CHAPTER 3

MATERIALS AND METHODS

3.1 INTRODUCTION

This chapter presents the methods followed for the catalytic cracking of vegetable oil, physicochemical analysis of the product obtained, fractional distillation of the OLP, structural characterization of the catalysts and kinetic aspects. The various analytical methods employed are also presented in detail.

3.2 CATALYTIC CRACKING

Commercial grade sunflower, castor and palm oil were purchased from the local market and used without any further treatment. The catalysts such as Co$_3$O$_4$, KOH, MoO$_3$, NiO, V$_2$O$_5$, and ZnO and Alumina (Al$_2$O$_3$) were purchased from Fisher scientific (India). Digital Heating Mantle (Manish scientific instruments, India) was used to carry out the experiments at different reaction conditions. The temperature was indicated and controlled using a digital temperature controller working in conjunction with two thermocouples with accuracy of ±2°C. The pressure that developed inside the reactor spreads the catalyst particle over the surface of the alumina and this will help to expose more active sites (catalyst pores). The exposition of more catalyst pores facilitates the mass transfer from the external pore mouth to the internal catalyst surface. The use of alumina to overcome mass transfer
limitations is reported in the literature (Singh & Vannice 2001; Zabeti et al 2009; Miyazaki & Balint 2011).

3.2.1 Selection of Vegetable Oil

Initially, the three different types of vegetable oils (palm, castor and sunflower) were checked for their suitability to catalytic cracking using metal oxide catalysts. The organic liquid products (OLPs) obtained from these three oils were clear and less viscous than the respective oils. Castor oil released little smoke with bad smell during the reaction while there was some bubble formation in the reactor when palm oil was used. The smoke and bubble formation might be associated with incompatibility of the oil to the experimental setup. Therefore, sunflower oil was preferred in all the subsequent investigations as it was found suitable to the experimental setup. Prior to use, the major fatty acid composition of the sunflower oil was determined using GC-MS analysis (Table 3.1).

Table 3.1 Major fatty acid compositions of sunflower oil used

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Chemical structure</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oleic acid</td>
<td><img src="image" alt="Oleic acid" /></td>
<td>58.4</td>
</tr>
<tr>
<td>Linoleic acid</td>
<td><img src="image" alt="Linoleic acid" /></td>
<td>23.5</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td><img src="image" alt="Palmitic acid" /></td>
<td>9.3</td>
</tr>
<tr>
<td>Stearic acid</td>
<td><img src="image" alt="Stearic acid" /></td>
<td>7.7</td>
</tr>
<tr>
<td>Pentadecanoic acid</td>
<td><img src="image" alt="Pentadecanoic acid" /></td>
<td>1.0</td>
</tr>
</tbody>
</table>
3.2.2 Cracking Conditions

The schematic diagram of the experimental setup used in this study is shown in Figure 3.1. Three-necked 250 ml round bottom flask was used as a reactor. Initially, 0.5 g of Al$_2$O$_3$ and 1.0 g of desired catalyst were placed in the flask. To this, 100 ml of oil was added and the flask was kept on a heating mantle. The desired temperature was set and pyrolysis of the oil was started after 15 min of heating. Thermocouples inserted through the side necks were used to measure temperature of the reaction mixture and vapor leaving the flask. The vapor condenses when it passes through a Liebig Drip Tip condenser fitted on the middle neck of the flask. The OLPs obtained were collected in the receiver, which was placed in the ice bath for further cooling.

Figure 3.1  Experimental setup: (1) Heating mantle (2) Three necked flask (3) Thermocouples (4) Condenser (5) Receiver (6) Ice bath and (7) Temperature controller
The dark residue containing glycerol and catalyst were disaggregated in the oil and retained in the flask. The %OLP was calculated using the following equation:

\[
\% \text{ OLP yield} = \frac{\text{Weight of OLP collected}}{\text{Weight of initial oil used}} \times 100 \quad (3.1)
\]

3.3 ANALYTICAL METHODS

The physical properties and chemical composition of the OLPs obtained are essential. These properties determine their usability in combustion engines.

3.3.1 Analysis of the Physical Properties

Specific gravity (SG) and density (\( \rho \)) of the OLPs were measured using hydrometer with DN range of 0.850 to 0.900. Ostwald viscometer was used to determine the kinematic viscosity (\( \nu \)) of the product. Higher heating value (HHV) of the OLP was measured by the Leco AC-350 equipment that was calibrated with benzoic acid and the ASTM D-240-02 method was followed. Flash point measurements were carried out using a Koehler mark apparatus and compared with ASTM D6751 (B100) standards.

3.3.2 Analysis of Chemical Composition

The types of hydrocarbon compounds present in the OLPs were analyzed using FTIR spectrometer. Perkin-Elmer Infrared model 337 spectrometer using NaCl window and polystyrene for calibration were employed. The acquisition of each spectrum provided 8 scans with a resolution of 4 cm\(^{-1}\).
The chemical compositions of the OLPs were analyzed using GC-MS (Agilent technologies, JEOL GCMATE II GC-MS with data system, double focusing instrument, conditions: capillary column (HP5); MS secondary electron multiplier (detection); evaporation 10 °C/min; oven temperature 50-250 °C and helium was used as carrier gas at a flow rate of 1.5 mL/min. Ionization voltage was set at 40V with optimal cycle time and attenuator (1/16)).

3.4 FRACTIONAL DISTILLATION

The OLPs synthesized was distilled and separated into four major components based on their distillation temperature (DT): DT < 80°C = light hydrocarbon; 80°C ≤ gasoline < 140°C; 140°C ≤ kerosene < 200°C; and heavy oil ≥ 200°C. These distillation temperature intervals were reported to give hydrocarbon fractions having properties similar to that of petroleum distillates (Santos et al 2010; Prado et al 2012). The amount of each component present was expressed as % fraction and was calculated using the following equation:

\[
\% \text{ fraction} = \frac{\text{Weight of each component}}{\text{Weight of total OLP}} \times 100 \tag{3.2}
\]

3.5 CHARACTERIZATION OF THE CATALYSTS

Based on their catalytic performance, three metal oxide catalysts (Co_3O_4, V_2O_5 and ZnO) were selected for further analysis. The structural modifications of these catalysts before and after catalytic cracking were investigated.

3.5.1 Scanning Electron Microscope (SEM) Analysis

Surface structures of the catalysts before use were characterized using scanning electron microscope (SEM) (VEGA 3 TESCAN Czech
Republic). The samples were mounted with double sided carbon tape on brass prior to the analysis for easy magnification.

To analyze the structural modification of the catalyst after use, each catalyst (1.0 wt.%) was used separately for catalytic cracking of the oil at 320°C for 40 min. The catalyst along with glycerol was precipitated in the reactor at the end of the reaction. The precipitate obtained was calcinated in a muffle furnace at 450°C for 3 h. The glycerol was removed during calcination and the weight of the catalyst recovered was found to be equal to that of weight of the catalyst used. The structural modifications of the catalysts during the reaction were compared with their respective structures before use.

3.5.2 FTIR Analysis of the Catalysts

In order to check the stability of the bonds in between the metal and oxygen, the fresh and calcinated catalysts were analyzed using FTIR spectrometer (Perkin-Elmer Infrared model 337).

3.6 REACTION KINETICS

The reaction kinetics of catalytic cracking of sunflower oil was investigated using the best catalyst (V$_2$O$_5$). In addition to the OLP, the % yield of gas and coke (g+c) formed during catalytic cracking of the oil was calculated using the following equation:

$$\text{% yield} = \frac{\text{Weight of desired product}}{\text{Weight of initial oil used}} \times 100 \quad (3.3)$$

where, desired product could be OLP or g+c formed during the reaction.
3.6.1 Catalytic Cracking Conditions

The independent reaction variables such as cracking temperature (603, 628 and 653 K) and residence time (15, 20, 25, 30, 35, and 40 min) were varied. The OLP and g+c obtained under each condition were used to find the kinetic parameters.

3.6.2 Reaction Kinetics Model

A lumping model proposed by Weekman & Nace (1970) with some modification was used to investigate the reaction kinetics of the catalytic cracking of sunflower oil. For simplification and less computational constraints, a 3-lump kinetic model which consider OLP, gas and coke as the components of the lumps was preferred in the present work. Based on the three-lump model, the cracking rate \( r_0 \) of the oil can be expressed as:

\[
r_0 = -\varphi (k_1 + k_2) C_0^n
\]

where, \( k \) is reaction kinetics constant, \( \varphi \) is the catalyst activity reduction (catalyst decay) and \( n \) represents the kinetic order.

In the present study, the first order reaction kinetics was adapted, and the rate of formation of OLP \( r_{OLP} \) and gas+coke \( r_{g+c} \) was defined as follows, respectively:

\[
\frac{dC_{OLP}}{dt} = k_1 C_0 - k_3 C_{OLP}
\]

\[
\frac{dC_{g+c}}{dt} = k_2 C_0 + k_3 C_{OLP}
\]
where, \( C_O \) is the concentration (wt.\%) of initial oil used in the reaction mixture, \( C_{OLP} \) and \( C_{g+c} \) is the wt.% OLP and g+c collected per initial oil used, respectively. Since the same and equal amount of catalyst applied in a batch reactor, and there was no observed reduction in catalyst activity, the effect of \( \varphi \) was ignored.

### 3.6.3 Analysis of the Lumps

Nonlinear least-squares curve fitting with Microsoft Excel Solver was employed to determine the reaction rate constants (Harris 1998). All values of the OLP and g+c (the dependent variables) were considered as having equal and unknown uncertainty (un-weighted) and each datum was given equal weight for curve fitting. Determination of reaction rate constants started by assigning a value 1 (dummy variable) for each constants (\( k_1 \), \( k_2 \) and \( k_3 \)). The least-squares criterion was used to find out value of \( k_1 \), \( k_2 \), and \( k_3 \) that minimize the relative mean square error (RMSE) between experimental and predicted values. The rate constants were used to calculate the activation energy values using the Arrhenius equation:

\[
k = Ae^{-\frac{E_a}{RT}} \tag{3.7}
\]

where, \( A \) is the frequency factor, \( T \) is the cracking temperature in Kelvin, \( E_a \) is the activation energy and \( R \) is the universal gas constant.