution mixed with DDA, and then TEOS was added dropwise with stirring. After 1 h, deionized water, MPTMS and H₂O₂ were sequentially added dropwise into the mixture with stirring and then the mixture was allowed to stand at 40 °C for 1 h. The molar compositions of synthesis mixture are summarized in Table 3.5. The resulting gel was aged at 40 °C for 3 d after



which it was precipitated in 100 mL of ethanol. The solid product was recovered by filtration, followed by drying under vacuum at 60 °C for 2 h. Finally, the template occluded in the mesopores of the composite was removed as in section 3.3.1. The composite was assigned as NR/HMS-SO₃H (x) where x represents the MPTMS/TEOS molar ratio used in the synthesis.

Table 3.5 Synthesis molar composition of NR/HMS-SO₃H composites.

Samples	Molar compositions						
	TEOS	DDA	H ₂ O	NR	MPTMS	H ₂ O ₂	THF
NR/HMS-SO ₃ H (0.1)	0.1	0.04	5.89	0.01	0.01	0.07	0.37
NR/HMS-SO ₃ H (0.2)	0.1	0.04	5.89	0.01	0.02	0.14	0.37
NR/HMS-SO ₃ H (0.4)	0.1	0.04	5.89	0.01	0.04	0.28	0.37

3.4 Material characterization procedure

3.4.1 Compositional and elemental analysis

Thermogravimetric/differential thermal analysis (TG/DTA)

The amount of NR and/or silica contained in the synthesis materials was determined by thermogravimetric/differential thermal analysis (TG/DTA), using a Perkin-Elmer Pyris Diamond thermogravimetric instrument. Approximately 10 mg of the sample was used and the temperature was ramped from room temperature to 1,000 °C at a heating rate of 10 °C min⁻¹ under a dry air flow.

Carbon, Hydrogen, Nitrogen and Sulfur (CHNS) analysis

The amount of sulfur incorporated in the mesoporous structure was evaluated using an Elementar Vario Micro Cube CHNS elemental analyser. The sulfanilic acid was used as standard with average value of 6 data to obtain corrective factor. Approximately 2 mg of the synthesis material was used analysing and corrected data with the corrective factor.



3.4.2 Surface functional groups analysis

Fourier-transform infrared spectroscopy (FTIR)

Fourier-transform infrared spectroscopy (FTIR) was applied for the identification of NR and/or functional groups in the synthesis materials using a JASCO FT/IR-4100 spectrometer equipped with a mercury cadmium telluride (MCT) detector. A self-supporting disk (20 mm, 10-20 mg) was placed in the quartz cell attached to a conventional closed-circulation system. The disk was pretreated by evacuation at 150 °C for 1 h. All the IR spectra were recorded under evacuation at 25 °C. A total of 64 scans over 400-4000 cm^{-1} at a resolution of 4 cm^{-1} were averaged for each spectrum.

Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (^{29}Si MAS NMR)

Nuclear Magnetic Resonance (NMR) has established itself as a major and unique analytical tool in the characterization on the structural features of solid materials. In case of sulfonic functionalized mesoporous materials, the presence of organo-sulfonic acid groups on the surface of materials and silica structure are confirmed using Solid-state ^{29}Si nuclear magnetic resonance (^{29}Si NMR) technique.

In solid-state NMR, it can generally deal with powder samples; that are samples consisting of many crystallites with random orientations. The nuclear spin interactions which affect solid-state NMR spectra, chemical shielding, dipole-dipole coupling and quadrupole coupling, are all dependent on the crystallite orientation. As a consequence, the NMR spectrum of a powder sample contains broad lines. Moreover, when the sample has several in equivalent nuclear sites, the powder patterns from each may overlap. The consequent lack of resolution in the NMR spectrum obscures any information that the spectrum may contain. From mentioned above, magic angle spinning (MAS) is a technique often used to perform experiments in solid-state NMR spectroscopy MAS is used extensively in the vast majority of solid-state NMR experiments where its primary task is to remove the effects of chemical shift anisotropy and to assist in the removal of heteronuclear dipolar coupling effects.



^{29}Si MAS NMR spectra were acquired on a JEOL-ECA400 NMR spectrometer at 79.4 MHz and a sample spinning frequency of 5 kHz to measure the relative concentration of silica species present in each material. The chemical shifts of the ^{29}Si MAS NMR spectra were quoted in parts per million (ppm) with tetramethylsilane as the internal standard. The resolution of the ^{29}Si MAS NMR spectra was sufficient for accurate peak assignments, and the relative peak area of each species was obtained by a curve-fitting analysis, using a series of Gaussian curves.

3.4.3 Structural analysis

X-ray Powder diffraction (XRD)

X-ray powder diffraction (XRD) is an instrumental technique used for identification of minerals, as well as other crystalline materials. XRD is a technique in which a collimated beams of nearly monochromatic X-rays is directed onto the flat surface of a relatively thin layer of finely ground material. XRD is a reliable technique that can be used to identify mesoporous structure. Typically, the XRD pattern of hexagonal symmetry shows five well-resolved peaks corresponding to lattice planes of Miller indices (100), (110), (200), (210), and (300). These XRD peaks appear at low angle (2-Theta angle between 0.5 and 3 degree) because the materials are not crystalline at atomic level, diffraction at higher angles is not observed.

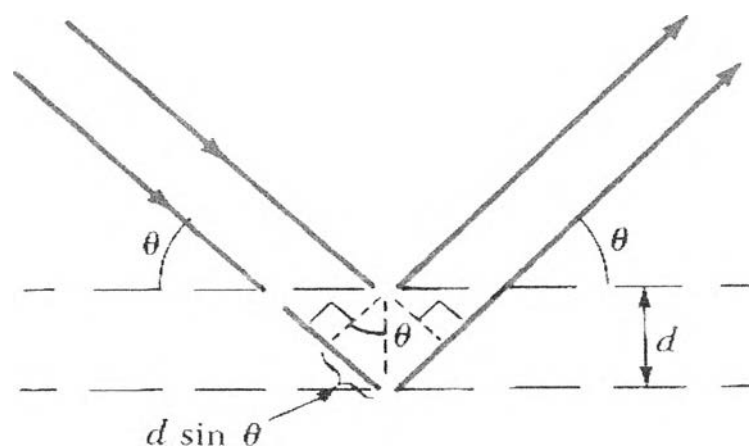


Figure 3.1 Diffraction of X-ray by regular planes of atoms.

Figure 3.1 shows a monochromatic beam of X-ray incident on the surface of crystal at an angle θ . The scattered intensity can be measured as a function of scattering angle 2θ . The resulting XRD pattern efficiently determines the different phases present in the sample. Using this method, Bragg's law is able to determine the interplanar spacing of the samples, from diffraction peak according to Bragg's angle using the equation 3.1.

$$n\lambda = 2d \sin\theta \quad (3.1)$$

Where the integer n is the order of the diffracted beam, λ is the wavelength; d is the distance between adjacent planes of the crystal (the d -spacings) and θ is the angle between the incident beam and these planes.

The structural information of the synthesis materials in this study was obtained using power X-ray diffraction (XRD). XRD patterns were obtained on a Rigaku Rint-Ultima III X-ray diffractometer employing Cu K α radiation and an X-ray power of 40 kV and 40 mA. The measurement was started from 2-Theta = 0.5 ° to 10 ° with a scanning step of 0.02° and a count time of 1 sec. The repeating distance (a_0) between pore centers of the hexagonal structure was calculated from the d -spacing of plane (100) (d_{100}) using the formula; $a_0 = 2d_{100}/\sqrt{3}$.

3.4.4 Textural properties and hydrophobicity measurement

N₂ adsorption-desorption measurement

The N₂ adsorption-desorption technique is used to classify the porous materials and its physical properties such as surface area, pore volume, pore diameter and pore-size distribution of solid catalysts. Adsorption of gas by a porous material is described by an adsorption isotherm, the amount of adsorbed gas by the material at a fixed temperature as a function of pressure. Porous materials are frequently characterized in terms of pore sizes derived from gas sorption data. The IUPAC classification of adsorption isotherms is illustrated in Figure 3.2.



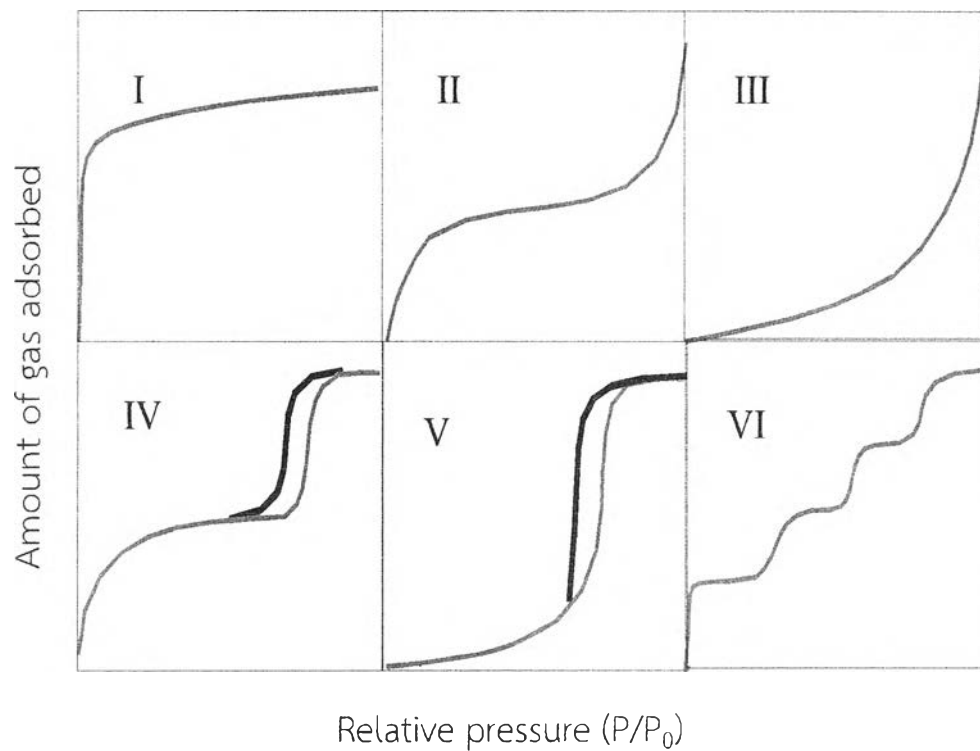


Figure 3.2 The IUPAC classification of adsorption isotherm.

The multipoint Brunauer, Emmett and Teller (BET) method is commonly used to measure total surface area using the equation in 3.2

$$\frac{1}{W[(P_0/P)-1]} = \frac{1}{W_m C} + \frac{C-1}{W_m C} (P/P_0) \quad (3.2)$$

Where W is the weight of nitrogen adsorbed at a given P/P_0 , W_m is the weight of gas to give monolayer coverage, and C is a constant that is related to the heat of adsorption. A slope and intercept are used to determine the quantity of nitrogen adsorbed in the monolayer and calculate the surface area. For a single point method, the intercept is taken as zero or a small positive value, and the slope from the BET plot is used to calculate the surface area. The surface area depends upon the method used, as well as the partial pressures at which the data are collected.

The textural properties of the synthesis materials were analyzed by nitrogen (N_2) adsorption-desorption measurement at $-196\text{ }^\circ\text{C}$ on a BEL Japan BELSORP-mini II instrument. The weight of the sample used (initially around 40 mg) was measured exactly after pretreatment at $150\text{ }^\circ\text{C}$ for 2 h. The Brunauer-Emmett-Teller (BET) method was employed to calculate the specific surface area (S_{BET}) in the relative pressure (P/P_0) range of 0.02–0.2 and the total pore volume (V_t) was obtained from the accumulative volume of N_2 adsorbed at a P/P_0 of about 0.990. The t -plot method was used to estimate the external surface area (S_{ext}). The primary mesopore volume (V_p) was calculated from the slope of linear portion of the t -plot in the relative pressure range above which N_2 was condensed inside the primary mesopores. The calculation of pore size (D_p) was performed by using the Barrett-Joyner-Halenda (BJH) method using the adsorption branch data of N_2 sorption isotherm.

H₂O adsorption-desorption measurement

The hydrophobic properties of the synthesized materials were studied by H_2O adsorption-desorption measurement. The weight of the sample used (initially around 60 mg) was measured exactly after pretreatment at $150\text{ }^\circ\text{C}$ for 2 h. The measurement was carried out by using a BEL Japan BELSORP-max instrument at $25\text{ }^\circ\text{C}$. The monolayer adsorbed volume (V_m) of H_2O was determined from analysis of adsorption data at a relative pressure below 0.2.

3.4.5 Electron microscopy

Scanning electron microscope (SEM)

Sample morphology was evaluated by scanning electron microscopy (SEM). The FE-SEM images were recorded on a Hitachi SU9000 scanning electron microscope operated at 30 kV. The samples on copper grids were observed without any metal coating.

Transmission electron microscopy (TEM)

TEM images were obtained from a JEOL JEM-2010F transmission electron microscope using an accelerating voltage of 200 kV. The TEM images were analysed for better resolution of mesopore arrangement in a two- and three-dimensional (2D and 3D) mode using the FemtoScan software (version 2.3.219). Wall thickness of mesopore channel was determined from the simulated 2D images. The distance of



20 nm was equivalent to 45 pixels. The data reported were average values of 20 different measured areas.

3.4.6 Particle size analysis

The particle size measurement was performed on a Nanotracs NPA252 particle size analyzer. The synthesis mixture after sol-gel process (~ 1 mL) was dispersed in deionized water. The number-average particle size (D_n) and the particle size distribution were analyzed using dynamic light scattering (DLS) mode.

3.4.7 Acidity measurement

The acid level of the functionalized materials was determined by acid-base titration. Typically, 0.5 g of sample was equilibrated with a 20-mL solution of THF and ethanol (50% (v/v)) under stirring at room temperature for 18 h. The resulting mixture was then titrated with 0.02 M NaOH aqueous solution. The acidity was calculated from Eq. (3.3);

$$N = \left(\frac{0.02 \times V}{1000 \times W} \right) \quad (3.3)$$

where N is the acidity (mmol g^{-1}), V is volume of NaOH solution consumed in the titration (mL) and W is sample weight (mg).

3.5 Esterification carboxylic acids and alcohols over acidic mesoporous silicas and composites

3.5.1 Study on the effect of type of acidic mesoporous catalysts

Esterification of various carboxylic acids with ethanol was carried out using SAC-13, HMS-SO₃H and NR/HMS-SO₃H as catalyst. This study used 3 types of carboxylic acids (acetic acid, octanoic acid and lauric acid) to esterification with ethanol. Esterification procedure was performed in a 50-mL three-neck round-bottom flask equipped with a reflux system and a magnetic stirrer. In a typical reaction, carboxylic acid and ethanol with 1:2 molar ratio of carboxylic acid: ethanol, were mixed in the flask. The reaction temperature was controlled using a silicone oil bath



at desired temperature as summarized in Table 3.6. Subsequently, the respective pre-treated catalyst (100 °C, 2 h) was added into the reaction mixture at 1 wt.% (based on the weight of carboxylic acid used). A certain quantity of the reaction mixture was withdrawn at different time intervals up to 8 h of the reaction course, immediately diluted with solvent, THF for acetic acid and ethanol esterification, pyridine for octanoic acid or lauric acid and ethanol esterification. And then, the sampling reaction mixture was prepared for composition analysis by gas chromatography (GC).

Table 3.6 Reaction condition of esterification carboxylic acids and ethanol.

Carboxylic acid /Alcohol	Esters	Reaction Temp.
Acetic acid/Ethanol	Ethyl acetate	80 °C
Octanoic acid/Ethanol	Ethyl octanoate	100 °C
Lauric acid/Ethanol	Ethyl laurate	120 °C

3.5.2 Study on the effect of catalyst amount

The effect of catalyst amount was studied as procedure in Section 3.5.1 in esterification octanoic acid with ethanol. The amount of catalyst was varied as 1 wt.%, 2 wt.%, 3 wt.% based on amount of octanoic acid.

3.5.3 Study on the effect of H₂O on catalytic activity

The effect of H₂O on catalytic activity of various acidic mesoporous catalysts was studied as procedure in Section 3.5.1 in esterification octanoic acid with ethanol. The amount of H₂O was added at initial with reactant mixture by using 5 wt.% based on amount of octanoic acid. In addition, the amount of catalyst was used 1 wt.% based on amount of octanoic acid.



3.6 Catalyst reusability of NR/HMS-SO₃H composite

After the course of octanoic acid and ethanol esterification in Section 3.5.1, the NR/HMS-SO₃H was recovered by a filtration, and washed with acetone to remove the organic phase covering on their surface from each reaction cycle, and then dried at 100 °C overnight before a new cycle was started with fresh reactants.

3.7 Reaction product analysis

The ester yield and residual carboxylic acid was determined by a Shimadzu GC-2014 gas chromatograph equipped with a 30-m DB-5 capillary column and a flame ionization detector (FID). The chromatograms of standard solution are shown in APPENDIX A.

The ester products were quantified according to an internal standard method. *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) was added into the liquid sample to convert the carboxylic acid to more volatile derivative, and then the sample volume was made up by adding *n*-heptane as solvent. The calculation of carboxylic acid conversion, percent ester yield, initial rate and turnover number (TON) can be seen in APPENDIX B.

Table 3.7 GC conditions for determination of residual carboxylic acid and ester content.

Condition	Value
Carrier gas (He) flow rate	3.0 mL/min
Total gas flow rate	38 mL/min
Column gas flow rate	0.69 mL/min
Detector temperature	200 °C (acetic acid and ethanol esterification) 250 °C (octanoic acid and ethanol esterification) 250 °C (lauric acid and ethanol esterification)
Split ratio	5
Injection port temperature	200 °C (acetic acid and ethanol esterification) 250 °C (octanoic acid and ethanol esterification) 250 °C (lauric acid and ethanol esterification)
Inject volume	1 μ L



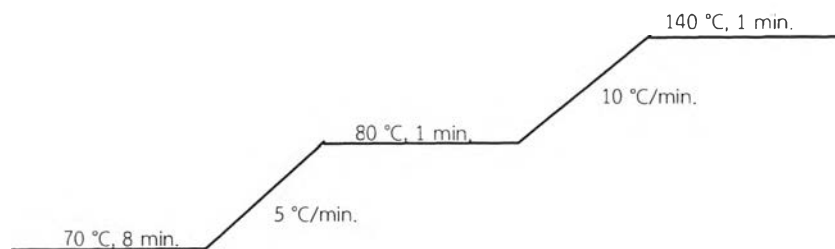


Figure 3.3 Temperature program of GC condition for acetic acid determination.

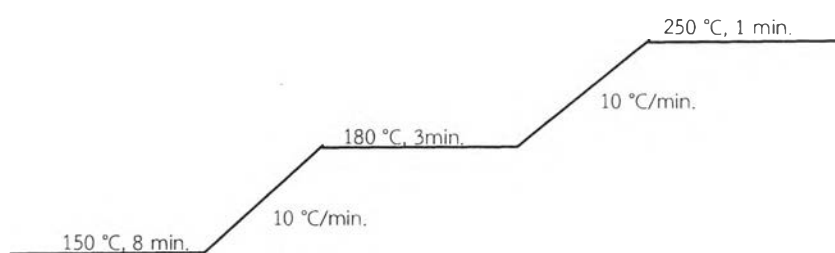


Figure 3.4 Temperature program of GC condition for octanoic acid and ethyl octanoate determination.

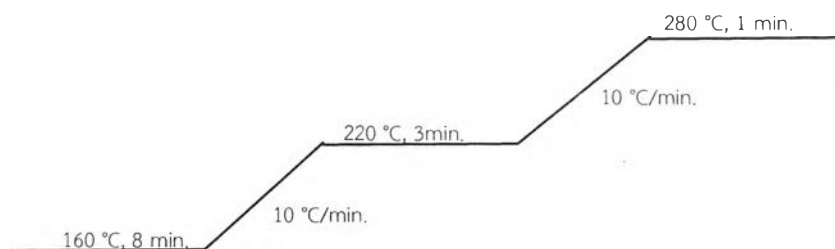


Figure 3.5 Temperature program of GC condition for lauric acid and ethyl laurate determination.

