

# Sulphated zirconia, an efficient solid acid catalyst for transesterification of triglycerides

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## Abstract

Sulphated zirconia, one of the most efficient solid acid catalysts, has been explored in present studies for transesterification reaction. The catalyst was synthesized by conventional precipitation method and characterized by XRD, TGA, FTIR and total acidity. The catalyst exhibits excellent activity for transesterification of model triglyceride triacetin as well as Jatropha oil with high selectivity towards the formation of monoalkyl esters. Influence of various reaction parameters such as triglyceride/alcohol molar ratio, catalyst amount, reaction temperature and reaction time on catalytic performance were studied over model triglyceride. The maximum 96 % yield of methyl acetate was achieved in 3 hours at 10 wt% catalyst loading with triglyceride to methanol ratio 1:15 and 70<sup>o</sup> C reaction temperature. The kinetic studies were also done and found that reaction follows first order kinetics and reaction rates are not mass transfer limited. The optimized reaction parameters were extended for biodiesel synthesis from Jatropha oil and FAME yield of 82 % could be successfully achieved. Hence, Sulphated zirconia is a promising catalyst for heterogeneous transesterification of triglycerides, which is more productive and environment-friendly as compared to conventional homogeneous transesterification. Copyright © 2017 VBRI Press.

**Keywords:** Transesterification, triacetin, sulphated zirconia, jatropha oil, biodiesel.

## Introduction

Renewable biofuels are gaining more and more importance in recent times due to the increased environmental concern and depleting fossil fuel resources. Biodiesel is liquid biofuel that can be developed from renewable biomass resources such as vegetable oils or fats [1]. It has similar physio-chemical properties with that of diesel-fuel and therefore, has the potential to be used as alternate fuel [2]. Transesterification by using homogeneous bases in presence of alcohol is a simple and conventional method for biodiesel synthesis. However, this method is associated with certain drawbacks such as the need of pretreated feedstock (to limit the moisture and free fatty acid content), post recovery and purification of products, soap formation, emulsifications etc. In order to overcome these limitations, use of solid heterogeneous catalyst is recommended [3, 4].

Numbers of heterogeneous catalysts both acid and base have been studied by many researchers for biodiesel synthesis. Since acid catalysts are least sensitive to free fatty acids /moisture content of feedstock and carry out both esterification and transesterification simultaneously are of greater interest as compared to base catalysts. Example of some of the solid acid catalyst studied for transesterification are sulfonic acid functionalized mesoporous SBA-15 [5-7], KIT-6 [8], Cs-exchanged heteropolyacids [9], tungstated zirconia [10,11],

zirconium phosphate [12], Nafion/Silica composite (SAC-13) [13] and sulphated zirconia [14].

Sulphated zirconia is one of the potential heterogeneous acid catalysts, not only for transesterification but also in several organic reactions such as etherification, cracking, hydrocracking etc [3]. Its ease of synthesis, high acid strength, good thermal stability and reusability are significant factors responsible for its enhanced activity under the mild reaction conditions. Sulphated zirconia is widely studied with respect to its synthetic procedure, influence of sulphur precursor, effect of drying and calcination temperature. These parameters directly affect the surface morphology, acidity and applicability of sulphated zirconia [15, 16]. Numbers of literature studies have reported the significant activity of sulphated zirconia for both esterification and transesterification reaction [17-19]. For example, Kiss et al. have studied the esterification of lauric acid in presence of various heterogeneous catalysts and demonstrated that sulphated zirconia is a promising catalyst with high activity, selectivity and stability as compared to other catalysts under the applied reaction conditions [20, 21]. Similarly, Rattanaphra and the group have studied sulphated zirconia catalyzed transesterification of rapeseed oil and esterification of myristic acid with methanol. The maximum 86% biodiesel was obtained in 60 min. of reaction time at the

temperature of 170° C and 22 bars pressure [22]. Another group of authors has reported the excellent activity of sulphated zirconia giving 98 % conversion of triglycerides in the presence of 0.5 wt% catalyst at lower temperatures 60° C but with increased reaction time i.e. 5 hours [23]. Suwannakarn et. al. has studied the stability and nature of active species on sulphated zirconia in transesterification [24]. One more contribution from Xiao and co-workers has demonstrated the use of sulfated zirconia for the transesterification of waste cooking oil with methanol [25]. Overall, the activity of sulphated zirconia for transesterification reaction has been reported by many researchers, but there are very few reports on the reaction mechanism, kinetics and activation energy of the reaction.

Present paper outlines the synthesis of sulphated zirconia and its characterization by various physico-chemical techniques such as X-ray diffraction (XRD), Thermo gravimetric analysis (TGA), Fourier transform infra-red (FTIR) and acidity determination. The catalytic activity was initially studied for transesterification of model triglyceride triacetin and then it was extended on complex triglyceride of Jatropha oil. The major reaction parameters such as triglyceride/alcohol molar ratio, reaction temperature, reaction time and catalyst amount were optimized over triacetin for maximum conversion. By using model triglyceride triacetin, we were able to gain the fundamental insight into the key reaction parameters such as reaction mechanism, reaction kinetics and activation energy.

## Experimental

### Materials

Zirconium(VI) oxychloride octahydrate (99%,  $ZrOCl_2 \cdot 8H_2O$ ) was purchased from Loba Chemie. Triacetin (99%) was obtained from Finar Chemicals. Ammonia (30% solution), sulphuric acid (98%), and methanol (99%) were procured from Merck, India. All the chemicals were of analytical grade and used as received. Jatropha oil was purchased from the local market and filtered through ordinary filter paper prior to use.

### Sulphated zirconia synthesis

Sulphated zirconia was synthesized by conventional precipitation method [26-28]. The process was started with preparing an aqueous solution of zirconyl oxychloride by dissolving 4 g zirconyl oxychloride in 25 ml water. Ammonia was added drop by drop to this solution till the pH of the solution was in the range of 8-10. The precipitate of zirconium hydroxide thus obtained was filtered and washed with hot distilled water until the filtrate became chloride free. ( $AgNO_3$  test was performed to ensure absence of chloride ions). The residue was dried in an oven at 110° C for 24 hours. The dried catalyst was then treated with 1 M sulphuric acid. For each gram of dried catalyst 15 ml 1 M sulphuric acid was used and then the solution was evaporated to dryness. The resultant mass was finally calcined in a muffle furnace at 550° C for 5 hours.

### Transesterification of triacetin

Transesterification was performed in two-neck round-bottom flask attached with a reflux condenser over magnetic stirrer. A mixture of triglyceride and methanol, with required molar ratio, was charged in a round bottom flask and heated to the reaction temperature. After attaining the steady temperature, required amount of catalyst was added to the reaction mixture. After completion of the reaction, the product mixture was centrifuged to separate the solid catalyst. Product analysis was carried out over Shimadzu gas chromatograph (GC 2025) equipped with RTX-1 capillary column (30m x 0.25 mm x 0.25  $\mu$ m). The GC oven temperature was varied between 45-220° C. Nitrogen was used as carrier gas. Injector and flame ionization detector temperature was set at 250° C and 280° C respectively. Identification of product components was done by comparison with standard samples and finally by gas chromatograph – mass spectrometry (Agilent GCMS 7890) under the same method.

### Catalyst characterization techniques

Prior to transesterification reaction, the catalyst was characterized by powder XRD over Panalytical X'pert by using  $CuK\alpha$  ( $\lambda = 1.54056 \text{ \AA}$ ) radiations. The angle ( $2\theta$ ) was measured in the step size of 0.02° with dwell time of 1s between 10° and 80°. Thermogravimetric analysis was carried out over Mettler Toledo Star system. For TGA analysis 6.8 mg sample weight was taken and 10° C/min heating rate was set. FTIR spectrum was recorded over PerkinElmer's spectrometer model 'Spectrum Two'. The samples were prepared as thin films on KBr salt plates and spectrum was recorded in the region of 400-4000  $cm^{-1}$ . The acidity of synthesized sulphated zirconia was determined by conventional acid-base titration method. In this method, 0.1 g of catalyst was suspended in 10 ml of 0.1 N sodium hydroxide solution and stirred at room temperature for 2 hours. After that, solid catalyst was separated and change in base strength was determined by titrating it against 0.1 N oxalic acid [29].

## Results and discussion

### Sulphated zirconia characterization

The powder XRD pattern of calcined sulphated zirconia is shown in Fig. 1. The diffraction peaks show the presence of both tetragonal as well as the monoclinic phase of crystalline zirconia. The tetragonal phase of zirconia is reported to be more active and more easily connected with sulfur containing groups as compared to the monoclinic phase [2, 27]. TGA spectrum of sulphated zirconia given in Figure S1 shows two major weight loss regions. First weight loss below 400° C temperature is due to desorption of surface adhered and interstitial water molecules, whereas the second major weight loss in the temperature range between 600-800° C is due to the decomposition of the sulphate group.

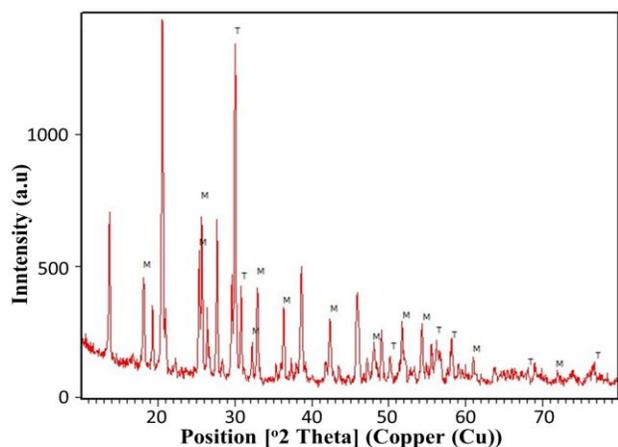


Fig. 1. XRD pattern of calcined sulphated zirconia.

FTIR spectrum shows characteristic bands at 1027, 1075 and 1264  $\text{cm}^{-1}$  due to the bidentate sulphate atoms connected to zirconium ion. Few more bands in the region of 700-400  $\text{cm}^{-1}$  are characteristic of crystalline zirconia. The broad peak at  $\sim 3200 \text{ cm}^{-1}$  is due to O-H stretching mode of hydrogen bonded water molecules. The peak at 1633  $\text{cm}^{-1}$  is due to the O-H bending mode of water molecules bonded with sulfate group and zirconia surface. The acidity of calcined sulphated zirconia determined by acid-base titration method was found as 2.14 mmol /g of base used.

#### Effect of reaction parameters

Transesterification is equilibrium limited and reversible reaction and hence generally alcohol is used in an excess amount to shift the reaction equilibrium to product side and achieve maximum conversion of triglyceride. Heterogeneously catalyzed transesterification needs higher molar ratio as compared to homogeneously catalyzed transesterification. In order to study the influence of triglyceride/alcohol molar ratio on triacetin conversion in presence of sulphated zirconia, the reaction was studied at 1:6, 1:9, 1:12, 1:15 and 1:18 molar ratios (Fig. 2). The rate of reaction was found to be increased with increase in molar ratio and reached maximum at 1:15 triacetin to methanol molar ratio. However, further increase in molar ratio to 1:18 did not markedly improve the conversion. This is due to the fact that molar ratio up to 1:15 sufficiently accelerates the reaction to effect the maximum conversion. Therefore, next increase in molar ratio does not support the increase in conversion.

The reaction temperature is another important and influential parameter that controls the triacetin conversion. Reaction temperatures in the range of 60° C to 90° C are evaluated in present study and results are shown in Fig. 3. The other fixed reaction parameters were set as triacetin to methanol molar ratio 1:15, catalyst amount 10 wt%, time 3 hours and stirring speed 1000 rpm. In heterogeneous system increasing the temperature helps to overcome the mass transfer limitations, thus helps to increase the triglyceride conversion. The initial increase in temperature from 60° C to 70° C increases the triacetin conversion from 76 % to 96 %, while further

increasing temperature up to 90° C does not enhance the triacetin conversion and hence 70° C is assumed to be the optimum temperature for reaction.

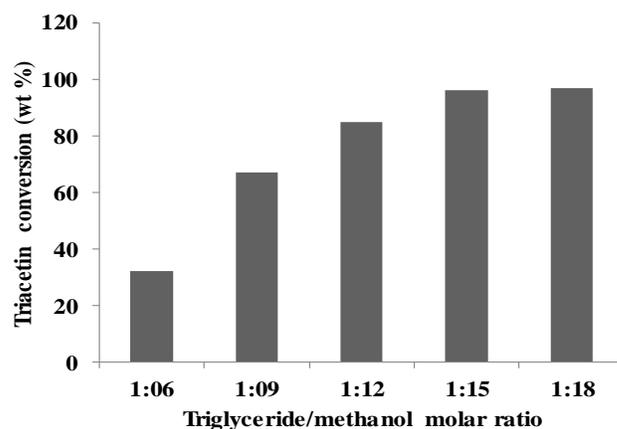


Fig. 2. Effect of Triglyceride/methanol molar ratio on triacetin conversion

[Reaction conditions- Catalyst amount 10 wt%, Reaction time 3 hours, Reaction temperature 70°C]

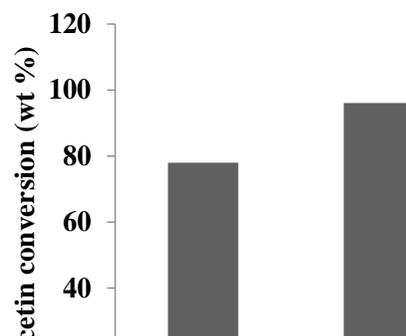


Fig. 3. Effect of reaction temperature on triacetin conversion

[Reaction conditions- Triglyceride/methanol molar ratio 1:15, Catalyst amount 10 wt%, Reaction time 3 hours].

Reaction time was studied as a function of triacetin conversion. The reaction mixture was analyzed at various time intervals and results are graphically presented in Fig. 4. Reaction reaches to the completion with maximum conversion in 3 hours of reaction time.

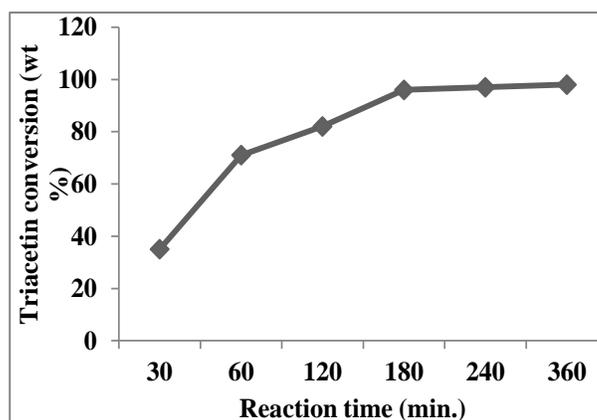
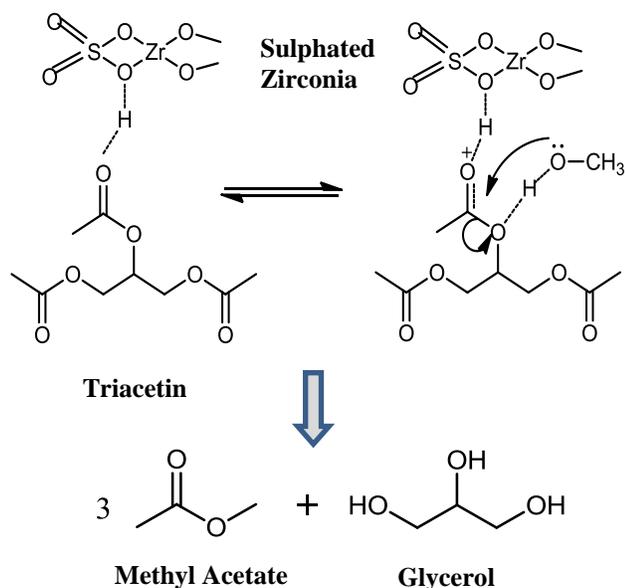


Fig. 4. Effect of reaction time on triacetin conversion

[Reaction conditions- Triglyceride/methanol molar ratio 1:15, Catalyst amount 10 wt%, Reaction temperature 70°C].

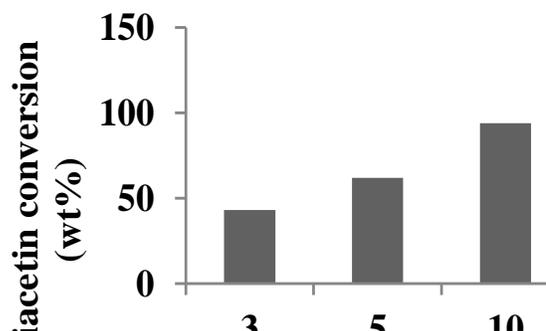
Transesterification of triacetin was studied in presence of varying amount of catalyst loading 3 wt%, 5 wt%, 10 wt% and 15 wt% and results are given in **Fig. 5**. The higher amount of catalyst will offer more number of active acidic sites and hence will increase the triglyceride conversion as expected. A similar trend was observed in present experimental results as well. Triacetin conversion increased from 43 % to 62 % with an increase of the catalyst loading from 3 wt% to 5 wt%. Further increase in catalyst amount 10 wt% gave maximum conversion 94 %. However, beyond that increase in catalyst loading 15 wt% resulted in an insignificant increase in conversion. So, 10 wt% catalyst loading is the optimum amount of catalyst in present reaction conditions.

From above studies, the optimum reaction conditions in order to achieve the highest triacetin conversion over sulphated zirconia were found to be 1:15 triacetin to methanol molar ratio, 10 wt% catalyst loading for reaction time 3 hours at 70° C reaction temperature. Overall reaction mechanism can be presented as below in **Scheme 1**.



#### Heterogeneity test of catalyst

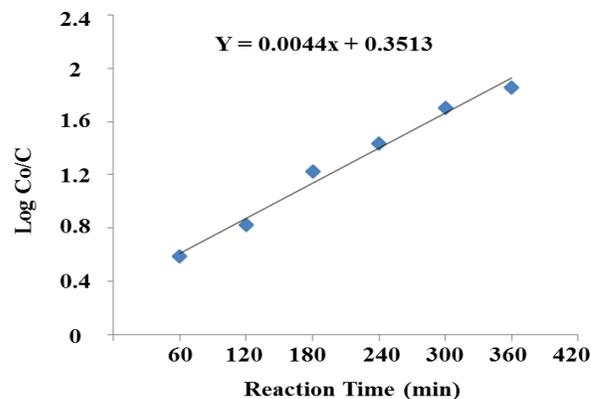
The leaching of active species from catalyst surface makes the catalyst unfavorable to be used as a heterogeneous catalyst. Heterogeneity test was carried out in order to confirm heterogeneous nature of sulphated zirconia. These studies were carried out by stirring the fresh catalyst with methanol at reaction temperature for 6 hours. The catalyst and methanol were separated by centrifugation followed by filtration. The recovered methanol was then used for transesterification of triacetin in absence of catalyst. The reaction mixture did not show any conversion even after 3 hours. On the basis of these results it can be confirmed that there was no leaching of any sulphur group from zirconia support and catalyst is truly heterogeneous.



**Fig. 5.** Effect of amount of catalyst loading on triacetin conversion [Reaction conditions- Triglyceride/methanol molar ratio 1:15, Reaction temperature 70°C, Reaction time 3 hours]

#### Reaction kinetics

In order to study the kinetics of transesterification of triacetin catalyzed by sulphated zirconia, the reaction was carried out under optimized parameters and products were evaluated at fixed time intervals using gas chromatography. In transesterification, methanol is used in an excess amount, and hence rate law is expected to follow the first order kinetics. Triacetin concentration decreases with increases in reaction time and therefore, the plot of  $\text{Co}/\text{C}$  against time shows a linear relationship (**Fig. 6**). It can be concluded from experimental observations that the reaction follows the first order kinetics.



**Fig. 6.** First order plot of transesterification of triacetin over Sulphated Zirconia.

**Table 1.** Physical constants of transesterification of triacetin reaction.

Temperature (K)	Rate constant (k) min <sup>-1</sup>	Pre-Exponential Factor (A) min <sup>-1</sup>	Activation Energy (Ea) K J mol <sup>-1</sup>
333	0.0252399	1.64	24.4
343	0.0367944		
353	0.0468985		
363	0.0520687		

### Activation energy

The effect of the reaction temperature is a most prominent factor in any catalytic process. In order to estimate the activation energy of the reaction, rate of transesterification reaction at various temperatures was studied. Graph of  $\ln k$  vs  $1/T$  was plotted and presented in Fig. 7. Arrhenius equation was used to calculate the activation energy and pre-exponential factor. Kinetic data such as rate constant, pre-exponential factor and activation energy are given in Table 1. The value of activation energy decides whether reaction rate is mass transfer dependent or chemical step dependent. It is reported that activation energy for mass transfer/diffusion limited reactions is in the order of 10-15 K J mol<sup>-1</sup>[30]. In present studies, activation energy was found to be 24.4 K J mol<sup>-1</sup> which indicates that reaction rate is controlled by chemical step.

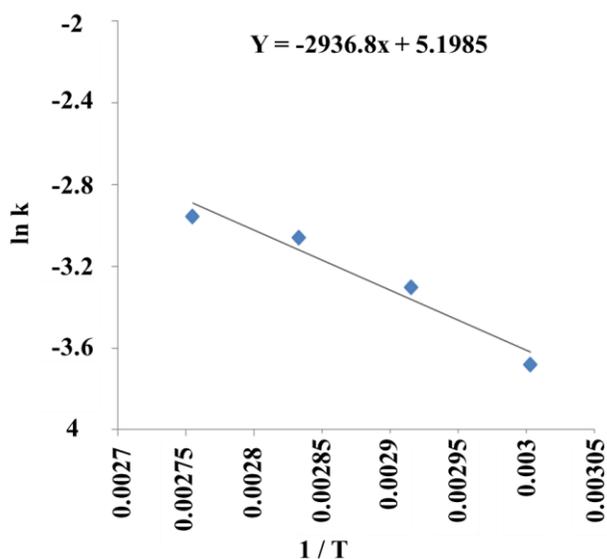


Fig. 7. Arrhenius plot of transesterification of triacetin over Sulphated Zirconia to determine activation energy

### Transesterification of Jatropha oil

The non-edible oil of Jatropha has the similar physico-chemical properties as that of petro-diesel and hence has the greatest potential to be used in biofuel production. It is perennial drought resistant low cost feedstock which can aid in improving the economic feasibility of biodiesel production.

In present studies, sulphated zirconia was used for transesterification of Jatropha oil. The typical reaction was carried out in 50 ml round-bottom flask equipped with a condenser and magnetic stirrer. The optimized reaction parameters over the model triglyceride triacetin were applied here except the reaction time. The oil and methanol were mixed in molar ratio 1:15, followed by 10 wt% catalyst additions; then the reaction was set at 70°C and studied for 3 hours, 6 hours and 9 hours and 12 hours reaction time. Fatty acid methyl ester (FAME) yield at various time intervals was found as 32 wt%, 56 wt%, 82 wt% and 83 wt% at 3, 6, 9 and 12 hours respectively.

Model triglyceride (triacetin) being smaller in size, the reaction took 3 hours of time for completion, compared to that under the same reaction conditions complex triglyceride of Jatropha oil took almost 9 hours for a maximum conversion. The catalyst superiority lies in the FAME yield of 82 % from Jatropha oil under the mild reaction conditions.

### Conclusion

The present studies conclude that sulphated zirconia synthesized via precipitation method exhibits significant activity towards transesterification of model triglyceride triacetin under mild reaction conditions, with maximum 96 % yield of monoalkyl ester. The catalyst is super acidic as well as heterogeneous in nature, confirmed through heterogeneity test. Transesterification of triacetin catalyzed by sulphated zirconia follows first order kinetics with 24.4 K J mol<sup>-1</sup> activation energy. Studies also reveal that the catalyst could be effectively used for biodiesel production from triglyceride feedstocks such as Jatropha oil without any pretreatment.

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