

Chapter 3

Experimental Procedures

3.1 Catalysts

Three commercial alumina based catalysts were chosen for this study, namely; Eta alumina (a commercially pure Syndol catalyst), ZSM-5 (a zeolite supplied by Süd-Chemie) and Siralox 40 (an amorphous silica alumina supplied by Sasol Germany).

3.2 Catalyst preparation

All three catalysts were crushed using a mortar and pestle and sieved to yield a fraction between 300 μm and 500 μm . The composition of the catalysts was assumed to be homogeneous for all size fractions since the fractions were taken from the bulk catalysts. The catalysts were calcined overnight in a muffle furnace at 400 °C. The catalysts were left to cool from 400 °C to ambient temperature.

3.3 Apparatus

3.3.1 Reactor

A bench scale fixed bed reactor system (Reactor 16) was used (Figure 3.1). Fixed bed reactors are one of two general types of plant-size reactors commonly used in industrial catalytic processes [Bartholomew et al., 2006]. The advantages of fixed bed reactors are:

1. They approach ideal plug flow;
2. There is little loss or attrition of catalyst;
3. A large variation in operating conditions and contact times is possible;
4. Long residence times to complete reaction and usually a high ratio of catalyst to reactants exist; and there is little wear on the equipment.

Fixed bed reactors' most serious disadvantages are their inefficient heat transfer with associated ineffective temperature control and difficulty in regenerating or replacing spent catalyst [Bartholomew et al., 2006].

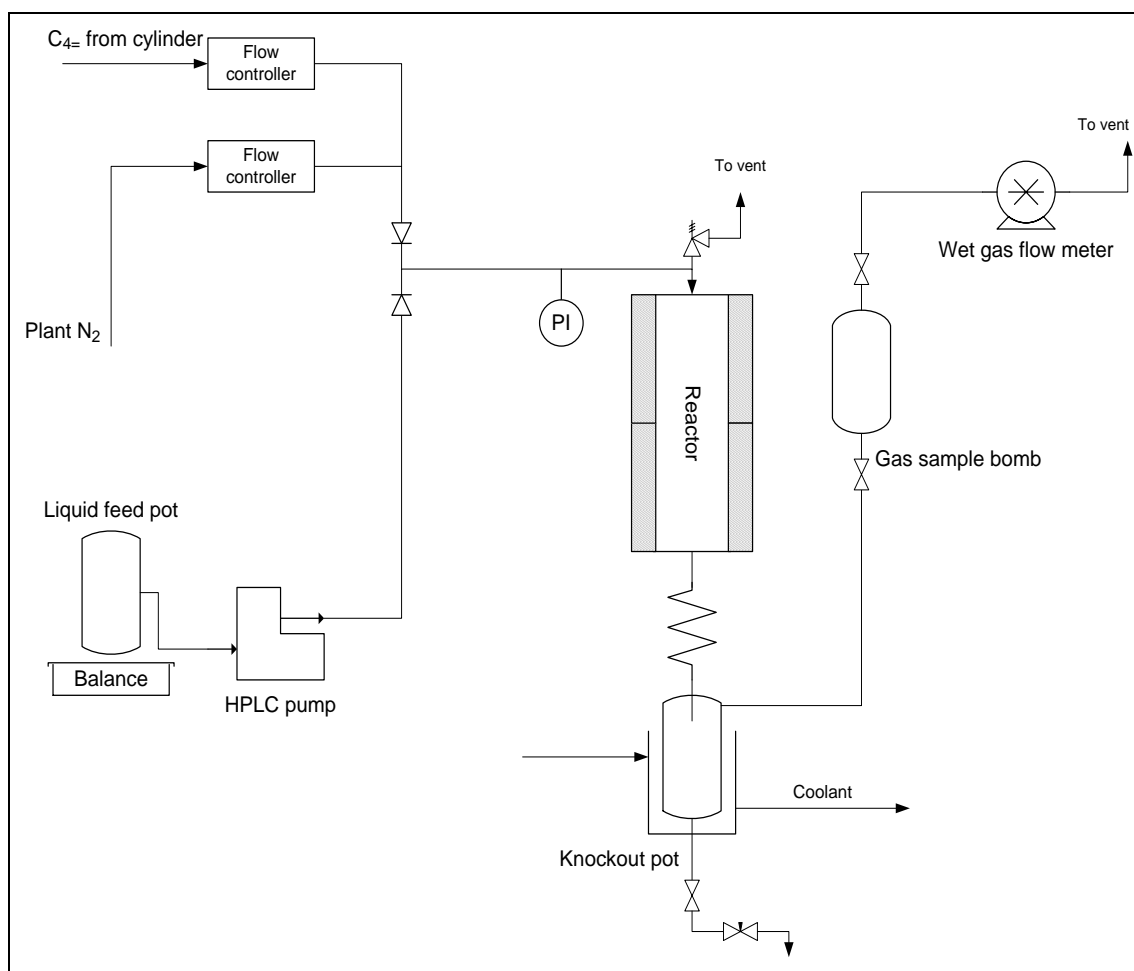


Figure 3.1: Process Flow Diagram of reactor system used in all experimental runs

3.3.2 Determining the loading zone

A temperature profile for Reactor 16 (R16), in which all experiments were conducted, was done. The optimal isothermal regions were established by doing the temperature profile at a heater temperature of 360 °C with no flow/feed through the reaction. It is evident that the area where the temperature was most constant and thus at optimal isothermal conditions, was between 10 and 14 cm from the bottom of the reactor. The catalyst was loaded in this relatively constant temperature area as discussed in section 3.3.3.

3.3.3 Loading the reactor

The internal diameter of the reactor tube was 15 mm and the reactor length was 265 mm. The reactor was placed upside down in the vice and glass wool was inserted at the top of the reactor and thereafter glass beads were loaded in the pre-heating zone. The reactor was then loaded with the specific catalyst of which the bed lengths of the Eta alumina, ZSM-5 and Siralox 40 catalysts were, respectively 28, 32 and 44 mm (details on these are given in the following three sections). After the catalyst was loaded, glass beads were added to fill the

remaining space of the reactor (exit zone) and glass wool was added again to secure the glass beads. The reactor was operated isothermally in all instances.

The lengths of the catalyst bed for each catalyst differed slightly because the catalysts have different densities. 1.5 g of the each catalyst was weighed and the volume of each was measured with a measuring cylinder. The catalyst bed was diluted with Silicon Carbide - a volume equal to that of the catalyst [Buchanan et al., 1987]. The method of loading each catalyst bed follows and the profiles for each catalyst are illustrated in Figures 3.2, 3.3 and 3.4, respectively:

Catalyst bed of the reactor for Eta alumina catalyst

The catalyst bed of the reactor was loaded with 1.5 g crushed Eta alumina catalyst, which was equal to 2.1 ml and mixed with 2.1 ml of Silicon Carbide (SiC). The length of the catalyst bed was 28 mm of the total length (265 mm) of the reactor. The catalyst loading diagram is shown in Figure 3.2.

Catalyst bed of the reactor for ZSM-5 catalyst

The catalyst bed of the reactor was loaded with 1.5 g of crushed ZSM-5 catalyst, which was equal to 2.4 ml and mixed with 2.4 ml of SiC. The length of the catalyst bed was 32 mm of the total length (265 mm) of the reactor. The catalyst loading diagram is shown in Figure 3.3.

Catalyst bed of the reactor for Siralox 40 catalyst

The catalyst bed of the reactor was loaded with 1.5 g crushed Siralox 40 catalyst, which was equal to 3.8 ml and mixed with 3.8 ml of SiC. The length of the catalyst bed was 44 mm of the total length (265 mm) of the reactor. The catalyst loading diagram is shown in Figure 3.4.

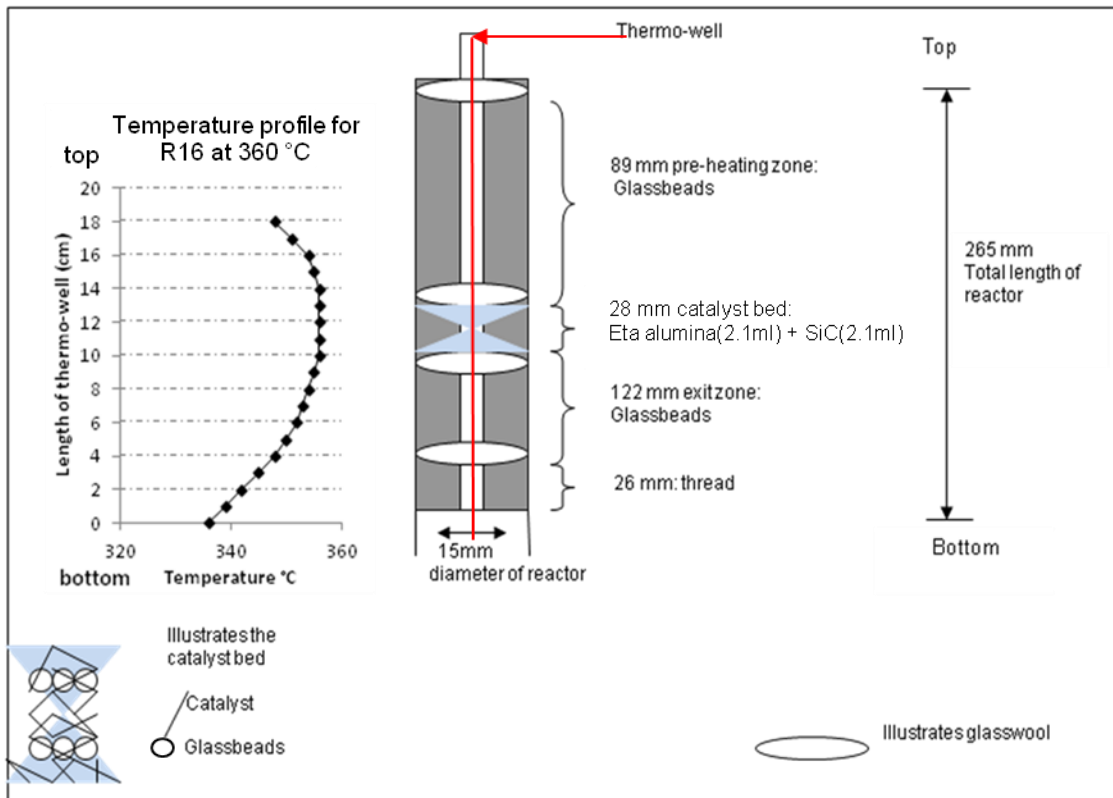


Figure 3.2: Temperature profile and loading diagram for Eta alumina catalyst

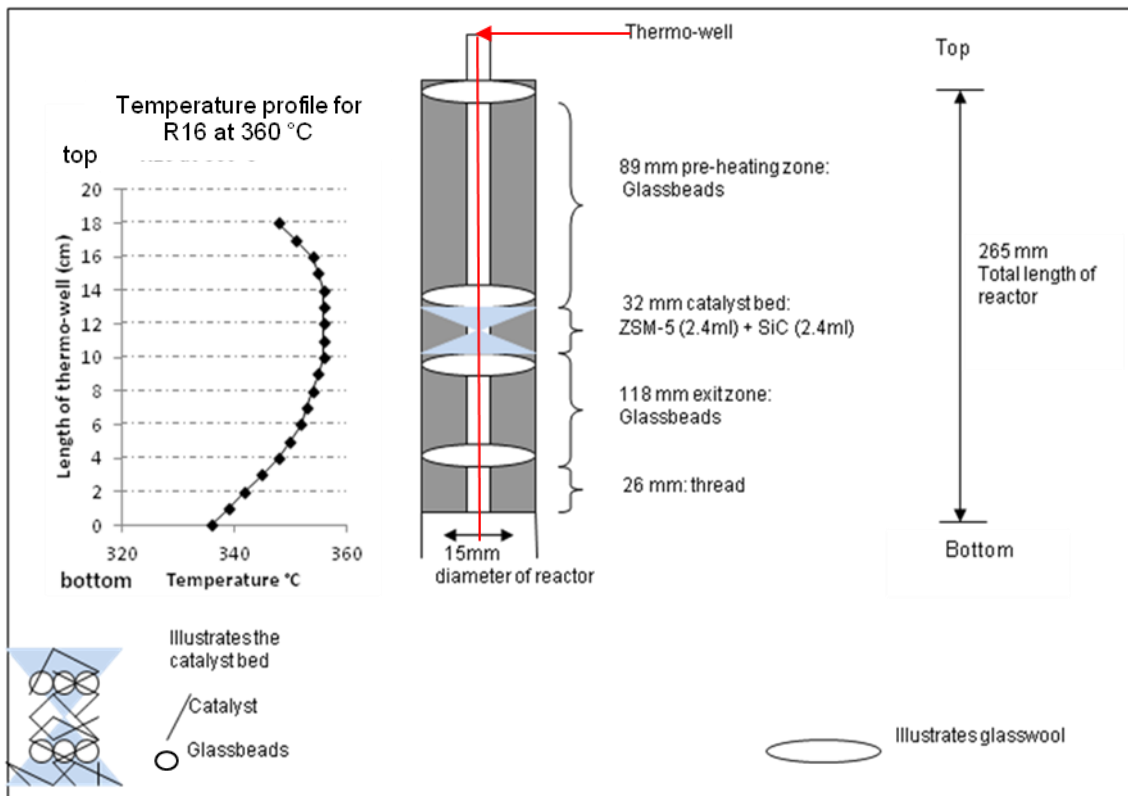


Figure 3.3: Temperature profile and loading diagram for ZSM-5 catalyst

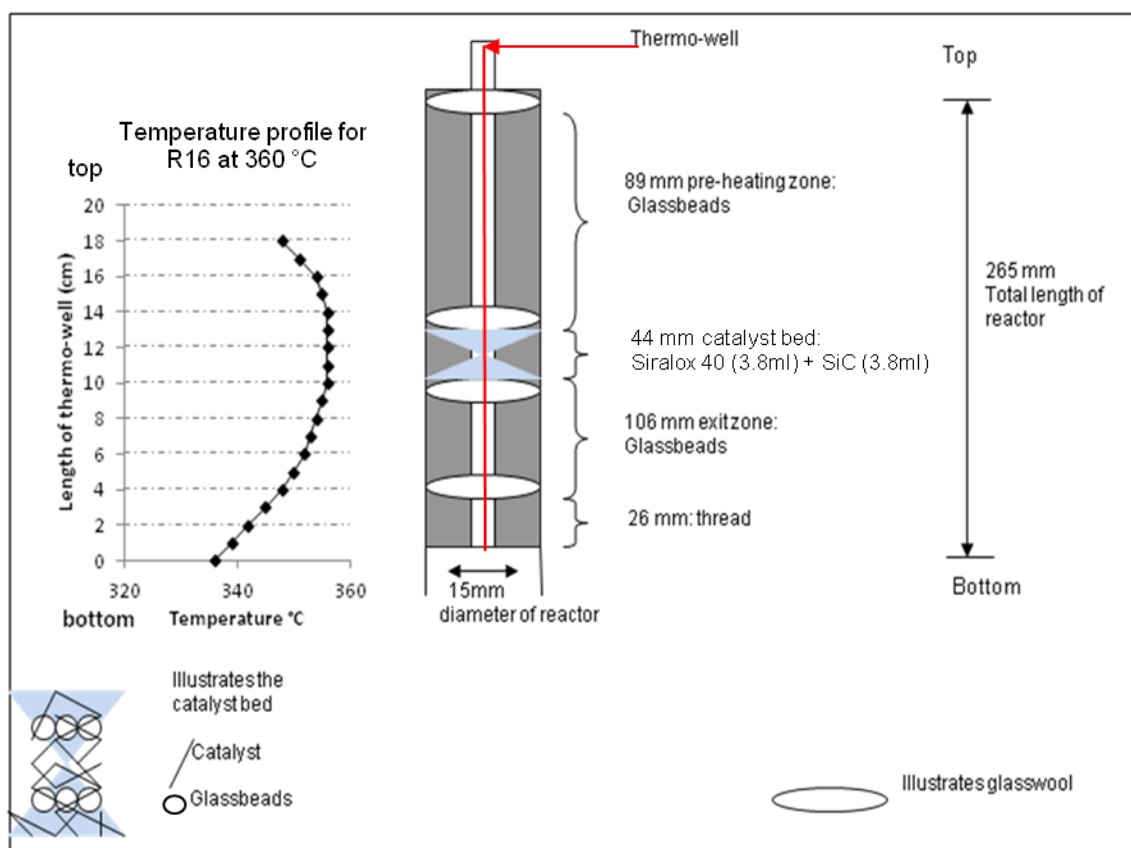


Figure 3.4: Temperature profile and loading diagram for Siralox 40 catalyst

3.3.4 Start up procedure for the various feeds

Before the experimental runs were started with the different feeds and catalysts, a blank run was done to confirm the inertness of the reactor system. This run, using 1-hexene is thoroughly described in Chapter 6.

The nitrogen Brooks flow meter was calibrated at 40 litres per hour (L/h). After the reactor was loaded, nitrogen was passed through the reactor at a flow rate of 32 L/h and a temperature of 400 °C for 16 hours. This was done to condition the catalyst.

1-Butene

The Brooks flow meter was calibrated to 15 L/h for 1-butene. Once the catalyst was conditioned the 1-butene was introduced at a flow rate of 3.3 L/h. This flow rate represents a weight hour space velocity (WHSV) of 5 hr⁻¹.

1-Hexene

Once the catalyst was conditioned the liquid feed containing 97% 1-hexene was introduced with an HPLC (High Performance Liquid Chromatography) pump. The 1-hexene was fed at a constant flow rate of 0.19 ml/min, *i.e.* a WHSV of 5 hr⁻¹.

1-Octene

Once the catalyst was conditioned the liquid feed containing 98% 1-octene was introduced with an HPLC (High Performance Liquid Chromatography) pump. The 1-octene was fed at a constant flow rate of 0.19 ml/min, *i.e.* a WHSV of 5 hr⁻¹.

The operating conditions were as follows: A weight hour space velocity (WHSV) of 5 hr⁻¹, isothermal temperatures of 300 °C; 350 °C and 400 °C and atmospheric pressure. By default, all experiments started at 300 °C. The feed was introduced and the temperature was kept constant at 300 °C for two hours. The temperature was then stepped up by increments of 25 °C until the desired temperature was reached. Experiments were performed for approximately 100 hours.

3.3.5 Chemical reagents and materials used

The chemicals used during this study are summarized in the Table 3.1. 1-Butene, 1-Hexene and 1-Octene were used as the feed material. Nitrogen was used for the conditioning and start-up of the reactor. All the *n*-octenes and *n*-hexenes displayed in Table 3.1 were used for identification purposes which will be discussed in paragraph 3.4.4.

Table 3.1
Chemicals

Chemicals	*Supplier	Purity
1-Butene	Poly 2 Plant (Midlands)	**±93%
1-Hexene	Merck	97%
1-Octene	Merck	98%
Nitrogen	Afrox	97%
<i>Trans</i> -2-octene	Aldrich	90+%
<i>Trans</i> -3-octene	Aldrich	97%
<i>Trans</i> -4-octene	Aldrich	97%
<i>Cis</i> -4-me-2-pentene	Aldrich	97%
2-me-2-pentene	Aldrich	97%
2-hexene	Aldrich	97%

*All suppliers are based in South Africa

**See Chapter 4 on feed composition of 1-butene

General, physical, stability and toxicology data for butene, hexene and octene were obtained from material safety data sheets (MSDS) as indicated in Annexure A.

3.4 Product Characterization

An off-gas sample was taken with a gas-tight syringe through a glass sample bomb fitted with a rubber septum (Figure 3.1). The volume of gaseous product passing through the reactor was measured with a flow meter and analysed using a 7890A RGA (Refinery Gas Analysis) Series Agilent GC System (GC-RGA). See Annexure B for a description of the RGA method used. The liquid product was collected in a knock-out pot which was cooled with a chiller set at -3 °C. The knock-out pot was emptied after each off-gas analysis and analyzed using a 6890 Series Agilent GC System (Gas Chromatography – Mass Spectrometer (GC-MS)) and a 6890 Series Agilent GC System (Gas Chromatography – Flame Ionization Detector system (GC-FID)). See Annexure C for a description of the GC-MS method used and Annexure D for a description of the GC-FID method used. Samples of these two streams (gas and liquid) were collected simultaneously and analyzed separately. The data obtained from the two streams were combined for mass balance purposes.

3.4.1 Refinery Gas Analysis (RGA)

The 7890A RGA Series Agilent GC System was used to analyse the off-gas that was sampled every 24 hours. The RGA system was used to determine the composition of the gases.

The RGA system was set up in such a manner that the FID detected all the hydrocarbons, one TCD (thermal conductivity detector) detected hydrogen components while the other TCD detected nitrogen, carbon monoxide, oxygen and carbon dioxide [Kealy et al., 2002]. The RGA system was calibrated with a commercially available reference and the calibration was verified every time the RGA was used. A flow diagram of the RGA system is shown in Figure 3.5.

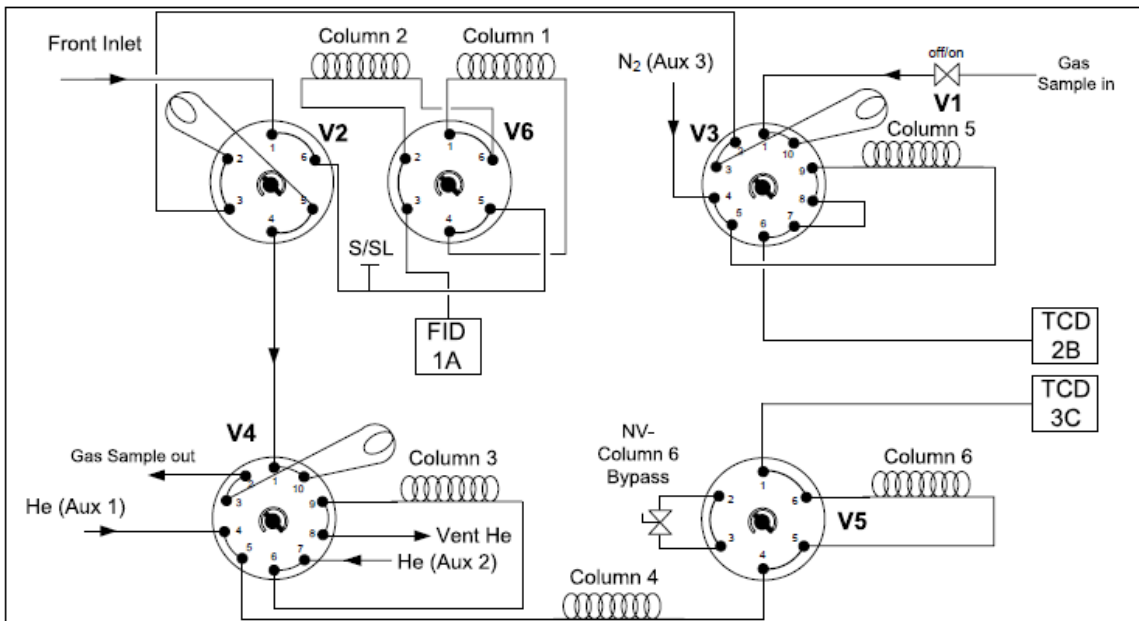


Figure 3.5: Flow diagram of Refinery Gas Analyzer

A description on the RGA method used is given in Annexure B.

3.4.2 Gas Chromatography – Mass Spectrometer (MS)

Liquid samples were taken every 24 hours during the experimental procedure. The 6890 Series Agilent GC system equipped with a mass selective detector (MSD) (Figure 3.6) was used to qualitatively and quantitatively identify the liquid compounds formed. A description on the GC-MS method used will be given in Annexure C.

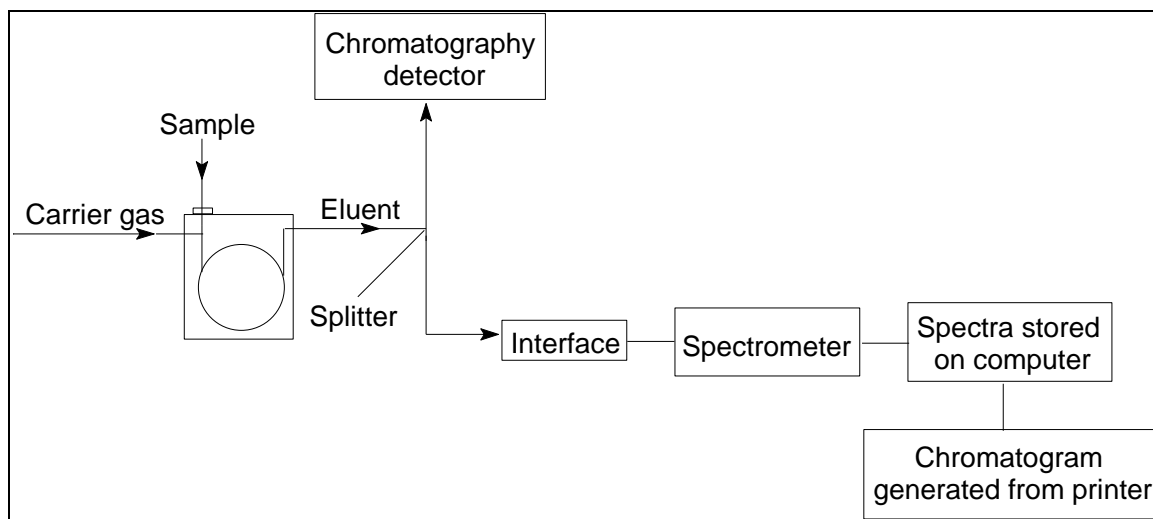


Figure 3.6: Block diagram of GC-MS system [Kealy et al., 2002]

3.4.3 Gas Chromatography – Flame Ionization Detector (FID)

Liquid samples were taken every 24 hours during the experimental procedure. The 6890 Series Agilent GC System with a FID detector was used to quantitatively determine the concentration of molecules or components in the solute. A description of the GC-FID method used is given in Annexure D.

3.4.4 Spiking with known compounds

For the accurate identification of compounds during the gas chromatographic analysis of the product streams, spiking with known compounds was included. The procedure of spiking is when known compounds of pure analytes are added to a sample [Kealy et al., 2002]. In the case of 1-hexene, drops of *cis*-4-methyl-2-pentene, 2-methyl-2-pentene and 2-hexene were added into separate vials and diluted with 1-hexene. In the case of experiments using 1-octene as a reagent, a drop of 1-octene, *trans*-2-octene, *trans*-3-octene, *trans*-4-octene was added into separate vials, diluted and mixed with a sample of which the compounds were known.

The known compounds were analysed on the GC and thereafter these drops of known compounds were added to a product and analysed on the GC. The chromatograms of the liquid product sample and the “spiked” sample (the mixture to which the drop was added) were overlaid and the peaks with increased areas were identified. Spiking was done to accurately determine the retention times of the compounds. A section on how this was done is fully described in Chapter 7.

3.4.5 Kováts indices

Professor Ervin Kováts developed the retention index system and the internationally designated Kováts retention indices in the 1900s [Kováts, 1958].

In gas chromatography, the use of Kováts indices helps to successfully and with a high degree of accuracy identify compounds present in a mixture. Kováts indices were used in this study to determine the retention times of *n*-octene compounds specifically because of the difficulty in identifying them. A detailed description follows in Chapter 7.

3.5 Catalyst Characterization

3.5.1 X-Ray Diffraction Analysis (XRD)

The pure catalysts were submitted for powder X-ray diffraction analysis to verify purity. The samples were packed in a stainless steel sample holder. A Philips X'Pert Pro multi-purpose diffractometer (XRD-2 system) was used to do the analysis. The data was collected at ambient temperature and atmospheric pressure. The crystalline phases present in the sample were identified using X'Pert HighScore Plus[®] software [X'Pert HighScore Plus, 2009].

3.5.2 Inductively Coupled Plasma Analysis (ICP)

The pure catalysts used were submitted for ICP (Inductively Coupled Plasma) analysis for the determination of amounts of Na, Mg, K, Ca, Ni, Mo and Si present in the samples.

The sample was digested in sulphuric and nitric acid using a Mars 240/50 CEM Mars Express closed vessel microwave and then quantified on the Perkin Elmer Optima 4300 DV ICP by comparing the intensity at characteristic wavelengths to that of a series of standards using yttrium as internal standard.

3.5.3 Thermal Gravimetric Analysis (TGA)

The pure and spent catalysts were analysed for fixed carbon contents using thermogravimetric analyses. A TGA (Thermal Gravimetric Analyser), 1 STAR^e system, Mettler Toledo with small furnace that can heat up to 1100 °C was used. Figure 3.7 represents a schematic diagram of the instrument.

The pure and spent catalysts were weighed and heated at 30 °C and kept for 3.0 min under an Argon flow of 150.0 ml/min. The temperature was increased from 30.0 °C to 110.0 °C at 50.0 °C/min under an Argon flow of 150.0 ml/min. The catalyst was kept at 110.0 °C for 3.0 min under an Argon flow of 150.0 ml/min. The temperature was increased from 110.0 °C to 900.0 °C at 50.0 °C/min under an Argon flow of 150.0 ml/min. The catalyst was kept at 900 °C for 20.0 min under an Argon flow of 150.0 ml/min. Thereafter air was introduced for the last step and the mass loss that occurred when air was introduced is due to the presence of fixed carbon.

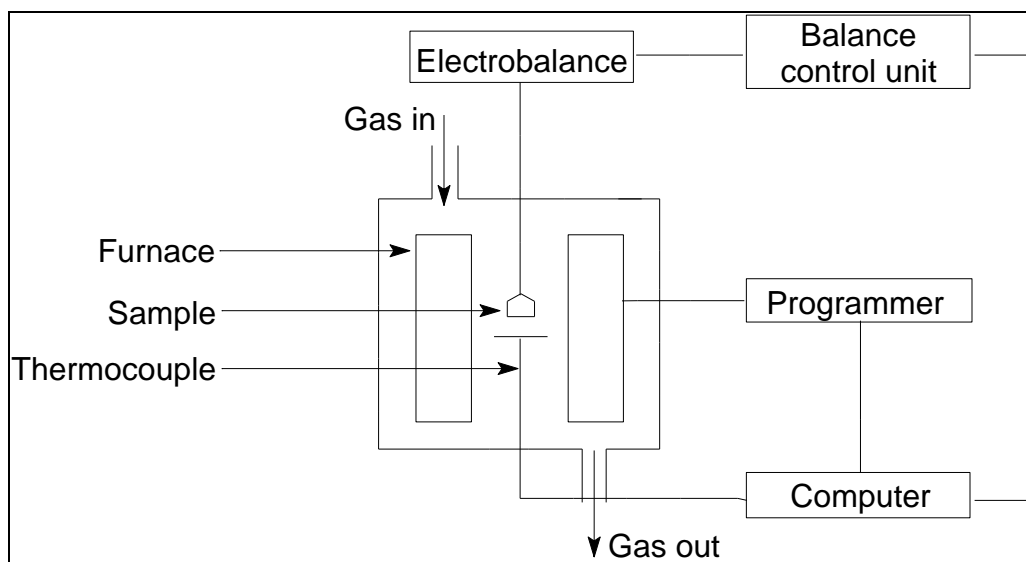


Figure 3.7: Block diagram of thermogravimetric instrument [Kealy et al., 2002]

3.5.4 Surface Area (SA) and Pore Volume (PV) Analysis

The Tri Star 3000 surface area analyzer system was used to collect surface area and pore volume data using nitrogen adsorption. Micromeritics software is used to recalculate the data points according to the Brunauer, Emmett and Teller (BET) equation [Haber, 1991]. The software calculates the surface area and pore volume for each sample after an experiment is completed.

Between 0.2 and 0.3 g \pm 0.01 g catalyst was weighed and placed in the Micromeritics Flow Prep 060 degasser. The catalyst was purged with nitrogen and degassed under a flowing stream of 50 ml/min for 12 hours \pm 1 hour at a temperature of 200 °C \pm 5 °C. After degassing, when the sample tube was cool enough to remove, it was placed in the Micromeritics Tri Star apparatus. A filter rod was immediately inserted into the sample tube to prevent oxygen uptake of the sample.

3.5.5 Surface Acidity

The catalysts were analysed for surface acidity using a NH₃ based TPD (Temperature Programmed Desorption) method for the determination of Brønsted Acidity [Jones et al., 1986] and a CO (Carbon monoxide) adsorption method for the determination of Lewis acidity [van Donk, 2002].

CO Adsorption method

The Diffuse Reflectance Infrared Fourier Transform (DRIFT) procedure was used to determine the amount of carbon monoxide adsorbed on the catalysts. A low temperature DRIFT reaction chamber from Harrick with ZnS windows of 1.5 mm in thickness was used to collect the DRIFT spectra. The spectra were recorded on a BRUKER TENSOR 27 spectrometer equipped with a Mercury Cadmium Telluride (MCT) detector of which the resolution was 4 cm^{-1} and sixty scans were collected per sample. The samples were pre-treated in the DRIFT cell. Pre-treatment was performed at $400\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$ in argon. This was done to remove all the adsorbed species such as water and carbonates from the samples. After drying overnight the cell was cooled to $\sim -195\text{ }^{\circ}\text{C}$ with liquid nitrogen. Background DRIFT spectra of the samples were collected. Pulses of $100\text{ }\mu\text{l}$ were introduced using a $100\text{ }\mu\text{l}$ Valco Instruments Corporation Incorporated (VICI) valve. $100\text{ }\mu\text{l}$ CO was pulsed into the argon system every sixty seconds until CO was observed in the off gas. The spectra obtained after introduction of CO was referenced to the background spectrum before the amount of CO desorbed was determined and converted to acidity (Absorbance units).

TPD method

The TPD analyses were performed on an AutoChem 2920 (Micromeritics, USA) instrument coupled to a Cirrus Mass Spectrometer. Approximately 50 mg of sample was placed in a quartz U-tube, kept in place by quartz wool. A thermocouple was inserted for continuous temperature measurements. The sample was activated first by heating to a temperature of $550\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C}/\text{min}$ whilst keeping it under helium. The sample was then cooled to the analysis temperature of $100\text{ }^{\circ}\text{C}$. Pulse-wise chemisorption of *n*-propylamine onto the sample was performed. The *n*-propylamine was kept at $22\text{ }^{\circ}\text{C}$ in a saturator whilst helium gas flowed at $10\text{ ml}/\text{min}$ to saturate the helium gas with the amine vapour. Twenty injections of *n*-propylamine vapour were dosed onto the sample. Data was collected during the temperature ramp from $100\text{ }^{\circ}\text{C}$ to $550\text{ }^{\circ}\text{C}$. A mass spectrometer was used to measure the amounts of propylene, ammonia and unreacted amine in the released gas phases.