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Reduction of NO_x and HC emissions in Waste Cooking oil Biodiesel using Nanoparticles of CsTPA

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Abstract. Recyclable Nanoparticles of Cesium Tungstophosphoric acid (CsTPA) for reduced NO_x emission in biodiesel using waste cooking oil of high acid value was investigated. The synthesized nano catalysts were characterized using FTIR, XRD, DLS, BET and SEM. The maximum yield of biodiesel reached 91% under optimized reaction conditions of 4% catalyst (w/w of oil), molar ratio of alcohol to oil of 10:1 for 4 hours at 65 °C. Engine performance and emission characteristics of fatty acid methyl esters investigated in a four stroke diesel engine showed a decrease in the Brake Thermal efficiency and Mechanical efficiency with respect to diesel. The heteropolyacid successfully decreased the HC and NO_x emissions in the biodiesel with an average reduction of 28 % and 10.3 % respectively. The nano catalyst also had excellent catalytic stability and reusability making it a promising catalyst for FAME production.

Introduction

The world has a very high energy need, of which a major percentage is fulfilled by the combustion of fossil fuels. But there are downsides to fossil fuels, as they are non-renewable and the exhaust from its combustion has a large volume of CO₂, NO_x, sulfur compounds, etc. which facilitates global warming [1, 2]. To keep up with the high energy demands and the depleting energy sources [3],



prospects of tapping energy from alternate sources like nuclear, solar, hydroelectric, wind, geothermal etc. are being studied extensively. All these alternate sources are not as universal as fossil fuels as it depends on several factors (like availability of sunlight, dams, geysers, funding for nuclear plants etc.). So the need arises to explore other alternatives that are available globally. The need for an easily procurable fuel substitute led to the projection of biodiesel as a global alternative fuel with properties similar to the conventionally used fuels [4, 5].

Biodiesel is obtained by transesterifying oils and fats using alcohols like methanol and ethanol with glycerin as a by-product [2, 6, 7]. All the hurdles faced by other energy sources are overcome by biodiesel as it is carbon neutral [8], biodegradable, renewable, reduces greenhouse effect [9], produces useful by-products and can be used as such in diesel engines without any further modifications [1, 10, 11]. The catalyst used can either be a chemical or a bio catalyst or an entirely non-catalytic process for its production [3, 6].

Biodiesel has been controversial as the feedstocks used for its production are oils from plants, such as corn, soya bean, sugarcane and palm. This has led to debate over the importance of food over fuel [12]. Large quantities of land, fresh water and fertilizers are used in this process which leads to deforestation, water and soil pollution. In recent years, research is being carried out to solve this problem by using non-edible oils and oils using algae as feedstock. But all these feedstocks require more land to grow and more water resources, making the production of biodiesel to be almost economically non-viable [13].

Waste Cooking Oils (WCO) have an advantage over other oil sources, as it needs neither land for cultivation nor large quantity of water to process the feedstock and it is less costly [14]. The world produces million tons of WCO every year from various sources [15]. WCO is considered as a pollutant because vegetable oils form a very thin layer on water bodies affecting the aquatic life [5]. Therefore, use of WCO as a feedstock for biodiesel will cut down on pollution from WCO disposal and fossil fuels [11].

Homogeneous base catalysts are being widely used in transesterification reactions for synthesis of biodiesel from edible and non-edible oils [16]. Even though the alcohol requirement is low for these catalysts, the process suffers from serious drawbacks as the catalyst is intolerant towards water molecules and Free Fatty Acids (FFA) and requires high energy [17]. Water present in the raw material leads to saponification of the oil to form soap which reduces the percentage of yield. There is

an increase in the volume of waste water generated using these catalysts, as the soap formed has to be removed by water washing [6]. Also, the catalyst is ineffective with oils and fats having higher Acid Value (AV) [5]. Hence, the AV of such oils and fats have to be reduced before using it for transesterification process.

Homogeneous acid catalysts like H_2SO_4 and phosphoric acid H_3PO_4 are also being used in the production of FAME[18]. The advantages of homogeneous acid catalysts over homogeneous base catalysts are that they are tolerant for water and high FFA in the raw feed[4, 6]. However, the requirement of higher catalytic volume, increased alcohol requirement and high processing temperatures are significant drawbacks. Apart from that, the catalyst is not reusable and by products like glycerol ethers are formed[5, 9].

Enzyme catalysts like lipase are used in an immobilized form to produce biodiesel to prevent contamination of the enzyme. This method is pretty effective but the produced glycerol inhibits the activity of the catalyst thus reducing its reusability [9, 19]. Also the catalyst shows low reactivity in the presence of water and alcohol also affects the immobilization of the enzyme. Another disadvantage is that the storage of the enzyme is difficult as enzymes are sensitive to the environment and involve very high production cost [20, 21].

Heterogeneous acid catalysts and renewable sources have been proven to be effective in converting low grade oils which contains multiple types of impurity and oils with higher acid value to methyl esters [9, 22]. The catalyst has shown good yield up to 96 % and is environment friendly. But the process requires high temperatures and leaching of catalyst into product restricts this process from being a commercial success [2, 5, 9, 20]. Heterogeneous base catalysts like alkali metal oxides and carbonates like MgO and CaO and base zeolites are very sensitive to high FFA. The FFA poisons the active sites and water hydrolyzes the FFA and slows the reaction rate [5, 19]. This makes the production cost higher and the catalysts hard to work with [2].

Heterogeneous solid acid catalysts in particular Heteropolyacids (HPA), are an excellent replacement for liquid acids reducing corrosion problems, highly water tolerant and ecofriendly [23]. Moreover, HPA with keggin structure possesses high thermal stability and high acidity which makes it a super acid and is also reusable [24]. Among the several synthesized HPA's, 12-tungstophosphoric acid (TPA) is found to have very high activity and has been used for catalyzing a number of reactions [24]. TPA has a low catalytic surface area and is highly soluble in water and alcohols, which makes it

difficult during the recovery of the catalyst [4, 11, 25, 26]. It has been noted that addition of alkali metals such as Potassium (K^+) and Cesium (Cs^+) ions to TPA is carried out in order to form salts with the respective metal ions [27, 28]. Cesium Tungstophosphoric acid ($CsTPA$) is thus tolerant to polar solvents and has a higher surface area due to its micro porosity and is preferred [29-31]. It has a longer catalytic life than other heterogeneous catalysts. Using Cesium Tungstophosphoric acid in biodiesel production is very effective as direct transesterification occurs and reduces the number of intermediate processes. [4, 24, 25, 32]

The present work focuses on producing biodiesel from WCO with high FFA (around 60 mg KOH/g) using synthesized nano particles of Cesium Tungstophosphoric acid as catalyst and also to study the engine performance and exhaust emission characteristics of the produced biodiesel. The synthesized catalysts were characterized and the process conditions were optimized for maximum yield. Fatty acid composition was determined using GC and the properties were analyzed as per ASTM standards. Reusability studies were performed for analyzing the efficiency of the catalyst for sustained activity.

2. Materials and Methods

2.1 Materials

WCO was procured from street food vendors in Chennai which served fast food. The collected WCO was subjected to pretreatment to remove suspended solid impurities. AV of the WCO sample was tested to be 60.12 mg KOH/g. Tungstophosphoric Acid (99.9 %) and Cesium Carbonate (99%) were purchased from LobaChemie Pvt. Ltd. Methanol (99.8 % purity by weight) was procured from Himedia Chemicals. Potassium Hydroxide (85 %) and Sodium Sulfate (99.9 %) were purchased from Merck Specialties Pvt. Ltd. Standard Supelco 37-component FAME mix was purchased from Sigma-Aldrich.

2.2 Synthesis of Catalyst

The acidic Cesium Tungstophosphoric acid catalyst ($CSITA$) was prepared by adding aqueous solution of 1M Cesium Carbonate ($CsCO_3$) to the aqueous solution of 0.8M Tungstophosphoric acid (TPA) by titration method under continuous rapid stirring [28, 33]. The solution formed a milky suspension which was aged for 20 hours at room temperature and evaporated to 100 °C. The white powder was further calcined at a temperature of 300 °C for a time period of 2

hours. Similar procedure was followed to synthesize Cesium Tungstophosphoric acid catalysts (CS2TA) and (CS3TA) by varying the concentrations of Cesium Carbonate (1.5M) and (2.5M) with aqueous solution of Tungstophosphoric acid.

2.3 Characterization Techniques

BRUKER-Alpha FTIR spectrometer with OPUS software using KBr pellet method for transmission measurements was used in the range of 400-4000 cm^{-1} at 24 scan per spectrum at 22 cm^{-1} resolution to record the FT-IR spectra which was translated into a plot of absorbance percentage against wave number. The GE XRD 3003 TT diffractometer system with XRDA31 software was used to analyze X-ray diffraction, peak positions and peak broadening of Cesium Tungstophosphoric acid (CsTPA) catalysts employing Cu K α radiation of wavelength 0.154178 nm and a scanning angle between 10-70°.

The morphology of samples were obtained from Field Emission Scanning Electron Microscopy (High Resolution) using HITACHI Model S-4800 fitted with an energy dispersive analytical system (EDS, EDAX HORIBA) with a working potential of 15 kV. Malvern Zetasizer Nano ZS96 analyzer with a count rate of 291.4 kcps was employed to analyze the particle size distribution in aqueous media by the method of Dynamic Light Scattering. Samples were dispersed using double deionized water at 25°C for 60 seconds in a disposable cuvette.

Micrometrics ASAP 2020 and Porosity analyzer using N₂ adsorption-desorption isotherm method were used to measure the surface area and pore size distribution respectively at a temperature of 77K. The samples were pretreated by degassing under vacuum at 373K for 3 hours. Barrett-Joyner-Halenda (BJT) method was employed for calculating the pore size distribution.

FAME conversion of WCO was analyzed using GC-FID (Young Lin Instruments, 6500GC System) with injector, Flame Ionization Detector (FID) and DB-WAX [polyethylene glycol (PEG)] - Capillary column. The length, diameter and film thickness of the column used were 30 m, 0.25 mm and 0.25 μm , respectively. The injection was executed in split mode with a split ratio of 10:1 at 0.1 minute. The temperature maintained in the injector and detector were 220 °C and 250 °C, respectively while the oven temperature was programmed at 100 °C with 3 minute holding. With a heating rate of 8 °C/min, the temperature was increased to 240 °C for 10 minutes holding time. Flow rate of Nitrogen (carrier gas), Hydrogen and Oxygen were maintained at 10, 30 and 300 mL/min

respectively. Supelco 37-component FAME mix in Dichloromethane was the standard used in GC analysis.

Properties of WCO and the esters of WCO were tested using the American Standard Testing Methods (ASTM). An electrical dynamometer coupled, single cylinder, water cooled, four stroke Kirloskar Diesel Engine with an engine power of 5 HP, speed 1500 rpm, bore diameter 0.0875m, stroke length 0.11m and a compression ratio measuring 16:5:1 was used for engine test of biodiesel. The engine was connected with AVS DIGAS 444 gas analyzer for exhaust gas emission studies.

2.4 Transesterification Reaction

Experiments were carried out by adding preheated oil to a mixture of preheated methanol and catalyst at 300rpm. The mixture was stirred for specified time duration and temperature and cooled in a separating funnel until it separated into methyl esters (upper layer) and glycerol (lower phase). After the completion of the reaction, the methyl esters were washed with water to produce clear biodiesel. This procedure was duplicated for optimizing the reaction conditions i.e., Catalyst Weight percentage (1.5-6 %), Molar ratio of WCO to Methanol (1:3-1:21), Reaction Time (3-6 h) and Reaction Temperature (50-75°C). The catalyst was separated and then reused. Methanol was recovered using a rotary evaporator.

3. Results and Discussion

3.1 Characterization Studies of Cesium Tungstophosphoric acid

FT-IR studies of synthesized nanoparticles (CS1TA, CS2TA and CS3TA) were recorded after calcination as shown in Fig.1. Generally, keggin structured heteropoly acids are elucidative in finger print region in FT-IR spectroscopy. By analysis of individual bands in the finger print region, it is possible to realize that four oxygen atoms make four characteristic bands in the 1200-700 cm^{-1} range. Appearance of the bands is based on the degree of hydration as well as the nature of counter cations present [34]. In keggin structured heteropolyacids, PO_4 tetrahedron is

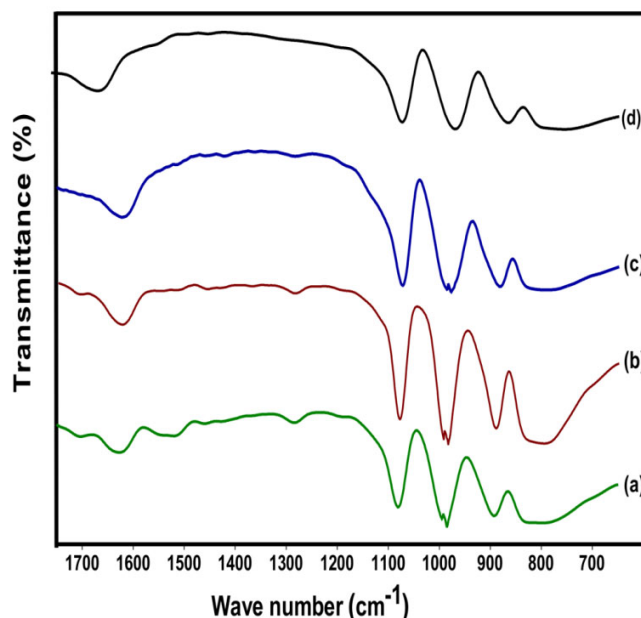


Fig.1: FT-IR Spectra of (a) CS1TA (b) CS2TA (c) CS3TA and (d) TPA

surrounded with 12 WO_6 octahedral with shared edges in W_3O_{13} triad group and corner between each triad via oxygen atom. Typical vibration peaks of keggin structured tungstophosphoric acid showed strong absorbance bands as: 1081 cm^{-1} (Stretching band of P-O in the central tetrahedron of PO_4), 983 cm^{-1} ($\text{W}=\text{O}_f$ terminal oxygen in the exterior WO_6 octahedron), 796 (bands for the $\text{W}-\text{O}_c-\text{W}$ corner sharing) and 893 cm^{-1} (bands for the $\text{W}-\text{O}_b-\text{W}$ bridge sharing) which coincide with literature [28]. The characteristic vibration of $\text{W}=\text{O}$ at 983 cm^{-1} split into 2 peaks at 985 and 993 cm^{-1} respectively which can be accounted for $\text{W}=\text{O}$ with H^+ (presence of H_2O) and interaction with Cs^+ ion. These results confirm the formation of CsTPA from Tungstophosphoric acid and Cesium carbonate.

XRD patterns of synthesized CS1TA, CS2TA, CS3TA and bulk TPA in the 2θ angle range between 10 - 70° is shown in Fig.2. The five reflection peaks between 25° to 40° can be accounted for the keggin structure of TPA. It can be seen that the location and crystalline structure of all the synthesized samples are very similar to bulk TPA. But the peaks are slightly inclined towards the higher angle in CS1TA, CS2TA and CS3TA which can be attributed to the presence of BCC structure of Cesium tungstophosphoric acid [32]. The XRD patterns of the crystalline phases in the synthesized samples were analysed and compared with JCPDS (Joint Committee of the Powder Diffraction

Standards) and the peaks confirmed the presence of keggin structured Tungstophosphoric acid in the synthesized samples (JCPDS No. 50-0305).

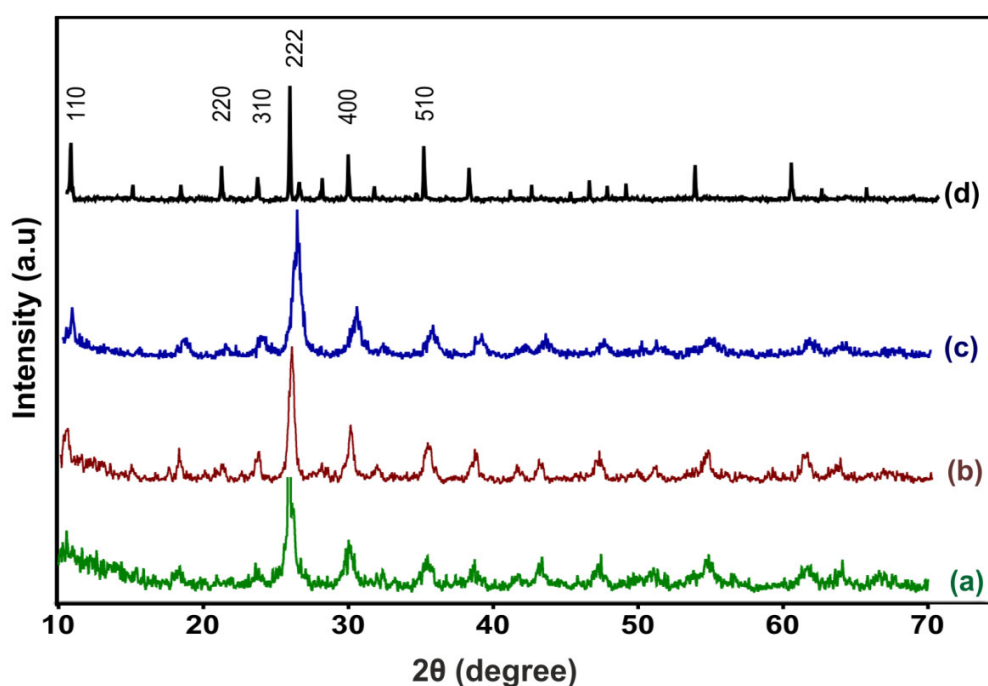


Fig.2: Powder XRD patterns of (a) CS1TA (b) CS2TA (c) CS3TA and (d) TPA

The average crystalline size of synthesized cesium tungstophosphoric acid and bulk TPA were also determined with the help of most intense peak using Debye-Scherrer's formula. Average crystalline size of CS1TA, CS2TA and CS3TA and bulk TPA were found to be 18.45, 13.28, 9.76 and 56.59 nm respectively. The X-ray diffraction studies show that CS3TA was found to have the lowest crystalline size when compared to CS1TA, CS2TA and bulk TPA.

Surface morphology studies of the synthesized catalysts CS1TA, CS2TA, CS3TA and bulk TPA using high resolution SEM, calcined at N_2 atmosphere is given in Fig.3(a-d). Fig.3 a&b depicts the SEM images of synthesized samples CS1TA and CS2TA which are spherically aggregate and have size below 100 nm. CS3TA was found to be spherical in nature with well-defined crystalline particle size less than 50 nm as shown in Fig.3c. SEM images of TPA as shown in Fig.3d shows particles with irregular shape. EDX spectra also recorded at various positions of samples indicate the

presence of elements Cesium, Oxygen, Phosphorus and Tungsten in all the synthesized samples as shown in Table 1.

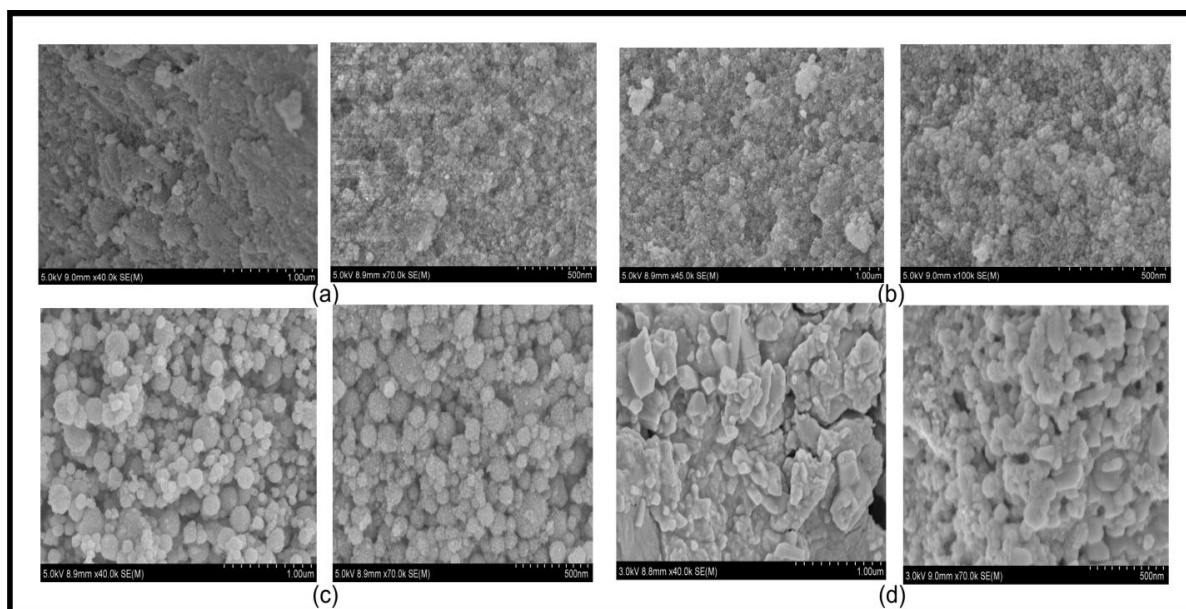


Fig.3: SEM images of (a) CS1TA (b) CS2TA (c) CS3TA and (d) TPA

Table.1: EDX quantification elements (a) CS1TA (b) CS2TA (c) CS3TA and (d) TPA

| Catalysts | Elements | | | | | | | |
|-----------|-------------|--------|-----------------|--------|-------------|--------|---------------|--------|
| | % of Cesium | | % of Phosphorus | | % of Oxygen | | % of Tungsten | |
| | Atomic | Weight | Atomic | Weight | Atomic | Weight | Atomic | Weight |
| CS1TA | 5.24 | 12.07 | 2.02 | 1.21 | 73.53 | 20.37 | 21.22 | 67.56 |
| CS2TA | 4.42 | 10.03 | 2.19 | 1.19 | 73.31 | 20.03 | 22.27 | 69.94 |
| CS3TA | 4.05 | 9.90 | 2.33 | 1.33 | 73.79 | 21.71 | 19.83 | 67.06 |
| TPA | - | - | 2.01 | 1.37 | 79.29 | 26.18 | 18.71 | 73.82 |

Dynamic Light Scattering (DLS) method measures the size as well as the Z-average of the nano particles using light scattered from a laser beam which passes through a colloidal suspension. The samples CS1TA, CS2TA, CS3TA and bulk TPA were dispersed in double deionized water to make a colloidal solution. The particle size and Z-average of bulk TPA was found to be 194 and 438 d.nm, respectively. Particle size of the catalysts increased from 194 to 506 d.nm when substituting TPA

with Cesium ions. Particle size of catalysts CS1TA, CS2TA and CS3TA was found to be 216, 239 and 506 d.nm respectively as shown in Fig.4. On the other hand, when decreasing the percentage of TPA, the Z-average of catalysts decreased from 438 to 154 d.nm. The Z-average of catalyst CS1TA, CS2TA and CS3TA was found to be 368, 160 and 154 d.nm respectively. Among the synthesized catalysts, CS3TA was found to have the lowest Z-average and highest particle size.

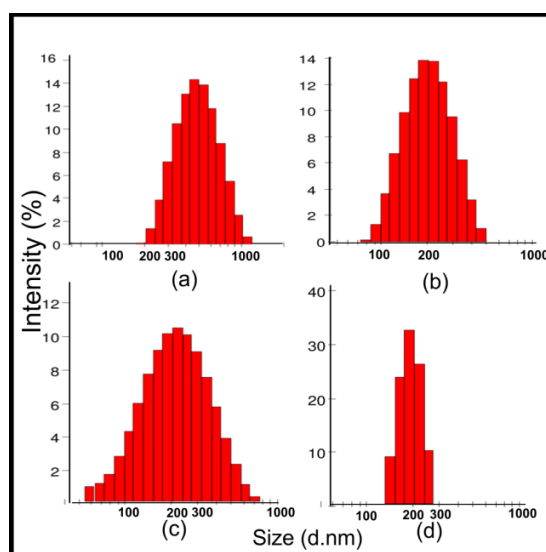
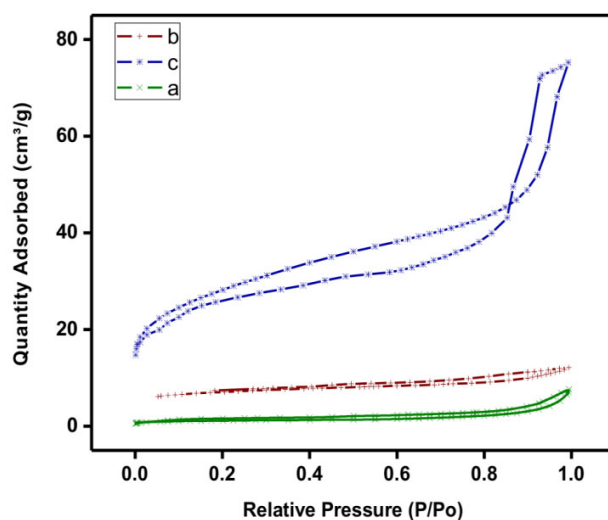


Fig.4: Average Particle Size Distribution of (a) CS1TA (b) CS2TA (c) CS3TA and (d) TPA

Surface area and pore size distribution studies using N_2 adsorption-desorption isotherms for all the synthesized catalysts are shown in Fig.5. Single and multi-point BET surface area, pore size and pore volumes of synthesised catalysts are given in Table 2. The single point surface area of catalysts CS1TA, CS2TA and CS3TA were found to be 3.75, 23.39 and 94.86 m^2/g , respectively. The multi-point BET surface area of catalysts CS1TA, CS2TA and CS3TA were found to be 5.81, 23.39 and 96.50 m^2/g , respectively. Since surface area is inversely proportional to pore size, we see from Table 2, that the pore size of the catalysts decreased with increase in surface area. On the other hand, the pore volume of the catalyst increased with increase in surface area.

Table-2: Single and multipoint BET, average pore size and pore volumes of synthesized catalysts**(a) CS1TA (b) CS2TA (c) CS3TA**

| Samples | Surface area (m^2/g) | | Pore size $d_{(\text{BET})}$ (nm) | Pore volume V_{BJH} (cm^3/g) |
|---------|--|----------------------|--------------------------------------|--|
| | Single point (BET) | Multi point (BET) | | |
| CS1TA | 3.75 | 5.81 | 12.41 | 0.0118 |
| CS2TA | 23.39 | 23.26 | 3.23 | 0.0187 |
| CS3TA | 94.86 | 96.50 | 4.82 | 0.1164 |

**Fig.5: N₂ Adsorption-Desorption of (a) CS1TA (b) CS2TA and (c) CS3TA**

Based on the characterization studies, catalyst CS3TA has high surface area, lower crystalline size, increased particle size and lower Z-average when compared to other catalysts and hence used for synthesis of biodiesel from WCO with high AV.

3.2 Optimization Studies of Process Variables

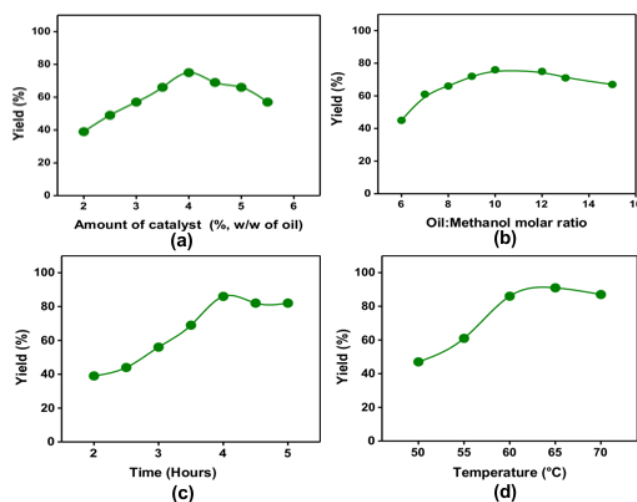


Fig.6: (a) Effect of catalyst Amount (b) Effect of methanol to oil molar ratio (c) Effect of duration of the reaction and (d) Effect of temperature of the reaction

Experiments were carried out by varying the amount of the catalyst in the range 2% to 5.5% (w/w of oil) while keeping the other reaction parameters constant at 9:1 alcohol to oil molar ratio for 5 hours at 60°C (Fig.6a). The yield increased from 39 to 75 %, with the increase in catalyst amount from 2 to 4% (w/w of oil). Increase in the yield could be attributed to the presence of more active sites for the transesterification reaction to take place [34]. However, when the amount of catalyst used for the conversion was increased to quantity higher than 4 % (w/w of oil), decrease in yield of FAME was noted. The decrease in yield may be due to the excess slurry formation making the mixture too viscous [35].

Due to the reversible and exothermic nature of the process, the molar ratio of alcohol was varied from 6:1 to 15:1 at constant catalyst concentration 4% (w/w of oil), 5 hours at 60 °C to get maximum yield. Yield percentage of biodiesel from WCO increased from 45 % to 75 % with increase in alcohol ratio from 6:1 to 10:1 as shown in Fig.6b. The yield % decreased beyond 10:1 which could be due to the increase in viscosity due to the accumulation of excess methanol in the mixture [36].

Effect of reaction time on FAME yield from WCO was studied by varying the time from 2-5 hours at a constant molar ratio of methanol to oil (10:1) and catalyst amount 4% (w/w of oil) at 60°C. It can be seen that the biodiesel yield increased to 86% with increase in reaction time as shown in

Fig.6c. Beyond 4 hours, the yield decreased slightly due to the blockage of pore openings of the catalyst with increase in time. Therefore, 4 hours was selected as appropriate transesterification time.

In order to study the influence of temperature on the yield, it was varied from 50 to 70°C and the effect on the transesterification process was studied as shown in Fig. 6d. With increase in temperature, the FAME yield increased to 91% at 65°C which might be due to the greater miscibility of methanol with oil and enhanced diffusion rate. Further increase in temperature to 70°C slightly decreased the yield from 91% to 84.9 %. This may be due to the vaporization of methanol which resists the reaction on the three phase interface [36]. The synthesized catalyst exhibited appreciable conversion of FAME even at low temperatures due to the high catalytic activity.

3.3 Reusable Studies of the catalyst

A remarkable feature of the heteropolyacid catalyst is its stability and sustained activity on repeated use. The catalyst was separated at the end of the reaction, stirred with methanol and hexane for 2 hours. It was dried at 120°C for 2 h to remove traces of moisture and reused. The results show a decrease in biodiesel yield by 4 to 16 % on recycling up to five cycles (Fig.7). The catalyst showed stable activity even after recycling.

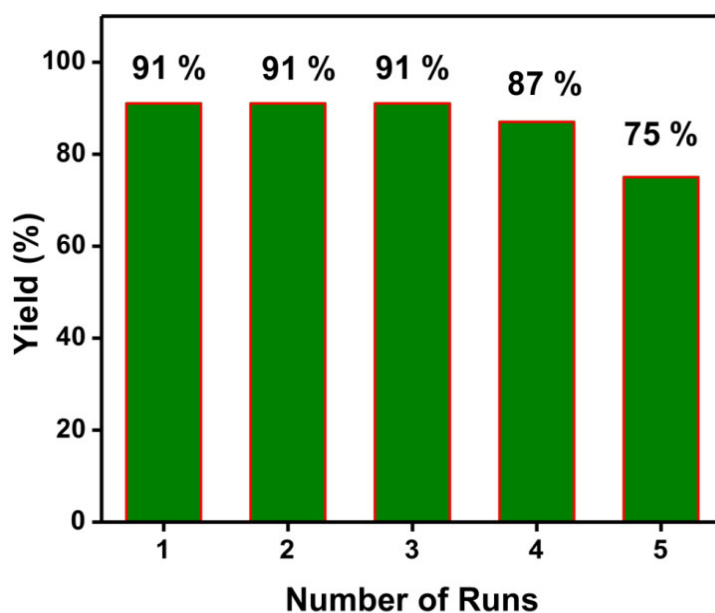


Fig.7: Reusability of catalyst CS3TA

3.4 Biodiesel properties

The important quality parameters of FAME obtained from WCO and raw WCO are shown in Table 3. All the measured values were in accordance with ASTM standards. The Cetane Number(CN) of FAME is found to be more than diesel. The cooking process and the molecular structure of WCO have an impact on the cetane number and other properties. Low-sulfur fuels play a vital role in reducing exhaust emissions. It can be seen that the sulfur content in the biodiesel is very low when compared with diesel, thus contributing to reduced emissions.

Table 3: Properties of Waste cooking oil, Biodiesel and Diesel

| Properties | Unit | Method | WCO | WCOME | DIESEL |
|------------------------|--------------------------------------|---------------|-------|-------|--------|
| Acid Value | mg of KOH/g | ASTMD974-14e2 | 60.32 | 0.81 | NA |
| Density | kg/m ³ (30 °C) | ASTM D1298 | 913 | 818 | 793 |
| Kinematic Viscosity | mm ² /S, 40 °C | ASTM D4016-14 | 5.4 | 4.8 | 3.5 |
| Calorific value | MJ/kg | ASTM D240 | 35.56 | 43.91 | 41.95 |
| Water content | % w/w | ASTM D2709 | 0.05 | 0.01 | 0.01 |
| Cloud point | ° C | ASTM D5772 | +8 | +6 | -14 |
| Pour point | ° C | ASTM D97 | +5 | +3 | -18 |
| Flash point | ° C | ASTM D93 | 208 | 124 | 75 |
| Fire point | ° C | ASTM D9390 | 220 | 133 | 82 |
| Sulfur content | Mass % | ASTM D5453 | 0.01 | 0.01 | 0.95 |
| Copper strip corrosion | 50 °C, 3 hours | ASTM D130-12 | 1 | 1 | 1 |
| Iodine value | g I ₂ 100 g ⁻¹ | ASTM D5768 | 72.5 | 96.2 | - |
| Cetane index | - | ASTM D976-06 | 42 | 53 | 49 |

3.5 Gas Chromatography analysis

The peaks in the WCOME chromatogram correspond to the presence of various esters in the sample and were identified by comparing with the standard FAME mixture. The compositions of FAME present in WCOME are shown in table-4 and Fig.8.

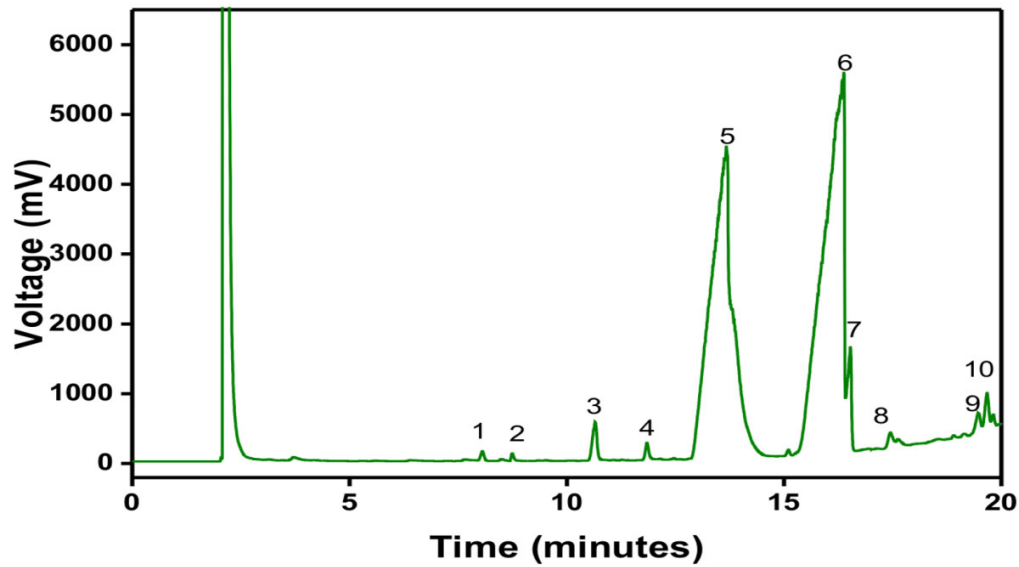


Fig.8: GC chromatogram of WCOME

Table-4: Composition of FAME obtained from WCO

| Peaks | Area (%) | Identified esters |
|-------|----------|----------------------------|
| 1 | 0.13 | Methyl dodecanate |
| 2 | 0.05 | Methyl tetradecanate |
| 3 | 1.05 | Methyl pentadecanate |
| 4 | 0.25 | Methyl octadecanate |
| 5 | 42.0 | Methyl 9-octadecenat |
| 6 | 53.9 | Methyl hexadecanate |
| 7 | 0.49 | Methyl 9-hexadecenat |
| 8 | 0.25 | Methyl 9,12-octadecadienat |
| 9 | 0.41 | Methyl eicosanate |
| 10 | 0.86 | Methyl 11-eicosenat |

3.6 Performance Studies

Brake Thermal Efficiency (BTE), Mechanical Efficiency (ME) and Brake Specific Fuel Consumption (BSFC) of biodiesel obtained from WCO and diesel were investigated.

Variation of BTE with respect to load percentages for diesel and WCOME is presented in Fig.9a. The BTE of an engine is inversely related to the fuel consumption. Results show an increase of BTE for WCOME and diesel with increase in load percentages. Better fuel consumption of both WCOME and diesel, leads to proper atomization, resulting in increase in power and reduction in heat loss. Lower BTE of WCOME is attributed to higher fuel consumption and low calorific value when compared to diesel [37]. The lesser heat content and the unsaturated condition of WCOME is another reason for reduction in BTE.

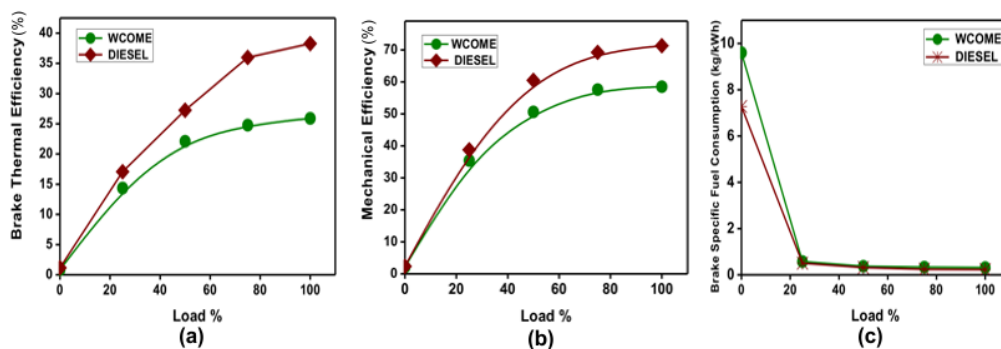


Fig.9: (a) BTE vs Load % (b) ME vs Load % and (c) BSFC vs Load %

The Mechanical Efficiency (ME) of WCOME and diesel were investigated with respect to load percentages as shown in Fig.9b. ME increased with increase in load percentages for both WCOME and diesel. But the mechanical efficiency of WCOME was slightly lower due to higher density, kinematic viscosity and low volatility which could have affected the atomization of the fuel. At 25 % load, the ME of WCOME was close to diesel but further increase in load % increased the ME for both WCOME and diesel. The average decrease in ME of WCOME was found BSFC of engine operated with both WCOME and diesel at various engine load percentages are given in Fig.9c. BSFC is inversely related to the BTE and has a tendency to decrease with increasing load percentages. Properties like kinematic viscosity, density, heating value and fuel injection influence the BSFC. The higher density of biodiesel leads to the plunger discharging more fuel in the fuel injection pump which eventually leads to increase in difference of BSFC between WCOME and

diesel. BSFC of both WCOME and diesel decreased by increasing the load percentages [38]. At 25 % of load, the variation between WCOME and diesel was found to be 13.8 %. Further increase in load conditions viz, 50 %, 75 % and 100 %, increased the variation of BSFC between WCOME and diesel by 17.8 %, 27.9 % and 29.3 %, respectively.

3.7 Emission Studies

Emission of Carbon monoxide (CO), Carbon dioxide (CO₂), unburned Hydrocarbon (HC) and Oxides of Nitrogen were investigated for both diesel and biodiesel obtained from WCO.

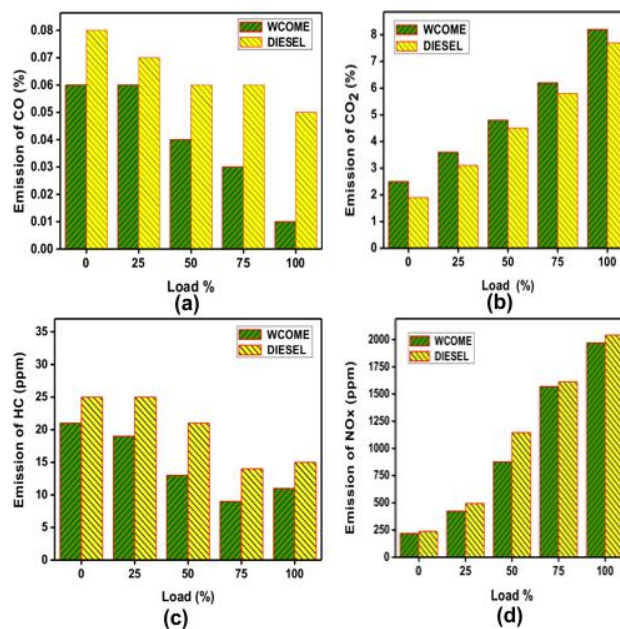


Fig.10: (a) CO emission vs Load % (b) CO₂ emission vs Load % (c) HC emission vs Load % and (d) NO_x emission vs Load %

Formation of CO is due to the partial oxidation from CO to CO₂ and insufficient burning of carbon atoms in the fuel. Emission of WCOME decreased for all load conditions with respect to diesel as given in Fig.10a. Concentration of oxygen in the fuel, engine speed and mixing of air and fuel are the influencing factors affecting the emission of CO [39]. The possibility of forming a fuel-rich zone is reduced due to the higher CN of biodiesel thus resulting in reduced CO emissions [40].

Variation of CO₂ emission of WCOME and diesel is shown in Fig. 10b. It is found that the emission of both WCOME and diesel increased with increasing load percentages. The high

concentration of CO₂ emission of FAME when compared with diesel is mainly attributed to the presence of high carbon and oxygen leading to complete combustion of biodiesel [41].

Fig. 10c depicts the variation of HC emissions for FAME and diesel from WCO. It is clear from the figure that, when the diesel engine is run on pure biodiesel the HC emissions are reduced [42]. The reason behind this reduction may be because of the increase in chain length of biodiesel (28 %) when compared to diesel [43]. CN also plays an important role in reducing the HC emissions. As the load percentage is increased, there is a considerable reduction in HC emission for WCOME due to higher CN leading to burning delay of fuel [44].

Emission of NO_x is a major concern in biodiesel synthesis. This is mainly due to combustion temperature, time and oxygen present in the fuel. Fig.10d shows the variation of NO_x emission levels with varying load percentages. It is found that the NO_x for both WCOME and diesel increased with increasing load percentages which might be due to increase in combustion temperatures and pressure inside the cylinder [45]. However, the concentration of NO_x was lower at all load percentages for WCOME than diesel with 23.5 % reduction at 50 % load [46]. This reduction in NO_x could be due to the catalytic activity of the synthesized heteropolyacid. It was encouraging to find an average reduction of 10.3 % when compared with diesel.

Conclusion

Catalytic activity of synthesized CsTPA nanoparticles for transesterifying high fatty acid WCO into biodiesel with lower NO_x and HC emissions was studied. The synthesized catalysts were characterized using FTIR, XRD, DLS, BET and SEM. CS3TA with high surface area (96.50 m²/g), lower crystalline size (9.76 nm) and lower Z-average (154 d.nm) was used for producing FAME from WCO. Reaction Parameters (temperature, alcohol/oil molar ratio, catalyst quantity and time) for maximizing the yield of WCOME were investigated. Highest yield of biodiesel was obtained at 65 °C, 4 hours at catalyst amount 4 % (w/w of oil) and 10:1 alcohol/oil molar ratio. FAME produced was in compliance with the ASTM standards. It was found that BTE and ME values were low for biodiesel than diesel. The average decrease in ME of WCOME was found to be 13.7 % when compared to diesel. HC emissions decreased by 28% in comparison with the conventional fuel. An average reduction in NO_x emission by 10.3 % was due to the catalytic activity of the synthesized heteropolyacid. Thus Cesium Tungstophosphoric acid, proved to be a potential reusable catalyst for producing eco-friendly biodiesel with improved performance and lower emissions.

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