CHAPTER 2

MATERIALS AND METHODS

Designed, Assembled and Installed a Biodiesel Pilot Plant made of Polypropylene Vessels for the Pilot Scale Production of Biodiesel
2.1 Introduction

The conventional homogeneous catalyzed industrial biodiesel production process is associated with operational problems and challenges [1]. For industrial purposes, heterogeneous catalysis is more suitable and it overcomes the problems associated with the homogeneous catalyzed biodiesel production [2]. Only limited successful reports are available for the large scale production of biodiesel via heterogeneous catalyzed route because of the high cost and non-availability of the catalyst as well as the tedious steps required in the catalyst development. Additionally, the catalyst production requires extra care in controlling pH, stirring rate, temperature etc [3]. Solid catalysts derived from natural resources or biomaterials as well as waste materials can effectively replace the conventional homogeneous catalysts thereby solving most of the hurdles in the biodiesel production processes [4]. Development of solid catalysts from renewable sources or from waste materials makes the process eco-friendly and economically viable [5]. Here we could develop 4 different sets of solid catalysts from waste materials; and among them, three sets are prepared by their reaction with alkali metal precursors. The catalyzed production of biodiesel from used cooking oil (UCO) and jatropha oil (JCO) is also effectively scaled up in the pilot plant designed and assembled in our laboratory. Simple methods and mild conditions are employed for the preparation of all the catalysts that makes the process greener, aiming the industrial scale-up straightforward and cost-effective. This chapter mentions the materials employed in the preparation of biodiesel and catalysts, characterization
and analytical techniques used to explore the nature and the active phases of the catalysts prepared, procedures of the laboratory scale experiments done for the investigation of the effect of reaction parameters and catalyst reusability in the biodiesel preparation, design and assembling of the parts of biodiesel pilot plant, detailed description of the scale up of the reaction under the selected conditions in the pilot plant, methanol recovery and purification of the biodiesel etc and also the fuel property analysis of the produced biodiesel samples.

2.2 Materials Used

All the materials used in the preparation of biodiesel in the laboratory scale and in the pilot plant including catalyst precursors are tabulated in the table 2.1. All the chemicals used were of analytical grade and only deionised water was used in the experiments.

Table 2.1 Materials used

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Material</th>
<th>Manufacturer/Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Waste Cooking oil</td>
<td>Catering centers at Pattambi</td>
</tr>
<tr>
<td>2</td>
<td><em>Jatropha curcas</em> oil</td>
<td>Extracted from <em>jatropha curcas</em> seeds using oil expeller (Rajkumar Agro Engineers Pvt Ltd, Nagpur, India)</td>
</tr>
<tr>
<td>3</td>
<td>Methanol</td>
<td>Merck Specialities Pvt. Ltd.</td>
</tr>
<tr>
<td>4</td>
<td>Isopropyl alcohol</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>5</td>
<td>Phosphoric acid</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>6</td>
<td>Con. HCl (35%)</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>7</td>
<td>Anhydrous sodium sulphate</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>8</td>
<td>Coconut husk</td>
<td>Local coconut farm</td>
</tr>
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</table>
### Materials and Methods

<p>| | | |</p>
<table>
<thead>
<tr>
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<tr>
<td>9</td>
<td>Areca nut husk</td>
<td>Local areca nut farm</td>
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<tr>
<td>10</td>
<td>Sodium hydroxide</td>
<td>NICE Chemicals Pvt. Ltd.</td>
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<tr>
<td>11</td>
<td>Rice husk</td>
<td>RARS pattambi</td>
</tr>
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<td>12</td>
<td>Anhydrous Lithium nitrate</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>13</td>
<td>Broken borosil® glass beakers</td>
<td>From our laboratory</td>
</tr>
<tr>
<td>14</td>
<td>Citric acid mono hydrate</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>15</td>
<td>Iodine monochloride</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
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<td>Potassium iodide</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>17</td>
<td>Sodium thiosulfate</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>18</td>
<td>Starch</td>
<td>NICE Chemicals Pvt. Ltd.</td>
</tr>
<tr>
<td>19</td>
<td>$N$-Methyl-$N$-(trimethylsilyl)trifluoroacetamide (MSTFA)</td>
<td>Sigma Aldrich Pvt. Ltd</td>
</tr>
<tr>
<td>20</td>
<td>Heptane</td>
<td>Merck Chemicals Pvt. Ltd</td>
</tr>
<tr>
<td>21</td>
<td>Biodiesel standards</td>
<td>Sigma Aldrich Pvt. Ltd</td>
</tr>
</tbody>
</table>

#### 2.3 Analytical techniques

The catalysts prepared by the reaction between waste materials and alkali metal precursors as well as by the combustion of coconut husks are analyzed using different techniques to find out their composition, structure and morphology in order to determine the active sites that are responsible for catalysis. Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron Microscopy (TEM), inductively coupled plasma-atomic emission spectroscopy (ICP-AES), temperature programmed desorption (TPD) of CO$_2$ etc are the various techniques used for the characterization of the prepared catalysts. Gas chromatography (GC) is used to evaluate the fatty acid methyl ester
(FAME) content in the biodiesel samples. FAME content in the biodiesel is compared with the quantity mentioned in the fuel specification of the biodiesel according to European (EN 14214) as well as American standards (ASTM D 6751). The percentage chemical composition of the biodiesel fuel was analyzed with gas chromatography-mass spectroscopy (GCMS). The fuel properties of biodiesel produced in the pilot plant, such as FAME content, acid value, iodine number, viscosity, water content, density etc are determined and compared with the standard fuel specifications.

2.3.1 Fourier transform infrared (FTIR) spectroscopy

Infra red spectroscopy is a spectroscopic technique used to identify the chemical compounds and to investigate and elucidate the composition of unknown samples by recording the absorption spectra of the substances in the near, mid and far infrared regions. This technique deals with the interaction of a molecule with radiation in the IR region of the electromagnetic spectrum. Molecular vibrations of the atoms in the compounds are responsible for the FTIR spectrum which is recorded with the intensity of infrared radiation as a function of frequency or wavelength. The spectrum is obtained by passing infrared radiation through the sample and analyzing the radiation absorbed/transmitted, which corresponds to the energy (frequency) of vibration of a part of the sample molecule and recorded as a peak. The light transmitted through the sample contains information about the material to be studied and this technique is irrespective of the phase of the material (solid, liquid or gas). The most useful IR region for sample
analysis lies between 4000 cm\(^{-1}\) to 400 cm\(^{-1}\) where we can study the fundamental vibrations and associated rotational vibrations of the molecules. The region 4000 cm\(^{-1}\)-1450 cm\(^{-1}\) is known as the functional group region, where the most useful information obtained from an IR spectrum is about the functional groups present within the molecule. IR region below 1450 cm\(^{-1}\) contains complicated series of absorption peaks mainly due to all manners of bending vibrations within the molecule, known as the fingerprint region; here the spectra tend to be more complex and much harder to assign. In the case of metal oxide related species, even stretching bands occurs below 1450 cm\(^{-1}\) and provides useful information about the structure of the materials [6-10].

In the present study, the catalysts prepared by the treatment of alkali metal precursors with different waste materials as well as catalysts derived from coconut husks were analyzed using FTIR spectral techniques. The FTIR spectra gave an idea about the chemical bonding, composition and material formation in the catalyst systems. The FTIR spectral analysis of the catalyst derived from coconut husk were done using NICOLET6700 FTIR Thermo scientific in the region of 400-4000 cm\(^{-1}\) by means of KBr pellet method. For the analysis of the catalysts derived from rice husk, areca nut husk and waste borosil\(^{®}\) glass, the FTIR spectra were recorded using THERMO NICOLET AVATAR 370 in the region of 400-4000 cm\(^{-1}\).
2.3.2 X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) is a non destructive analytical technique employed for the qualitative and quantitative analysis of the crystal structure and chemical composition of the materials and thin films. X-ray diffraction technique investigates the crystal structure and atomic spacing of the materials by quantifying the scattered intensity of the X-ray beam hit on the sample as a function of incident and scattered angle. It is based on constructive interference of monochromatic X-rays and a crystalline sample. X-rays are electromagnetic radiation with wavelengths between about 0.02 Å and 100 Å and they are of higher energy that can penetrate to the matter more easily. Their ability to penetrate to the matter depends on the density of the matter. When X-ray radiation passes through the matter, it interacts with the electrons in the atoms, resulting in its scattering. If the atoms are organized in planes (i.e., the matter is crystalline) and the distances between the atoms are of the same magnitude as the wavelength of the X-rays, constructive and destructive interference will occur. The interaction of X-rays with crystalline substances produces diffraction pattern when constructive interference takes place and is called X-ray diffraction and the condition can be expressed by Bragg's law, \( n\lambda = 2d \sin \theta \), where, ‘\( \lambda \)’ is the wavelength of X-rays, ‘\( d \)’ is the inter-planar distance and ‘\( \theta \)’ is the angle of diffraction. X-ray diffraction is of two types, powder and single crystal diffraction. Here we are using the powder diffraction technique to analyze the catalysts. The powder sample is assumed to be consisted of a number of crystallites which are oriented in a random manner. When
monochromatic X-rays are allowed to fall on the powder sample, diffraction takes place from the planes which are properly oriented at the correct angle to satisfy the Bragg's law. The observed diffraction pattern is recorded by a diffractometer. The diffraction pattern thus formed is unique for each material. If the sample consists of different phases, then each phase produces its own diffraction patterns. Lattice spacing for different planes and percentage of amorphous and crystalline phases of samples can be obtained from XRD analysis [11-15].

In the present study, the crystal structure, crystalline phase and chemical composition of the prepared solid catalysts is determined using XRD analysis. The active phase responsible for the catalytic activity of the catalysts in the transesterification reaction is also verified from by the XRD measurements and is compared with the standard JCPDS database. The powder diffraction patterns of the catalysts derived from coconut husk ash and rice husk ash were recorded on a Bruker AXS D8 Advance diffractometer using Cu Kα radiation as X-ray source (Kα =1.542 Å). In XRD analysis, all the samples were scanned in the 2θ range of 3°-80°. Rigaku Mini flex 600 diffractometer is used for the XRD analysis of the catalysts from arecanut husk and waste glass.

2.3.3 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is an advanced non destructive technique used to analyze the surface structure of solid samples by magnifying the image of the samples to a resolution range
of few nanometers using high energy electron beams. In the SEM analysis, the electron beam is produced with the help of an electron gun and is swept in a raster over the surface of the specimen. The interaction of electron beam with surface atoms of the sample will produce signals corresponding to secondary electrons, back scattered electrons, characteristic X-rays, cathodoluminescence, auger electrons, specimen current, transmitted electrons etc, depending on the nature of the sample and it provides informations about the surface morphology, composition and electrical conducting properties of the samples. The signals developed by the instrument is recorded on a screen as a three dimensional image containing the morphology of the sample. Generally, SEM analysis is conducted under vacuum and the samples are prepared by coating on a carbon tape (conducting) and in the case of non conducting samples, sputter coating with gold is used [16-20]. On combination with EDS, we can find out the percentage composition of the elements in the samples.

Surface morphology of the catalytic systems prepared in the present work were analyzed by the Jeol JSM - 6390LV scanning electron microscope. From the SEM analysis, macroporous structures of the solid catalysts are revealed which is beneficial for the activity of catalysts in the transesterification reaction. The elemental analysis and hence the percentage composition of the catalytic systems prepared from coconut husk was performed with the SEM-EDS combination using OXFORD XMX N energy dispersive spectrometer.
2.3.4 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a high magnification and ultra resolution microscopic technique used to analyze the morphology and topography of the samples. It gives a clear picture about the microstructure of the specimens including crystalline structure and composition. In the operation, TEM resembles the working of an optical microscope, where the electron beams are used instead of light rays and the electromagnetic condenser lenses replaces the normal optical lenses. Compared to the optical microscope, TEM gives high magnification of about one million times and ultra resolution even in less than 1 nanometer range.

In TEM, high energy electron beam produced by the electron gun is focused on the sample through the condenser lens and the electrons transmitted after the interaction with the sample are magnified and focused to the imaging device to get a two dimensional black and white image of the sample. Depending upon the structure and nature of the materials, the interaction of electron with the sample may cause diffraction, transmission and scattering which produces scattered electrons i.e., elastic and inelastic scattered electrons, transmitted electrons, X-rays, Auger electrons, etc. For a sample to show a good TEM image, it must be transparent to the electron (thin or porous materials) and must be able to withstand vacuum.

Using TEM, we can identify the particle size, grain and crystallite size, particle size distribution as well as lattice fringes and hence the structure of the material can be illustrated [21-25]. The TEM
Analysis of the catalysts was done using Jeol JEM - 2100 transmission electron microscope. The macroporous nature of the catalysts beneficial for the activity in the transesterification is also confirmed from the TEM analysis.

2.3.5 Inductively coupled plasma-atomic emission spectroscopy (ICP-AES)

By the inductively coupled plasma-atomic emission spectroscopic (ICP-AES) technique, the metal composition in the sample can be analyzed. ICP-AES is an emission spectroscopic technique usually used to detect the metals present even at minor or trace quantity in the sample. Around 60 elements can be analyzed at a time using a single source. In this technique, inductively coupled plasma is used to excite the atoms or ions in the sample to higher energy levels and returned to the ground state by emitting the radiation characteristic to the elements. Normally, samples for analysis are prepared by making a solution with concentrated acids and the diluted sample solution is aspirated to the instrument. Atomization or ionization of the elements will be achieved and they reach the plasma with the help of argon gas at an elevated temperature of about 7000 °C; here the excitation of the outer shell electrons takes place. These excited electrons emit radiation having a wavelength characteristic to the element with intensity corresponding to the concentration of the element [26-30]. In the present study, we use SPECTRO ACROS simultaneous ICP spectrometer in the spectral range 130 nm to 770 nm to a approximate resolution of 0.009 nm and Thermo Electron IRIS
INTREPID II XSP DUO in the spectral range 165 to >1000 nm of resolution 0.005 nm at 200 nm for the elemental analysis of catalyst derived from coconut husk and waste borosilicate glass respectively. ICP-AES analysis gave the percentage composition of the elements present in the catalyst and thus confirmed its nature.

2.3.6 Temperature-programmed desorption (TPD) of CO₂

The basicity or acidity of the catalysts can be analyzed using temperature programmed desorption (TPD) technique. This method of analysis was introduced by Amenomiya and vetanovic in 1963. In this method, desorption of adsorbed gases on the samples occurs by means of programmed heating and eluted gas is analyzed. In a typical TPD experiment, a definite amount of the catalyst is kept in a reactor and heated to a programmed temperature with the aid of a furnace. At first an inert carrier gas, usually argon, nitrogen or helium flows over the catalyst and a suitable adsorbate is then injected to the carrier column where it gets adsorbed on the surface of the catalyst. After a sufficient time of exposure, the gas that is not adsorbed is flushed out of the system. Then the catalyst is heated where the temperature rises linearly with time. A suitable gas chromatographic detector is used to analyze the changes in the carrier gas stream. As the catalyst is heated, the adsorbate is desorbed into the carrier gas stream and is detected by the detector. The spectrum thus obtained depends on the nature of the catalyst, heating rate and surface coverage. In TPD, the strength of basic or acidic sites in the sample can be calculated from the amount of desorbed gas. The information obtained from the desorption studies
includes the surface concentration and the nature of the active sites. Higher the desorption temperature of CO$_2$, stronger will be the basic sites because strongly bound molecules have high binding energies which increases the desorption temperatures. The catalysts usually shows weak, medium and strong basic sites corresponding to desorption peaks obtained at a temperature range of room temperature to 200 °C, 200 °C-400 °C and above 400 °C respectively [31-34].

The basicity of the catalysts prepared from waste borosilicate glass and arecanut husk were investigated using the instruments BELCAT II Version 0.4.5.16 and Micromeritics Chemisorb 2750 respectively via temperature programmed desorption (TPD) of CO$_2$ by using Helium as the carrier gas. The amount of CO$_2$ desorbed is taken as a measure of the basicity and the desorption temperature indicated the strength of basic sites [35].

2.3.7 Gas chromatography

Chromatographic methods are used to separate mixtures of compounds based on their physical properties. The important chromatographic methods are gas chromatography (GC) and liquid chromatography (LC, often termed as high-performance liquid chromatography (HPLC)). In GC, the mixture is separated mainly based on the difference in the polarity, boiling point and the structure of the individual compounds. To carry out a GC analysis, the sample is usually dissolved in low concentrations in an organic solvent and then injected into the gas chromatograph. In some cases, the sample needs to be derivatized with a specific reagent in order to obtain a useful gas
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c chromatogram. Derivatization with MSTFA is required for biodiesel analysis. The main intention of the derivatization is to make the sample volatile. After injection of the volatile sample into the gas chromatograph, it is carried through the column by a carrier gas and the components are separated. A column is a long, thin path (usually capillary tube) that contains a material with which the sample components interact more or less strongly depending on their structure (may be polarity). The separated components reach the detector while heating; one of the common detectors, i.e. flame ionization detector, is used in the present study. When the detector detects a material eluted from the column at a certain retention time, this will be shown by a peak in the chromatogram. Generally, the integrated value of the peak amplitude over time is proportional to the amount of material. This constitutes the usefulness of GC in quantifying the amounts of components in a mixture. Glycerol and mono- and diacylglycerols containing free hydroxyl groups, is not performing well in the GC. Derivatization improves their performance considerably. Derivatization can provide better resolution between compounds with similar properties. Often standards are used in GC, which are known compounds that will indicate the presence of those compounds in the mixture based on their retention time in the column. Standards are therefore very useful in establishing the presence of specific compounds in a mixture [36-40].

Here biodiesel is analyzed using Thermo Fisher Trace GC 700 Gas Chromatograph equipped with MXT biodiesel TG column and flame ionization detector as per the standard procedure. The condition
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for GC analysis of biodiesel sample of the present study as per ASTM D 6584 specification is given below.

**Injector**

Cool on column injection: Programme, oven track  Sample size: 1μL

Mode: Splitless Column Flow: 30 mL/min , Injection Volume: 1 μL

**Injector Temperature Programme**

<table>
<thead>
<tr>
<th>Temp1</th>
<th>Time1</th>
<th>Rate1</th>
<th>Temp2</th>
</tr>
</thead>
<tbody>
<tr>
<td>55 °C</td>
<td>1 min</td>
<td>15°/min</td>
<td>180 °C</td>
</tr>
<tr>
<td>Time2</td>
<td>Rate2</td>
<td>Temp3</td>
<td>Time3</td>
</tr>
<tr>
<td>0 min</td>
<td>7°/min</td>
<td>230 °C</td>
<td>0 min</td>
</tr>
<tr>
<td>Rate3</td>
<td>Temp4</td>
<td>Time4</td>
<td>Rate4</td>
</tr>
<tr>
<td>30°/min</td>
<td>360 °C</td>
<td>10 min</td>
<td>0°/min</td>
</tr>
</tbody>
</table>

**Detector**

Type: Flame Ionization  Temperature : 350 °C  Carrier Gas : Nitrogen

**Oven**

Column: MXT® biodiesel TG column

**Oven Temperature Programme**

<table>
<thead>
<tr>
<th>Temp1</th>
<th>Time 1</th>
<th>Rate1</th>
<th>Temp 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>55 °C</td>
<td>1 min</td>
<td>15°/min</td>
<td>180 °C</td>
</tr>
<tr>
<td>Time 2</td>
<td>Rate2</td>
<td>Temp 3</td>
<td>Time 3</td>
</tr>
<tr>
<td>0 min</td>
<td>7°/min</td>
<td>230 °C</td>
<td>0 min</td>
</tr>
<tr>
<td>Rate 3</td>
<td>Temp 4</td>
<td>Time 4</td>
<td>Rate4</td>
</tr>
<tr>
<td>30°/min</td>
<td>360 °C</td>
<td>10 min</td>
<td>0°/min</td>
</tr>
</tbody>
</table>
2.3.8 Gas chromatography-mass spectrometry

The percentage composition of each of the methyl esters present in the biodiesel were evaluated by gas chromatography–mass spectrometry (GC-MS). It is an analytical method that combines the features of gas chromatography and mass spectrometry to identify different substances within a test sample. The GC-MS instrument separates chemical mixtures in the GC component and identifies the components at the molecular level in the MS component. It is one of the most accurate tools for analyzing organic samples. In the GC, mixture will separate into individual substances when heated. As the separated substances emerge from the column opening, they flow into the MS. MS identifies the compounds by determining the mass of the analyte molecule and then by comparing it with the standard mass spectral library of known mass spectra of known compounds, covering several thousand compounds. MS is considered as the only definitive analytical detector in GC [41-45]. Here the UCO biodiesel was analyzed using PerkinElmer Autosystem XL GC TurboMass Gold Mass Spectrometer with TurboMass 6.1.0.1963 software and JCO biodiesel using Agilent 6890 GCMS with MSD chemstations software for investigating the fatty acid profile in the samples.

2.4 Purification of oil feedstock

UCO was collected from a local catering center. It was filtered using a fine cotton cloth to remove all the insoluble impurities. JCO was expelled from *jatropha curcas* seeds and filtered by means of an oil expeller and filtration unit (Rajkumar Agro Engineers Pvt Ltd,
Nagpur, India). Both the oils are then subjected to degumming to remove the soluble gums inherently present in the oil feedstocks.

2.5 Initial studies on the influence of reaction variables on the transesterification reaction of oil feedstocks

A series of transesterification reactions were performed in the laboratory scale by varying the reaction parameters such as reactants’ molar ratio, catalyst/oil weight percentage, the temperature at which the reaction was conducted, and the duration of the reaction. In a typical run, 5 g of oil (UCO/JCO) (usually with FFA < 1% attained via pretreatment) was mixed with the desired amount of catalyst and methanol in a 50 mL RB flask fitted with a water condenser. The reaction was carried out at a specified temperature with constant stirring at 450 rpm. After each run, the reaction mixture was centrifuged for 15 minutes and the top methyl ester phase was separated from the dense glycerol phase after removing the settled catalyst. 3 mL of deionized water was added to the methyl ester part for washing in order to remove any impurities if present. The washing process was repeated 3 times and the obtained biodiesel was dried over anhydrous sodium sulphate. The reactions were also repeated with oils having varying amount of FFA and water content in order to study the effect of these parameters on the catalytic activity.

2.6 Reusability of the catalyst

One of the highlights of the solid heterogeneous catalyst is its reusability. Solid catalyst can be recovered by means of simple
filtration and can be reused directly or by activating at its calcination temperature [46-50]. In the present study, reusability of the most active catalysts in each series is investigated under one of the best suited reaction conditions. After the reaction, the contents were centrifuged and filtered. The catalyst residue was washed with methanol to remove the contaminated impurities and after that, the catalyst was dried and activated at its calcination temperature for 1 h. Then, the second cycle of the transesterification process was conducted using the regenerated catalyst and the procedure was repeated after each reaction till the catalyst loses its activity.

2.7 Biodiesel analysis

For the use of biodiesel as an alternate fuel for petrodiesel, the FAME content in the biodiesel should be greater than 96.5% as per the European specification of standard biodiesel fuel. In the present study, the FAME content and hence the fuel quality of the biodiesel is determined mainly by the GC analysis. Thermo Fischer Trace GC 700 gas chromatograph equipped with MXT biodiesel column and flame ionization detector is used to determine the FAME content in the biodiesel by a test method of ASTM D 6584 [51-53]. Sample preparation for GC measurements is the important step in biodiesel analysis. The glycerol, mono-, di- and triglycerides must be derivatized to reduce their polarity and improve the thermal stability of the molecule. The derivatization technique used is silylation. The derivatization reagent used is MSTFA. The reaction involves the replacement of the active hydrogen of the hydroxyl group by a trimethylsilyl group. The derivatization procedure for both standards and samples is identical. 100 mg of biodiesel samples were weighed
into a clean dry 10 mL septa vial followed by internal standards and it was derivatized exactly with 100 µL of MSTFA. The mixture was shaken well and allowed to stand at room temperature for 15-20 min. Approximately 8 mL of n-heptane was added to the vial and mixed well. One microlitre of the reaction mixture was then injected into the cool-on column port and the analysis was started. Injector program was oven track, (details are mentioned in section 2.3.7). Mono-, di-, and triglycerides were determined by a comparison with mono-olein, diolein, and triolein standards. Chromatogram and peak integration reports were collected and the FAME content was determined [54-56].

2.8 Biodiesel pilot plant: design and assembling

With a thorough knowledge and experience in the laboratory scale biodiesel preparation, we can scale up the entire biodiesel production process to pilot scale. Here we have designed a pilot scale set up having a production capacity of 15 L biodiesel per run. Figure 2.1 shows the schematic of the designed pilot plant (SNGS model1).

In the pilot plant, we ensured the presence of different components/operational facilities required in the laboratory scale biodiesel preparation. The biodiesel pilot plant consists of the following parts/vessels; provision for feedstock pretreatment (j), transesterification reactor (e), catalyst filtration port (f), glycerol settling vessel (g), methanol recovery unit (k) and provision for the purification of biodiesel (o, m & p). The entire vessels and valves are made of polypropylene (PP), which are resistant to biodiesel and a range of chemicals. The connections are done using tygoethane tubing, which is also resistant to a range of chemicals and biodiesel. The top of
all the main vessels (pretreatment tank, reaction vessel and methanol distillation tank) are equipped with a condensers made of PVC pipe and copper coil. Cold water (from chiller (s)), is circulated through the condensers using a tulu pump for the condensation of methanol in the pretreatment vessel, reaction vessel and methanol recovery tank.

Fig 2.1 Schematic representation of Biodiesel pilot plant SNGS model1

фикс - Valve, a - Oil tank, b - Pretreated oil tank, c - Methanol tank, d - Condenser, e - Reaction vessel, f - Catalyst separation port, g - Glycerol settling tank, h - Acid tank, i - Condenser, j - Pretreatment vessel, k - Methanol distillation tank, l - Condenser for methanol from distillation tank, m - Hot water tank, n - Recovered methanol tank, o - Water washing tank, p - Drying tank, q - Waste water tank, r - Pure biodiesel tank, s - Chiller, t₁ & t₂ - pump, u - vacuum pump
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There is a provision for the removal of solid catalyst from the reaction mixture after the reaction, a filtration port (f), where the catalyst is separated by filtration under suction. The liquid mixture of biodiesel, methanol and glycerol is allowed to separate to two layers in the separation/settling tank (g). Two motor pumps (t₁ & t₂) are engaged; one for the supply of pretreated oil to the reaction vessel via tank (b) and the second for the pumping of glycerol separated biodiesel to the methanol distillation tank (k). The top of the methanol distillation tank is equipped with a condenser (l) and it is connected to the methanol collection tank (n). The vacuum pump (u) employed for providing suction during filtration of the catalyst is also used for giving vacuum for the distillation of methanol. Washing tank (o), hot water tank (m) and drying tank (p) are meant for the purification of the crude biodiesel.

All the components of the pilot plant engaged in the production of biodiesel are properly mounted on a stand according to the design. The connections of the vessels through valves are done using tygoethane tubing. Electric connections are assembled in a control panel which controls and monitors the temperature as well as regulates the speed of mechanical stirrers inside the tanks. The photograph of the pilot plant assembled with all the vessels and accessories are shown in the figure 2.2.
2.9 Different components of biodiesel pilot plant

2.9.1 Pretreatment and Reaction vessels

The transesterification reaction vessel and esterification pretreatment vessel are exactly same with only changes in the number of openings and valves in the top portion. Both are conical bottom cylindrical 50 L polypropylene vessels equipped with a mechanical stirrer (1100 W motor). The stainless steel (SS) stirring rad in the
reaction vessel composed of two stainless steel crosses in the end at a distance of 7 cm in between. The bottom cross is projected to the valve tubing to avoid settling of the solid catalyst in the valve tubings. Teflon stirring rod of the same type is used in the pretreatment vessel. The speed of the stirrer is variable and has a maximum stirring speed of 700 rpm. In the pretreatment vessel, the required temperature is achieved by using a 2 kW dry coil heater kept inside a medium thick glass tube (since SS corrodes in concentrated acids) and in the reaction vessel, 2 kW SS immiscible coil heater is used. The top of both the vessels are equipped with water condensers made of copper coil covered with a PVC jacket. Chilled water is circulated through the copper coils to ensure the condensation of methanol vapors inside the PVC tube during the reaction. This provision avoids the risk in operating the vessels since there is no high pressure generation, where the excessive formation of methanol vapors are avoided by its continuous condensation. The PVC condensers are sealed to prevent the accumulation of atmospheric moisture on the copper coils. The oil and the methanol for the biodiesel production are transferred from the corresponding storage vessels to the pretreatment/reaction vessels via tygoethane tubing (tygothane polyurethane 1” ID x 1 3/8” OD). The images of both the pretreatment and reaction vessels and their accessories are shown in the figure 2.3 and figure 2.4 respectively. Drawing of the vessel is also shown in figure 2.3.
2.9.2 Filtration and Settling unit

There is a provision for the removal of solid catalyst from the reaction mixture after the reaction, a filtration port (f) made of PP, where the catalyst was separated by filtration using whatman no.1 filter.
paper under suction. A vacuum pump (u) is connected to the settling tank for providing suction in the catalyst separation stage. This will also helps for the easy layer separation of the glycerol-biodiesel mixture. The filtration port is a flat bottom cylindrical vessel having sieve like provision. Filter paper was properly placed at the bottom of the vessel. The liquid mixture of biodiesel, methanol, and glycerol after filtration can be allowed to settle in the separation tank (g). After the settling, the glycerol separated biodiesel layer can be pumped to the methanol distillation tank (k) via pump t_2. The image of filtration and settling units are provided in the figure 2.5.

![Filtration and settling unit](image)

**Fig 2.5 Filtration and settling unit**

### 2.9.3 Methanol recovery unit

In the present pilot plant, there is also a provision for the recovery of excess methanol used for the reaction, which makes the
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entire process cost effective. The methanol distillation tank (k) contains a 2 kW SS coil heater. The top of the methanol distillation tank is equipped with a condenser (l) made of PVC and copper coil, and it was connected to the methanol collection tank (n). The copper coil was connected to the distillation tank via a 4 cm diameter SS 316 tube. The entire system was sealed to achieve the required vacuum. The excess methanol can be collected (in tank n) here under vacuum at a temperature of 50 °C. The same vacuum pump (u) is meant for the filtration of the catalyst. Figure 2.6 shows the image and schematic of the methanol recovery unit and the condensation port respectively.

Fig 2.6 Methanol recovery unit and schematic of condensation port
2.9.4 Biodiesel purification

Beside the major components, there is a provision for the purification of the biodiesel produced in the pilot plant. Washing tank \( o \) equipped with stirrer, hot water tank \( m \) equipped with heating coils and drying tank \( p \) are meant for the purification of the crude biodiesel.

In summary, we have skillfully designed and expertly assembled the components of the pilot plant for the pilot scale economic production of biodiesel which has the promise of easy industrial scale up. Thus constructed biodiesel pilot plant is designated as SNGS Model 1. Since the components are made of PP vessels, it makes the entire unit become cost effective, light weight and offers a lot of promise for an easy and economical industrial scale up. The pilot plant is a skid mount unit, which is movable and can be easily transported from one place to other. The temperature inside the vessels is controlled digitally and the maximum temperature engaged in the biodiesel production is 65 °C. Continuous condensation of methanol inside the reaction vessels avoids the high pressure generation inside the vessels and hence the entire process is safe. The filtration port ensures the separation of solid catalyst and the catalyst may be recycled and reused, which makes the process further green and economical. Methanol recovery unit in the biodiesel pilot plant is another peculiarity and thus the recovered excess methanol can be reused. The production capacity of the biodiesel pilot plant is 15 L biodiesel/run. The entire set up was cost effective, eco-friendly and highly feasible for the industrial scale up.
2.10 Catalyst preparation unit

A cylindrical PP vessel equipped with heating coils and mechanical stirrer is used for the bulk scale preparation of the catalyst. The capacity of the PP vessel is 120 L. The stirring speed of the mechanical stirrer is varied by a controller and the required temperature inside the vessel is controlled and maintained using digital temperature controller. The catalyst preparation vessel set up is also employed for the degumming of the oil feedstock. The photograph of the set up is shown in the figure 2.7.

Fig 2.7 Degumming and catalyst preparation unit
2.11 Degumming of oil feedstocks

Degumming of filtered oil (JCO/UCO) was done to eliminate phospholipids and was performed by thermal treatment with water with the assistance of a degumming agent, phosphoric acid [57, 58]. Figure 2.8 shows the settled gum from the oil

Fig 2.8 Degumming of used cooking oil in the laboratory scale

In bulk, degumming was done in the catalyst preparation unit, which is a cylindrical PP vessel equipped with heating coils and mechanical stirrer (section 2.11, figure 2.7). In this process, the filtered oil was first heated to a temperature of 60 °C. As the temperature was achieved, 0.01% phosphoric acid by weight of oil was added to the oil and the mixture was then stirred for 30 minutes with heating. 2 wt% of water was added to the above mixture followed by increasing the temperature and maintained at 70 °C-80 °C for 15 minutes [59, 60]. Gums present in the oil settled at the bottom were drained off. The oil was dried using anhydrous Na$_2$SO$_4$. 
2.12 Biodiesel production in the pilot plant

The detailed procedure for the biodiesel production in the pilot plant is provided below. JCO and UCO were used as the feedstocks for the biodiesel production over different catalysts. The different stages in the biodiesel production are discussed in the following sections.

2.12.1 Pretreatment of Degummed Oil

There is no change in the experimental procedure between laboratory scale and pilot scale pre esterification reactions, the only difference is in the equipments where the reaction was carried out. In the laboratory scale, experiments were conducted in round bottom flasks made up of Borosil glass that was fitted with Liebig condenser. Temperature was maintained in the oil bath where the reactions were performed. The figure 2.9 shows the pretreatment process in the laboratory scale set up.

Fig 2.9 set up of pretreatment of used cooking oil in laboratory scale
In the pilot plant, experiments were performed on PP vessels. Separate provisions were available for each step of the biodiesel production process. At first, degummed oil (from tank a) was added to the pretreatment vessel (j). Adequate amount of methanol (6:1 w.r.t oil) (from methanol storage tank b) and acid (HCl, 6 wt%) (from acid storage tank h) were added to the oil in the pretreatment vessel and then mixed thoroughly with stirring. Pretreatment was done at a temperature of 50 °C for 1 h [61, 62]. Water was poured to the vessel following the pretreatment and after layer separation, bottom layer was discarded and washing was repeated thrice to remove remaining acid from the oil. The washed pretreated oil was then transferred to the storage tank via pump (t1). The pretreated oil was made water free using anhydrous Na₂SO₄.

2.12.2 **Transesterification reaction in the pilot plant; catalyst and glycerol separation**

The pretreated oil (~15 kg) was passed to the reaction vessel (e) and was mixed with specified amount of methanol (from tank c) with stirring. Required amount of catalyst was added through the opening on the top of the reaction vessel while stirring and the reaction mixture was heated to the desired reaction temperature for specified reaction time. Then the reaction mixture was transferred into the filtration port (f) and the catalyst was separated by filtration under suction. The liquid mixture of biodiesel, methanol, and glycerol were collected in the separation tank (g) and allowed to settle the glycerol with layer
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separation. The lower glycerin layer was drawn off from the bottom of the separation tank.

2.12.3 Methanol recovery

The crude biodiesel was then passed into the methanol distillation vessel (tank k) via pump (t₂). The unreacted methanol was recovered under vacuum at a temperature of 50 °C and was collected (tank n).

2.12.4 Purification of biodiesel

The methanol separated biodiesel was passed to the washing tank (tank o) to purify with warm deionized water from the hot water tank (m). As in the case of a homogeneous catalyzed process, there is no step required to neutralize the biodiesel since the catalyst was already separated. Washing with water was performed with gentle agitation so as to ensure complete removal of any traces of methanol, glycerol or any other impurities present in the biodiesel. The washed biodiesel was then passed to the moisture remover tank (p), where the remaining water was separated using anhydrous sodium sulfate. Pure biodiesel was then collected and stored.

2.13 Determination of fuel properties of biodiesel

Two major fuel specifications establishing the quality requirements for mono alkyl ester based biodiesel as fuels are the ASTM D 6751 in USA and the EN 14214 in Europe [63-67]. Fuel properties of the biodiesel made in the pilot plant were determined
using standard test procedures. The fuel properties like ester content, free and total glycerol, mono, di and triglycerides etc were analyzed by GC analysis (method ASTM D 6584) and some of the other parameters such as acid value, iodine number, water content, density, viscosity etc, were determined using standard analytical test methods described in the following sections and thus obtained biodiesel properties can be compared with standard fuel specifications to assess its quality [63-68].

2.13.1 FAME content

FAME content is meant to be a guide to the purity of biodiesel by way of measuring the conversion of triglycerides to methyl esters. In order to commercialize biodiesel as pure biofuel or blending stock for diesel fuels, it must meet the standard specifications for biodiesel fuel (FAME content of 96.5% by EN 14214). Ester content was usually analyzed using GC [63-68]. Mono-, di-, and tri- glycerides are also determined by the GC analysis.

2.13.2 Total and free glycerol

The most important criterion for a good-quality biodiesel is the completion of the transesterification reaction. The incomplete reaction will cause the presence of bound glycerol in the form of un-reacted triglycerides and intermediate mono- and di- glycerides. Another contaminant found in biodiesel is the free glycerol, which was not removed during the water washing of biodiesel.

The combination of the bound and free glycerol is referred to as total glycerol. These datas are calculated directly from the gas
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chromatogram on the basis of the ASTM D 6584, which is the prescribed standard method for measuring free and total glycerol. The total glycerol in a biodiesel sample is calculated using the formula [63-68].

\[
\text{Total glyceride} = G + (0.25 \times \text{MG}) + (0.15 \times \text{DG}) + (0.10 \times \text{TG})
\]

G - Free glycerol, MG - Monoglyceride, DG - Diglyceride, TG - Triglyceride

Besides the acylglycerols, residual alcohol (methanol) can contaminate the final biodiesel product. Amount of methanol can also be analyzed via GC.

2.13.3 Acid value

Acid value of the oil/fat/biodiesel sample indicates quantitatively the presence of free fatty acid in it. It is generally estimated by neutralizing the FFA in the sample with KOH solution of known concentration. Titration method is employed here to determine the FFA content in the sample. In a typical procedure, 1 g of biodiesel sample was accurately weighed in an Erlenmeyer flask and was dissolved in 10 mL isopropyl alcohol. Then, to the mixture, two drops of phenolphthalein was added and thoroughly shaken. It was then titrated with standardized KOH solution until a permanent pink color appears. The acid value was calculated from the titer value using the following formula [63-68].

\[
\text{Acid Value} = \frac{(A \times N \times 56.1)}{W}
\]
Where, ‘A’ represents Volume of KOH solution, ‘N’ represents the normality of the KOH solution and ‘W’ represents the weight of the biodiesel sample. According to the standard fuel specifications, the acid value should be less than 0.50 mg KOH/g (ASTM D 6751).

2.13.4 Water content

Water content is a detrimental factor affecting the quality of biodiesel by causing its auto oxidation, hence increasing the FFA concentration [63-68]. Water content in the biodiesel sample was analyzed by drying the sample using calcium chloride [69]. 10 mL of biodiesel sample is added to the previously weighed dry beaker and the mass of the sample is accurately weighed on a four digit electronic balance. Next, 1g of calcium chloride was separately weighed and added to the beaker containing the biodiesel sample. Then the beaker was kept inside a hot air oven at a temperature of 100 °C for 1 h. After that, the sample was cooled and accurately weighed and mass of the dried biodiesel sample alone was calculated [69].

\[
\text{Water Content} = \left( \frac{d}{t} \right) \times 100
\]

Where: d, represents the difference in oil weights in g.

\[t, \text{ represents the mass of the oil before heating in g.}\]

2.13.5 Iodine number

Iodine value (IV) or iodine number of oil is the measure of total unsaturation in the fatty acid chain and it is one of the quality determining factors for the use of biodiesel in diesel engines. IV is
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determined by calculating the number of moles of iodine added directly to the double bonds present in the fatty acid chain [63-67]. In a typical procedure for IV determination, 1 g of biodiesel sample was accurately weighed in an Erlenmeyer flask and about 25 mL of Wij’s solution was added to this sample. The solution was thoroughly mixed and kept at room temperature for 30 minutes. After that, 10 mL of 15% KI solution was added and again shaken for 2 minutes. The solution was then titrated with 0.1 N sodium thiosulfate. When the color of the solution becomes pale yellow, 1 mL of starch solution was added as the indicator. Then titration was continued until the blue color of the solution was disappeared and then the volume of the thiosulfate solution used up was noted. Similarly, a blank titration was also conducted without using biodiesel sample. From the titre values, the iodine number was calculated using the following formula [63-68].

\[
\text{Iodine value} = \frac{\text{Eq. wt of iodine} \times \text{vol. of Na}_2\text{S}_2\text{O}_3 \times \text{Normality of Na}_2\text{S}_2\text{O}_3 \times 100 \times 10^{-3}}{\text{Weight of biodiesel sample}}
\]

2.13.6 Viscosity

Viscosity of the biodiesel sample was determined using Ostwald’s viscometer apparatus. Ostwald viscometer is a commonly used viscometer, which consists of a U-shaped glass tube held vertically. For more accurate measurements, it is held in a controlled temperature bath. The liquid biodiesel sample was allowed to flow through its capillary tube between two etched marks (A and B) and the time of flow of the liquid was measured using a stopwatch.
Similarly the time of flow for reference sample, usually water was also calculated. The viscosity is calculated from the relation,

\[
\eta/\eta^* = dt/d^*t^*
\]

Where: \(\eta^*\) is viscosity coefficient of the reference sample (water), \(d^*\) is the density of the reference sample, and \(t^*\) is the time of flow of the reference sample. The other variables are viscosity coefficient (\(\eta\)), density (\(d\)), and time of flow (\(t\)) of the biodiesel sample [63-68].

### 2.13.7 Density

Density is mass of the substances occupying unit volume. It is an important fuel property, which is directly related to the engine performance and emission characteristics. The density was determined by measuring the volume of biodiesel accurately and its weighing was performed in a four digital electronic balance. 10 mL of biodiesel sample was accurately measured and transferred to a pre-weighed dried beaker and weighed the total mass. From the difference between weight of sample and beaker, the weight of the sample alone can be found out [63-68]. Then, the density of biodiesel sample is calculated using the formula,

\[
\text{Density} = \frac{w}{v}
\]

Where, ‘\(w\)’ represents the weight and ‘\(v\)’ represents the volume of the biodiesel sample.
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