CHAPTER III
EXPERIMENTAL

3.1 Materials and Equipments

3.1.1 Materials

Waste automobile tires (Bridgestone TURANZA GR-80) were first scraped and then sieved into the range of 20-40 mesh (425-850 μm).

3.1.2 Equipments

1. Oven and furnace
2. Vacuum Pump
3. Gas sampling bag
4. Rotary evaporator
5. Funnel and suction
6. Hydraulic pelletizer
7. Hot plate with stirrer
8. Bench-scale autoclave reactor
9. Sieves (20,40 and 60 U.S. mesh (ASTM))
10. LECO® Elemental Analyzer (TruSpec®S)
11. Surface Area Analyzer (SAA)
12. X-ray diffraction (XRD)
13. X-Ray Fluorescence (XRF)
14. Field Emission-Scanning Electron Microscope (FE-SEM)
15. Temperature Programmed Desorption (TPD)
16. Thermogravimetric/Differential Thermal Analysis (TG/DTA)
17. LECO® Elemental Analyzer, CHNS-932

3.2 Chemicals and Solvents

1. Tetrarthylorthosilicate (TEOS, 99 %, Merck)
2. Hexadecyltrimethylammonium bromide (CTAB, 99+ %, Aldrich)
3. Ethanol (EtOH, AR grade, RCI Labscan)
4. Aqueous ammonia solution (NH_4OH, 30 %, Merck)
5. Hydrochloric acid (HCl)
6. Sodium hydroxide (NaOH)
7. Nitric acid (HNO_3 65 %, RCI Labscan)
8. Carbon disulfide (CS_2)
9. n-Pentane ($CH_3(CH_2)_3CHk_3$, Assay $\geq$ 99 %)
10. Nitrogen gas (N_2)
11. Hydrogen gas (H_2)

3.3 Experimental Procedures

3.3.1 Catalyst Preparation

Al-MCM-41, Al-SBA-15, Si-MCM-41, Si-MCM-48, untreated char and $5MHNO_3$-treated char were prepared. Particularly, Si-MCM-41 and Si-MCM-48 were synthesized using the synthesis methods, and pyrolysis char was treated using the acidic treatment in the next following sub-sections. After preparation, all catalysts were pelletized, and then sieved to obtain a particle size in the range of 40-60 mesh (250-425 μm) prior to their utilization.

3.3.1.1 Commercial Al-MCM-41 and Al-SBA-15

Commercial Al-MCM-41 and Al-SBA-15 materials were supplied by Green Stone Swiss Co., Limited (Shanghai, China). They were calcined at 540 °C for 6 h with the heating rate of 2 °C/min to remove impurity prior to their utilization.

3.3.1.2 Synthesis Methods of Si-MCM-41 and Si-MCM-48

Si-MCM-41 material was synthesized using the procedure of Meléndez-Ortiz et al. (2014) whereas Si-MCM-48 was prepared using the procedure of Kibombo et al. (2014). Both materials were synthesized in the similar conditions. The difference was just only the ratio of the precursors as shown in Figure 3.1.
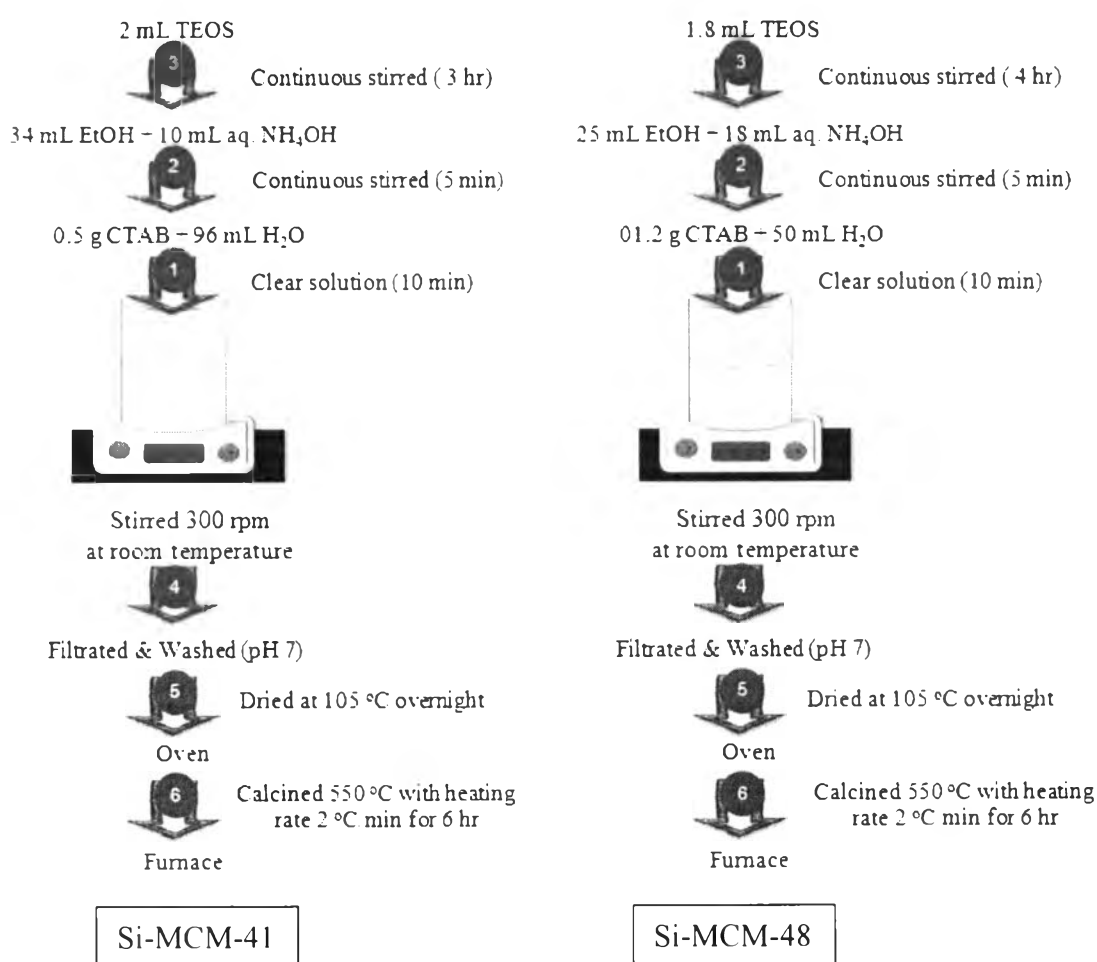

2 mL TEOS	1.8 mL TEOS
Continuous stirred (3 hr)	Continuous stirred (4 hr)
34 mL EtOH – 10 mL aq. NH$_4$OH	25 mL EtOH – 18 mL aq. NH$_4$OH
Continuous stirred (5 min)	Continuous stirred (5 min)
0.5 g CTAB – 96 mL H$_2$O	01.2 g CTAB – 50 mL H$_2$O
Clear solution (10 min)	Clear solution (10 min)
Stirred 300 rpm at room temperature	Stirred 300 rpm at room temperature
Filtrated & Washed (pH 7)	Filtrated & Washed (pH 7)
Dried at 105 °C overnight	Dried at 105 °C overnight
Oven	Oven
Calcined 550 °C with heating rate 2 °C min for 6 hr	Calcined 550 °C with heating rate 2 °C min for 6 hr
Furnace	Furnace
Si-MCM-41	Si-MCM-48

Figure 3.1 Synthetic Si-MCM-41 and Si-MCM-48.

3.3.1.3 Treatment Method of Pyrolysis Char

The acidic modification of pyrolysis char for removing sulfur contents and some metallic compounds was decried by Soltani *et al.*, (2014). The synthetic flow chart is presented as follows.
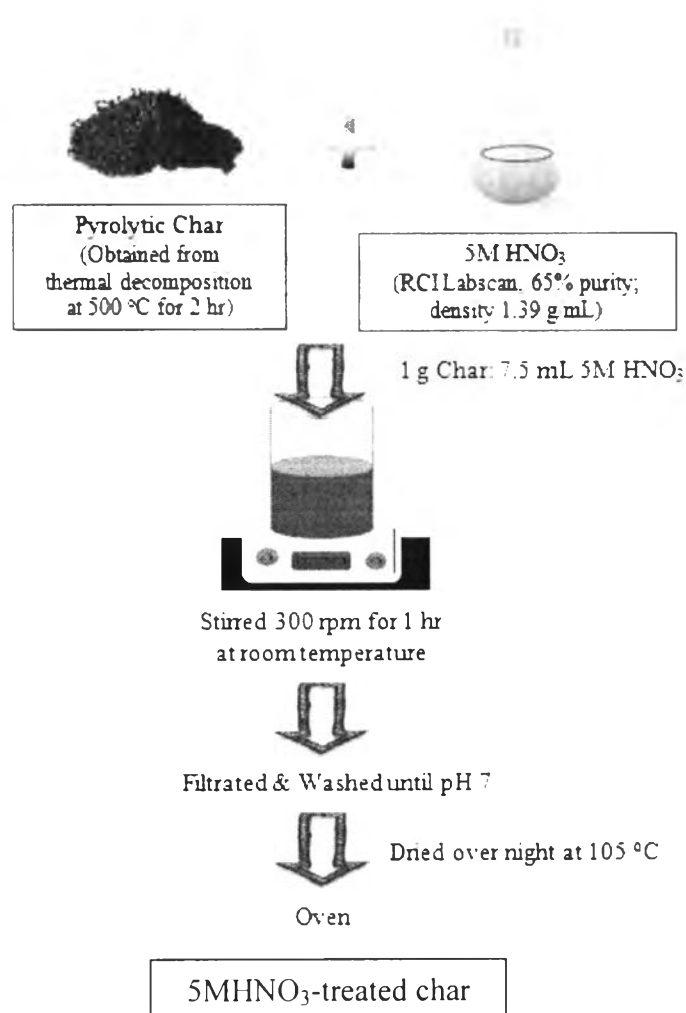

Figure 3.2 of pyrolysis char.

Figure 3.2 Acidic modification of pyrolysis char.

3.3.2 <u>Catalyst Characterization</u>

This work focused on the cracking ability of the mesoporous catalyst; thus, Surface Area Analyzer (SAA), X-ray diffraction (XRD) with small angle mode, X-Ray Fluorescence (XRF), Field Emission-Scanning Electron Microscope (FE-SEM), Temperature Programmed Desorption (TPD), Thermogravimetric/Differential Thermal Analysis (TG/DTA), and LECO® Elemental Analyzer-CHNS-932 (CHNS-analyzer) were used. The conditions of all instruments were showed bellow:

3.3.2.1 Surface Area Analyzer (SAA)

The surface area analyzer with the Brunauer-Emmett-Teller (BET) technique was employed to determine surface area, total pore volume and pore diameter of meso-catalyst, using Thermo Finnigan/Sorptomatic 1990, which is based on the physical adsorption of nitrogen gas. The sample is initially out-gassed to remove the humidity and volatile adsorbents adsorbed on the catalyst surface under vacuum at 300 °C at least 18 hours prior to analysis steps. After that surface area and pore diameter are obtained from the twenty-two-point nitrogen adsorption and desorption isotherm plot. Then, pore diameter distribution is calculated using the BJH method (using 0.05-0.1 g of sample).

3.3.2.2 X-ray diffraction (XRD)

The x-ray diffraction was used to characterize the crystallinity of catalysts. The patterns of the samples were obtained on a Rigaku RAD-C diffractometer using nickel-filtered Cu Kα X-ray source radiation (λ=1.5405Å) and operated at 40 kV and 100 mA under the following conditions: scan mode CONTINUOUS, slit (SS) 1° (DS) 1° (RS) 0.3 mm and present time 1s. And the step size was scanned by speeding 2° min^{-1} while the 2θ range was measured from 0.4° to 7° for small-angle mode, and 10° to 60° for wide-angle mode.

3.3.2.3 X-Ray Fluorescence (XRF)

The x-ray fluorescence spectrometry (AXIOS PW4400), which is a non-destructive analytical technique, was used to identify and determine the concentrations of elements present in the solid and powder samples. The samples were mixed with boric acid with the sample to boric acid mass ratio of 1:3, and then hydraulically pressed to give a flat surface. The conditions were set as follows:

internal flow of 4.10 min^{-1}, external flow of 2.49 min^{-1}, cabinet temperature of 29.97°C, primary temperature of 19.00°C, vacuum of 10.10 Pa, x-ray generation of 50 kV (60 mA), 150 μm of collimator, angle of 10.0002 degree, gas flow 0.90 h^{-1}, and gas pressure of 1020.8 hPa.

3.3.2.4 Field Emission-Scanning Electron Microscope (FE-SEM)

The microstructure of the catalysts was identified by the field-emission scanning electron micrographs, Hitachi Model S4800. The electrons were backscattered or emitted from the specimen surface to the samples that were placed on a stub and coated with gold by using ion-sputtering device. The specimen was scanned with a narrow beam of electrons. The quantity of electrons scattered as the primary beam bombards each successive point of the metallic specimen surface was measured by an electron detector and used to modulate the intensity of a second electron beam and forms an image on a TV screen.

3.3.2.5 Temperature Programmed Desorption (TPD)

The temperature programmed desorption analyzer was used to characterize total acidity and acid strength of catalyst. The catalyst was first pretreated at 150 °C for 30 minutes with He. Then, the system was cooled to 100 °C. Completed adsorption of NH_3 was occurred by using 1.13 % NH_3/N_2 for 1.5 hr. After that, 30 ml/min of He was flown for 30 minutes at 100 °C to remove the physical adsorption of NH_3. Finally, the system will be cooled to 40 °C then started the temperature programmed desorption from 40 °C to 800 °C with the heating rate of 10 °C/min.

3.3.2.6 Thermogravimetric/Differential Thermal Analysis (TG/DTA)

The thermogravimetric/differential thermal analysis was used to determine the weight of coke formation on catalysts. The sample was heated from the room temperature to 800 °C with the heating rate of 10 °C/min. Nitrogen and oxygen flow rate is set about 20 ml/min and 20 ml/min, respectively.

3.3.2.7 LECO® Elemental Analyzer, CHNS-932

The LECO® Elemental Analyzer, CHNS-932 was used to determine carbon, hydrogen, nitrogen, and sulfur contents in feed material, tire derived oil and spent catalyst. As the first, the 0.1 grams of sample was added to

ceramic boat. After that the boat was put into the analyzer with heating from room temperature to 600 °C. Then, it was hold for 15 min and further to 1,350 °C.

3.3.2.8 Back titration

The acidity of pyrolysis char was determined by using back titration (Makrigianni *et al.,* 2015). First, 0.1 g of char sample was placed in 40 mL of the 0.1 M NaOH and then stirred with 300 rpm at room temperature for 24 h. After that the solution was filtrated in order to remove char sample out, and 10 mL solution was collected to analyze. The phenolphthalein was dropped into the solution before titration with 0.1 M HCl. When the solution turn from colorless into slightly pink, the end point of titration was reached (3 replicates). The total acidity (mol/g) of char sample was calculated using Eq. (3.1) (Liu *et al.,* 2013), where [HCl], V_{HCl}, and m are concentration of hydrochloric acid (mol/L), volume of HCl (L), and mass of char sample (g).

$$\text{Acidity} = \frac{[\text{HCl}] \times V_{HCl}}{m} \qquad (3.1)$$

3.3.3 Pyrolysis Process

The pyrolysis process was shown in Figure 3.3. The reactor was divided into two zones: the lower zone was the pyrolysis zone where waste tire sample was placed, and the upper zone was the catalytic zone where a catalyst was packed. The reactor was heated from room temperature with 10 °C/min to the final temperature at 500 °C and 350 °C for lower and upper zones, respectively, and kept for 120 min at atmospheric pressure. Nitrogen gas was flown all the time at a flow rate of 30 ml/min to sweep the pyrolysis products to condensers and a gas sampling bag. The condensers were immersed in an ice-salt bath to collect the condensable products while the non-condensable products were passed through the condensers and collected by the gas sampling bag.
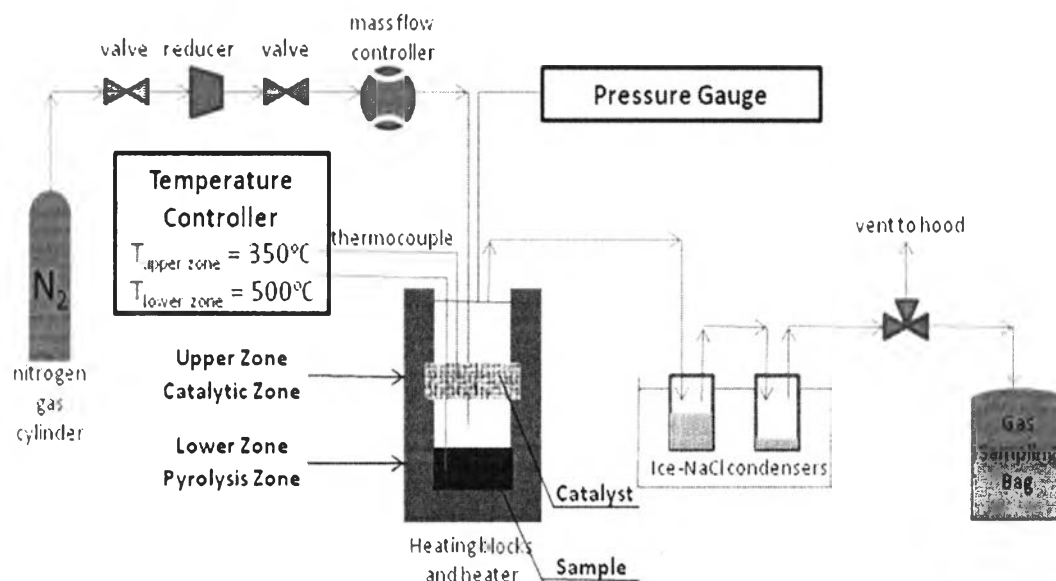
Figure 3.3 Schematic of the pyrolysis process (Yuwapornpanit, 2014).

3.3.4 Product Analysis

3.3.4.1 Liquid Analysis

Tire-derived oil was dissolved in n-pentane with the oil to n-pentane mass ratio of 1:40 before leaving for 18 hr in order to separate asphaltene out. The obtained oil is called maltene. After that the asphaltene was filtered out by using a 0.45 μm teflon membrane under vacuum system. The membrane and asphaltene were dried in an oven at 60 °C for 24 hr and weighed to determine the asphaltene content. Then, the *n*-pentane was evaporated from the maltene solution obtained after filtering by using a rotary vacuum evaporator at 50 °C. The remained oil was analyzed by using the LECO®Elemental Analyzer for sulfur content. Then, 30 μL maltene was diluted in 2 mL carbondisulfide (CS_2) before analyzing by GC×GC-TOF/MS and SIMDIST GC.

a) Two-dimensional Gas Chromatography with Time of Flight Mass Spectrometer (GC×GC/TOF-MS)

Table 3.1 Analysis conditions of GCxGC-TOF/MS

Conditions	Set Point
Oven Program	main GC oven: 50 °C, hold 2 min ramp 5 °C/min to 310 °C, hold 10 min secondary oven: 60 °C, hold 2 min ramp 5 °C/min to 320 °C, hold 10 min
Modulator	
- Time	4s for cycle time, 0.5s for holding time in repeat position
- Cryogen Coolant	nitrogen (UHP, 99.999%) (set at least -80 °C of modulation trap temperature)
Detector voltage	1600 V
Injector	
- Temperature	250 °C
- Splitless	1 µL
Carrier Gas	helium 99.99 % (flow rate 1 mL/min)
Mass Range Collection	30-500 m/z (transfer 100 spectra/s)
Data Processing	S/N = 10
Similarity	700 up
Percentage Area Calculation	Dt

The diluted maltene was analyzed to identify the chemical components using GC×GC/TOF-MS. The conditions are shown in Table 3.1. The Agilent gas chromatograph 7890 (Agilent Technologies, Palo Alto, CA, USA) was composed of a Pegasus® 4D TOF/MS (LECO, St. Joseph, MI, USA) and a thermal modulator. The instrument was operated by the cooperation of two GC columns. The 1st column was a non-polar Rtx®-5Sil MS with 30 m length × 0.25 mm ID × 0.25

μm film thickness installed in the main oven. The 2nd column was a polar Rxi$^{\text{R}}$-17 MS with 1.79 m length × 0.15 mm ID × 0.10 μm film thickness installed in the second oven. Total Ion Chromatograms (TICs) of maltenes obtained from GCxGC/TOF-MS were plotted in forms of 2D (Contour Plots) and 3D (Surface Plots) in order to observe the distribution of hydrocarbon groups in the chromatograms.

Table 3.2 PIANO standard

Components	Conc. (wt%)	Components	Conc. (wt%)
n-pentane	2.227	Toluene	2.576
n-hexane	2.421	Ethylbenzene	2.504
n-heptane	2.411	p-xylene	3.374
n-octane	2.426	Propylbenzene	2.423
n-nonane	2.446	Cumene	1.864
n-decane	2.387	3-ethyl toluene	1.953
n-undecane	1.761	1,2,4 trimethyl benzene	1.772
n-dodecane	2.189	1,3,5 trimethyl benzene	1.482
Isopentane	2.176	n-butyl benzene	2.456
2-methyl pentane	1.731	Isobutyl benzene	2.275
3-methyl pentane	1.798	1,2,4,5 tetramethyl benzene	1.261
2,2 dimethyl butane	1.609	n-pentyl benzene	2.417
2,3 dimethyl pentane	2.914	Cyclohexane	2.422
2,4 dimethyl pentane	1.823	Methylcyclohexane	2.425
2,2,4 trimethyl pentane	2.295	Ethylcyclohexane	2.461
2-methyl-1-heptene	1.344	Propylcyclohexane	2.419
Benzene	2.425	N-butylcyclohexane	1.208
		N-pentylcyclohexane	2.387

The external standard (PIANO, Spectrum Quality Standards, Ltd.) was also used for calibrating the peaks of GCxGC/TOF-MS chromatogram. The standard concentration (known concentration) of each component is reported in Table 3.2. The PIANO standard was firstly diluted in CS_2 in the PIANO standard/CS_2 volume ratio of 1:10 and then the 30 μL diluted standard was further diluted in 2 mL CS_2 prior to analysis with GCxGC/TOF-MS instruments. The average peak area of petrochemical products (BTEXC), detected from GCxGC/TOF-MS, is reported in Table 3.3.

Table 3.3 Average peak area of some petrochemical products (BTEXC) in PIANO standard detected from GCxGC/TOF-MS

Components	Retention Time (s)		Avg. Peak Area	Avg. Peak Area percentage (%)
	1D	2D		
Benzene	435-440	2.02-4.65	4,359,114	1.713
Toluene	655-1835	0.30-2.55	3,263,826	1.288
Ethylbenzene	940-945	0.32-2.43	7,726,809	3.050
p-xylene	970	2.36	6,955,656	2.754
Cumene	1120	2.31	6,241,609	2.459

The quantification of component is shown in Eq. (3.2) where [STD], A_{STD}, and A_{comp} are defined as known concentration of PIANO standard (wt%), average peak area of standard detected from GCxGC/TOF-MS, and peak area of component detected from GCxGC/TOF-MS, respectively.

$$\text{Component Concentration (wt\%)} = \frac{A_{comp}[STD]}{10A_{STD}} \qquad (3.2)$$

b) *Simulated Distillation Gas Chromatography (SIMDIST GC)*

The maltene was analyzed for simulating true boiling point curves using a Varian GC-3800 simulated distillation gas chromatograph (SIMDIST-GC) equipped with a 15 m × 0.25 mm × 0.25 μm WCOT fused silica capillary column and FID. The maltene was analyzed according to the ASTM D2887 method as reported in Table 3.4: The true boiling point curves were cut into petroleum fractions according to their boiling points as reported in Table 3.5.

Table 3.4 Analysis conditions of SIMDIST GC

Conditions	Set Point
Initial temperature (°C)	30
Time at initial temperature (min)	0.01
Heating rate (°C/min)	20
Final temperature (°C)	320
Holding time (min)	8.50

Table 3.5 Hydrocarbon ranges divided into the simulating true boiling point by using SIMDIST GC

Hydrocarbon Ranges	Boiling Point (°C)
Gasoline	< 149
Kerosene	149-232
gas oil or diesel	232-343
light vacuum gas oil or fuel oil	343-371
heavy vacuum gas oil	> 371

3.3.4.2 Gas Analysis

Gas Chromatography, Agilent Technologies 6890 Network GC system, using HP-PLOT Q column: 30 m x 0.32 mm diameter (ID) and 20 μm film thicknesses with FID detector and He carrier gas was used to analyze incondensable gas products collected by a gas sampling bag as reported in Table 3.6.

Table 3.6 Analysis conditions of GC/FID

Conditions	Set Point
Initial temperature (°C)	70
Time at initial temperature (min)	8
Heating rate (°C/min)	20
Holding time (min)	16
Final temperature (°C)	200
Holding time (min)	30

The standard gas containing methane (1 %), ethylene (1 %), ethane (1 %), propylene (0.5 %), propane (1 %), mixed C4 (2 %), and mixed C5 (1 %) was used for calibrating GC/FID and examining the response factors. The response factors were calculated on the weight basis using methane as the standard. The mass of each gas component (G_i) was calculated using Eq. (3.3) and then, the response factor of each gas component was calculated using Eq. (3.4), where A is defined as the detected area from GC/FID. The response factors are reported in Table 3.7.

$$G_i = (4.0220 X 10^{-7})(\%_i)(Mw_i) \tag{3.3}$$

$$f_i = \left(\frac{A_{std}}{A_i}\right)\left(\frac{G_i}{G_{std}}\right)(f_{std}) \tag{3.4}$$

Table 3.7 Response factors of gases

Gas	Retention Time (s)	Response Factor (f_i)
Methane	2.755-2.759	1.0000 ± 0.0000
Ethylene	3.605-3.606	0.9779 ± 0.0014
Ethane	4.006-4.008	0.9663 ± 0.0022
Propylene	9.225-9.237	0.8555 ± 0.0013
Propane	9.722-9.736	0.9610 ± 0.0017
Mixed-C4	13.681-15.195	0.9271 ± 0.0039
Mixed-C5	16.804-18.280	0.9841 ± 0.0000