



## Eco-friendly process for preparation of biodiesel from WFO over MTSA-Si catalyst: An innovative approach for the utilization of side product

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### ABSTRACT

Present work aimed for the synthesis of a promising MTSA-Si catalyst and its application for biodiesel preparation using WFO. It has been illustrated from the experimental results, the most favorable reaction conditions for the biodiesel preparation using WFO are (i) 1:10 oil to methanol molar ratio, (ii) 5% MTSA-Si catalyst (*w/w*), (iii) 130 °C reaction temperature and (iv) 10 h reaction time, for the 98.22% yield of biodiesel. The side product raw glycerin was further transformed into the triglycerides over MTSA-Si catalyzed lauric acid esterification. The fuel properties of biodiesel were estimated and correlated fuel standards.

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### Introduction

Currently, alternative energy research community across the world is insisting for an exploration of alternative energy resources in order to minimize consumption of the traditional energy resources by virtue of their everlasting depletion and growing destructive concussion on the climate [1]. The manufacturing of second generation biofuel from non edible oils likes, *Jatropha curcas*, *Sterculia foetida*, *Ceiba pentandra* and *Cerbera manghas*, as well as waste frying oil has been become the key of energy insufficiency to counter any reduction in the supply of edible oil resources to the food manufactory [2–4]. Biodiesel is being produced from the reaction of vegetable oil or animal fats with a shorter chain alcohol like methanol or ethanol in presence of a relevant catalyst. The global energy insistence is increasing day-to-day, while the repertory of conventional fuels such as coal and petroleum are reducing constantly. Besides, the consumption of conventional fuels motives the global warming by raising the effects of greenhouse gases notably. Biodiesel is a non-toxic, biodegradable and green alternative by virtue of its lower emission figurations. Contradictory to these dominance, the most significant disadvantage of biodiesel is its higher cost than conventional fuels [5,6]. Such alternative fuel has received considerable attention due to its being produced from non-conventional sources and it potentially lower down the climatic impact in association to conventional diesel fuel [7]. Biodiesel synthesis is mainly executed by the transesterification of oils over homogeneous, heterogeneous and enzymatic catalysts [8]. The currently

well established manufacturing facilities for biodiesel synthesis are mainly based on homogeneous base catalysis [9]. The noncorrosive, eco-friendly and reusable nature of heterogeneous acid and alkali [10] catalysts makes them more suitable for the biodiesel synthesis with respect to homogeneous acid catalysts. However, they are associated with some limitations for their commercial scale production likes, (i) complex synthesis process and (ii) difficulties in handling in application to commercial scale plants [11]. The booming production of WFO from domiciliary as well as industrial sectors is a maturing scrape globally by virtue of its oxidation and hydrogenation characteristics. Waste frying oil commonly abundant of free fatty acids, polymeric material and disintegration products, besides triglyceride, diglycerides and monoglycerides. This residue is habitually discharged into the water, arising the problems for drainage water treatment units and energy mislay, or is intersperse into the food cycle through animal feeds, hence, becoming a potential cause of human health problems [12].

There are considerable applications of waste frying oil, such as in the production of soap, in production of energy through anaerobic digestion, in thermal cracking [13], recently, in the synthesis of biodiesel fuel [14], and much more. Waste frying oil (WFO) is the provocative alternative resource for the biodiesel synthesis due to its inherent in shortening expenses and environmental percussion of biodiesel when correlated with traditional feedstocks. Therefore, waste frying oil as an adequate raw material for biodiesel preparation has attracted significant attention recently due to its reasonable price and smooth availability [15]. The physicochemical properties of WFO are tabularized in Table 1.

In recent times, the usage of solid acid catalysts were describe in literature as a most favorable key for biodiesel production, because it could potentially eliminate some reaction steps like complex isola-

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**Table 1**  
Physicochemical properties of WFO [16–19].

Properties	Test standards	Value
Physical state	–	Liquid
Color	–	Deep oily
Calorific index (MJ/kg)	IS:1448:(P:33):1991	38.314
Peroxide index (O <sub>2</sub> /kg)	AOCSCD8-53	10.00–25.25
Specific gravity (g/cm <sup>3</sup> )	ASTM D854-10	0.92
Density @ 20 °C (kg/m <sup>3</sup> )	ASTM D1298, ASTM D4052-91, IS:1448:(P:32):1992	897.0
Acid index (mg KOH/g)	ASTM D664	3.0
Iodine index (g I <sub>2</sub> /100 g)	AOCSCD1-25 1993	102.3
Kinematic viscosity @ 40 °C (mm <sup>2</sup> /s)	ASTM D 445, IS:1448:(P:25):1976	54.53
Saponification index (mg KOH/g)	AOCSCD3 2003	192
Average molecular weight of FFA (g/mol)	–	275.5
Mean molecular weight (g/mol)	–	864.5
Flash point (°C)	ASTM D92-94, IS:1448:(P:21):1992	Not less than 250
Pour point (°C)	ASTM D 97	–9.7
Cloud point (°C)	ASTM D 2500, EN 23015	–8.2
Fatty acid compositions	ASTM D1585-96	19.7%

tion, corrosion issue, toxicity and environmental contemplation [20]. Magnificently, a solid acid catalyst used for biodiesel production should offer a higher acidic density of active sites, admirable thermal stability, larger pore size and pore volume, lower cost and hydrophobic exterior [21]. The heterogeneous acidic catalysts have been reported and examined for biodiesel synthesis are the inorganic material based such as zeolite [22,23], niobic acid [24] and sulfated zirconia [25]. However, these catalysts offer smaller pore size and pore volume, which restrict the penetration of the longer chain fatty acid molecules, and hence they are unsuitable for the synthesis of biodiesel. Whereas, the strong acidic ion-exchange resins, i.e., Amberlyst-15 and Nafion-NR50 [26], offer a large fraction of sulfonic acid groups but their application is very limited by virtue of their higher preparation cost and lower thermal stability. While, solid acid catalysts prepared from polystyrene [27] and polyvinyl alcohol crosslinked with sulfosuccinic acid [28] also offer remarkable activity for the esterification of fatty acids using methanol regarding biodiesel production. But leaching of active site from catalysts into the reaction system is a major and uncleaned concern. Hence, it is adorable to prepare solid acid catalysts with a higher thermal stability and higher density of active sites.

Currently, the considerable sense behind uncommercialization of biodiesel is its higher preparation expense than conventional diesel [29,30]. The higher preparation expense of biodiesel is principally in view of its being produced from refined oils with low levels of FFA contents. A potential approach for lessening down the biodiesel expense is to utilize lower expense oils composed of higher concentration of FFA, recycled or waste oil and side products of edible oils refineries [31,32]. The crude glycerol- a side stream of biodiesel synthesis is also spoiled with the unspent methanol, unspent glycerides, moisture and catalyst, that compulsorily be separated out to acquire its commercial assessment. As per the environmental protection Act, the raw glycerol must be dumping out in a shorter period of time or to be sold at minimum price, in addition the cost of dumping is also to much expensive [33]. Very insufficient experiments have been carried out to transform the raw glycerin to effective products [34].

In the view of reported studies, we have observed that melamine is a cheaper and commercially feasible chemical, its offers three primary amino (–NH<sub>2</sub>) groups; hence, it could easily react with sulfurochloridic acid to yield melamine trisulfonic acid (MTSA) at ambient conditions. Besides, synthesized MTSA was sensibly added

with silica gel to reinforce the MTSA-Si via formation of inter molecular hydrogen bonding with silica gel. Therefore, an attempt has been made to examine transesterification of waste frying oil to biodiesel over MTSA-Si catalyst. Besides, biodiesel based crude glycerol was also transformed into the TGLA via esterification of lauric acid using MTSA-Si catalyst. Usually, the activity of solid acid catalyst does not influence by the presence of higher levels of FFA contents. Hence, this advance may be helpful to synthesize biodiesel from waste oil based stocks with lower cost as well as feedstocks with higher levels of FFA contents. Generally, solid acid catalyst could show remarkable catalytic activity in esterification and transesterification of oils concurrently. Over and above, heterogeneous nature of MTSA-Si catalyst, it could be simply isolated from the reaction mass and reused for five successful cycles after smooth filtration and reactivation. It has been found from the experimental results, the optimum reaction conditions for the biodiesel preparation via transesterification of WFO are (i) 1:10 oil to methanol molar ratio, (ii) 5% MTSA-Si catalyst (w/w), (iii) 130 °C reaction temperature and (iv) 10 h reaction time for the 98.22% yield of biodiesel.

## Materials and method

### Materials

Waste frying oil (single time used sunflower oil) was obtained as an open-handed gift from Jay Sardar Restaurant, Rajkot, Gujarat, India. Lauric acid (99% purity) and anhydrous dichloro methane (99.8% purity) were supplied by Sterling Lab care Pvt. Ltd, Surat, Gujarat, India. Methanol (AR grade) was purchased from Advent Chembio Pvt. Ltd. Sulfurochloridic acid, melamine and silica gel (99% purity) were supplied by Aashka Scientific Co., Surat, Gujarat, India. Methanol less crude glycerol was produced using current biodiesel synthesis procedure.

### Analytical instrumental methods

The FT-IR analyses of fresh and regenerated MTSA-Si have been carried out on a (Model, Shimadzu FIIR-8400S) FT-IR spectrophotometer. However, the FT-IR analysis of biodiesel and TGLA were carried out on a (Model- RZX Perkin-Elmer) FT-IR spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR analysis were carried out on a (Model, Bruker Biospin, Switzerland 400 MHz liquid state NMR spectrometer) FT-NMR spectrometer. Large angle X-ray diffraction (XRD, Rigaku, Miniflex) study was carried out by using X-ray diffractometer. The surface area of the MTSA-Si was measured on a (Micromeritics ASAP 2020) porosimeter. The thermal stability of MTSA-Si was recognized by Thermogravimetric analysis (Model: Perkin Elmer TGA-7, IIT madras). Surface and structural morphologies of the fresh and regenerated MTSA-Si catalysts were predicted by scanning electron microscope (SEM, Model, Hitachi S3400N). The total acidity of the MTSA-Si was measured by neutralization titration. The biodiesel (%) yield was estimated by gas chromatography analysis. The SUP-ELCO C<sub>8</sub>-C<sub>24</sub> component FAME mixture was employed as a standard for recognition and determination of the peaks retrieved in the WFO based biodiesel in gas chromatography analysis (YL 6500GC).

### Experimental

#### Preparation of MTSA-Si

A 250 mL three neck suction flask (FBF) was charged with sulfurochloridic acid (5 mL, 75.2 mmol). The melamine powder (3.16 g, 25.07 mmol) was charged in little fractions over a time slot of 45 min at ambient conditions under nitrogen atmosphere (g) and constant

stirring. As a result, the hydrochloric acid (g) was elaborated from the reaction flask immediately. On the completion of addition of melamine, the reaction mixture was rattled for 45 min and the remaining side product hydrochloric acid (g) was removed by vacuum. The mixture was triturated with dichloro methane (20 mL) and then filtered. The powdery residue was again treated with dichloro methane (20 mL) and dried under vacuum oven. The melamine trisulfonic acid (MTSA, 8.2 g, 90%) was obtained as an off-white powder. Then after, 15.2 g silica gel (200–400 mesh) was mixed with off-white MTSA and stirred for 30 min for the formation of an intermolecular hydrogen bond to support the MTSA-Si [35]. At last, a dried and grayish powdery material composed of MTSA-Si was obtained (23.1 g). The scheme for synthesis of MTSA-Si is given in Fig. 1.

#### Preparation of biodiesel

All the transesterification reactions were executed in a laboratory autoclave (Amar, close SS reactor), assembled with pressure indicator, temperature controller, internal cooling system, online sampling valve, automatic and manually chilling systems. The 289 g of WFO was transferred into the reactor of autoclave and preheated at 55 °C

in order to reduce the viscosity of WFO, hence it could be homogeneously stirred in an autoclave. The MTSA-Si-methanol mixture was carefully transferred in an autoclave and stirred at 700 rpm with the interest to restraint the mass transfer constraint. The biodiesel synthesis experiments have been conducted at different oil: methanol molar ratio (1:6, 1:7, 1:8, 1:9, 1:10 and 1:11), reaction temperature (100, 110, 120 and 130 °C), catalyst (MTSA-Si) loading (3, 4, 5 and 6% w/w) and reaction time (4, 5, 6, 7, 8, 9, 10 and 11 h). All transesterification reactions were performed at endogenous pressure till the achievement of the optimum conversions. The reaction scheme for biodiesel synthesis is illustrated in Fig. 2.

On the completion of the transesterification reaction, the MTSA-Si was isolated from the reaction slurry by simple filtration. The unspent methanol was also completely removed by distillation and the mixture was thoroughly transferred to a separating funnel for a gravitational settling of biodiesel as well as glycerol, as demonstrated in Fig. S1.

From Fig. S1, it has been clearly observed that due to difference in the densities of biodiesel and glycerol, the biodiesel comes out at top layer and glycerin as well as traces of MTSA-Si catalyst settled

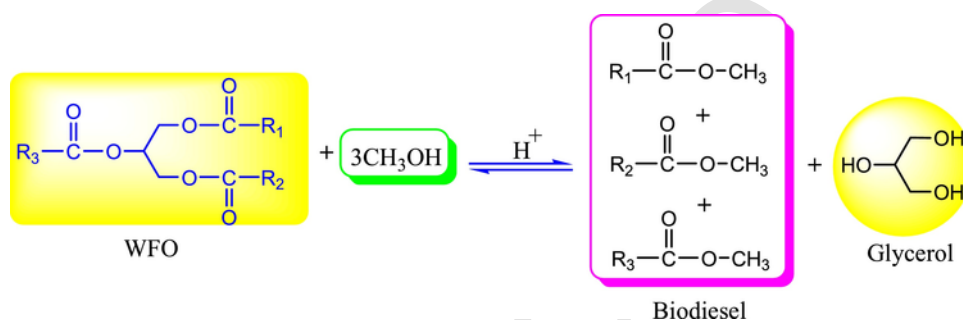


Fig. 1. Transesterification of WFO to biodiesel.

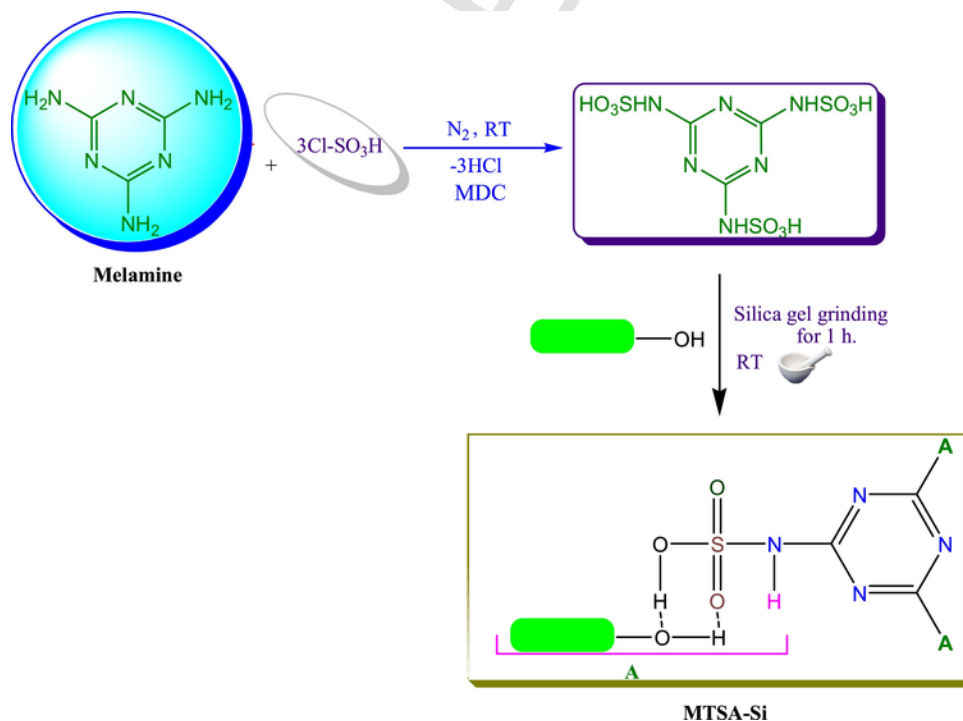


Fig. 2. Reaction scheme for the synthesis of MTSA-Si.

down at the bottom layer. The biodiesel layer was refined by using demineralised water and then treated with anhydrous  $\text{Na}_2\text{SO}_4$  in order to make it free from moisture. Therefore, 100 mL of biodiesel was mixed with 1.0 g of anhydrous  $\text{Na}_2\text{SO}_4$  and stirred for 30 min. Then after, the mixture was allowed for gravitational settling (24 h). The decanted moisture free biodiesel was isolated with the service of a vacuum pump for the expulsion of solid impurities traces. The resultant biodiesel has been stored in a glass bottles for further analysis and applications.

#### Esterification of raw glycerol to TGLA

Esterification is an equilibrium restrained reaction. In pursuance to reduce the equilibrium restrain, commonly an esterification of lauric acid is executed by taking alcohol in excess to enhance the forward reaction [36]. Besides, the expulsion of water during esterification is significantly required, as it is being produced as a side stream and will act as a poison for the catalyst as well as can also promote the reverse reaction. Hence, it could unnecessarily increase the reaction time for the optimal yield of desired esters. The esterification is an equilibrium constrained reaction. The required conversion of desired esters could be attained with the isolation of either water or esters. In order to rectify this problem of present study, an anhydrous sodium sulphate (0.1 mol) was charged in a reactor along with glycerol and lauric acid with a view to encounter water makeup during esterification.

Therefore, in the present work, a 100 mL three neck flat bottom flask was charged with a mixture of lauric acid (3 mol), crude glycerol (1 mol), anhydrous sodium sulphate (0.1 mol) and MTSA-Si (0.8 g) catalyst. The mixture was stirred at  $100^\circ\text{C}$  for the 7 h. Finally, the reaction mixture was cooled down to an ambient temperature and MTSA-Si catalyst was filtered off from the reaction media. The filtrate was poured into a cold water to isolate the resultant triglycerides. Due to the density difference, triglyceride of lauric acid comes out at upper layer in water. In addition, the unspent lauric acid is further coming out at upper layer. Therefore, it was separated from the TGLA and 92.28% yield was reported. The reaction scheme for the preparation of TGLA is demonstrated in Fig. 3.

#### Biodiesel (%) yield estimation

The waste frying oil based biodiesel samples were preserved under  $\text{N}_2$  (g) atmosphere at  $4^\circ\text{C}$  in a glass sample vials for GC analysis. The heptadecanoate was selected as an internal standard for quantifiable determination. On the determination of FAMES of the biodiesel samples, the peak areas were used to estimate the FAME content of each and every sample by Eqs. (1) and (2) [37].

$$\text{Conversion (C)} = \left[ \frac{\sum A - A_{IS}}{A_{IS}} \right] \times \left[ \frac{C_{IS} \times V_{IS}}{m} \right] \times [100] \quad (1)$$

where,  $\sum A$  is the total peaks area,  $A_{IS}$  is the internal standard (methyl heptadecanoate) peak area,  $C_{IS}$  is the concentration of the compositional standard solution (mg/mL),  $V_{IS}$  is the volume of the internal standard solution used (mL) and  $m$  is the mass of the biodiesel sample (mg).

$$\text{Yield (\%)} = \left[ \frac{M_{\text{Biodiesel}} \times C}{M_{\text{Oil}}} \right] \times [100] \quad (2)$$

where  $M_{\text{Biodiesel}}$  is the mass of pure methyl esters obtained,  $M_{\text{Oil}}$  is the mass of waste frying oil used and  $C$  is the fatty acid methyl ester concentration determined as described in above Eq. (1). The gas chromatogram of WFO based biodiesel is given in Fig. S2. It has been recognized from the gas chromatograph of waste frying oil based biodiesel, the biodiesel mixture is composed of methyl esters of corresponding fatty acid likes, methyl oleate, methyl linoleate, methyl lenolenate and methyl behenate.

## Results and discussion

#### Transesterification of WFO to biodiesel

The synthesis of biodiesel from the transesterification reaction using a suitable catalyst is a highly convenient process. The transesterification reaction for biodiesel synthesis can be carried using different methods and is widely described as the incorporation of shorter chain alcohol to lipids in the presence of acid or base catalyst [38]. Maneechakr et al. have synthesized biodiesel from waste cooking oil over a novel sulfonic modified carbon spheres catalyst under ultrasonic transesterification. From the experimental results, they found 90.8% biodiesel yield with 11.5 wt% catalyst loading, 8.8 min reaction time and  $117^\circ\text{C}$  reaction temperature under ultrasonic conditions [39]. Therefore, in this study, the biodiesel preparation reactions were performed at diversified oil: methanol molar ratio (1:6, 1:7, 1:8, 1:9, 1:10 and 1:11), reaction temperature (100, 110, 120 and  $130^\circ\text{C}$ ), MTSA-Si loading (3, 4, 5 and 6% w/w) and reaction time (4, 5, 6, 7, 8, 9, 10 and 11 h). The results of (%) yield of biodiesel with varying reaction parameters are summarized in Table 2.

#### Effect of oil to methanol molar ratio

With a view to study the influence of oil to methanol molar ratio, all transesterification experiments have been carried out at different

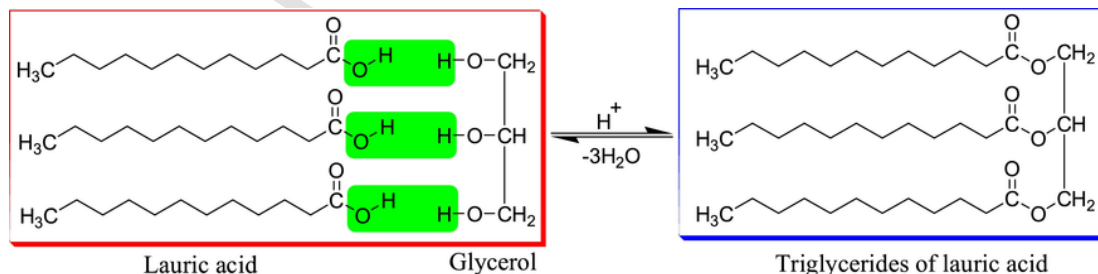


Fig. 3. Reaction scheme for the esterification of crude glycerol to TGLA.

**Table 2**  
Result of (%) yield of biodiesel with varying reaction parameters.

Entry	O:M molar ratio	MTSA-Si loading (% w/w)	Reaction temp. (°C)	Reaction time (h)	Biodiesel yield <sup>a</sup> (%)
1	1:6	3	100	4	22.28 ± 0.99
2	1:7	3	100	4	31.24 ± 0.91
3	1:8	3	100	4	45.29 ± 1.19
4	1:9	3	100	4	61.21 ± 1.25
5	1:10	3	100	4	74.33 ± 0.66
6	1:11	3	100	4	69.44 ± 0.91
7	1:10	4	100	4	79.53 ± 0.98
8	1:10	5	100	4	83.48 ± 0.78
9	1:10	6	100	4	80.11 ± 1.33
10	1:10	5	110	4	83.50 ± 0.79
11	1:10	5	120	4	85.98 ± 0.99
12	1:10	5	130	4	87.11 ± 1.29
13	1:10	5	130	5	89.10 ± 1.11
14	1:10	5	130	6	91.58 ± 0.90
15	1:10	5	130	7	93.25 ± 0.97
16	1:10	5	130	8	95.59 ± 1.33
17	1:10	5	130	9	96.68 ± 1.39
18	1:10	5	130	10	98.22 ± 0.88
19	1:10	5	130	11	98.22 ± 0.69

<sup>a</sup> (n = 3) All experiments have been carried out in triplicates.

oil to methanol molar ratio (1:6, 1:7, 1:8, 1:9, 1:10 and 1:11). From Table 2, it has been realized that as methanol to oil molar ratio increases, it directly influence the biodiesel yield (%). The (%) yield of biodiesel is increased with the increasing in the methanol to oil molar ratio. The maximum (%) yield of biodiesel was noticed with 1:10 oil to methanol molar ratio. The oil to methanol molar ratio down to 1:10 directly enhances the reversible reaction. Therefore, the main sense behind decrement in the (%) yield of biodiesel down to 1:10 oil to methanol molar ratio is the reversible nature of the transesterification reaction. It has also been noticed that the decrement in the % yield of biodiesel beyond the 1:10 oil to methanol molar ratio. This may be associated with the polar feature of catalyst and methyl alcohol. Therefore, as the methanol to oil molar ratio increases, the polarity of the reaction is increases gradually. The reaction mechanism of transesterification clearly recommends that the protonation of oil takes place first. However, the polarity of the reaction is increases as the concentration of methyl alcohol increases. Therefore, instead of oil phase, the MTSA-Si directly moves to the methyl alcohol phase. Hence, interactions of methanol towards catalyst phase become quite stronger than interactions of methanol towards oil phase. Therefore, the diminishment in the (%) yield of biodiesel was observed beyond the 1:10 oil to methanol molar ratio. The graphical representation of the influence of oil to methanol molar ratio on the (%) yield of biodiesel has been illustrated in Fig. 4.

#### Effect of reaction time (h)

In order to study the influence of reaction time (h) on the (%) yield of biodiesel, all the transesterification reactions of oil were also studied using different length reaction time comprising 4, 5, 6, 7, 8, 9, 10 and 11 h. From, the experimental results, it has been perceived that 1:10 oil to methanol molar ratio shows maximum yield of biodiesel (74.33%). Therefore, 1:10 oil to methanol molar ratio was selected as an optimum ratio to study biodiesel synthesis using different reaction times. From the experimental result, it can be concluded that, in the case of 4 h reaction time, the highest (%) yield of biodiesel perceived was 87.11%. Whereas, in the case of 5 h reaction time, the maximum (%) yield of biodiesel sensed was 89.10%. In the case of 6 h reaction time, the maximum (%) yield of biodiesel recognized was 91.58%. In the case of 7 h reaction time, the highest (%) yield of biodiesel observed was 93.25%. In the case of 8 h reaction time, the highest (%) yield of biodiesel sensed was 95.59%. Whereas,

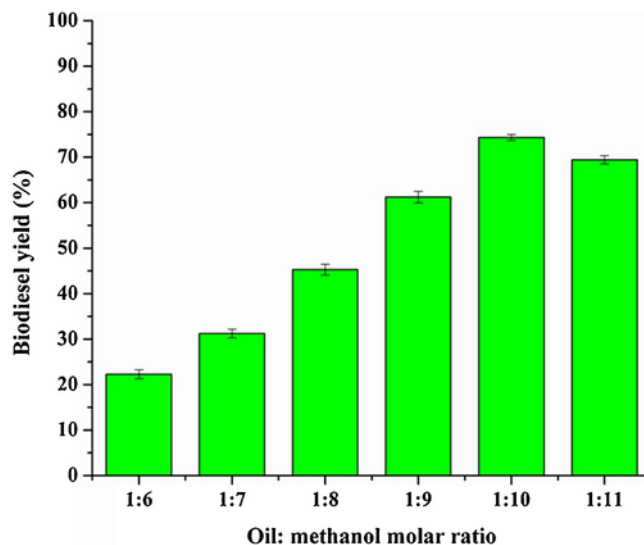


Fig. 4. Influence of oil to methanol molar ratio on the (%) yield of biodiesel.

in the case of 9 h reaction time, the maximum (%) yield of biodiesel recognized was 96.68%. In the case of 10 h reaction time, the highest (%) yield of biodiesel remarked was 98.22%. However, in the case of 11 h reaction time, the highest (%) yield of biodiesel observed was 98.22%. Therefore, the reaction time beyond 10 h does not show any remarkable enhancement in the (%) yield of biodiesel. The similar (%) yields of biodiesel were obtained using 10 h and 11 h reaction times at identical operation conditions. The graphical representation of the influence of reaction time (h) on the (%) yield of biodiesel has been illustrated in Fig. 5.

#### Effect of MTSA-Si loading (% w/w)

In order to study the influence of catalyst dosage (% w/w) on the transesterification, all experiments have been performed at varying catalyst dosages (3, 4, 5 and 6% w/w). From Table 2, it has been realized that as catalyst concentration (% w/w) increases, the (%) yield of biodiesel increases. In the case of 3% catalyst dosage (w/w), the (%) yield of biodiesel was observed to be 74.33% at optimum oil to methanol molar ratio. Whereas, in the case of 4% catalyst dosage (w/

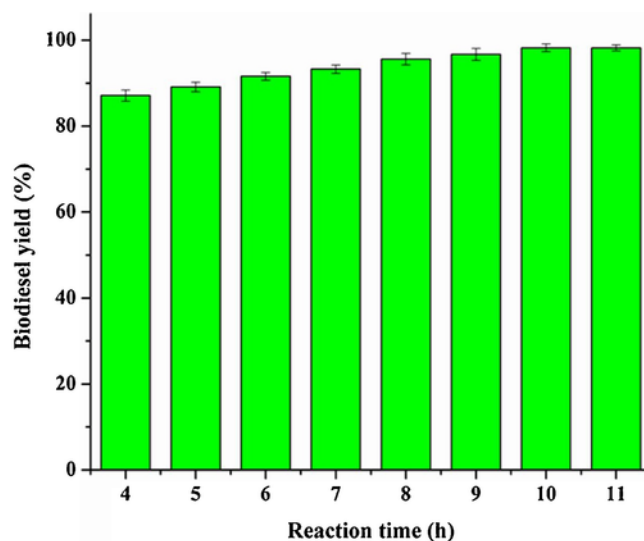


Fig. 5. Influence of reaction time (h) on the (%) yield of biodiesel.

w), the (%) yield of biodiesel was remarked to be 79.53% at optimum oil to methanol molar ratio. In the case of 5% catalyst dosage (*w/w*), the (%) yield of biodiesel was recognized to be 83.48% at optimum oil to methanol molar ratio. Whereas, in the case of 6% catalyst dosage (*w/w*), the (%) yield of biodiesel was perceived to be 80.11% at optimum oil to methanol molar ratio. Hence, the catalyst concentration beyond 5% (*w/w*) does not show any remarkable enhancement in the (%) yield of biodiesel. Therefore, it has been realized from the experimental results, as catalyst dosage (% *w/w*) increases, the (%) yield of methyl laureate increases. The influence of MTSA-Si loading (% *w/w*) on (%) yield of the biodiesel has been demonstrated in Fig. 6.

#### Effect of reaction temperature (°C)

With an intention to study the influence of reaction temperature (°C) on the (%) yield of transesterification reaction, all experiments have been carried out at varying reaction temperatures (100, 110, 120 and 130 °C). From Table 2, it has been realized that as reaction temperature (°C) increases the (%) yield of biodiesel increases. In the case of 100 °C reaction temperature, the (%) yield of biodiesel was found to be 83.48% at optimum oil to methanol molar ratio. Whereas, in the case of 110 °C reaction temperature, the (%) yield of biodiesel was realized to be 83.50% at optimum oil to methanol molar ratio. In the case of 120 °C reaction temperature, the (%) yield of biodiesel was realized to be 85.98% at optimum oil to methanol molar ratio. However, in the case of 130 °C reaction temperature, 5% (*w/w*) MTSA-Si and 10 h reaction time, the (%) yield of biodiesel was realized to be 98.22% at optimum oil to methanol molar ratio. Hence, the reaction temperature beyond 130 °C does not show any remarkable enhancement in the (%) yield of biodiesel. The effect of reaction temperature (°C) on the (%) yield of biodiesel has been given in Fig. 7.

Overall, from experimental results, the optimum reaction conditions within the selected frameworks for the preparation of biodiesel from WFO were found to be, (i) 1:10 oil to methanol molar ratio, (ii) 130 °C reaction temperature, (iii) 10 h reaction time and (iv) 5% (*w/w*) of MTSA-Si catalyst for 98.22% biodiesel yield.

#### Esterification of raw glycerol to TGLA

Raw glycerol is the large-scale side stream of the biodiesel manufacturing unit. In routine, for every 100 pounds of biodiesel produc-

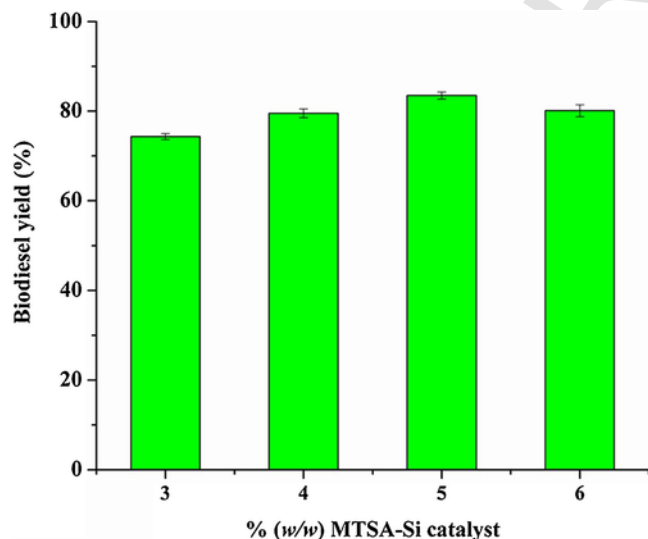


Fig. 6. Influence of % MTSA-Si (*w/w*) on the (%) yield of biodiesel.

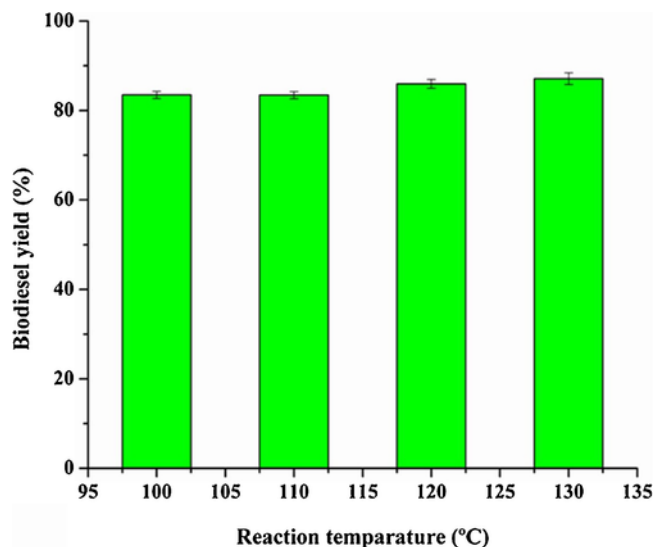


Fig. 7. Influence of reaction temperature (°C) on the (%) yield of biodiesel.

tion, proximately 10 pounds of raw glycerol is being produced. The raw glycerol is an uneconomical to refine for its application in food, pharmaceutical and cosmetics industries, biodiesel producers must seek alternative methods for its disposal. [40]. Glycerol is being produced as a side stream as a result of the transesterification of oil along with biodiesel. Hence, the biodiesel manufacturers are staying with a serious problems regarding to dispose of crude glycerol produced from biodiesel production as a side product. On other side, the biodiesel manufacturers are facing a serious trouble regarding the availability of a cheaper feedstock for biodiesel production. Besides, the refining of raw glycerol in the biodiesel production unit is a major and uncleared issue. Hence, it is a new engineering challenge for the developing biodiesel production unit to dispose of the crude glycerol. Therefore, in present work, we made a small attempt to convert the biodiesel derived crude glycerol to triglycerides of lauric acid (TGLA) using MTSA-Si catalyst. It has been found from the results of esterification of raw glycerin, the optimal reaction conditions for the maximum (%) yield of TGLA are, (i) 1:3 glycerol to lauric acid molar ratio, (ii) 2% MTSA-Si catalyst (*w/w*), (iii) 100 °C reaction temperature and (iv) 7 h reaction time.

The distillation technique has been employed to isolate the methanol from crude glycerol. The MTSA-Si amount was selected based on the maximum (%) yield of the TGLA and minimum compositions of unspent lauric acid and glycerin in the TGLA. On completion of reaction, the reaction mixture was cooled down to room temperature and MTSA-Si catalyst was filtered off from reaction mixture by vacuum filtration. The filtrate was carefully transferred in to separating funnel containing distilled water. By virtue of the density difference of the TGLA and water, the TGLA comes out at top layer and water settled down at bottom layer. Besides, the unspent lauric acid also comes out at top layer. Hence, it was isolated from the TGLA and 92.28% yield has been reported.

Crude glycerol is readily attainable in the trading market with very lower expenses or almost no expenses. Besides, the separation and refining of crude glycerol is very tedious process and involves several steps for its isolation and purification, hence, it requires higher expenses and multitudinous manpower as well. On other side, the commercial grade lauric acid accessible in the trading market with some higher expenses. But the expense of the lauric acid is earlier protected by glycerol, if glycerol is crude. Because, the refining expenses of crude glycerol is much greater than the expenses of industrial grade lauric acid. The superior advantage affiliated with this

protocol is the production of water as a side stream rather than some toxic products. Hence, this process could offers climatic feasibility as well. Therefore, this process may prove beneficial to the commercial manufacturers of TGLA and biodiesel as well, as TGLA could be an abundant feedstock for the biodiesel manufacturers.

#### Reaction mechanism for transesterification of WFO

The transesterification reaction is preferably catalyzed by bronsted acid catalysts, like, sulfonic and sulfuric acids based materials and their reaction mechanism is well explained by many researchers [41]. The mechanism of WFO transesterification could be accomplished via below mentioned steps. This step consists of (i) Protonation to one of the terminal carbonyl group by the MTSA-Si catalyst (ii) Nucleophilic attack of the alcohol towards terminal carbonyl group leads to generate a tetrahedral intermediate (iii) Proton migration and breakdown of the intermediate lead to generate one molecule of biodiesel and one molecule of diglycerides. The migrated proton again absorbed by the MTSA-Si catalyst in order to regenerate and reactivate it for the next use. This entire arrangement will replay twice to form three molecules of biodiesel and one molecule of glycerol. The mechanism scheme for the transesterification of waste frying oil is given in Fig. 8.

#### Reaction mechanism for esterification of raw glycerol

The fischer-speier esterification is a simple esterification reaction carried out by using carboxylic acid with alcohol in the presence of an adequate acid catalyst. The esterification of lauric acid and glycerol completely follows fischer-speier esterification [42]. The mecha-

nism of glycerol and lauric acid esterification could be completed via four steps, in the first step, acid catalyst will protonate the lauric acid molecule via elimination of the proton form MTSA-Si catalyst, in the second step, the nucleophilic attack of oxygen (from glycerol) will take place to form tetrahedral intermediate. In the third step, tautomerization of the tetrahedral intermediate takes place. Finally, in the fourth step, the removal of one molecule of water and deprotonation of tetrahedral intermediate leads to produce the monoglycerides of lauric acid. The eliminated proton again absorbed by the MTSA-Si catalyst in order to regenerate and reactivate it for the next use. This entire arrangement will replay for twice to form TGLA and three moles of water. The mechanism scheme for the esterification of crude glycerol is demonstrated in Fig. 9.

#### FT-IR analysis of MTSA-Si

The FT-IR spectra of fresh and regenerated MTSA-Si have been demonstrated in Fig. 10.

The FT-IR spectra of fresh and regenerated MTSA-Si catalyst were confirmed with the presence of characteristics bands at  $3342.75\text{ cm}^{-1}$  (OH stretching of Si-OH, intermolecular H-bond),  $3146.00\text{ cm}^{-1}$  (N-H stretching),  $2712.01\text{ cm}^{-1}$  (C-H stretching),  $1728.28\text{ cm}^{-1}$  (C=O stretching),  $1687.77\text{ cm}^{-1}$  and  $1525.74\text{ cm}^{-1}$  (N-H bending),  $1400.37\text{ cm}^{-1}$  (S=O stretching),  $1361.79\text{ cm}^{-1}$  (S-O stretching),  $1170.83\text{ cm}^{-1}$  (SO<sub>2</sub> asymmetric stretching of SO<sub>3</sub>H group),  $1087.89\text{ cm}^{-1}$  (O-Si-O stretching) and  $976.01\text{ cm}^{-1}$  (SO<sub>2</sub> symmetrical stretching) respectively [43]. No remarkable variations were realized in FT-IR spectra of fresh and regenerated catalysts, they affirmed the confinement of skeleton structure on all accounts of the esterification and transesterification.

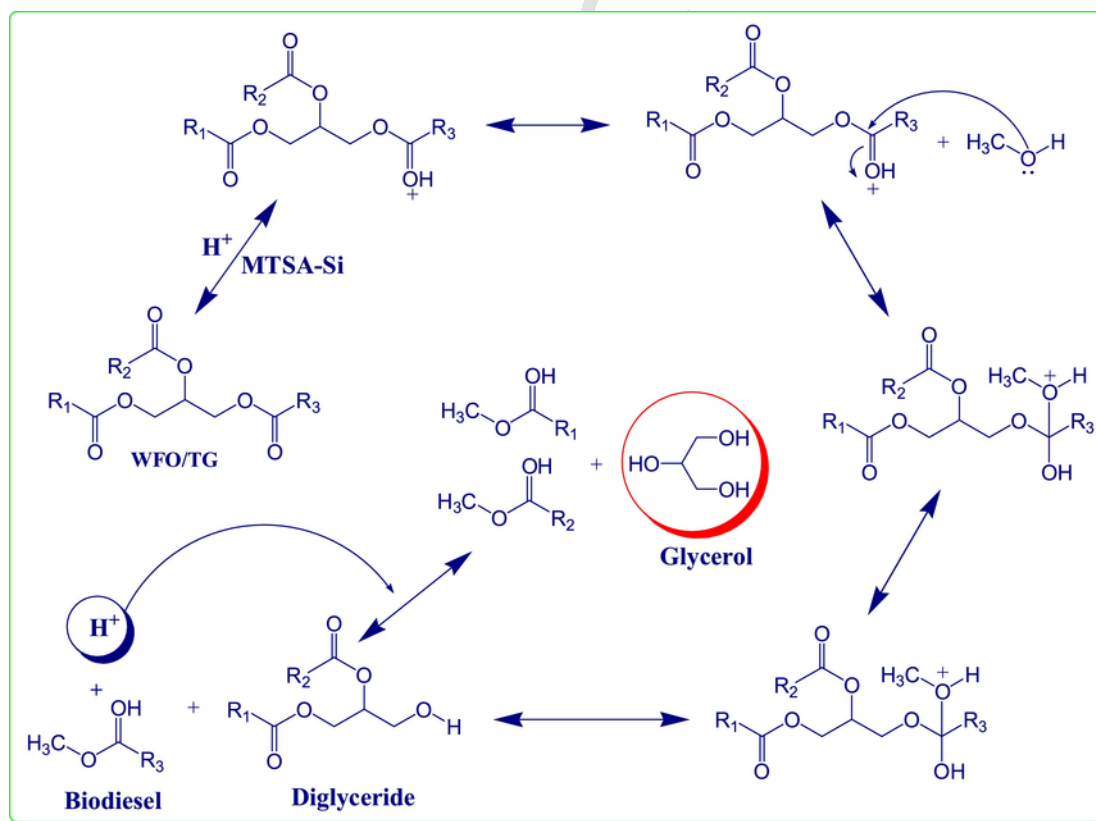


Fig. 8. Mechanism for MTSA-Si catalyzed transesterification of WFO. Where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> are carbon chains of different fatty acids.

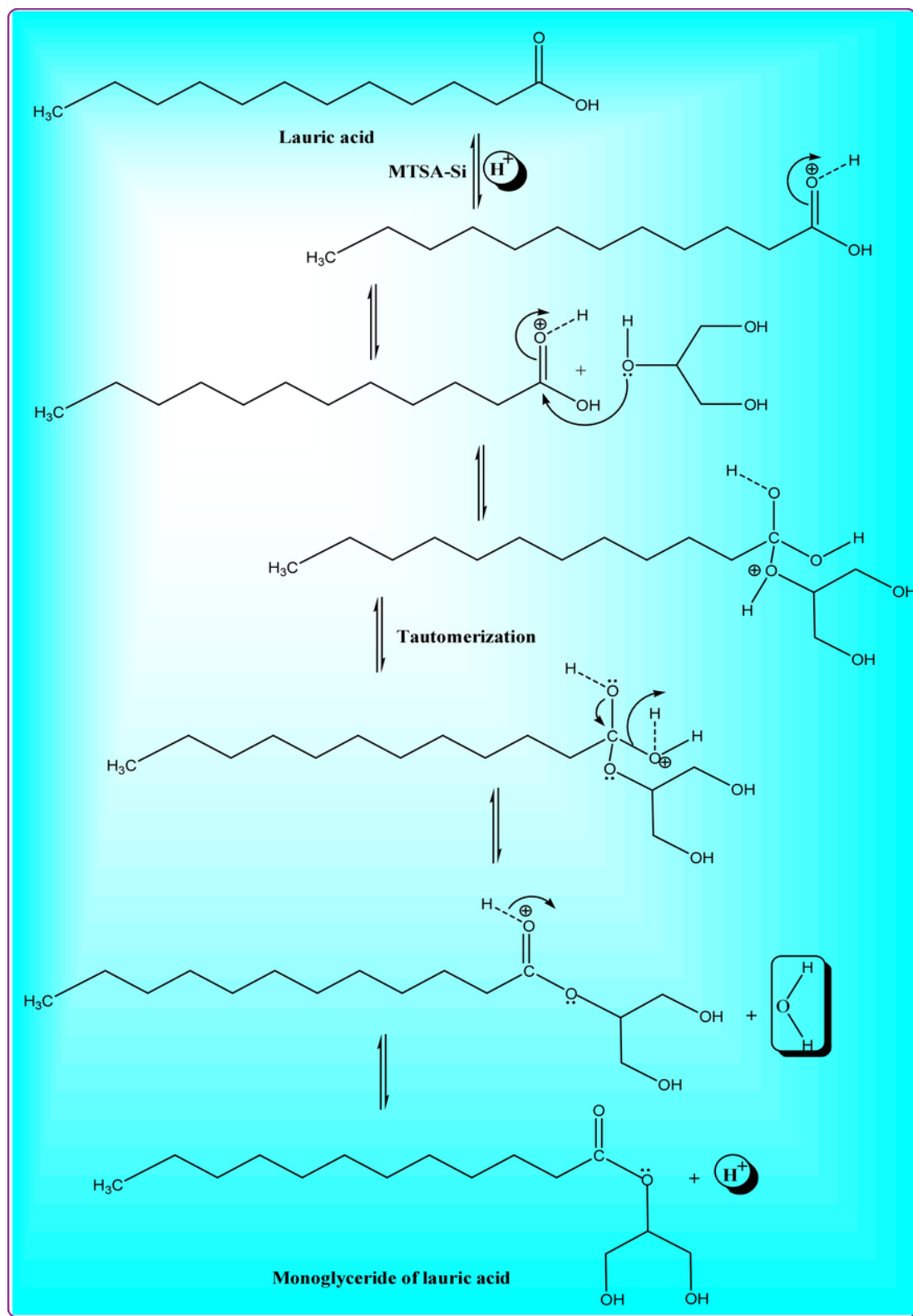


Fig. 9. Mechanism scheme for MTSA-Si catalyzed esterification of crude glycerol to TGLA.



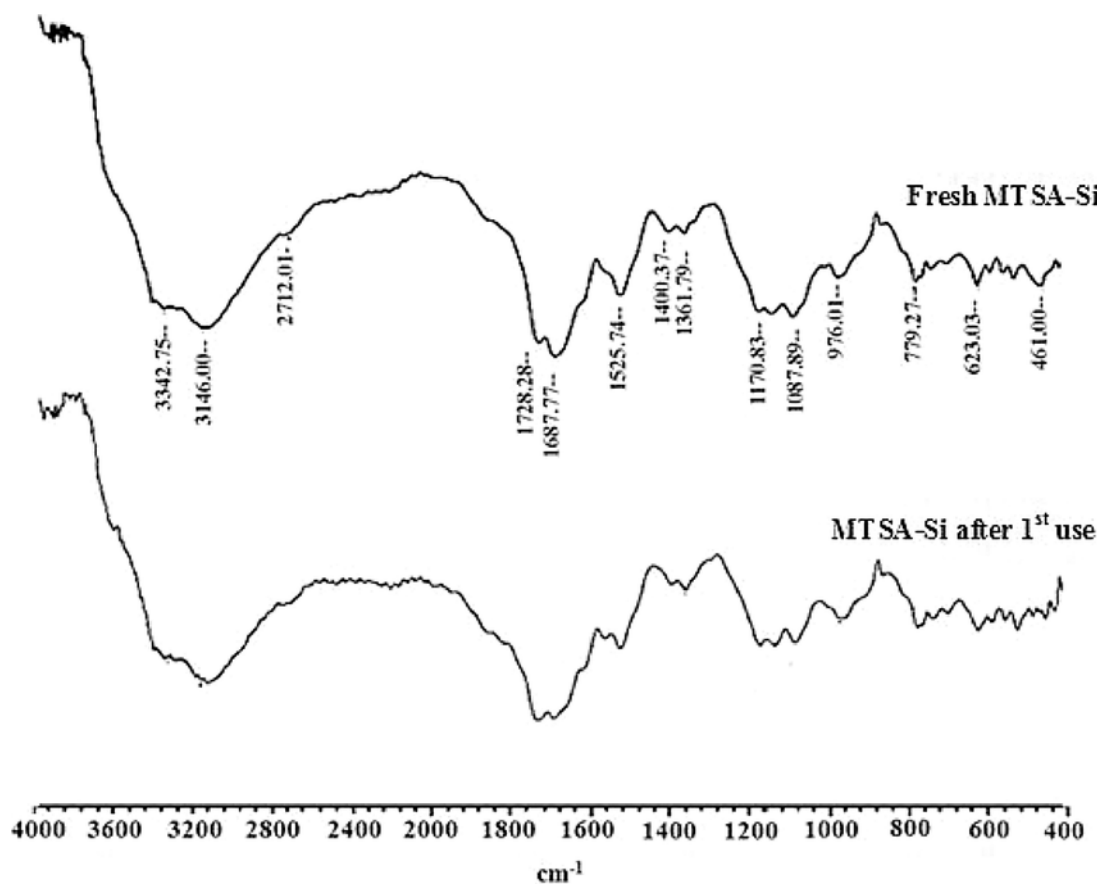


Fig. 10. FT-IR spectra of fresh and regenerated MTSA-Si.

#### Morphological study of MTSA-Si

The surface morphology of fresh and regenerated MTSA-Si catalysts was recognized using the scanning electron microscope. From SEM micrographs, it has been found that a silica gel molecule offers an irregular pentamerous framework. However, the melamine trisulfonic acid molecules offers irregular flakes like framework structure. It has also been found that the particles size of melamine trisulfonic acid turns to smaller and particles gravitated to assemble after chloro-sulfonation. Additionally, the melamine trisulfonic acid molecules are well arranged in circumforaneous of irregular pentamerous shape silica gel molecules. No indicative changes were ascertained in SEM micrographs of fresh and regenerated MTSA-Si, they affirmed the confinement of skeleton structure throughout the esterification and transesterification. SEM micrographs of fresh and regenerated MTSA-Si catalysts are demonstrated in Fig. 11.

#### Powder X-ray diffraction study of MTSA-Si

The texture properties of fresh and regenerated MTSA-Si were evaluated by XRD analysis. The spectra displayed natural diffraction peaks suggesting crystallinity of MTSA-Si. The X-Ray diffractograms displays characteristics diffraction pattern showing crystalline planes of MTSA-Si. The characteristics peaks found at 18.94 2 $\theta$  (deg.), 20.84 2 $\theta$  (deg.), 22.76 2 $\theta$  (deg.), 25.14 2 $\theta$  (deg.), 26.50 2 $\theta$  (deg.), 28.04 2 $\theta$  (deg.) and 29.60 2 $\theta$  (deg.) are attributed to the presence of crystalline silica gel (JCPDS-29-1129). Whereas, sharp peaks

recognized at 30.38 2 $\theta$  (deg.), 32.10 2 $\theta$  (deg.), 36.64 (deg.), 38.12 2 $\theta$  (deg.) and 39.74 2 $\theta$  (deg.) are characteristics of melamine (JCPDS-00-005-0127). In the case of X-Ray diffractogram of regenerated MTSA-Si catalyst, the intensity of peak at 25.14 2 $\theta$  (deg.) and 26.50 2 $\theta$  (deg.) are slight decreased. This may attributed to the leaching of active centers ( $H^+$ ) from the MTSA-Si surface or slight modification in the structure of MTSA-Si. Otherwise, no indicative major changes were ascertained in the XRD patterns of fresh and regenerated MTSA-Si, they affirmed the confinement of skeleton structure throughout the esterification and transesterification. The wide angle X-Ray diffractograms of fresh and regenerated MTSA-Si have been demonstrated in Fig. 12.

#### Surface area determination of MTSA-Si

The results of specific surface area, pore size and pore volume have been tabularized in Table 3.

It has been clearly observed from Table 3, the BET surface area ( $S_{BET}$ ) of MTSA-Si was found to be 108.94 m<sup>2</sup>/g. The BET isotherm of MTSA-Si found naturally of Type-IV at lower  $p/p_0$  values directing the presence of mesopores in MTSA-Si catalyst. The pore volume and pore size of MTSA-Si was found to be 0.1071 cm<sup>3</sup>/g and 15.88 Å respectively. The pore size and surface area reveals the existence of sulfonic acid groups ( $-SO_3H$ ) on the pore surface of melamine species. This fact is in identical with the reported literature [44]. The BET adsorption-desorption isotherm of MTSA-Si has been demonstrated in Fig. 13.

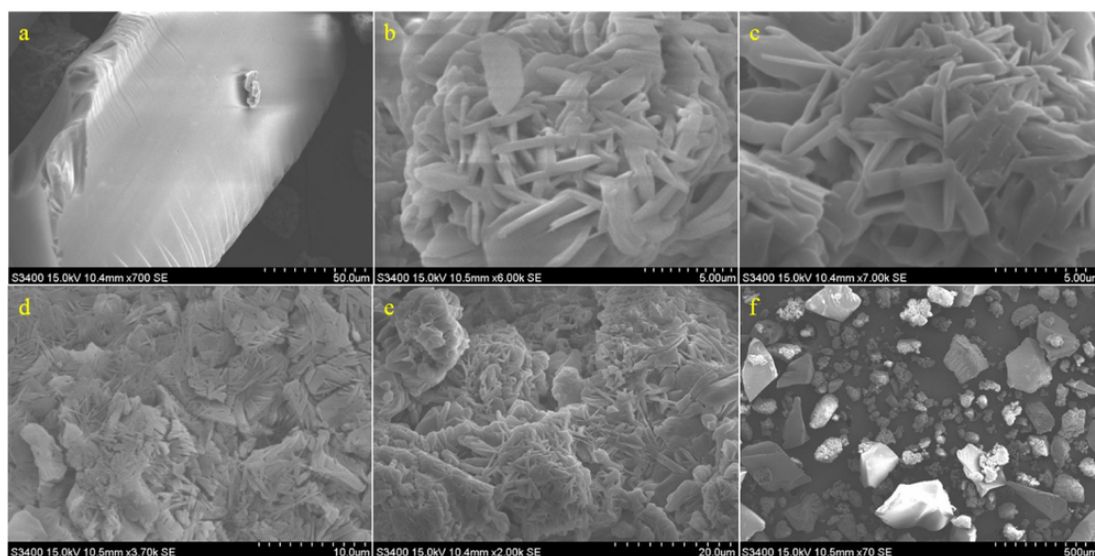


Fig. 11. SEM micrographs of (a) silica gel, (b) fresh MTSA-Si and (c–f) regenerated MTSA-Si.

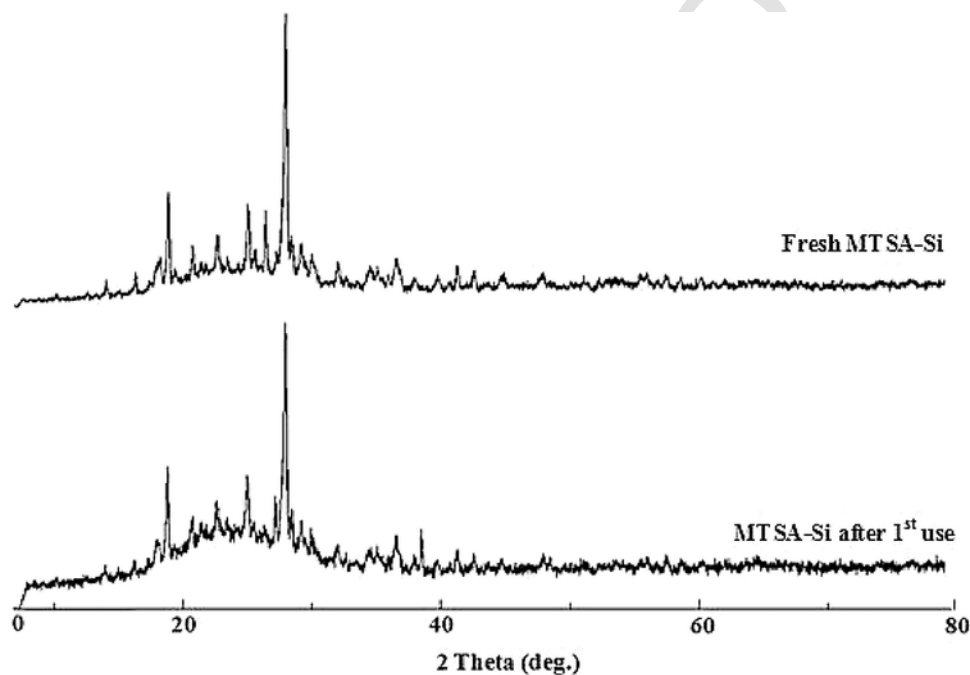


Fig. 12. Large angle X-ray diffractograms of fresh and regenerated MTSA-Si catalysts.

**Table 3**  
Surface area and pore volume of MTSA-Si.

Sr. no	Catalyst	BET surface area ( $m^2/g$ ) $S_{BET}$	Total PV ( $cm^3/g$ ) $V_{total}$	DFT pore size ( $\text{\AA}$ )
1.	MTSA-Si	232	0.1071	15.88

#### Acidity measurement study

The acidity of solid acid catalyst is a very significance property for the heterogeneous catalysis. Solid acid catalysts may contain both lewis and bronsted acidic sites. Both nature and strength of acid sites

play an important role in expressing catalytic activity of many solid acid catalysts. Hence, the measurement of surface acidity of solid catalysts is of immense importance from technological point of view because it not only helps to characterize a catalyst sample but also provides a method of screening of a catalyst sample for optimal yield in a process. Accordingly, a large number of methods are accessible for the estimation of acidity of solid acid catalysts. The total acidity of the MTSA-Si catalyst was found to be  $1.1 \text{ mmol g}^{-1}$ , which was estimated through the neutralization titration. In a 500 mL glass beaker, 0.6 g MTSA-Si catalyst was added along with 4 mL 2 N aqueous NaCl and stirred those at ambient conditions for 24 h in order to allow the ion exchange in the solution. Then after, the solids were filtered off from the aqueous solution and washed thrice with distilled

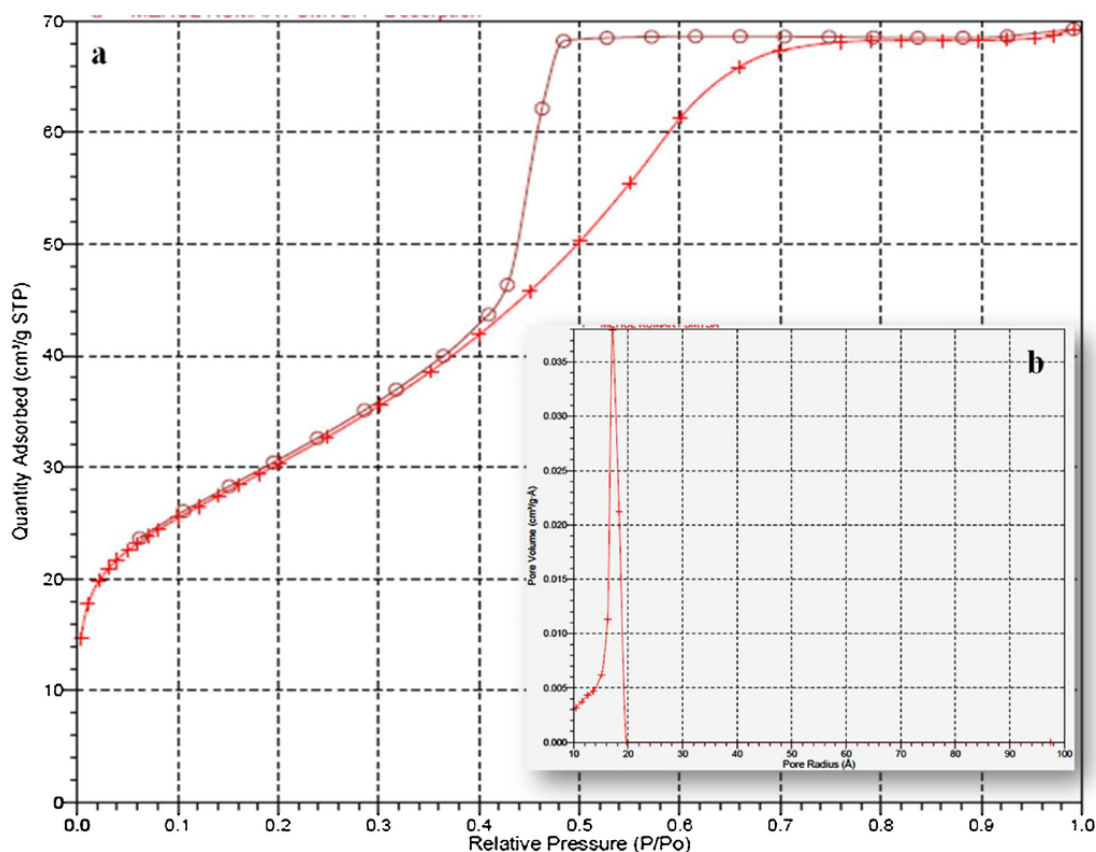


Fig. 13. (a) BET isotherm of MTSA-Si and (b) pore size distribution of MTSA-Si.

water (15 mL). The collective filtrate was titrated with 0.01 N NaOH using phenol red as an indicator [42].

#### Thermal stability study of MTSA-Si

The thermogravimetric analyzer (TGA) is an essential laboratory tool used for determination of thermal stability of materials and compositions of volatile compounds by keeping track record of the weight loss that occurs when material is heated. The thermal stability of MTSA-Si was estimated by thermogravimetric analysis. From the TGA thermogram of MTSA-Si, it has been found that the 10.72% weight loss occurs in a temperature range of 30–210 °C is pertaining to the molecular moisture decomposition, 26.46% weight loss occurs in a temperature range of 210–550 °C is pertaining to the melamine decomposition and 12.75% weight loss occurs in a temperature range of 570–920 °C is pertaining to the decomposition of sulfonic acid group (–SO<sub>3</sub>H) attached to the melamine. In the present study, the maximum reaction temperature employed for the transesterification and esterification reactions are 130 °C and 100 °C respectively. Whereas, the weight loss (7.306%) has been observed in the range of temperature 30–210 °C and it's due to the decomposition of molecular moisture. From the TGA thermogram, it could be recognized that the thermal stability of MTSA-Si is not much influenced at 130 °C reaction temperature. Therefore, the MTSA-Si offers a remarkable thermal stability also. The TGA thermogram of MTSA-Si has been expressed in Fig. 14.

#### FT-IR analysis of biodiesel

The FTIR spectrum of waste frying biodiesel is confirmed with the presence of characteristics bands at 2924.09 cm<sup>-1</sup> (CH<sub>3</sub> stretching), 2854.65 cm<sup>-1</sup> (CH<sub>2</sub> stretching), 2360.87 cm<sup>-1</sup> (C=C stretching), 1743.65 cm<sup>-1</sup> (C=O), 1458.18 cm<sup>-1</sup> (CH bending), 1195.87 cm<sup>-1</sup> and 1172.72 (C–O) and 725.23 cm<sup>-1</sup> (CH rocking) respectively [43]. The FT-IR spectrum of synthesized biodiesel is given in Fig. S3.

#### <sup>1</sup>H NMR analysis of biodiesel

The purity of waste frying biodiesel is further confirmed by the presence of characteristics peaks at 5.22–5.28 (unsaturated olefinic –CH=CH– protons) ppm, 3.57 (CH<sub>3</sub>O-methoxy protons) ppm, 3.36 (OCH<sub>2</sub> protons) ppm, 2.69 (CH protons) ppm, 2.19–2.23 (OCH protons) ppm, 1.91–1.98 (β-CH<sub>2</sub> protons) ppm, 1.52–1.56 (α-CH<sub>2</sub> protons) ppm and 1.18–1.23 (CH<sub>3</sub> protons) ppm respectively [45]. The <sup>1</sup>H NMR spectrum of biodiesel has been given in Fig. S4.

#### <sup>13</sup>C NMR analysis of biodiesel

The purity of waste frying biodiesel is confirmed by the presence of characteristics peaks, including, 173.88–173.91 ppm (C=O carbons), 127.79–129.92 ppm (olefinic carbons), 76.80–77.43 ppm (CDCl<sub>3</sub>-solvent), 51.11 ppm (O–CH<sub>3</sub> carbon) and 27.05–33.90 ppm (aliphatic carbons) respectively [46]. The <sup>13</sup>C NMR spectrum of biodiesel is given in Fig. S5.

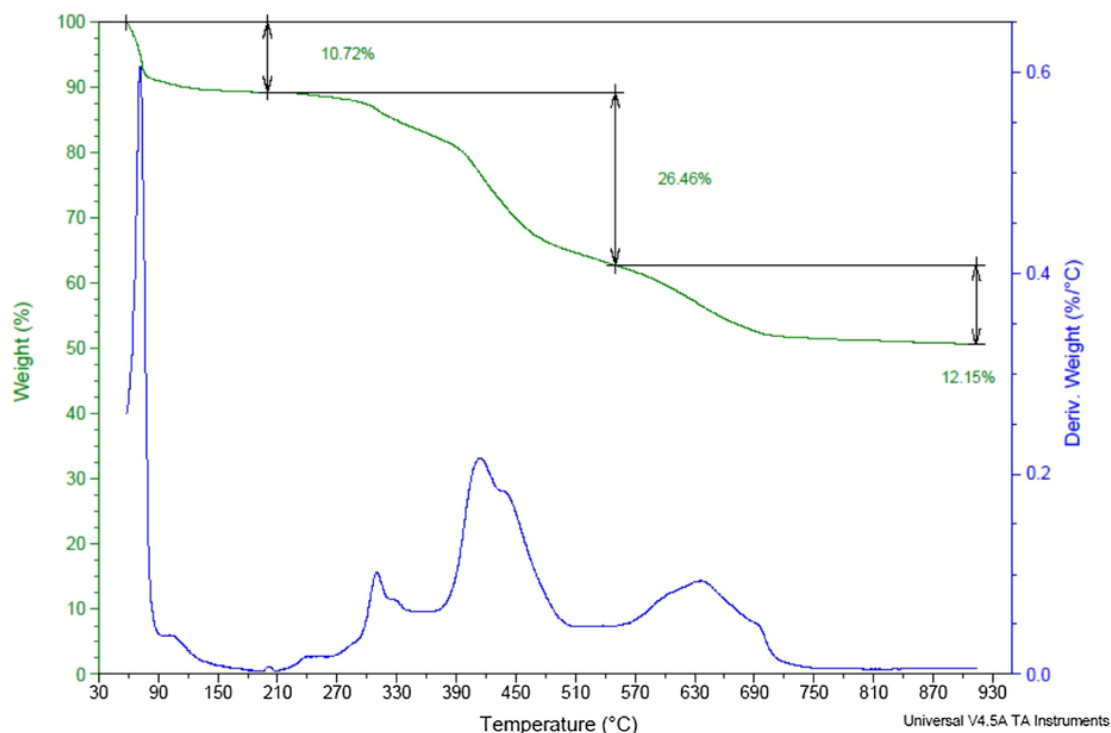


Fig. 14. TGA profile of MTSA-Si.

#### FT IR analysis of TGLA

FTIR spectrum of TGLA is confirmed with the presence of characteristics bands at  $2924.09\text{ cm}^{-1}$  ( $\text{CH}_3$  stretching),  $2854.65\text{ cm}^{-1}$  ( $\text{CH}_2$  stretching),  $2360.87\text{ cm}^{-1}$  ( $\text{C}=\text{C}$  stretching),  $1712.79\text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ),  $1458.18\text{ cm}^{-1}$  ( $\text{CH}$  bending),  $1188.15\text{ cm}^{-1}$  ( $\text{C}-\text{O}$ ) and  $725.23\text{ cm}^{-1}$  ( $\text{CH}$  rocking) respectively [43]. The FT-IR spectrum of TGLA has been demonstrated in Fig. S6.

#### $^1\text{H}$ NMR analysis of TGLA

The purity of TGLA is confirmed by the presence of characteristics peaks corresponding to 3.54 ( $\text{O}-\text{CH}_2$ ) ppm, 2.51 ( $\alpha\text{-CH}_2$  protons) ppm, 2.12–2.22 ( $\beta\text{-CH}_2$  protons) ppm, 1.96 ( $\text{CH}_3$  protons) ppm, and 1.22–1.47 ( $\text{CH}$  protons) ppm respectively [45]. The  $^1\text{H}$  NMR spectrum of TGLA is given in Fig. S7.

#### $^{13}\text{C}$ NMR analysis of TGLA

The purity of TGLA is further confirmed by the presence of characteristics peaks, including, 172.80–174.41 ppm ( $\text{C}=\text{O}$  carbons), 127.51–129.26 ppm (olefinic carbons), 50.79 ppm ( $\text{CH}_3$  carbon), 69.26 ppm ( $\text{O}-\text{CH}_2$  carbon) and 28.56–39.91 ppm (aliphatic carbons) respectively [46]. The  $^{13}\text{C}$  NMR spectrum of TGLA has been depicted in Fig. S8.

#### Reusability of MTSA-Si

The widespread and easy commercialization of any fuel is strictly depends on their manufacturing cost. With a view to shorter down the expense of biodiesel and TGLA synthesis, the MTSA-Si was examined for their potential reusability for the esterification and transesterification reactions. Hence, in this approach, after each run, the MTSA-Si catalyst was isolated from the reaction mass through vac-

uum filtration and treated thrice with dichloro methane in order to eliminate some impurity like, the surface restrained moisture, unspent triacylglyceride, diacylglycerides, monoacylglyceride, glycerol and unspent methyl alcohol. Before reuse, dichloro methane treated MTSA-Si was kept in a tray dryer at  $110\text{ }^\circ\text{C}$  for 20 h in order to acquiesce elimination of organic solvent traces and reactivation of active centers ( $\text{H}^+$ ) on the melamine surface. It has been recognized from the results of esterification and transesterification reactions, the MTSA-Si catalyst could have a potential to reuse five times without indicative disappearance of catalytic activity. However, the slight subtraction in the (%) yields of biodiesel and TGLA have been recognized on the repetitive runs of MTSA-Si. The percolation of active centers ( $\text{H}^+$ ) or modification of MTSA-Si structure at given reaction temperature could play significant role in the deactivation of MTSA-Si catalyst. It has been found from the repetitive runs and spectral analysis of the MTSA-Si catalyst (Figs. 10–12), the melamine preserves its structure through the esterification and transesterification reactions without any serious distortion. In the case of biodiesel synthesis, a fresh MTSA-Si catalyst could shows highest conversion up to 98.22%. While, it's first, second, third, fourth and fifth repetitive run could shows highest conversions up to 94.25%, 89.33%, 86.52%, 83.69% and 78.45% respectively. The influence of MTSA-Si run on the (%) yield of biodiesel has been illustrated in Fig. 15.

Whereas, in the case of TGLA synthesis, a fresh MTSA-Si catalyst could shows highest conversion up to 92.28%. While, it's first, second, third, fourth and fifth repetitive run could shows highest conversions up to 89.11%, 86.33%, 81.28%, 77.45% and 70.18% respectively. The influence of MTSA-Si run on the (%) yield of TGLA has been illustrated in Fig. 16.

#### Comparison of catalytic activity of MTSA-Si

Table 4 shows the comparison of catalytic performance of MTSA-Si with reported results of the various solid acid catalysts employed for the transesterification of oil to biodiesel.

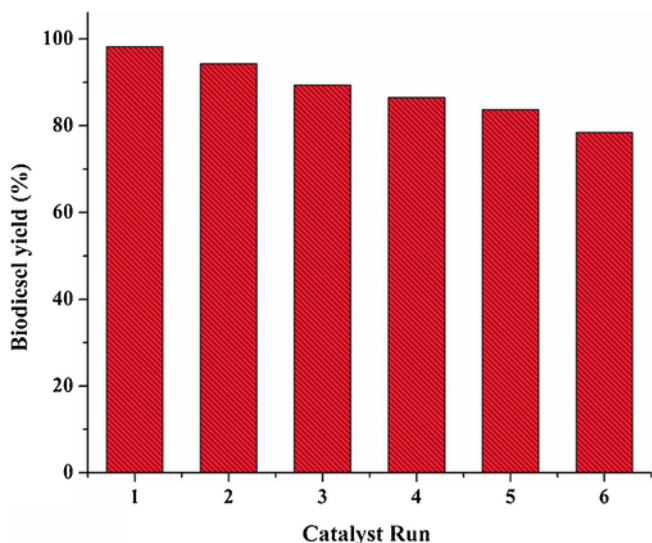


Fig. 15. The effect of catalyst run times on (%) yield of biodiesel.

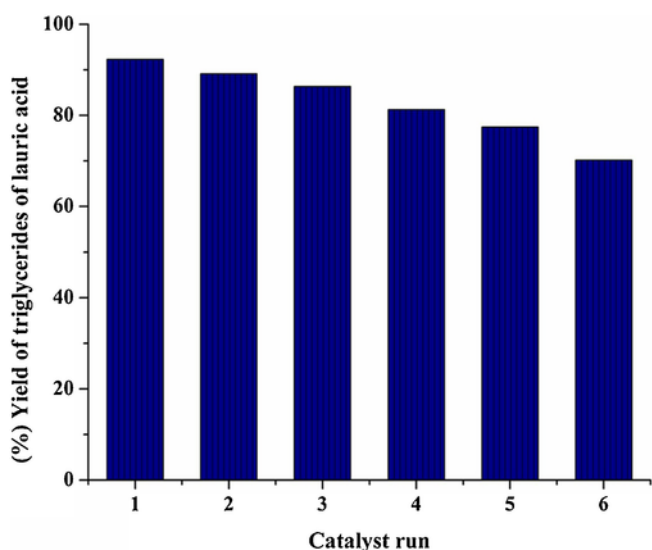


Fig. 16. The effect of catalyst run times on (%) yield of TGLA.

From Table 4, it could be observed that MTSA-Si catalyst shows remarkable catalytic performance for the transesterification of waste frying oil for synthesis of biodiesel. In present study, the best results achieved at optimum reaction conditions like, (i) 130 °C reaction temperature, (ii) 1:10 oil to methanol molar ratio, (iii) 5% (w/w) catalyst and (iv) 10 h reaction time, for the 98.22% biodiesel yield. It has also been found from Table 4, the results of the present study are comparable to the results of reported literature of the solid acid catalysts, where comparatively precise reaction parameters (too high reaction temperatures and oil to methanol molar ratio) were reported [47–49,51–54].

#### Moisture absorption test for MTSA-Si

The MTSA-Si was also studied for its moisture absorption susceptibility. In this process, the required amount of MTSA-Si catalyst was put up in a glass vessel under saturated humidity at atmospheric temperature for several days in order to acquiesce the absorption of moisture on the MTSA-Si surface. The MTSA-Si samples were weighted at regular interval of times. The absorbing moisture rate ( $W\%$ ) of the samples were determined by Eq. (3).

$$W\% = \left[ \frac{56 \Delta m}{18 m_0} \right] \times [100] \quad (3)$$

where,  $\Delta m$  refers to the increased weight and  $m_0$  refers to the initial weight of the MTSA-Si sample. The influence of exposure time (h) on the moisture absorption of MTSA-Si is illustrated in Fig. S9.

From Fig. S9, it has been observed that moisture absorption rate ( $W\%$ ) is increased gradually with increased in moisture exposure time (h). The melamine trisulfonic acid (MTSA) catalyst offers three hydroxyl (–OH) groups in association to the three sulfonic acid groups. Hence, as a result of polar texture of catalyst, the MTSA-Si catalyst could easily absorb the moisture from constant humidity surroundings.

#### Estimation of fuel properties of biodiesel

The most important fuel properties which influence the engine performance of the diesel engine are like, the process taking place in the engine, (i) ignition quality, (ii) serenity of starting, (iii) production and flaming of the fuel-O<sub>2</sub> mixture, (iv) formation of burn out gas and its quality and (v) the calorific index. The cool climate properties like, (i) cloud point, (ii) pour point and (iii) cold filter plugging point. The storage and transportation properties like, (i) oxidative and thermal stability, (ii) flash point, (iii) an ordination period, (iv) micro-

Table 4

Comparison of catalytic activity of MTSA-Si with reported literature.

Sr. no	Catalyst	Reaction conditions				Biodiesel yield (%)	Ref.
		Reaction temp. (°C)	Catalyst % (w/w)	O/M molar ratio	Reaction time (h)		
1.	MTSA-Si	130	5.0	1:10	10	98.22	Present work
2.	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> -Nb <sub>2</sub> O <sub>5</sub>	200	3.0	1:18	20	94.00	[47]
3.	Zr-PMOs	209	12.8	1:48.5	6.0	85.00	[48]
4.	[(CH <sub>2</sub> ) <sub>4</sub> SO <sub>3</sub> HPy-HSO <sub>4</sub> ]	170	2.0	1:12	5.0	92.00	[49]
5.	H <sub>3</sub> PW <sub>12</sub> O <sub>40</sub> /SBA-15	65	0.3	1:2	12	75.0	[50]
6.	Propyl-SO <sub>3</sub> H SBA-15	190	5.0	1:6	15 min	38.0	[51]
7.	Arene-SO <sub>3</sub> H SBA-15	190	5.0	1:6	15 min	56.0	[51]
8.	Me/Arene-SO <sub>3</sub> H SBA-15	190	5.0	1:6	15 min	58.0	[51]
9.	EBD-100	65	1.0	1:12.2	24	100	[52]
10.	EBD-200	65	1.0	1:12.2	24	100	[52]
11.	EBD-300	65	1.0	1:12.2	24	81.0	[52]
12.	Ti/SiO <sub>2</sub> nanoflowers	65	5.0	1:30	4.0	98.0	[53]
13.	Lithium-doped ceria supported SBA-15	65	10.	1:40	4.0	>98.0	[54]

bial degradation and (v) percolation limit temperature. The wear properties like, (i) lubricity, (ii) cleaning effect, (iii) viscosity, (iv) density and (v) consonance with materials employed to prepare a fuel. The physicochemical properties of biodiesel can be estimated by the fatty acid profiles of corresponding oils. The fuel properties of biodiesel can alter substantially from one oil to oil in virtue of its slight higher molar mass than conventional diesel [55]. Some fuel properties of WFO based biodiesel and its comparison with ASTM fuel standards has been tabularized in Table 5.

The flash point and fire point (ASTM D6751) were measured with help of cleveland open cup tester (Pensky-martens). The cetane number (ASTM D 976) was estimated by cetane number analyzer (AFIDA 2805). The iodine value (AOCS CD1-25 1993) and acid value (ASTM D664) were estimated through titration methods. The calorific value (IS:1448:(P:33):1991) was determined by an oxygen bomb calorimeter (model 6772, Parr instrument Ltd, USA). Kinematic viscosity was estimated using viscometer bath (ASTM D6751, Aditya 01). The density (D4052-91) of biodiesel was predicted by hydrometer method (D1298). The cloud point is an exclusive cold flow property that is recognized in ASTM D6751 standards [56]. From Table 5, it has been found that all fuel properties are in consonance with the test limits, which were defined by ASTM and AOCS fuel standards.

## Conclusion

Herein, a promising MTSA-Si catalyst was prepared via chlorosulfonation of melamine and evaluated for the transesterification of WFO for biodiesel synthesis. It has been realized from experimental results, the optimum reaction conditions for the biodiesel preparation are (i) 1:10 oil to methanol molar ratio, (ii) 5% MTSA-Si (*w/w*), (iii) 130 °C reaction temperature and (iv) 10 h reaction time for the 98.22% yield of biodiesel. As MTSA-Si could simultaneously catalyze esterification and transesterification, hence, it does not demands refined feedstocks. Currently, the biodiesel manufacturers are facing a serious problem to dump the crude glycerol produced as a side product during biodiesel production and availability of a cheaper feedstock for biodiesel production. Therefore, we made a small attempt to convert the biodiesel based crude glycerol to triglycerides of lauric acid using MTSA-Si catalyst. It has been illustrated from the experimental results, the optimal reaction conditions for the maximum (%) yield of TGLA (92.28%) are, (i) 1:3 glycerol to lauric acid molar ratio, (ii) 2% MTSA-Si (*w/w*), (iii) 100 °C reaction temperature and (iv) 7 h reaction time. Hence, this protocol offers duple advantages; i.e (i) crude glycerol is effectively transformed into corresponding triglycerides and (ii) synthesized triglycerides could be used

**Table 5**

Fuel properties of WFO based biodiesel based on ASTM and AOCS fuel standards.

Sr. no	Properties	Unit	Method	Value	ASTM limits
1.	Flash point	(°C)	ASTM D6751	133	>130
2.	Fire point	(°C)	ASTM D6751	141	>140
3.	Pour point	(°C)	ASTM D 97	-16	-15
4.	Cetane index	-	ASTM D 976	49	52.0
5.	Iodine value	g I <sub>2</sub> /100 g	AOCS CD1-25 1993	91	120
6.	Calorific value	MJ/kg	IS:1448:(P:33):1991	39.85	-
7.	Total acid number	mg KOH/g	ASTM D 664	0.78	0.8
8.	Kinematic viscosity @ 40 °C	mm <sup>2</sup> /s	ASTM D6751	4.21	1.9-6.0
9.	Density @ 25 °C	Kg/m <sup>3</sup>	ASTM D4052-91	867	860-900
10.	Cloud point	(°C)	ASTM D6751	9.8	-

as cheaper feedstock for biodiesel production. Besides, the MTSA-Si could successfully be used for five repetitive runs without any serious distortion of their performance for esterification and transesterification.

## Acknowledgement

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.jiec.2018.03.036>.

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