3.1 Synopsis of methodology

In present chapter, materials and methodologies adopted for synthesis and characterization of catalyst, transesterification for biodiesel production and biodiesel characterization have been discussed. The catalysts for the present study were synthesized via co-precipitation and physicochemical methods. Then physicochemical characterization of catalysts was investigated using various spectroscopic techniques. Furthermore, the catalytic activity of synthesized catalysts in transesterification of the feedstocks, namely used vegetable oil and kusum oil was assessed through optimization and reusability study. The kinetics and thermodynamic studies along with green chemistry matrix were studied for biodiesel synthesis. The synthesized biodiesel samples were characterized by NMR (^{1}H and ^{13}C), GC-MS and physicochemical properties by using ASTM standards.

3.2 Materials

Chemicals: Barium nitrate (BaN_2O_6), aluminium nitrate hydrate ($AlN_3O_9 \cdot xH_2O$), ammonia solution, potassium carbonate (K_2CO_3), alumina (Al_2O_3), methanol (CH_3OH), sodium sulfate (Na_2SO_4) etc. chemicals were purchased from Merck Limited, Mumbai, India. All the chemicals were of analytical grade.

Feedstocks: The feedstock used vegetable oil (UVO) was collected from hostel canteens of the I.I.T. (BHU), Varanasi. After collection, it was filtered and dried in a hot air oven at 110 °C for 2 h to remove impurities in form of suspended food particles and moisture content respectively. Another feedstock, crude kusum oil was obtained from local market of Ranchi city, Jharkhand. The important physicochemical properties of the feedstocks are represented in Table 3.1.

Table 3.1 Important physicochemical properties of used vegetable oil (UVO) and kusum oil feedstocks

Properties	Used vegetable oil	Kusum oil
Color	Gardner color of 15	Gardner color of 13
Acid Value (mg KOH/g)	2.52	20.19
Density (g/cm^3)	0.913	0.893
Kinematic viscosity (40 ℃) mm^2/s	34.2	39.8
Saponification number (mg KOH/g)	185.9	184.3
Calorific value (MJ/kg)	41.3	39.24

3.3 Synthesis of heterogeneous base catalysts

3.3.1 Synthesis by co-precipitation route

Co-precipitation is the most effective synthesis process of precursors of catalyst constituting of more than one components. In co-precipitation method, more than one components are simultaneously separated out from their aqueous solutions. The alkaline salts require acidic solution and acidic salts are precipitated by basic solution. The control of pH is basic requirement for effective precipitation. The inorganic salts such as nitrates, carbonates or chlorides are used as metal precursors in co-precipitation method because of their high solubility in aqueous media. Commonly, the metal hydroxides and carbonates are precipitated from their precursor salt solutions by addition of an alkaline precipitating agents

such as ammonia or sodium bicarbonate. These metal hydroxides and carbonates are irreversibly converted into mixed metal oxides by performing calcination in temperature rage 400-900 °C [Jong, 2009].

3.2.2 Synthesis by physicochemical route

The physicochemical route is one of the commonly used methods for the synthesis of crystalline bulk materials. It is environmental friendly process as no toxic or wastes are generated. It is cost effective, facile and scalable approach. In physicochemical route, the solid state reactants react chemically at elevated temperatures by yielding a stable product material. Initially, the starting materials such as oxides and carbonates are mixed together in stoichiometric proportions thoroughly using mortar pestle or ball mill (for large samples > 20 mg). To achieve the homogeneous mixture of reactants during grinding, adequate amount of volatile organic solvent, acetone was added. After that, the obtained solid state powder mixture is calcined at high temperature using muffle furnace.

3.4 Catalyst characterizations

The physical and chemical properties of synthesized catalysts were investigated by various spectroscopic characterization techniques and were detailed as follows:

3.4.1 Thermal characterization (TG-DTA)

Thermogravimetric (TG) and differential thermal (DT) analysis are thermo-analytic techniques that interpret the variation in physicochemical properties of materials with temperature scanning. Physical changes include phase change such as melting, vaporization, crystallization, transitions between crystal structure, volume change by expansion and contraction and change

in mechanical behaviour, whereas chemical changes include new product formation, oxidation, decompositions, corrosion, chemisorption and dehydration. The thermogravimetric analysis records the changes in the mass of the sample as a function of temperature (or time) at a heating rate in controlled atmosphere. The plot of weight change (mg) against temperature is known as the thermogravimetric curve or thermogram. Differential thermal analysis monitors the difference in temperature in between materials under study and thermally inert reference and records as a function of programmed change of temperature. An endothermic event, takes place when the sample temperature is lower than the reference, whereas, in endothermic event sample temperature will be exceeded over the reference. The area under the DTA peaks is related to enthalpy change of the thermal event (ΔH). The differential temperature is plotted against temperature or time in differential thermal curve or thermogram [Gabbott, 2008].

Thermal characterization, TG-DTA were performed using SETSYS Evolution-2400 (SETARAM Inc. France) instrument in the temperature range of 27-1000 ºC at a heating rate of 10 ºC min^{-1} under the flow of dry air.

3.4.2 X-ray diffraction (XRD)

X-ray diffraction is a powerful non-destructive technique used to analyze the crystal structure, phase and preferred crystal orientation of crystalline materials. The X-ray diffractogram is recorded by the construction of interference of monochromatic X-ray beams diffracted at their corresponding angular position 2θ, determined by Bragg's law, from each set of lattice planes in sample.

$$2d \sin\theta = n\lambda \tag{3.1}$$

Here, n (an integer) is the "order" of diffraction, λ is the wavelength of the incident X-rays, d is the interplanar spacing of the crystal and θ is the angle of incidence [Warren, 1990].

The peak intensity in pattern gives the information of the distribution of atoms in long-range order within the lattice. X-ray diffractogram is a characteristic pattern associated with individual material. X-ray diffraction patterns enable the phase identification of a large variety of crystalline materials with the help of JCPDS (The Joint Committee on Powder Diffraction Standards) file. The average crystallite size can also be calculated from X-ray diffraction patterns with help of Debye-Scherrer equation by considering the intense diffraction peak:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad\qquad (3.2)$$

Where D is the average crystallite size, λ is the wavelength of the X-ray beam and β is the line broadening at full width at half maxima (FWHM) in radian and θ is the Bragg angle in degree.

X-ray powder diffraction (XRD) patterns of the synthesized catalyst were collected on a Rigaku MiniFlex300/600 powder diffractometer (Cu Kα radiations) with an applied voltage of 40kV and 15 mA anode current. The XRD patterns were recorded between 20º and 80º in 2θ and scan rate was 10 º/min with step width of 0.02 degree (2θ). The diffractogram was analyzed using the standard JCPDS files.

3.4.3 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a distinctive technique employed to interpret the structural elucidations and surface functional species of the catalyst. In addition,

it may also provide information about the quality and impurities present in the sample. The chemical bonds in a molecule produce unique infrared spectra of various vibrations between the bonded atoms. The wavelength of light absorbed is characteristic of the chemical bond in solid, liquid and gases samples [Griffiths and Haseth, 2007]. Most of the inorganic compounds gives the simple IR spectra in the range of 500-1500 cm^{-1} whereas organic compounds give descriptive IR spectra in range 1000-4000 cm^{-1}.

The FT-IR analysis was performed on ALPHA BRUKER Eco-ATR equipped with ZnSe attenuated total reflection (ATR) accessory over a scanning range of 500-3500 cm^{-1} with 4 cm^{-1} resolution.

3.4.4 Scanning electron microscopy- Energy dispersive X-ray spectroscopy (SEM-EDX)

In scanning electron microscopy analysis, the sample surface is finely scanned with a highly focused electron beam (primary). The resulting primary electron bombardment (0.5-30 kv) enters into sample surface and generates many low energy secondary electrons. The sample surface topography image at a gray scale can be constructed by measuring secondary electrons intensity as a function of the position of scanning primary electron beam. In addition to the emission of secondary electrons, backscattering of high energy primary electrons and the creation of elemental specific X-rays are also generated by primary electron bombardment. The intensity of backscattered electrons results in characteristic peaks of unique energy and can be correlated to the atomic number of the elements. Hence, qualitative (the type of elements) as well as quantitative (the percentage of the concentration of each element of the sample) compositional information can be obtained in form of elemental mapping.

Particle morphology, size and elemental composition of catalyst sample were analyzed by NOVA Nano SEM 450 equipped with EDAX-Ametek detector.

3.4.5 Textural characterization (BET-BJH)

The information regarding textural characteristics such as surface area, pore size and pore volume of the synthesized catalyst samples were evaluated by BET-BJH method. The specific surface determined by BET method relates the multilayer physical adsorption of small gaseous molecules such as nitrogen on the relative surface of the porous solids as a function of relative pressure. The specific surface area in (m^2/g) includes the external surface and pore surface and provides the information of surface porosity and particle size. The pore volume against diameter distribution was the result of adsorption-desorption of the BJH isotherm. The adsorbed amount of vapour at a relative temperature close to unity in the pore of the solid sample gives the information regarding total pore volume. The average pore size is estimated from the pore volume [Brunauer et al., 1938].

The total surface area, pore volume and average pore diameter of the synthesized catalysts were evaluated by nitrogen adsorption/desorption isotherms at −197 °C by the Brunauer–Emmet–Teller (BET) method using ASAP 2020 V3.02 H Micromeritics instrument (Micromeritics instruments corporation, USA). Isotherms were recorded to attain several points BET-surface area. Samples were degassed for 3h at 200 °C to remove the moisture. Pore size distributions of the catalysts were also determined from the adsorption branch of the isotherms in accordance with the Barrett–Joyner–Hallenda (BJH) method.

3.4.6 Basic strength and amount determination

Hammett indicator experiments were used to quantify the basic strength and the amount {Number of basic sites (mmol) in a unit weight of the solid} of the sample. The Hammett indicators used were bromothymol blue (H_=7.2), phenolphthalein (H_=9.3), 2, 4-dinitroaniline (H_=15.0), and 4-nitroaniline (H_=18.4). Typically, 25 mg of the catalyst sample was shaken with 1.0 ml of a solution of Hammett indicator followed by dilution with 10 ml of methanol and left for 2.5 h to equilibrate. Basicity of the catalyst was calculated by the titration method of Hammett indicator-benzene carboxylic acid (0.02 mol/L anhydrous methanol solution) and delineated in terms of Hammett basicity function (H_) as scaled by pKb value of indicators. The basic strength of the catalyst was taken to be higher than the weakest indicator that has undergone a colour change and lower than the strongest indicator that did not undergo colour change [Hammett and Deyrup, 1932].

3.5 Biodiesel synthesis

In present study, used vegetable oil biodiesel was synthesized by transesterification reaction, whereas kusum oil biodiesel was synthesized by esterification followed by transesterification reaction as described in the following section. Both the esterification and transesterification reactions were carried out on laboratory scale batch set-up using three-neck round bottom reactor equipped with water-cooled condenser, thermometer and mechanical stirrer. The reactor was immersed in temperature controlled water bath.

3.5.1 Biodiesel synthesis from used vegetable oil

Biodiesel was synthesized via single-step transesterification of used vegetable oil as the feedstock comprises the permissible limit of free fatty acid (2.52 mg KOH/g) according to

ASTM standards (<4 mg KOH/g). In a typical reaction, a specific amount of catalyst was activated by dissolving it into methanol and heating at 45±0.5 ℃ temperature through stirring in the reactor for 30 min followed by addition of 10 ml of UVO. The catalyst-methanol-oil mixture was heated at 65±0.5 ℃ for a certain time period. To overcome the mass transfer limitations in the triphasic reaction mixture, continuous stirring was maintained. After completion of the reaction, the catalyst was filtered using Whatman filter paper (grade 42) and excess methanol was collected by rotary evaporator for reuse. Then, the filtrate was taken into a separating funnel and left for 6 h for phase separation. The bottom layer containing glycerol and high-density impurities was decanted off and the upper layer containing FAMEs was washed with hot distilled water (60±0.5 °C). It was dried in hot air oven at 110 ℃ for 2 h followed by passing through anhydrous Na_2SO_4.

3.5.2 Biodiesel synthesis from kusum oil

3.5.2 (a) Degumming process

In general, crude vegetable oils contain some viscid defilement such as phospholipids known as gum. These gums are undesirable and removal of these impurities i.e. degumming is an imperative process, before the application of oils for biodiesel synthesis. The phosphoric acid degumming process was deployed for the removal of phosphatides from the crude kusum oil. In this process, 14% diluted phosphoric acid was added into the oil (by 0.5% volume) at elevated temperature (70 ℃) and stirred for 30 min with an agitation speed of 800 rpm. The gums were precipitated and observed at the bottom of oil-acid mixture which was separated via filtration process. The degummed kusum oil was washed 2-3 times with preheated distilled water (80 °C) and dried in a hot air oven at 110 °C for 2 h.

3.5.2 (b) Esterification reaction

Kusum oil biodiesel was synthesized via two-steps chemical process i.e. acid catalyzed esterification followed by alkali-catalyzed transesterification as the feedstock comprises high free fatty acid content of 20.19 mg of KOH/g. The esterification, a pretreatment step was performed to lessen the FFA in the feedstock to the ASTM norms permissible limit (4 mg KOH/g) by converting into corresponding esters (FAME). Without prior pretreatment step, a fatty solid product was formed as a result of saponification during direct transesterification. Initially, 200 ml of degummed kusum oil was heated in the reactor to the temperature of 45 ± 0.5 ºC for 15 min. Afterwards, 1.5% v/v H_2SO_4 as an acid catalyst and methanol in 1:10 molar ratio with oil was added followed by stirring at 650 rpm at 65 ± 0.5 ºC for 60 min. Once the reaction was accomplished, the mixture was poured into a separating funnel and allowed to stand for overnight to separate esterified oil from excess alcohol, sulfuric acid, water and impurities via decantation. The upper separated layer of esterified oil was washed with preheated (60 ± 0.5ºC) distilled water and dried in a hot-air oven at 110 ºC for 2 h. The acid value of esterified oil was found to 0.67 mg KOH/g and this oil was further undergone for transesterification reaction.

3.5.2 (c) Transesterification reaction

Initially, the activation of a designated amount of catalyst was performed by dispersing it into methanol through constant stirring in the reactor at 45 ± 0.5 ºC for 20 min. Now, the esterified kusum oil (10 ml) was added into the catalyst- methanol mixture and refluxed at 65 ± 0.5 ºC

for certain reaction time. During the reaction, above mixture was stirred constantly to maintain uniformity and mass transfer limitations. Once the reaction was completed, excess methanol was removed by rotary evaporator and solid catalyst was separated from the residual mixture using Whatman filter paper (grade 42). Following this, the filtrate was poured into a separating funnel and left for 6 h. Methyl esters were collected from the upper layer while glycerol and impurities from high-density bottom layer. The methyl ester phase was then washed with hot distilled water (60±0.5 °C) by spraying over the surface followed by drying in a hot air oven at 110 ºC for 2 h and finally passed through anhydrous Na_2SO_4.

3.5.3 Optimization Study

To enhance the catalytic performance of the synthesized catalyst in transesterification reaction, optimization study of reaction variables such as methanol: oil molar ratio, catalyst dose, temperature, the reaction time and stirring speed were investigated. As observed, reaction time is an important variable, hence in the present study time dependent optimization of methanol: oil molar ratio, catalyst dose, temperature and stirring speed with respect to biodiesel conversion were performed.

3.5.3 (a) Effect of methanol: oil molar ratio

To investigate effect of methanol: oil molar ratio, it was varied as 12:1- 24:1 for used vegetable oil and 9:1- 21:1 for kusum oil at 0-180 min of reaction time using $BaAl_2O_4$ catalyst while for $K_2Al_2O_4$ catalyst, 9:1-21:1 for used vegetable oil and 6:1-18:1 for kusum oil at reaction time 0-90 min were varied. Other reaction variables, namely catalyst dose, temperature and stirring speed were kept constant at optimized values [Tan et al., 2015; Shrirame et al., 2011].

3.5.3 (b) Effect of catalyst dose

The catalyst dose was varied between 1-5 wt% for used vegetable oil and 0.5-4.5 wt% for kusum oil at varying reaction time (0-180 min) in transesterification using $BaAl_2O_4$ catalyst. Whereas, catalyst dose 1-3 wt% for used vegetable oil and 0.5-2.5 wt% for kusum oil at differing reaction time (0-90 min) were considered for $K_2Al_2O_4$ catalyst. Other reaction variables methanol: oil molar ratio, temperature and stirring speed were set at optimized value throughout the experiments [Kumar et al., 2018; Pullen and Saeed, 2015].

3.5.3 (c) Effect of temperature

Reaction temperature was varied from 35 to 65±0.5 °C for both the feedstocks: used vegetable oil and kusum oil in transesterification using $BaAl_2O_4$ catalyst at 0-180 min of reaction time as well as using $K_2Al_2O_4$ catalyst at 0-90 min of reaction time. Other reaction variables methanol: oil molar ratio, catalyst dose and stirring speed were taken constant at optimized conditions throughout the experiments [Birla et al., 2012].

3.5.3 (d) Effect of stirring speed

The effect of stirring speed has been studied by varying it between 300 rpm to 700 rpm for used vegetable oil and kusum oil using $BaAl_2O_4$ catalyst with varying reaction time (0-180 min) and using $K_2Al_2O_4$ with varying reaction time (0-90). The methanol: oil molar ratio, catalyst dose and temperature were taken as optimized value during all experiments [Agrawal et al., 2012; Nayebzadeh et al., 2016].

3.5.4 Kinetics and thermodynamic studies

To investigate rate, required activation energy and free energy, the kinetics and thermodynamic studies of transesterification reaction were performed using Arrhenius and Erring equations. For the purpose, multiple batch reaction varying reaction time and temperature were performed.

3.5.4 (a) First-order kinetics

The overall rate of transesterification reaction can be expressed in terms of reactant by following equation (3.3):

$$r = d[TG]/dt = -k\,[TG]^n \tag{3.3}$$

Here TG is the concentration of triglycerides; t is the reaction time (min); n is the order of the reaction and k is the rate constant of reaction [Malani et al., 2017]. A kinetic model was developed for the transesterification reaction using following assumptions;

- Isobaric and isothermal reaction conditions during reaction

- Excess methanol molar concentration which is remain constant throughout the reaction

- Irreversible reaction assumption due to high methanol concentration

Under the above assumptions, transesterification reaction tends to follow pseudo-first order kinetic model and equation fitted to the conversion data of FAME can be expressed as under:

$$\frac{\ln(1-x)}{t} = -k \tag{3.4}$$

Where, x is the fraction of conversion of triglycerides at time t. k is the rate constant value and it can be calculated from the slope of the plot of -ln (1-x) vs. t at the different studied temperature [Feyzi and Shahbazi, 2017].

3.5.4 (b) Activation energy calculation

Since, the reaction rate has positive dependence with the reaction temperature. Furthermore, the activation energy required for the process was also investigated by using Arrhenius equation

$$k = A \exp (-Ea/RT) \qquad (3.5)$$

A is the frequency factor and R is the universal gas constant (8.314 J $K^{-1}Mol^{-1}$). The logarithmic form of equation 3.5 can be written as:

$$\ln k = \ln A - \frac{Ea}{RT} \qquad (3.6)$$

The Arrhenius plot of ln k versus 1/T (100/K) gives a straight line. The activation energy and frequency factor (A) were quantified from the slope (-Ea/R) and intercept (ln A) by linear fitting [Nautiyal et al., 2014; Choudhury et al., 2014].

3.5.4 (c) Thermodynamic studies

To interpret the important features of transesterification reaction such as enthalpy (ΔH), entropy (ΔS), and the Gibbs free energy (ΔG), thermodynamic studies were performed. Eyring-Polanyi equation was used to calculate the Gibbs free energy as following which describe the temperature dependence of reaction rate-

$$k = K.k_B \frac{T}{h} exp^{-\Delta G/RT} \qquad (3.7)$$

Where, k, K, k_B, T, h, ΔG and R are rate constant, transmission coefficient (usually taken as unity), Boltzmann's constant ($1.381*10^{-23}$ J.K^{-1}), absolute temperature (Kelvin), Plank constant ($6.626*10^{-34}$ J·s), free energy of activation, and Universal Gas Constant (8.3145 J/mol K) respectively [Deshmane and Adewuyi, 2013]. Taking the natural logarithm of equation 3.7 and substituting $\Delta G = \Delta H - T\Delta S$ gives

$$\ln \frac{k}{T} = \frac{-\Delta H}{R}.\frac{1}{T} + [\ln K + \ln \left(\frac{kB}{h}\right) + \frac{\Delta S}{R}] \tag{3.8}$$

Equation 3.8 describes the relationship between enthalpy and entropy with the rate constants. The Eyring-Polanyi plot (straight line with negative slope) in between 1/t versus ln k/T gives the intercept and slope values equal to $[\ln \frac{kB}{h} + \frac{\Delta S}{R}]$ and $\frac{-\Delta H}{R}$ respectively.

3.5.5 Green matrix formulation

The quantitative assessment on environmental impact of biodiesel synthesis reactions, Environmental-factor (*E*-factor) and Process mass intensity (PMI) were deliberated. These green chemistry matrix significantly consider the waste disposal of the synthesis processes used. E-factor is defined as ''the mass ratio of waste to desired product'' and PMI is ''the total mass utilized in the process divided by the mass of product''.

The E-factor and PMI of methyl transesterification reactions of used vegetable oil and kusum oil feedstocks using $BaAl_2O_4$ and $K_2Al_2O_4$ catalysts have been calculated as follows (Eqution 3.9 & 3.10):

$$E - factor = \frac{\text{weight of waste (mg)}}{\text{weight of product (mg)}} \tag{3.9}$$

A higher E factor value of a process means more wastes are generated and, consequently, lesser green approach of process having negative environmental impact. Moreover, to raise the accuracy, the issues like solvent reusability and catalyst recyclability are omitted by E-factor.

$$Process\ mass\ intensity\ (PMI) = \frac{weight\ of\ mass\ used\ in\ process\ (mg)}{weight\ of\ product\ (mg)} = E - factor + 1$$

(3.10)

The reaction efficiency, stoichiometry, amount of solvents and all reagents are considered in calculation of PMI.

3.5.6 Reusability and regeneration of catalysts

The reutilization test of heterogeneous catalyst is an imperative aspect to make its use cost-effective and preferable over a homogeneous catalyst. In order to investigate the reusability of catalyst, the spent catalyst was recycled in the consecutive five batch runs under optimized reaction conditions. The catalyst was removed after completion of each catalytic experiment and regenerated by washing with anhydrous methanol, dried at 110 °C for 5 h in hot air oven followed by calcination at 600 °C for 3 h. During regeneration, washing and heat treatment steps were carried out to remove reaction media molecules from the surface of the catalyst [Nayebzadeh et al., 2016].

3.6 Biodiesel characterizations

3.6.1 Nuclear magnetic resonance study

Nuclear Magnetic Resonance spectroscopy is a powerful analytical tool to elucidate molecular structure. ^{1}H and ^{13}C NMR analysis were performed on BRUKER 500 (advance

III HD) and CDCl$_3$ was used as a solvent and tertramethylsilane as internal reference. The conversion of triglycerides in feedstocks into methyl esters was calculated using the following equation proposed by G. Knothe, 2006[1].

% conversion = 2 I$_{(CH3)}$ / 3 I$_{(\alpha\text{-}CH2)}$ * 100 %   (3.11)

Where I$_{(CH3)}$ is the integral value of methoxy methyl ester peak at 3.68 ppm (singlet peak) and I$_{(\alpha\text{-}CH2)}$ is the integral value of α-methylene peak at 2.3 ppm (triplet peak) respectively.

3.6.2 Gas chromatography-mass spectroscopy (GC-MS) analysis

The Gas chromatography-mass spectroscopy is an important tool to investigate the fatty acid methyl ester compositions of synthesized biodiesel from used vegetable oil and kusum oil feedstocks. The GC-MS studies were performed on Gas Chromatography (Agilent 7890 B) and Mass Spectroscopy ((Agilent 5977 A). HP-1 column was used for the separation. (GC-MS). The carrier gas helium was used with flow rate of 3 ml per min. Temperature ramping was started from 70 °C to 300 °C with 3 °C per min ramping rate. The obtained data were compared with the NIST database for identification of fatty acid methyl esters in synthesized biodiesel samples.

3.6.3 Physicochemical characterizations

The important physicochemical characteristics such as acid value, density, kinematic viscosity at 40 °C, calorific value, flash point, fire point, cloud point, pour point and cetane number of the synthesized biodiesel were evaluated by following the procedures as specified by American Society for Testing and Materials (ASTM) standard. The properties of synthesized biodiesel are influenced mainly by quality of feedstock, free fatty acid composition of the feedstock, type of production and purification procedure. Therefore,

installation of standards of fuel quality is a mandatory step to protect biodiesel consumers and producers as well as to support the development of biodiesel industries [Knothe, 2006][2]. Table 3.2 presents the ASTM test methods used to evaluate the physicochemical properties of biodiesel as well as its limit of standard in comparison to the diesel fuel.

Table 3.2 ASTM specifications of biodiesel as diesel fuel

Property	Units	Test method	ASTM D 6751	Diesel fuel
Acid value	mg KOH/g	ASTM D 664	≥0.5	0.36
Density	g/cm^3	ASTM D 4052	0.86 to 0.89	0.840
Kinematic viscosity (40 ºC)	mm^2/s	ASTM D 445	1.9 to 6.0	2.98
Calorific value	MJ/kg	ASTM D 240	>35	44
Flash point	°C	ASTM D93	>120	52
Fire point	°C	ASTM D93	-	89
Cloud point	°C	ASTM D2500	-3 to12	-
Pour point	°C	ASTM D97-05	-15 to16	-
Cetane number	-	ASTM D976	>47	40

3.6.3 (a) Acid value

Acid value is defined as the number of milligram of KOH required for neutralizing free fatty acids present in 1 g of oil or fat. It is the free fatty acid amount present in sample which is responsible for corrosion of internal combustion engine and fuel supply system. The very low

acid value (≥0.5) of biodiesel is desirable for fuel application in engine. The acid value was determined as per ASTM D 664 test method by an acid-base titration using KOH as titrant.

3.6.3 (b) Density

Density is the ratio of mass to volume expressed in g/L. It is notable fuel quality parameter which directly influences the performance characteristics of fuel such as cetane number and heating value. Fuel injected in fuel chamber is measured with respect to volume, so the change in density will influence the engine output power due to difference in mass of injected fuel. Biodiesel is denser than diesel fuel. The density of biodiesel was determined as per ASTM D 4052 standard using digital densitometer.

3.6.3 (c) Kinematic viscosity

Kinematic viscosity is an important measurement which affects the incomplete atomization of fuel in the combustion chamber resulting in deposition of particles in engine parts and ultimately reducing engine performance. Higher the viscosity, such tendency will be higher and that also causes a difference in injection timing and spray patterns during fuel ignition. The kinematic viscosity was evaluated by capillary viscometer which measures the resistance of the fluid to flow due to fraction using ASTM D 445 test method at 40 °C.

3.6.3 (d) Calorific value

Energy content of biodiesel is lower both on mass and volume basis as compared to the diesel fuel. Density reciprocally affects the fuel consumption in order to gain the same power from engine. Calorific value of a fuel is the amount of energy (in form of heat) released during combustion of unit quantity of fuel. High calorific value is dignified as better combustion of fuel that facilitates high-energy content and improved engine performance.

Biodiesel possesses a lower calorific value than diesel fuel as measured by ASTM D 240 test method by bomb calorimeter.

3.6.3 (e) Flash point and fire point

Flash point and fire point of fuel are important characteristics related to the ignition temperature of fuel. High flash and fire points are desirable in handling, storage and transportation safety and prevent unexpected explosion during combustion. On the other hand, high flash and fire point ensure high purity of biodiesel by removal of excess methanol. Residual methanol in biodiesel causes a significant elevation of these ignition properties. Flash point and fire point of biodiesel were determined as per ASTM D 93 test method using Pensky-Martens closed cup tester.

3.6.3 (f) Cloud point and pour point

The other fuel quality parameter is cold flow property which is denoted in terms of cloud point and pour point. Cloud point of a fuel is the temperature at which the liquid fuel becomes cloudy because of solidification of saturates and is responsible for clogging in engine fuel lines and filters causing problem in engine operability. The pour point is the temperature at which liquid loses its flow characters and become semisolid. The reason behind displaying higher cloud points and pour points of biodiesel is the presence of a significant amount of saturated fatty compounds which have consequentially higher melting temperature than unsaturated fatty compounds. Cloud point and pour point of biodiesel were determined as per ASTM D2500 and ASTM D 97-05 test method respectively.

3.6.3 (g) Cetane number

The ignitability of fuel is typically characterized by its cetane index, and a high cetane index results in a shorter ignition delay. Ignition delay is an important phenomenon, which is the time between start of injection and start of combustion. Shorter ignition delay is advantageous in better fuel-air mixing, lower NOx emissions and lesser occurrence of knocking phenomena in combustion process. The cetane number of biodiesel was determined as per ASTM D 976 test method using following equation;

$$CN = 454.74 - 1641.416\,D + 774.74\,D^2 - 0.554\,B + 97.803\,(\log B)^2 \tag{3.12}$$

Where, D is density and B is mid-boiling temperature of the biodiesel.