PREPARATION OF HETEROGENEOUS CATALYST FOR THE TRANSESTERIFICATION OF WASTE COTTON SEED OIL

A

Thesis Submitted

In partial fulfillment for the award of the degree for

MASTER OF SCIENCE

IN

CHEMISTRY

Submitted By:
Ms. Satwinder Kaur
(301102013)

Under the supervision of:
Dr. Amjad Ali
Associate Professor

SCHOOL OF CHEMISTRY AND BIOCHEMISTRY
THAPAR UNIVERSITY
JULY, 2013

Acknowledgement

I would like to express my special thanks of gratitude to my teacher Dr. Amjad Ali, Associate Professor in School of Chemistry and Biochemistry for giving me this amazing opportunity and being a great supervisor. Without his guidance and persistent help this dissertation would not have been possible. I convey my special thanks to Dr. Satnam Singh, Head (School of Chemistry and Biochemistry) for allotting me the field of my interest for this thesis work.

I would not forget to remember Ph.D scholars Ms. Mandeep Kaur and Ms. Navjot Kaur for their unlisted encouragement and moreover their support and guidance till the completion of the project. I am highly obliged to the laboratory staff, Mr. Chander Singh for their help in every possible way.

Finally, an honourable mention goes to my family and friends for their understandings and supports on me in completing the project.

Satwinder Kaur

Place: Patiala

Date: 11.7.2013

Regards,

(SATWINDER KAUR)

CANDIDATES DECLARATION

I hereby declare that the work being presented in the thesis entitled, **"PREPARATION OF HETEROGENEOUS CATALYST FOR THE TRANSESTERIFICATION OF WASTE COTTON SEED OIL"**, being submitted by Ms. Satwinder Kaur to **Thapar University, Patiala**, in partial fulfillment of the requirement for the award of the degree of **Masters of Science in Chemistry in the School of Chemistry and Biochemistry, Thapar University, Patiala,** is my own work during the period of January 2013 to July 2013, under the supervision of **Dr. Amjad Ali,** Associate Professor, School of Chemistry and Biochemistry, Thapar University, Patiala. I have not submitted the matter embodied in this thesis for the award of any other degree.

Satwinder Kaur

Patiala **Satwinder Kaur**

Date: 11.7.2013

This is to certify that the above statement made by the candidate is correct and true to the best of our knowledge.

Dr. Amjad Ali
Associate professor and Supervisor
SCBC,
Thapar University, Patiala

Dr. Satnam Singh 11/7/13
Head, SCBC
Thapar University, Patiala

CERTIFICATE

This is to certify that the thesis entitled **"PREPARATION OF HETEROGENEOUS CATALYST FOR THE TRANSESTERIFICATION OF WASTE COTTON SEED OIL"**, being submitted by Ms. Satwinder Kaur to **Thapar University, Patiala**, in partial fulfilment of the requirement for the award of the degree of Master of Science in Chemistry, is a bonafide work carried out under my supervision, and that no part of this thesis has been submitted for the award of any other degree.

Dr. Amjad Ali
Associate professor and Supervisor
SCBC,
Thapar University, Patiala

Dr. Satnam Singh 21/7/10
Head, SCBC
Thapar University, Patiala

Dr. S. K. Mohapatra
Dean, Academic Affairs
Thapar University, Patiala

LIST OF CONTENT

ABSTRACT

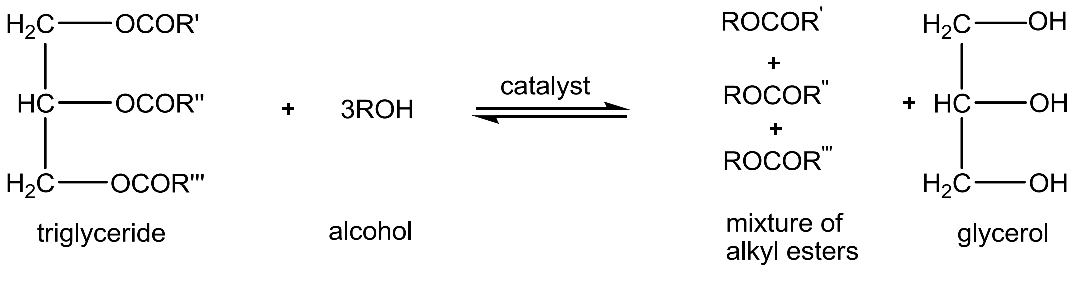
A series of WO_3/SiO_2–600 catalysts has been prepared by impregnating 5–25 wt% sodium tungstate dihydrate in silica by wet chemical method. Prepared WO_3/SiO_2–600 catalysts has been characterized by powder X–ray diffraction, scanning electron microscopy, BET surface area, and Hammett indicator test studies in order to correlate the catalyst structure and acidic strength with its activity. The prepared 20–WO_3/SiO_2–600 has been employed as heterogeneous catalyst for the transesterification of waste cotton seed oil (containing 4.9 wt% free fatty acid contents) with methanol. Under optimal reaction conditions *viz.*, methanol/oil molar ratio of 80:1, catalyst to oil weight fraction of 5 % and 65 °C reaction temperature, a 98±2 % fatty acid methyl ester (FAME) yield was obtained in 5 h of reaction duration. Under the same reaction conditions, the activation energy was found to be 37.71 kJ mol^{-1}. Few physicochemical properties of the prepared biodiesel sample from waste cottonseed oil have been studied and compared with EN standard values.

1. INTRODUCTION

Decreasing fossil fuel resources and increasing environment problems like depletion of ozone layer and global warming are the diverse reasons for the search of an alternate fuel such as biodiesel. Biological fuels such as, biomass, vegetable oil, compressed natural gas (CNG), liquefied natural gas (LNG) and liquefied petroleum gas (LPG) are being studied for the production of biodiesel [1]. However, vegetable oils are a good option [2], but oils have higher viscosity than conventional fuel which leads to engine fouling [3]. Hence, the oils are incapable to use directly as a fuel. So, a search begins to generate fuel similar in properties to that of diesel fuels but that are much greener and ecofriendly, so biodiesel came into concern.

Biodiesel is biodegradable and reduces the emission of hydrocarbons, carbon dioxide, carbon monoxide, and SO_X in exhaust gases [4]. It is environment-friendly, as CO_2 emitted by combustion of biodiesel is continuously fixed by plants and can be recycled by next generation crop, hence formed a closed carbon dioxide cycle [5], on the other hand, CO_2 emitted by petroleum diesel was fixed from the atmosphere during earth formative years. Additional advantages of the biodiesel are its high lubricity and higher cetane number in comparison to the conventional diesel fuel.

The word biodiesel comes from two terms bio + diesel; Bio refers to biological in origin and diesel refers to the fuel. Chemically biodiesel is fatty acid alkyl esters and produced via transesterification of vegetable oil (triglyceride) with alcohol in the presence of catalyst as shown in Scheme 1. Glycerol formed in this reaction is another important product and often used in cosmetics and pharma industry.



Scheme 1. Transesterification reaction of vegetable oil/fat in the presence of alcohol.

Theoretically any triglyceride may be used for the transesterification reaction, however, to avoid fuel *vs* food situation, use of edible oil is not advisable for the biodiesel production. In India, non edible oils such as jatropha and karanja oils are mainly used for the biodiesel production. Among alcohols, methanol is the most frequently used, due to ease of availability, high reactivity, and cheaper price. In recent past use of ethanol is also gaining the popularity owing to its lesser toxicity and renewability.

Among catalysts, homogenous base catalyst (e.g. NaOH and KOH) are used at industrial scale biodiesel production. This process yielded the acceptable biodiesel yield in relatively shorter reaction duration, although sensitive to the presence of free fatty acids (FFA) and moisture contents in the feedstock. Moreover, same catalyst yielded the biodiesel contaminated with catalyst and hence, required huge amount of water for the product washing and leads to generate excessive amount of effluents. In order, to circumvent the problems associated homogeneous catalysts now research has been directed for the development of the heterogeneous catalysts.

2. LITERATURE SURVEY

Biodiesel, chemically known as fatty acid methyl ester (FAME), is produced by the transesterification of vegetable oils or animal fats with methanol in presence of catalyst. Pure vegetable oil was tested for the first time as fuel by Rudolf Christian Karl Diesel hundred years before. However, due to discovery of the fossil fuel during the same period much attention has not been paid on the application of vegetable oil as an alternate to the diesel fuel. Due to increasing crude oil prices, environmental concern, and diminishing fossil fuel resources, vegetable oils and fats are being studied on a large scale now a days. Though there are various methods for the production of biodiesel such as dilution, microemulsions, pyrolysis, catalytic cracking and transesterification, however, transesterification with short carbon chain alcohols in presence of a catalyst is the most frequently employed process [6].

Stoichiometrically, three moles of methanol are required for the complete transesterification of one mole of triglyceride. Due to reversible nature of the reaction, a higher molar concentration of methanol is usually employed to obtain higher ester yield [7].

Acid, base and enzyme catalysts can be used for transesterification reaction. The acid and base catalyzed transesterification reactions could be further divided into homogeneous and heterogeneous catalysts categories. In enzyme-catalyzed transesterification methods, oils with high acid content can be used and glycerol formed as the byproduct can be recovered easily. Also, there are no side reactions produced in this case, however, due to high enzymes cost it is not economically viable at commercial scale [8].

2.1 HOMOGENEOUS CATALYSED TRANSESTERIFICATION

At industrial scale biodiesel is mainly produced by employing homogenous alkali catalyst (NaOH, KOH, etc.,) for the transesterification reactions. The main advantage of using homogeneous alkali catalysts is their high activity even under ambient conditions, lower cost and readily availability. However, these catalysts are highly sensitive to water and free fatty acid (FFA) content present in feedstock. High water content leads to soap formation, which causes reduction of ester yield and the separation of glycerol from methyl ester is difficult. The increase in viscosity and formation of emulsion [9,10] create many problems for purification and product recovery.

2.1.1 HOMOGENEOUS BASE CATALYSED TRANSESTERIFICATION

Few researchers reported the comparison of NaOH and KOH catalysts and their activity. Dorado et al. [11] focused on biodiesel production from different types of vegetable oils such as palm oil, animal fat with 5.12% FFA, Spanish olive oil with 2.24% FFA and a mixture of German vegetable oil with 1.28% FFA and KOH as catalyst during a two-step transesterification reaction. Their reported yield was 89–95%. The two-step transesterification process is better than one-step reaction since it needs a lower reaction temperature, less alcohol and amount of catalyst and reached a higher conversion [12].

2.1.2 HOMOGENEOUS ACID CATALYSED TRANSESTERIFICATION

The homogeneous acid catalysts (HCl, H_2SO_4 etc.,), unlike their base counterparts, are insensitive to FFA (free fatty acids), and they normally employed for the transesterification of vegetable oil having more than 1 % FFA contents. [13]. However, major problem with acids catalysts are their less reactivity and deactivation by the water, which is also a side product during the acid catalysed esterification reaction. Moreover, it causes the corrosion of the reactor and hence, costly acid resistance reaction vessel is required.

Freedman et al. [14] investigated the transesterification of soybean oil with methanol, 1 wt% sulfuric acid at 65 °C, molar ratio of 30:1 methanol/soybean oil and it took 69 h for 90% conversion of biodiesel. Canakci and Gerpen [15] evaluated that increasing the molar ratio, reaction temperature, weight of catalyst and reaction time in acid catalysed transesterification process causes higher conversion of waste cottonseed oil.

Acid catalysts are usually employed for the two step transesterification of feed stock with high FFA contents (> 1 wt%). In the first step acid catalyst is employed for the esterification of FFA with alcohol followed by acid neutralization and transesterification by base catalyst.

2.2 HETEROGENEOUS CATALYSED TRANSESTERIFICATION

In order to overcome the problems associated with homogeneous catalysts, research has been focused for the development of heterogeneous catalyst in recent past.

The heterogeneous catalysts have several advantages over homogeneous catalysts such as they could be recovered from the reaction mixture easily, reusable, and leads to the formation of non contaminated product and hence product formed required lesser purification steps.

Broadly heterogeneous catalysts could be divided in two categories viz., heterogeneous base catalyst and heterogeneous acid catalyst.

2.2.1 HETEROGENEOUS BASE CATALYSED TRANSESTERIFICATION

There are different types of heterogeneous base catalysts used in literature for the transesterification reactions such as calcium oxide [16], MgAZr [17], nano-magnetic KF/CaO-Fe_3O_4 [18], modified CaO by trimethyl chlorosilane (TMCS) [19], and supported solid base catalyst such as Eu_2O_3/Al_2O_3 [20], KI/Al_2O_3 [21], Na/NaOH/γ-Al_2O_3 [22]. Guo et al. [23] investigated the use of sodium silicate as solid base catalysts for the transesterification to achieve 95% yield at optimum conditions of 3.0 wt% catalysts, 7.5:1 molar ratio of methanol to oil, 60 °C reaction temperature, 60 min reaction time, and 250 rpm mixing intensity.

Sodium molybdate (Na_2MoO_4) used as heterogeneous catalyst for the transesterification of soybean oil under relatively mild conditions of low temperatures, short times, and normal pressure with fatty acid methyl esters (FAMEs) yields higher than 95% conversion. The catalyst was easily recovered and recyclable for another catalytic reaction without significant loss in activity [24].

2.2.2 HETEROGENEOUS ACID CATALYSED TRANSESTERIFICATION

In literature, several heterogeneous acid catalysts such as sulfated zirconia [25], TiO_2/SiO_2 [26], sulfonated polystyrene compounds [27] are reported by many research groups. Wang et al. [28, 29] investigated biodiesel production with two methods. The first method, involved FAME production from waste cooking oil with solid acid catalyst in a two–step process. In the first step 10:1 molar ratio of methanol to oil is taken at 95°C in the presence of 2 wt% ferric sulphate catalyst for conversion upto 97% however, in the second step 1 wt% KOH catalyst was used at 65 °C. In the second method, FAME is produced in a conventional acid catalyst system. The conventional method had around 90% conversion with 20:1 molar ratio of methanol to oil and 10 h reaction time. Cao et al. [30] produced biodiesel from high acid value and water content of waste cotton seed oil (WCO) and heteropoly acid as catalyst. This process had around 87% conversion for transesterification. The transesterification was carried out at 65 °C temperature, 70:1 molar ratio of methanol to oil, and 14 h reaction time. Jacobson et al. [31] attempted to search for a powerful solid acid catalyst for simultaneous transesterification and Esterification reactions where among (MoO_3/SiO_2, MoO_3/ZrO_2 and $WO_3/SiO_2/\gamma–Al_2O_3$ and ZS/Si) the zinc stearate immobilized on silica gel (ZS/Si) was more active than others, with 98% conversion. The optimum condition was, 18:1 molar ratio of methanol to oil, 600 rpm mixing intensity, 3% w/w catalyst, and 200 °C reaction temperature. Park et al. [32] used WO_3/ZrO_2 catalyst and WCO for biodiesel production. The highest conversion was 85% in a packed bed reactor, and the optimal condition was 75 °C reaction temperature and 20 h reaction time. But the conversion reduced to 65% in the next run and remained constant for up to 140 h.

Thus literature reported heterogeneous solid acid catalysts required high methanol to oil molar ratio, more reaction duration, high reaction temperature for the significant FAME yield. Further, the catalysts were found to show poor reusability due to the leaching of the active species from the catalysts support. In order to prepare a reusable catalyst for the transesterification of the waste cooking oil, In present study, sodium tungstate dihydrate has been impregnated over SiO_2 and prepared catalyst was characterized by FTIR, powder XRD and SEM techniques.

3. OBJECTIVES

1. To prepare tungsten impregnated silica as solid catalyst by wet impregnation method.

2. Transesterification of waste cottonseed oil using prepared 20–WO_3/SiO_2–600 solid catalyst.

3. To study the kinetics of reactions.

4. To study the physiochemical properties of the prepared biodiesel samples.

4. MATERIALS AND METHODS

Waste cottonseed oil (WCO) was collected from restaurants located at Patiala. The free fatty acid (FFA) and saponification value of waste cottonseed oil were determined by following reported methods [5] and values were found to be 4.9 % (w/w) and 190.2 mg of KOH/g, respectively.

Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$), tetraethyl orthosilicate (TEOS), Cetyl trimethyl ammonium bromide (CTAB) and methanol (99.8%) were purchased from Merck, India. Silica gel of reagent grade quality, for thin layer chromatography (TLC) was obtained from SD fine Chem Limited and used as such without further purification. Hexane, ethyl acetate and acetic acid used as solvent system for TLC were purchased from Loba Chemie, India and methyl oleate (99%) used as a biodiesel standard was procured from Sigma–Aldrich.

Powder X–ray diffraction (XRD) data was collected on Panalytical's X'Pert Pro with Cu Kα radiation. The samples were scanned in the range of $2\theta = 5–80°$ at the scanning speed of 2 °/min. The crystallite size of the catalyst particles were determined by following the Debye–Scherrer equation as given in equation 1.

$$\tau = 0.9\lambda / \beta \cos\theta \qquad (1)$$

Where, τ is the mean crystallite size (nm); λ is the X–ray wavelength; β is the line broadening at half of the maximum intensity (FWHM), θ is the Bragg angle.

Scanning electron microscopy (SEM) was performed on FESEM JEOL JSM 6510LV JAPAN to collect the SEM images of the catalysts. The surface area pore size and pore volume of the catalyst were determined by using the adsorption/desorption method at 77 K by the standard Brunauer–Emmett–Teller (BET) method using Micromeritics Tristar 3000 equipment. Prior to the analysis samples were degassed at 473K for 90 min under nitrogen atmosphere to remove the physisorbed moisture from the catalysts.

Fourier transform–infrared spectra (FTIR) were recorded on Perkin Elmer–Spectrum RX1 spectrophotometer. Fourier transform-nuclear magnetic resonance (FT–NMR) spectra of prepared biodiesel and waste cotton seed oil were recorded on a Bruker Avance–II (400 MHz) spectrophotometer. ^{1}HNMR was performed to calculate the % yield of FAME formation [33, 34]. The acidic strength of the catalysts was determined by simple acid base titration methods. In a typical experiment, 25 mg WO_3/SiO_2–600 catalyst was dissolved in 25 mL, 0.1M NaOH and resulting mixture was stirred for an hour. The catalyst would neutralize NaOH equivalent to its acidity. Remaining concentration of NaOH was determined by titration with standard HCl solution. Finally, the amount of NaOH neutralized by the catalyst was determined and represented as acidity of the catalyst as mmol of NaOH/g of catalyst [35].

4.1 CATALYST PREPARATION

To prepare sodium tungstate dihydrate impregnated SiO_2 solid catalyst, first mesoporous silica was prepared by the method reported in the literature with slight modification [36]. In a typical preparation, 2M solution of NaOH solution was mixed with 480 ml of distilled water and to this 4 g of CTAB, as surfactant, was added and resulted mixture was stirred with heating at 50 ºC. The solution become homogeneous after 30 min and to this 19.3 g of TEOS was added drop wise to form white slurry. The resulted mixture was filtered after 12 h, and white solid thus obtained was washed with distilled water, dried at ambient temperature and finally calcined at 600 ºC for 4 h to yield the mesoporous silica.

Mesoporous silica thus prepared has been employed as support for the immobilization of tungstate ions. In immobilization experiment, 10 g of prepared silica was suspended in 40 mL of deionised water, and to this 10 mL aqueous solution of $Na_2WO_4.2H_2O$ of desired concentration was added. The resulted slurry was stirred for 2 h, then washed with deionized water. Slurry was evaporated to dryness, heated at 120 ºC for 24 h and finally calcined at 600 ºC for 3 h. A series of WO_3/SiO_2 was prepared by varying the tungsten concentrations in the range of 5.0 to 25 wt%. The catalysts thus prepared were designated as x–WO_3/SiO_2–600, where x represents the wt% of tungsten in SiO_2.

4.2 TRANSESTERIFICATION OF WASTE COTTON SEED OIL

In a typical transesterification reaction, vegetable oil and methanol in 1:80 molar ratio and 5 wt% (catalyst/vegetable oil) were taken in a two neck, 50 mL round–bottom flask equipped with a water-cooled condenser and reaction mixture was stirred till the completion of the reaction at 65 °C.

The progress of the reaction and primary characterization of the products were carried out by thin layer chromatographic (TLC) technique using hexane/ethylacetate/aceticacid (90:9:1) as the mobile phase and silica gel as the stationary phase.

Biodiesel shows a higher mobility than vegetable oil with the selected solvent system, and complete conversion of vegetable oil to biodiesel was supported by the disappearance of the spot on the TLC plate. Further biodiesel so produced was characterized and quantified by ^{1}HNMR spectroscopy, following the literature reported protocol as given in equation 2.

$$\% \text{ Cme} = 100\ [2I_{me} / 3I_{\alpha CH2}] \qquad (2)$$

I_{me} and $I_{\alpha CH2}$ are the areas under the peaks corresponding to –OCH_3 protons and α–methylene protons, respectively in the proton NMR of FAMEs.

4.3 REACTION KINETICS

One molecule of the triglyceride required three molecules of alcohol for the complete transesterification and hence the order of the reaction should be four. However, in order to shift the equilibrium in forward direction this reaction is usually employed in presence of excess alcohol. Hence, transesterification is assumed to follow pseudo–first order reaction kinetics [37] as given in equation 3.

$$-\ln(1-X_{me}) = kt \qquad (3)$$

Where, k is the apparent first order rate constant (min^{-1}), X_{me} is the conversion of oil into FAME at time t,

To calculate the activation energy, reactions were carried out at four different temperatures, viz., 35, 45, 55 and 65 ºC. The conversion of WCO at different reaction times was obtained and activation energy was calculated by fitting the appropriate data in equation 4.

$$\ln k = \ln A - Ea/RT \qquad (4)$$

Where, E_a is the activation energy (kJ mol^{-1}), A is the pre–exponential factor (min^{-1}), R is the gas constant (8.314×10^{-3} kJ K^{-1} mol^{-1}) and T is the reaction temperature (°K).

5. RESULTS & DISCUSSION

5.1 CATALYST CHARACTERISATION

Acidic Strength

The acidic strength of pure silica was found to be 0.51 mmol of NaOH/g of catalyst. It remains silent towards the transesterification of triglyceride. The incorporation of tungsten on silica surface was found to enhance the acidic strength of tungsten impregnated silica as given in Table 1. The maximum acidic strength was observed in case of 20–25 wt% tungsten impregnated Silica, prepared at 600 °C calcination temperature.

Table 1. Comparison of BET surface area, acidity, for the WO_3/SiO_2-600 catalysed transesterification reactions.

Catalyst	***BET surface area ($m^2\ g^{-1}$)***	***Acidity (x 10^{-3} mmoles of NaOH/ g of catalyst)***
SiO_2	300.2	0.510
5–WO_3/SiO_2–600	228.2	0.925
10–WO_3/SiO_2–600	197.0	0.928
15–WO_3/SiO_2–600	162.2	0.947
20–WO_3/SiO_2–600	132.1	0.992
25–WO_3/SiO_2–600	119.4	0.992

*(**Reaction conditions**: methanol to oil ratio = 80:1 at 65 ºC reaction temperature, 5 wt% catalyst with respect to oil)*

Powder X-Ray Diffraction

The XRD patterns of WO_3/SiO_2 catalysts prepared by varying the tungsten concentration (5–25 wt%) are compared in Figure 1. The XRD pattern of pure silica shows a broad peak at $2\theta = 22.3^\circ$ to indicate its amorphous nature. The impregnation of sodium tungstate dihydrate over silica leads to formation of the highly crystalline WO_3/SiO_2 as could be seen from the appearance of sharp peaks in the XRD patterns. The XRD patterns of the 5–25 wt% tungsten loaded silica shows the diffraction peaks at $2\theta = 16.9^\circ$, 21.9°, 27.7° and 32.5°, and these are characteristics of the orthorhombic phase of tungsten trioxide (JCPDS No. 001–0486).

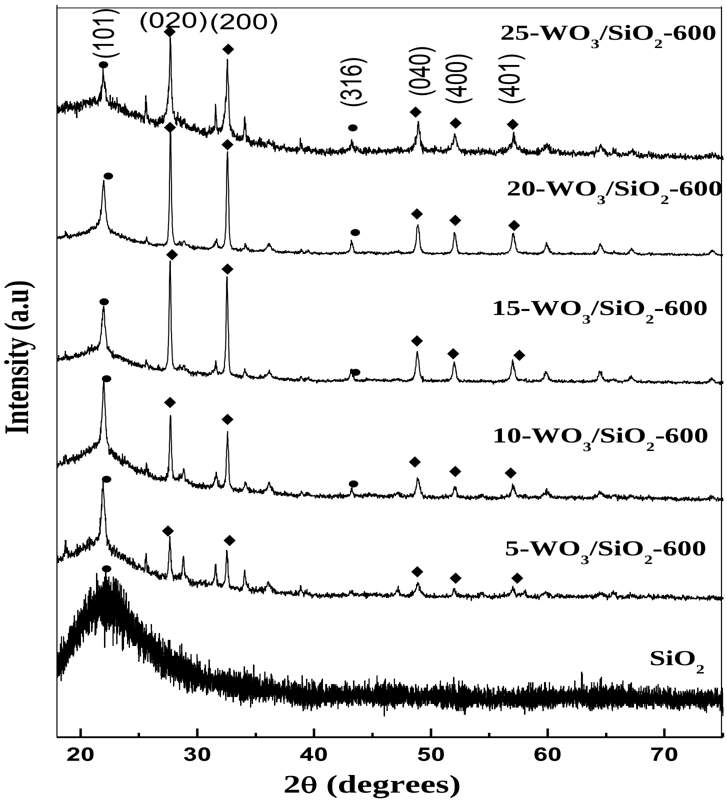


Figure 1. **Comparison of XRD patterns of prepared silica and (5–25 wt%) sodium tungstate dihydrate impregnated silica calcined at 600 °C. [SiO_2 (•) and WO_3 (♦)]**

The crystallite size of 5 – 25 wt% WO_3 impregnated SiO_2 was determined by XRD line breadth of crystal plane (020) by following Debye–Scherrer method [38]. The crystallite size increases gradually (Table 2) as the sodium tungstate dihydrate impregnation was increased in silica.

Table 2. Comparison of Crystallite sizes of (5–25 wt %) WO_3/SiO_2–600 catalysts.

Catalyst	*Crystallite size (nm), plane (020) at 2θ = 27.4 °*
5–WO_3/SiO_2–600	29.3
10–WO_3/SiO_2–600	32.4
15–WO_3/SiO_2–600	33.1
20–WO_3/SiO_2–600	38.7
25–WO_3/SiO_2–600	40.2

FTIR Spectroscopy

The comparison of the FTIR spectrum of the prepared catalysts is shown in Figure 2. A broad band observed at 3400 cm^{-1}, in all the samples is due to the stretching vibration of Si–O–H bond and water molecules adsorbed on the silica surface. A weak band around 1640 cm^{-1} is due to the bending mode of adsorbed water molecules while band around 1085 cm^{-1} may be due to the asymmetric stretching vibration of siloxane bond (Si–O–Si). The band at 800–805 and 468–472 cm^{-1} was attributed to symmetric stretching and bending modes of bulk Si–O–Si bond.

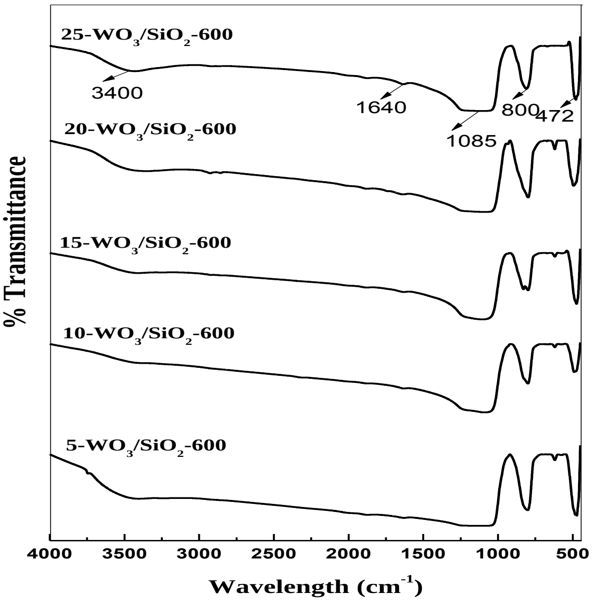


Figure 2. **FTIR patterns of (5–25 wt%) sodium tungstate impregnated silica calcined at 600 °C.**

SEM Images

The SEM images of the pure silica and 20–WO_3/SiO_2–600, have been compared in Figure 3. The silica particles have formed in spherical or oval shape with particle size of ~0.5 μm, as shown in Figure 3a. The chemical impregnation of sodium tungstate over silica causes the agglomeration of the particles and distortion from the spherical geometry as shown in Figure 3b. The average particle size of the prepared 20–WO_3/SiO_2–600 was found to be 1.2 μm.

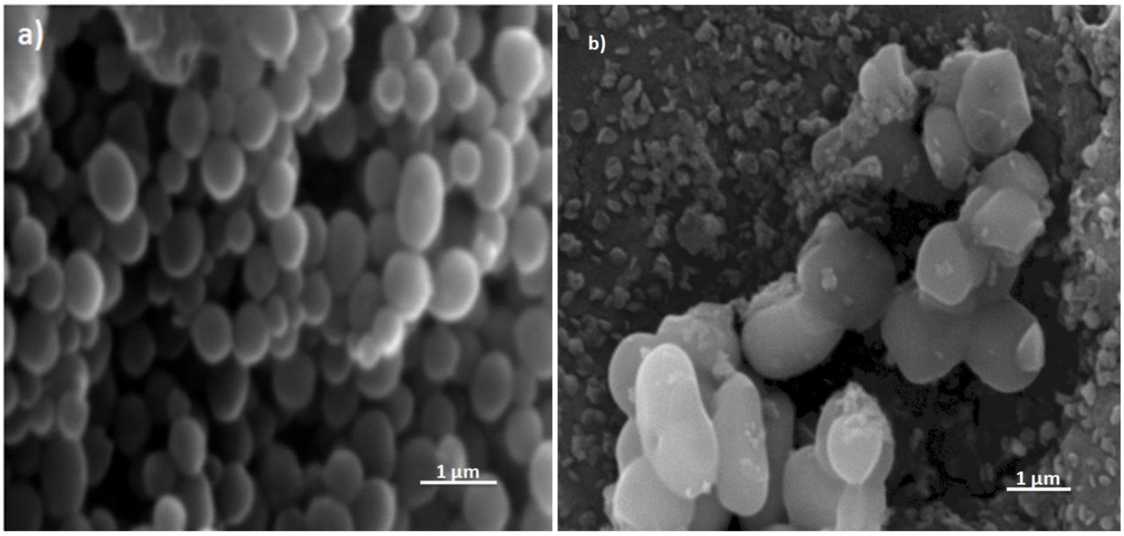


Figure 3. **SEM Images of a) prepared nano silica b) 20–WO_3/SiO_2–600**

6. FAMEs CHARACTERIZATION BY PROTON NMR

The efficiency of the selected catalyst, 20–WO_3/SiO_2–600, has been tested for the transesterification of waste cottonseed oil (WCO). The FAMEs was characterized and quantified by proton NMR technique, as same technique is quick, simple, non destructive and not required any derivatization of the products.

The ^1H NMR spectrum of WCO shows a multiplet at 4.1–4.3 ppm due to the presence of glyceridic protons. The peaks in the range of 0.8–2.8 ppm in the proton NMR spectra of FAMEs and vegetable oil are due to the protons of saturated hydrocarbon chain as shown in Figure 4. The unsaturated protons of fatty acid carbon chain appear at 5.3 ppm in same spectrum. In proton NMR spectrum of FAMEs, a new peak appears at 3.6 ppm due to –OCH_3 protons, and peaks corresponding to the glyceridic protons were no longer found, to support the formation of fatty acid methyl ester upon transesterification of oil with methanol.

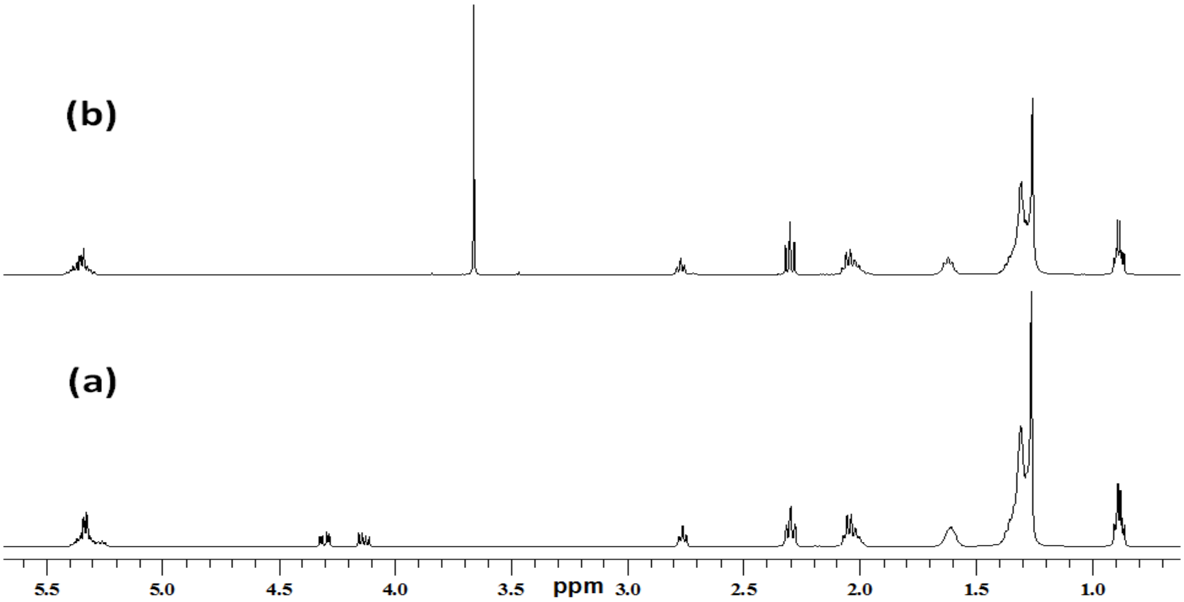


Figure 4. Comparison of the ^{1}H NMR spectra of (a) waste cottonseed oil (b) FAMEs.

6.1 Catalytic Activity

The efficiency of the selected catalyst, 20–WO_3/SiO_2–600, has been tested for the methanolysis of WCO. The reaction parameters for the same reaction have been optimized to achieve the complete transesterification (98±2%) of oil with methanol in minimum possible time. The FAMEs were characterised and quantified by proton NMR technique, as same technique is quick, simple, non destructive and not required any derivatization of the products.

The transesterification reactions have been performed by varying one parameter at a time out of the followings: (i) impregnated sodium tungstate concentration, (ii) catalyst concentration, (iii) reaction temperature, and (iv) methanol to oil molar ratio (v) Effect of reaction time

Effect of FFA on catalytic activity and the reusability of the catalyst have also been studied.

6.1.1 Effect of Impregnated sodium tungstate dihydrate in silica

To determine the optimum amount of sodium tungstate dihydrate impregnated in prepared silica, a series of catalysts were prepared by varying the amount of sodium tungstate from 5 to 25 wt% in SiO_2. Transesterification reactions were performed at 65 °C, employing 80:1 methanol to oil molar ratio and 5 wt% (oil/catalyst) catalysts. The time required for the complete transesterification of WCO was found to reduce from 30 to 5 h as the tungsten concentration in SiO_2 support was increased from 5 to 20 wt%. The increase in FAME yield on increasing the tungsten concentration in support could be due to the increase in acidic sites of the catalyst as shown in Table 1. A further increase in tungsten concentration (from 20 to 25 wt %) was not found to increase the yield of biodiesel produced as shown in Figure 5. Hence, 20–WO_3/SiO_2–600 catalyst was employed to optimize other parameter for the complete transesterification of WCO to FAMEs.

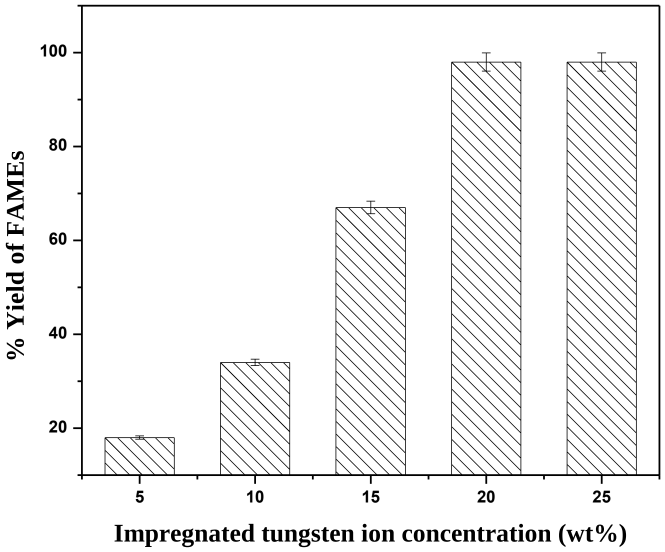


Figure 5. **Effect of sodium tungstate dehydrate concentration in SiO_2 on the FAMEs yield for the complete transesterification of WCO (Reaction time = 5 h, catalyst amount = 5 wt%, temperature = 65 °C, MeOH/oil molar ratio = 80:1).**

6.1.2 Effect of Catalyst Amount

The amount of catalyst required for any process has significant economical and environmental effect. To determine the optimum catalyst concentration, transesterification reactions were performed at 65 °C, employing a 80:1 methanol to oil molar ratio, in the presence of 20–WO_3/SiO_2–600 by varying its concentration from 1 to 6 wt% (catalyst/oil). Time required for the complete conversion of WCO to FAMEs was found to be reduced from 48 h to 5 h, when the catalyst amount was increased from 1 to 5 wt%. Further increase in catalyst concentration (5 to 6 wt%) doesn't reduce the reaction time significantly as shown in Figure 6. Hence, transesterification reactions were further studied with 5 wt% catalyst concentration (oil/catalyst) for optimizing the other parameters.

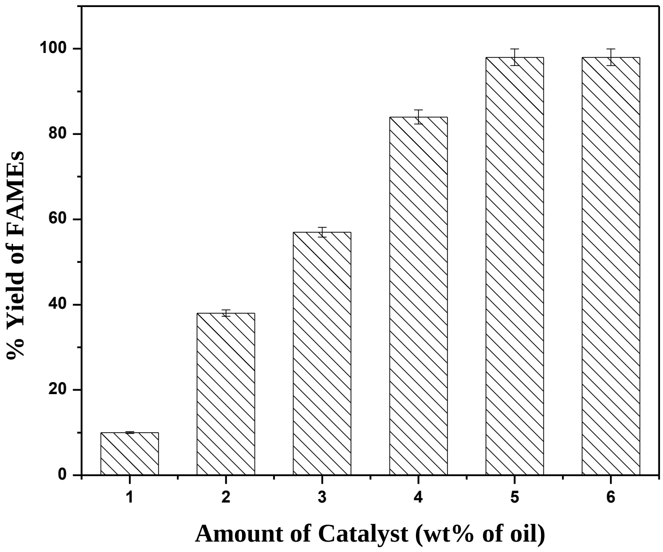


Figure 6. Effect of catalyst concentration on the FAMEs yield for complete transesterification of WCO to biodiesel (Reaction time = 5 h, temperature = 65 ºC, MeOH/oil molar ratio = 80:1).

6.1.3. Effect of methanol to oil molar ratio

The effect of methanol/oil molar ratio is one of the important parameter in transesterification reaction as it affects the methyl ester yield as well as the cost of biodiesel production. The theoretical minimum methanol to oil ratio should be 3:1 for the complete conversion of vegetable oil to biodiesel. Due to reversible reaction transesterification is performed with an excess of methanol to achieve maximum methyl ester yield. Heterogeneous catalysts usually catalysed the transesterification reaction at a slower rate and took more time for the completion of the reaction. The use of higher alcohol to oil molar ratio (e.g., 200:1 or 500:1) to improve the yield of transesterified product in less time have been reported in the literature [39] when reactions were catalysed by heterogeneous catalysts.

To determine the optimum methanol/oil molar ratio the reactions were performed with 10:1 to 100:1 methanol to oil molar ratios at 65 °C using 5 wt% of 20–WO_3/SiO_2–600 catalyst. The rate of transesterification reaction increases as methanol/oil ratio was increased from 10:1 to 80:1. The reaction was found to complete in 5 h with 80:1 molar ratio of methanol/oil. Further increase in reaction temperature doesn’t reduce the reaction time significantly as shown in Figure 7, and hence, 80:1 methanol to oil molar ratio was found to be optimum.

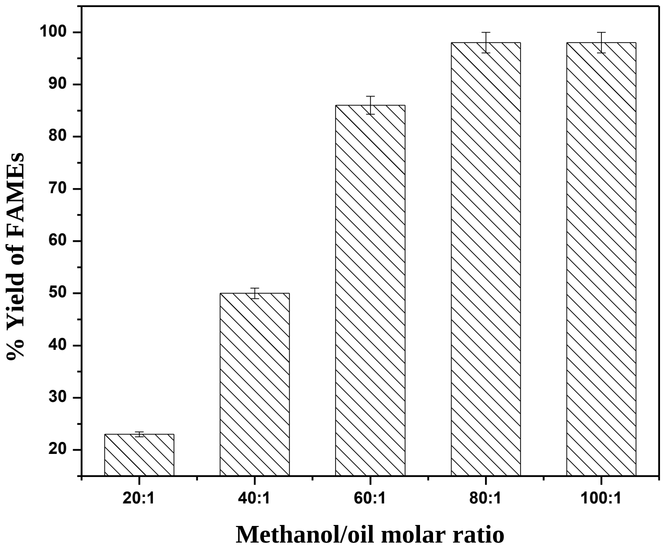


Figure 7. Effect of the oil/methanol molar ratio on the FAMEs yield for complete transesterification of WCO to biodiesel (Reaction time = 5 h, temperature = 65 ºC, catalyst amount = 5 wt%).

6.1.4. Effect of reaction temperature

In order to determine the optimum activity of the prepared catalyst, reactions were performed in temperature range of 35–75 °C. Although, 20–WO_3/SiO_2–600 was able to complete the transesterification of WCO even at room temperature (35 °C), but required longer reaction duration (3 days). However, time required for the complete transesterification decreased to 5 h on increasing the temperature from 35 to 65 °C. Further increase in reaction temperature doesn’t reduce the reaction time significantly as shown in Figure 8. Thus a 80:1 methanol to oil molar ratio, in presence of 5 wt% catalyst (with respect to oil), at 65 °C reaction temperature yielded the complete conversion (> 98 %) of vegetable oil into FAMEs in 5 h.

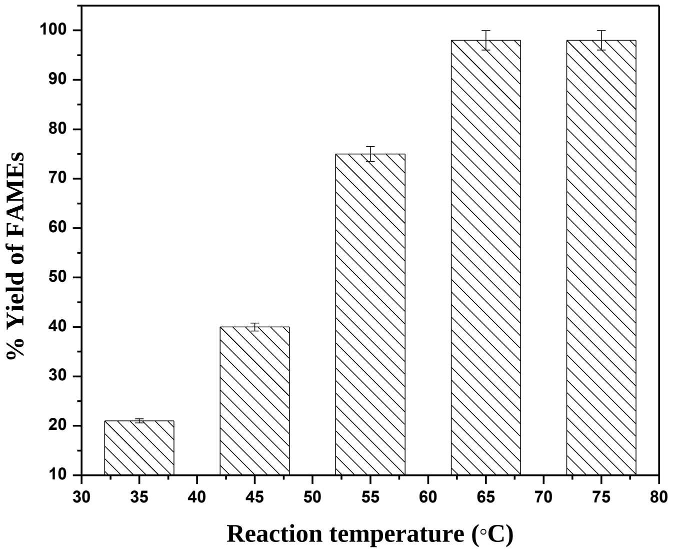


Figure 8. Effect of reaction temperature on the FAMEs yield for complete transesterification of WCO to biodiesel (Reaction time = 5 h, catalyst amount = 5 wt%, MeOH/oil molar ratio = 80:1).

6.1.5. Effect of FFA on the catalytic activity

The methanolysis of WCO when performed by homogeneous catalysts (NaOH or KOH) soap formation took place instead of biodiesel production. However, the prepared catalyst 20–WO_3/SiO_2–600 leads to the completion of the transesterification reaction of the WCO. In order to find out the maximum FFA tolerance of the same catalyst, the transesterification reactions of WCO (having 4.9 wt% FFA) was performed in presence of palmitic acid (up to 3 wt%). The catalyst 20–WO_3/SiO_2–600 was found to resist the presence of up to 3 wt% added FFA and yielded complete transesterification of the WCO, as shown in Figure 9. However, a further increase in the FFA (> 3 wt%) was found to deactivate the catalyst and only partial conversion of oil in to FAMEs was achieved even after 48 h.

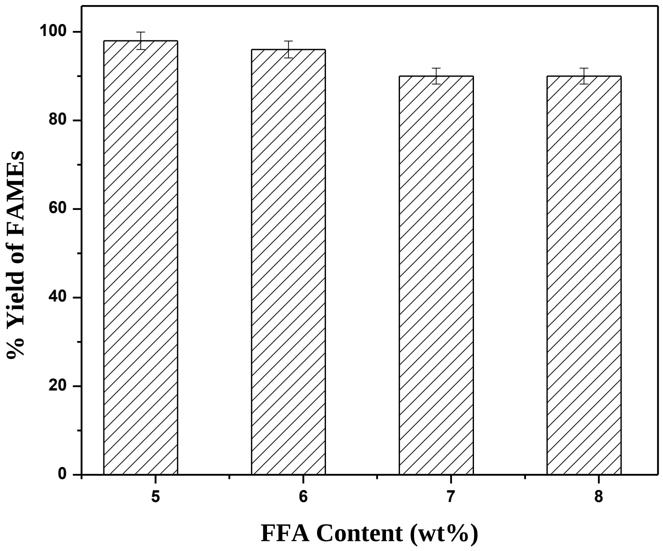


Figure 9. **Effect of FFAs on the catalyst activity for the transesterification of WCO (Reaction conditions: Catalyst amount = 5 wt%; Temperature = 65 °C, MeOH/oil molar ratio = 80:1).**

6.1.6. Evaluation of the Recyclability and Homogeneous contribution

To test the reusability of 20–WO_3/SiO_2–600 catalyst, it was recovered from the reaction mixture by filtration, washed with hexane and dried at 140 °C and then calcined at 600 °C. The catalyst thus recovered was used for four runs, respectively, under the same experimental condition and regeneration method. Upto third run of the recovered catalyst, it leads to the complete conversion of the WCO with methanol. In the fourth run, activity of the catalyst decreases may be due to the leaching of metal ion into the product from the support.

In order to quantify the homogeneous contribution of the catalytic activity, the catalyst, 20–WO_3/SiO_2–600 (500 mg), was refluxed with appropriate amount of methanol for 5 h at 65 °C and then separated from methanol through filtration. Same methanol has been used for the transesterification of WCO (MeOH/oil = 80:1, m/m) at 65 °C to evaluate the homogeneous contribution. Under these experimental conditions no conversion of the WCO to fatty acid methyl ester has been achieved as shown in Figure 10 and hence, the possibility of the partial homogeneous contribution in the catalytic activity could be ruled out.

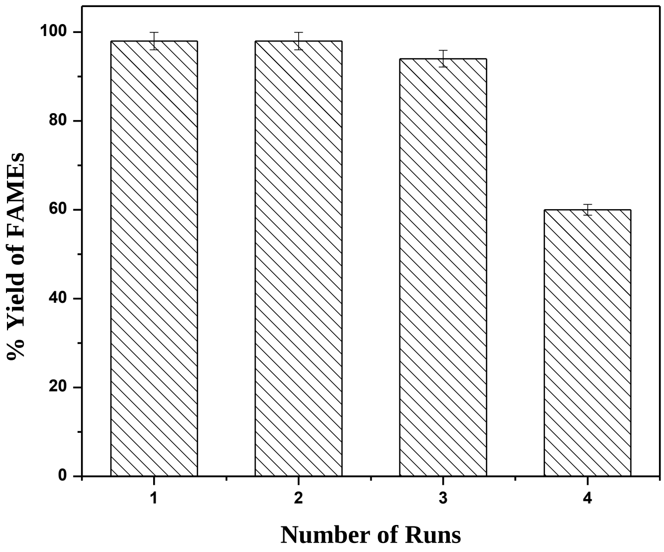


Figure 10. Reusability studies of 20–WO_3/SiO_2–600 catalyst with WCO (Reaction conditions: Catalyst amount = 5 wt%; Temperature = 65 °C, MeOH/oil molar ratio = 80:1).

6.2 Kinetics of 20–WO_3/SiO_2–600 catalyzed transesterification

The transesterification of triglycerides in presence of excess alcohol has been reported to follow pseudo–first order kinetic model [40]. The kinetics of the 20–WO_3/SiO_2–600 catalysed transesterification of WCO has been studied at different temperatures by plotting a graph between $-\ln(1-X_{me})$ *vs* ‘t’ as given in Figure 11.

The linear nature of these plots support the (pseudo) first order kinetic model is followed by the 20–WO_3/SiO_2–600 catalyzed reaction. The apparent first order rate constants form these plots were found to be 0.033 min^{-1} at 65 ºC.

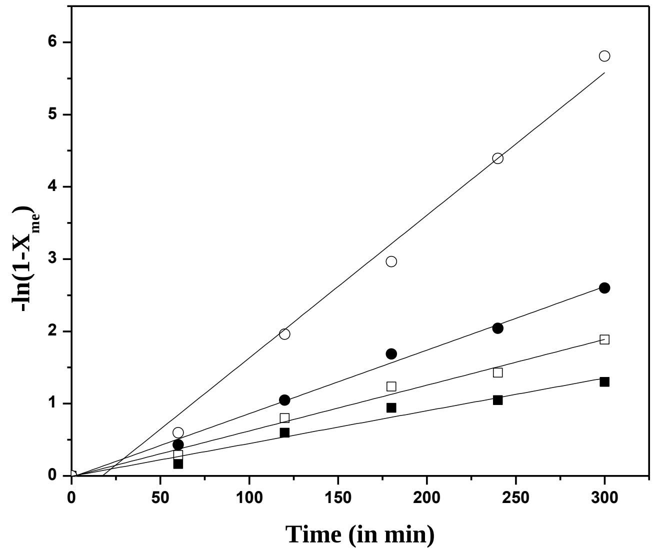


Figure11. Plots of –ln(1–X) *vs* time at different temperatures (Reaction conditions: Catalyst amount = 5 wt%; MeOH/oil molar ratio = 80:1).

The Arrhenius model was employed to estimate the activation energy (E_a) and pre–exponential factor (A) for transesterification of WCO following the equation 2. A plot between ln k *vs* 1/T is shown in Figure 12, and the values of E_a and A from the same graph was found to be 37.71 kJ mol^{-1} and 3.2×10^{10} min^{-1}, respectively. The value of E_a was found within the range (33–84 kJ mol^{-1}) of reported values [41, 42] for the transesterification of vegetable oils.

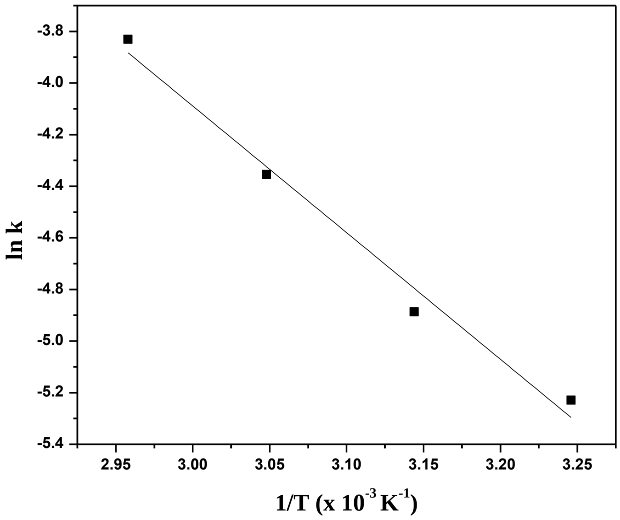


Figure.12. Arrhenius plot of lnk *vs*. 1/T for the transesterification of WCO with methanol.

7. Physicochemical properties of the FAMEs

Few important properties of FAMEs produced from the transesterification of WCO in presence of 20–WO_3/SiO_2–600 have been evaluated following the standard test methods as given in Table 3. The observed values of the studied properties of prepared FAMEs were found within the limits of the EN 14214 specifications.

Table 3. Physicochemical properties of the FAMEs prepared from WCO.

S.No.	Parameters	FAMEs	EN14214	Test method
1	Ester content (%)	>98 %	96.5	^{1}H–NMR
2	Flash point (ºC)	110	100–170	ASTM D93
3	Pour point (ºC)	1	–5 to10	ASTM D2500
4	Kinematic viscosity at 40 ºC (cSt)	4.50	1.9–5.0	ASTM D445
5	Density at 31 ºC (g/mL)	0.88	0.86-0.90	ISI448 P:32
6	Ash (%)	NIL	0.02	ASTM D874

7. Conclusions

Present work demonstrates the preparation of a series of tungsten metal ion impregnated SiO_2 catalysts and investigation of their catalytic activities towards transesterification of waste cottonseed oil. The catalyst exists in nanocrystalline form as supported by powder XRD and SEM studies. The catalyst, 20–WO_3/SiO_2–600, required 5 h for the complete transesterification of waste cottonseed oil with methanol (1:80 molar ratio) at 65 °C. The catalyst has been reused for three successive catalytic runs without significant loss in catalytic activity. In short, the prepared solid catalyst has the potential to convert the cheap feedstock, having higher amount of FFAs, into biodiesel. The physicochemical properties of the prepared biodiesel sample have been tested and observed values were found to be within the limits of EN standards.

REFERENCES

1. K. Narasimhara, A. Lee, K. Wilso. *J Biobased Mater Bio.* 2007, **1**, 19.
2. A. K. Agarwal and L. M. Das, *J Eng Gas Turb Power*. 2001, **123**, 440
3. Y. C. Sharma, B. Singh, S. N. Upadhyay, *Fuel*. 2008, **87**, 2355.
4. M. G. Kulkarni and A. K. Dalai, *Ind Eng Chem Res,* 2006, **45**, 2901.
5. D. Kumar and A. Ali, *Energ Fuel*, 2010, **24**, 2091.
6. M. N. Varma and G. Madras, *Ind Eng Chem Res.* 2007, **46**, 1.
7. Y. C. Sharma, B. Singh, S. N. Upadhyay, *Fuel*. 2008, **87**, 2355.
8. C. Silva, T. A. Weschenfelder, S. Rovani, J. V. Oliveira, *Ind Eng Chem Res*. 2007, **46**, 5304.
9. K. S. Liu, *J Am Oil Chem Soc*. 1994, **71**, 1179.
10. H. N. Basu, M. E. Norris, US Patent.1996, 5525126; 1996.
11. M. P. Dorado, E. Ballesteros, J. A. Almeida, C. Schellet, H. P. Lohrlein, R. Krause, *Trans* ASAE. 2002, **45,** 525.
12. G. Cayh, S. Kusefoglu, *Fuel Process Technol.* 2008, **89**, 118.
13. B. Freedman, E. H. Pryde, T. L. Mounts, *J Am Oil Chem Soc*. 1984, **61**, 1638.
14. B. Freedman, R. O. Butterfield, EH. Pryde, *J Am Oil Chem Soc*. 1986, **63**, 1375.
15. M. Canakci, J. H. van Gerpen, American Society of Agricultural Engineering, Annualm international meeting, Sacramento, California, USA, July 30- August 1, 2001, paper number-016049.
16. L. C. Meher, M. G. Kulkarni, A. K. Dalai, S. N. Naik, *J Lipid Sci Technol*. 2006, **108**, 389.
17. Y. Li, S. Lian, D. Tong, R. Song, W. Yang, Y. Fang, *Appl Energy*. 2011, **88**, 3313.
18. S. Hu, Y. Guan, Y. Wang, H. Han, *Appl Energy*. 2011, **88**, 2685.
19. Y. tang, M. Meng, J. Zhang, Y. Lu, *Appl Energy.* 2011, **88**, 2735.
20. X. Li, G. Lu, Y. L. Guo, YQ. Wang, Z. G. Zhang, X. H. Liu, *Catal Commun.* 2007, **8**, 1969.
21. W. I. Xie, H. T. Li, *Appl Catal A.* 2006, **255**, 1.
22. H. J. Kim, B. S. Kang, M. J. Kim, U. M. Park, D. K. Kim, J. S. Lee, *Catal Today*. 2004, **93**, 315.
23. F. Guo, Z. G. Peng, J. Y. Dai, Z. I. Xiu, Fuel Process Technol. 2010, **91**, 322.
24. S. Nakagaki, A. Bail, V. C. Santos and V. H. R. Souza, *Appl Catal A.* 2008, **351**, 267.
25. J. Jitputti, B. Kitiyanan, P. Rangsunvigit, K. Bunyakiat, L. Attanatho, P. Jenvanitpanjakul, *Chem. Eng. J.* 2006, **116**, 61.

26. M. Cozzolino, R. Tesser, M. DI Serio, M. Ledda, G. Minutillo, E. Santacesaria *Surf, Sci. Catal.* 2006, **162**, 299.

27. R. A. Soldi, A. R. S. Oliveira, L. P. Ramos, M. A. F. Cesar-Oliveira, *Appl. Catal, A.* 2009, **361**, 42.

28. Y. Wang, S. Ou, P. Liu, F. Xue, S. Tang, *Mol Catal A.* 2006, **252**, 107.

29. Y. Wang, S. Ou, P. Liu, Z. Zhang, *Energy Convers Manage*. 2007, **48**, 184.

30. F. Cao, Y. Chen, F. Zhai, J. Li, J. Wang, Z. Wang, *Biotechnol Bioenergy* 2008, **101**, 92.

31. K. Jacobson, R. Gopinath, L. C. Meher, A. K. Dalai, *Appl Catal B* 2008, **85**, 86.

32. Y. M. Park, D. W. Lee, D. K. Kim, J. Lee, K. Y. Lee, *Catal Today.* 2008, **131**, 238.

33. G. Gelbard, O. Bres and R. M. Vargas, *J Am Oil Chem Soc*. 1995, **72,** 1239.

34. G. Knothe, *J Am Oil Chem Soc*. 2001, **78**, 1025.

35. A. K. Singh, S. D. Fernado, *Energy Fuel.* 2008, **22,** 2067.

36. Q. Cai, Z. S. Luo, W. Q. Pang, Y. W. Fan, X. H. Chen, F. Z. Cui, Chem. Mater. 2001, **13**, 258.

37. B. Freedman, O. Royden, B. Everest H. Pryde, 2 Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, IL 61604.

38. S. B. Qadri, E. F. Skelton, D. Hsu, A. D. Dinsmore, J. Yang, HF, Gray *Phys Rev B.* 1991, **60**, 9191.

39. S. Yan, H. Lu, B. Liang, *Energy Fuels*. 2008 **22** 646.

40. M. Balat, H. Balat, Progress in biodiesel processing, *Appl. Energ.* 2010, **87,** 1815.

41. B. Freedman, R. Butterfield, E. Pryde, *J. Am. Oil. Chem. Soc*. 1986 **63** 1375.

42. R. Song, D. Tong, J. Tang, C. Hu, *Energy Fuels*. 2011, **25,** 2679.