# Parametric study of esterification of high free fatty acid rice bran oil using aluminum doped sulfated zirconia

**Rajiv Arora*[a], Amrit Pal Toor[b] and Ravinder Kumar Wanchoo[b]**

[a]*S. B. S. State Technical Campus, Firozpur-152 001, Punjab, India*

*E-mail:* rajiv_fzr@yahoo.com

[b]Dr. S. S. Bhatnagar Univ. Inst. of Chemical Engg. & Technology, Panjab University, Chandigarh-160 022, Punjab, India

Conventionally, biodiesel is produced by the alkaline catalyzed transesterification of edible oils. The cost of these edible oils is quite high. Though the cost of waste and high free fatty (FFA) acid oils is almost one half to one third that of refined oils, the production cost increases due to additional steps for lowering the FFA to less than 2% for further transesterification to biodiesel. In this study, the esterification technique for the reducing FFA of rice bran oil (RBO) with 70% FFA using strong heterogeneous catalyst aluminum (Al) doped sulfated zirconia has been investigated. Several process affecting parameters like catalyst calcination temperature, stirrer speed, catalyst loading, oil to methanol molar ratio, reaction temperature and re-action time were optimized in order to minimize FFA of oil. The FFA conversion of 95.26% was achieved at 338.15 K, RBO to methanol molar ratio 1:9, catalyst loading 3 wt% in 180 min of reaction time. Consequently, this esterification step reduces the FFA of the oil and thus increases the possibility of producing biodiesel at lower price.

Keywords: Esterification, biodiesel, rice bran oil, heterogeneous catalyst, kinetics.

## Introduction

Biodiesel is produced by the reaction between triglycerides and lower alcohols such as methanol in the presence of a strong basic catalyst. This reaction is known as 'Transesterification' and this reaction produces a by-product, glycerin. The triglycerides (TG) used are generally derived from various types of edible oils like sunflower, rapeseed, palm oil, soybean and peanut oil. Animal fats are also used as raw material for biodiesel (also known as fatty acid methyl ester) production. The cost of waste and high free fatty acid oils is almost one half to one third that of refined oils, but the production cost increases due to additional steps for converting free fatty acids to esters. Using low cost oils as raw material, such as waste oils, acid oils, crude oils or high FFA RBO can produce the biodiesel at much lesser cost[1].

High FFA RBO can be one of the prominent low cost oil for the manufacturing of commercial biodiesel. The annual world paddy cultivation produces about 48 million tons of rice bran, from which approximately 9.2 million tons of crude RBO could be extracted. Rice bran contains 14–26% oil and the FFA in crude RBO from fresh rice bran is approximately 6–8%[2]. Since active enzymes are present in rice bran, FFA value of rice bran increases at the rate of 1–6% every day during storage. The crude rice bran oil can only be refined to produce edible oil only if the FFA content in the crude oil is less than 10%. It is not feasible to extract RBO without delay after the milling of rice, due to which huge quantity of oil is not extracted and the high FFA rice bran is used as ingredient in animal feed.

Various homogeneous and heterogeneous catalysts were used during the esterification of high FFA oils[3–8]. Among these, sulfated zirconia is an effective and significant catalyst as it possesses strong acidity, referred as super-acidity[9–11]. Sulfated zirconia is having excellent catalytic activity in many significant industrial unit processes such as cracking, acylation, trans-esterification and esterification. Sun *et al.*[12] and Vahid *et al.*[13] investigated the properties of sulfated zirconia/Al-doped sulfated zirconia and showed that

the calcinations generates nano-sized particle having higher surface area, catalytic activity and stability. In the present work, the process variables like catalyst calcination temperature, stirrer speed, catalyst concentration, reaction temperature, RBO to methanol molar ratio and and time were optimized with the objective of reducing the FFA of RBO using Al-doped sulfated zirconia as nano-catalyst.

*Materials and method:*

Dewaxed and Degummed high FFA rice bran oil was collected from solvent extraction unit of Partap Group of Industries, Ambala (India). The acid value was determined and it was 140 mg KOH/g RBO, corresponding to 70% FFA. The mean molecular weight of high FFA rice bran oil is calculated as per the FFA and Triglyceride (TG) weight fraction, with molecular weight 282 for FFA and 870 for TG[9,10]. The chemicals used in catalyst preparation and esterification reaction were zirconium oxychloride octahydrate, $ZrOCl_2 \cdot 8H_2O$ (99.9% purity, Merck), $(NH_4)_2SO_4$ (99% purity, Merck), $Al_2(SO_4)_3 \cdot 18H_2O$ (99.9% purity, Merck), methyl alcohol (99.0% purity, S D Fine, India), potassium hydroxide (KOH, 99.9% pure, Merck), ethyl alcohol (99.9% pure), diethyl ether and indicator (phenolphthalein). All the reagents and chemicals used during the study were of analytical grade and were used without further purification.

*Catalysts preparation:*

Aluminum (Al)-doped sulfated zirconia was prepared using solvent-free method. Zirconium oxychloride octa-hydrate and ammonium sulfate were mixed in molar ratio 1:6. $Al_2(SO_4)_3 \cdot 18H_2O$ was added to the mixture in the molar ratio 1:0.2 ($ZrOCl_2 \cdot 8H_2O$:$Al_2(SO_4)_3 \cdot 18H_2O$) and mixed thoroughly in mortar pestle for 20 min at 25°C. The resulting mixture was kept at 25°C for 18 h and then calcined for 5 h at various temperatures between 400°C to 600°C.

*Experimental procedure:*

The esterification reaction was performed in a 500 ml temperature controlled batch reactor of borosilicate glass working under total reflux. 100 g of RBO was pre-heated to the required reaction temperature. Varying quantities of catalyst (1.0 to 4.0% wt) were mixed in methanol and the mixture thus formed is allowed to react with pre-heated oil. Methanol to RBO molar ratio from 3 to 15 was studied during different experiments. The reaction time for the esterification reaction was 4 h with constant stirring and sample collection at regular intervals. To remove the impurities, the samples were washed with distilled water, followed by drying and then acid value was checked. All the esterification reactions were performed at atmospheric pressure. The standard error obtained for duplicate set of reactions was in the range of 1.0–2.0% .

*Free fatty acid value calculation:*

The sample taken during the esterification experiment was dissolved in ethanol-diethyl ether solution and the resulting solution was titrated against standard KOH solution of known normality using phenolphthalein as an indicator. The acid value ($A_v$) of the sample was calculated as under:

$$A_V = \frac{M_W \times c \times v}{m} \tag{1}$$

where $c$ is the molar concentration of KOH, $M_W$ is the molecular weight of KOH, $m$ is the weight of sample (in g) and $v$ is the volume (in ml) of KOH used in the titration process. The fractional FFA conversion was calculated as under:

$$X = \left(1 - \frac{A_v}{A_{vo}}\right) \tag{2}$$

where $X$ is the fractional FFA conversion and $A_{vo}$ is the initial acid value of RBO before the esterification reaction.

## Results and discussion

The esterification of FFA in RBO with methanol using homogeneous/heterogeneous catalyst is a reversible reaction:

$$R_1 - COOH + CH_3 - OH$$
$$\xleftarrow{\quad catalyst \quad} R_1 - COO - CH_3 + H_2O$$
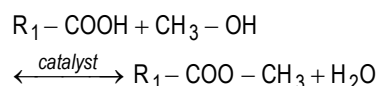
In the current study, $R_1$ is the linear chain of 11–17 carbon atoms with a variable number of unsaturations which further depends on the type of the raw oil.

A parametric study was performed so as to ascertain the optimum parameters for the esterification of FFAs in RBO. The parameters included: effect of calcination temperature, stirring speed, catalyst loading, RBO to methanol ratio, esterification reaction temperature and reaction time. Absence or presence of mass transfer effect was studied by performing experiments at different stirring speeds.

*Effect of catalyst calcination temperature:*

The calcination temperature of Al-doped sulfated zirconia is important parameter for the conversion of FFA in RBO.

As shown in Fig. 1, catalyst calcination temperature was varied from 400°C to 600°C and esterification reactions were carried out at 65°C, 1:9 oil to methanol molar ratio, 600 rpm stirring speed and 3 wt% catalyst concentration. The maximum conversion was achieved at calcination temperature of 500°C. Catalyst calcined at 500°C was used in all further experiments.
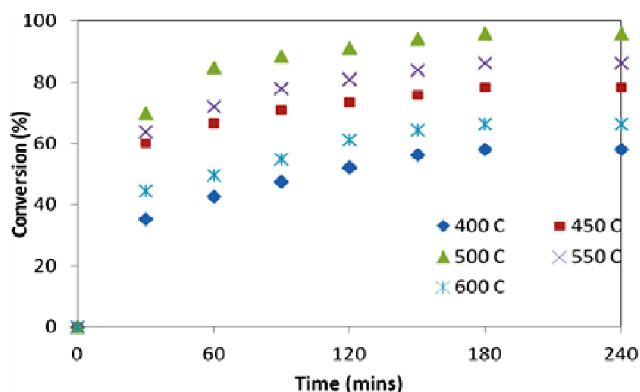


**Fig. 1.** Effect of calcination temperature of Al-doped sulfated zirconia on conversion of FFA at 3.0% (w/wt of oil) of catalyst, 1:9 oil to methanol molar ratio and at 65°C.

*Catalyst characterization:*

*Powder X-ray diffraction (XRD):* Crystalline size of the Al-doped sulfated zirconia was determined by the XRD over a $2\theta$ range from 5° to 90° with continuous scanning. The following Scherrer's equation was used to calculate crystalline size

$$D = \frac{0.9\,\lambda}{\beta \cos \theta}$$

where $D$ is the crystallite size in nm, $\lambda$ is the X-ray wavelength in nm, $\beta$ is the corrected half-width of the peak profile and $\theta$ is the corrected half-width of the diffraction peak angle. Two similar studies using sulfated zirconia as catalyst reported the well distinguished peaks at $2\theta = 30$ and $50.4$ confirming the presence of tetragonal phases of $ZrO_2$[2,13]. In the XRD graph for the Al-doped sulfated zirconia (Fig. 2), the presence of two distinct peaks at $2\theta = 30.22$ and $50.25$ confirmed the tetragonal phase of the catalyst. The crystallite size was found to be 9.8 nm. The XRD peaks and the results are consisted with the results published by the other researchers for the metal doped sulfated zirconia (Vahid *et al.*, 2012; Kaur *et al.*, 2015).
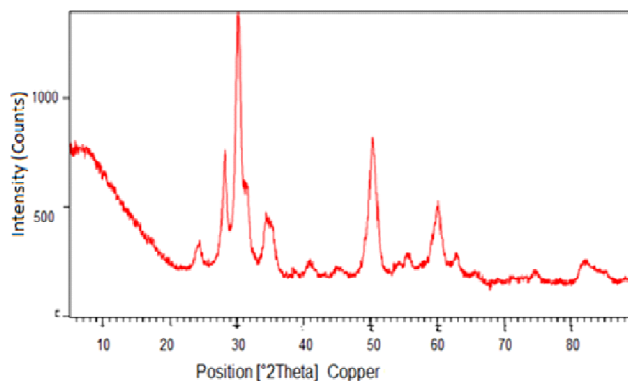
**Fig. 2.** XRD of Al-doped sulfated zirconia catalyst calcined at 500°C for 4 h.

*Scanning Electron Microscopy (SEM) analysis:*

The surface morphology of the Al-doped sulfated zirconia was performed by SEM analysis and the images are shown in Fig. 3. The SEM image of Fig. 3(a) and 3(b) shows the formation of about particles of about 2–10 μm size. Adding aluminum and sulfate in the zirconia have resulted the irregular shapes (flake like structure) as shown in Fig. 3(b). The thickness of the flakes was also in the range of 100 to 500 nm.
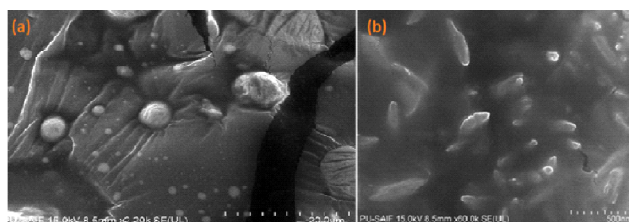


**Fig 3.** SEM images (a and b) of Al-doped sulfated zirconia catalyst calcined at 500°C for 4 h.

*Effect of external mass transfer:*

The solubility of methanol in RBO is very less; and agitation is needed to avoid mass transfer resistance to control the esterification process. Experiments were performed at various stirring speeds ranging from 300 to 700 rpm (at 3 wt% catalyst, 1:9 oil to methanol ratio and 338 K). The results for the effect of stirring speed are shown in Fig. 4, and it can be observed that when the stirring speed was changed from 300 rpm to 600 rpm, there was an increase in ester formation but when the speed was above 600 rpm, it was found that there is no further increase in FFA conversion.
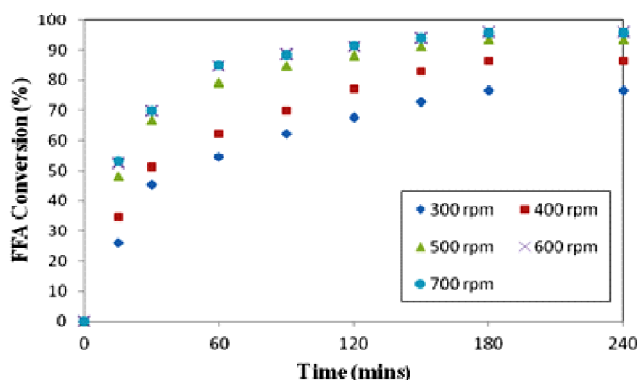
**Fig. 4.** FFA conversion at different agitator speed with 1:9 oil to methanol ratio, catalyst concentration 3.0 wt% and at temperature 338 K.

This indicates the absence of external mass transfer limitations above 600 rpm. Therefore, a speed of 600 rpm was therefore afterward used to examine the influence of other variables.

*Effect of catalyst concentration:*

In general, the conversion efficiency of the esterification reaction depends on how frequently the reactants and the catalyst contact. As the catalyst dosing is increased, the frequency of contact also increases which resulted higher rate of esterification reaction. Experiments were performed at different catalyst concentrations in the range of 1.0–4.0 (wt%) at a temperature of 338 K, oil to methanol molar ratio of 1:9 and at stirrer speed of 600 rpm. The change in FFA conversion was shown in Fig. 5. It was also found that at 4% catalyst loading, the conversion rate of FFA to methyl ester was almost similar to that obtained at 3% catalyst loading. Therefore the optimum value of catalyst loading was taken as 3.0%
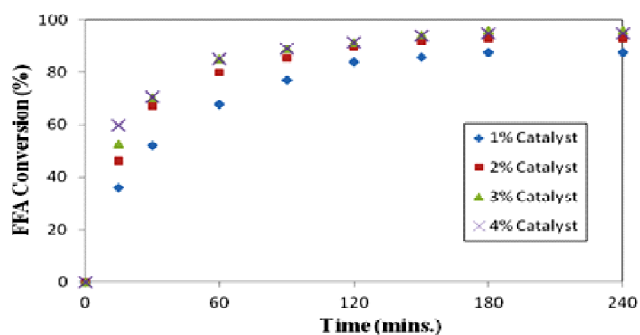


**Fig. 5.** FFA conversion with change in catalyst concentration at 600 rpm, 338 K and 1:9 oil/methanol molar ratio.

and further esterification reactions were carried out using the catalyst loading of 3.0%.

*Effect of oil to methanol molar ratio:*

To shift the equilibrium towards the formation of methyl ester (Biodiesel), methanol was taken in excess quantity over RBO. When the quantity of methanol is increased, the equilibrium value for the esterification shifts towards the formation of the products i.e. fatty acid methyl esters and water which means higher conversion of FFA to methyl esters[2]. Also, if the methanol to RBO molar ratio is increased, the viscosity of the solution mixture decreases. Consequently reactants mixes with catalyst in a better manner which increases the mass transfer rate. The FFA conversion at various time with change in RBO to methanol molar ratios is shown in Fig. 6. It can be observed that there was an increase in conversion as RBO to methanol ratio is increased from 1:3 to 1:9 and thereafter remained constant and then decreased owing to the excess amount of methanol available for reaction. Hence 1:9 was considered as optimum molar concentration for all other experiments.
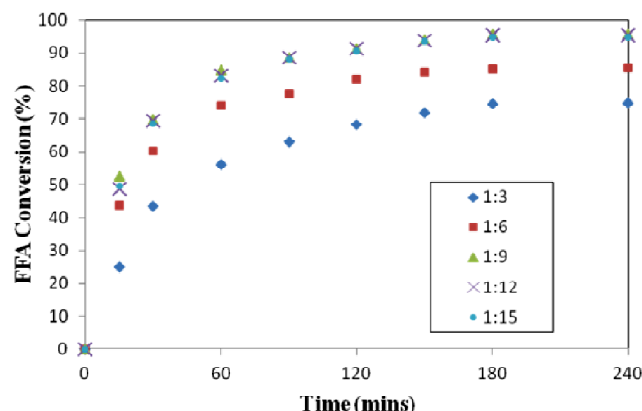


**Fig. 6.** FFA conversion with change in oil to methanol molar ratio at catalyst loading at 3.0 wt% at 600 rpm and 338 K.

*Effect of temperature:*

Influence of temperature was investigated by keeping oil to methanol ratio of 1:9 and catalyst concentration of 3.0 wt% as optimized. Since the esterification of FFA with methanol is exothermic; an increase in the temperature will definitely increases the rate of reaction. Also, at higher temperature, the viscosity of the solution is decreased and thereby increases the diffusion of material through the pores. The results for the influence of reaction temperature are shown

in Fig. 7. Reaction temperature evidently influences esterification and the highest FFA conversion was obtained at 338 K. A further higher temperature can increase the rate of reaction, but in that case, the reactions need to be performed using a pressure above atmospheric level. In the current study, the reaction temperature above boiling point of methanol (338 K) cannot be used as the methanol starts evaporating under atmospheric pressure conditions. Also, it has been found that there is no increase in FFA conversion after 180 min.
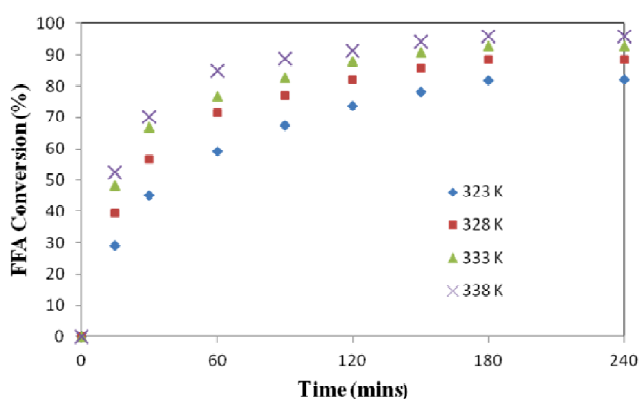


**Fig. 7.** FFA conversion with temperature at 1:9 oil/methanol molar ratio at catalyst loading at 3.0 wt% at 600 rpm.

## Conclusions

In this work, nano-sized Al-doped sulfated zirconia catalyst was examined for the esterification of RBO having 70% FFA. The effects of catalyst calcinations temperature, catalyst concentration, stirring speed and methanol to oil molar ratio on reduction in FFA of rice bran oil with methanol using nano-sized Al-doped sulfated zirconia as heterogeneous catalyst were studied. Highest FFA reduction of 95.26% was obtained with the optimum stirring speed 600 rpm, catalyst concentration 3.0 wt%, oil to methanol molar ratio 1:9 and at a reaction temperature of 338 K in 180 min.

## References

1. S. Zullaikah, C. C. Lai, S. R. Vali and Y. H. Ju, *Bioresour. Technol.,* 2005, **96**, 1889.

2. R. Arora, A. P. Toor and R. K. Wanchoo, *Chem. Biochem. Eng. Q*, 2015, **29(4)**, 617.

3. J. Ni and F. C. Meunier, *Appl. Catal. A: Gen.,* 2007, **33**, 122.

4. T. A. Peters, N. E. Benes, A. Holmen and J. T. F Keurentjes, *Appl. Catal. A: Gen.,* 2006, **297**, 182.

5. T. Sejidov, Y. Mansoori and N. Goodarzi, *J. Mole. Catal. A: Chem.*, 2005, **240**, 186.

6. P. Shah, A. V. Ramaswamy, K. Lazar and V. Ramaswamy, *Appl. Catal. A: Gen.*, 2004, **273**, 239.

7. G. Kuriakose and N. Nagaraju, *J. Mole. Catal. A: Chem.,* 2004, **223**, 155.

8. E. Lotero, Y. Liu, D. E. Lopez, K. Suwannakarn, D. A. Bruce and J. G. Goodwin, *Ind. Eng. Chem. Res.,* 2005, **44**, 5353.

9. F. Garin, L. Seyfried, P. Girard, G. Maire, A. Abdulsamad and J. A. Sommer, *J. Catal.,* 1995, **151**, 26.

10. N. Katada, T. Tsubaki and M. Niwa, *Appl. Catal. A: Gen.*, 2008, **340**, 76.

11. G. D. Yadav and J. Nair, *Microp. Mesop. Mat.*, 1999, **33**, 1.

12. Y. Sun, S. Ma, Y. Du, L Yuan, S. Wang and J. Yang, *J. Phy. Chem. B*, 2005, **109**, 2567.

13. R. Vahid, N. Saghatoleslami, H. Nayebzadeh and A. Maskookib, *Chem. Biochem. Eng. Q,* 2012, **26(2)**, 71.