Electronic Supplementary Material (ESI) for RSC Advances.

One pot transesterification and esterification of waste cooking oil *via* ethanolysis using Sr:Zr mixed oxide as solid catalyst

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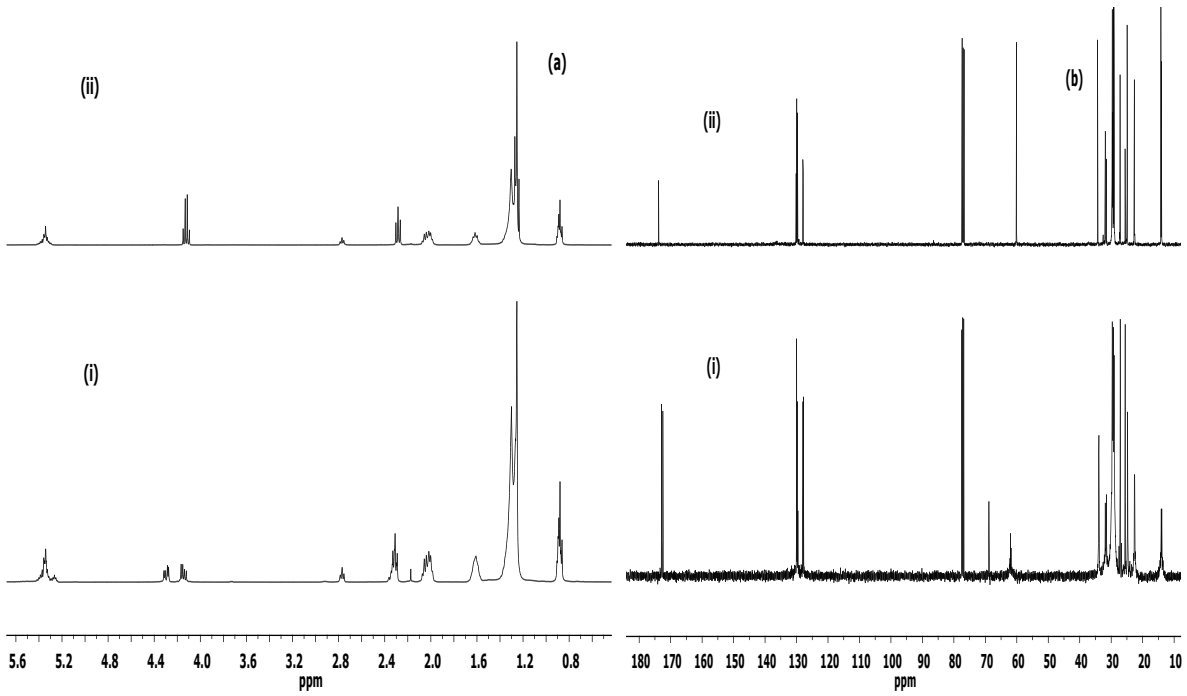

Fig. S1. Comparison of (a) ^{1}H-NMR and (b) ^{13}C-NMR spectra of (i) waste cottonseed oil with its (ii) ethyl esters.

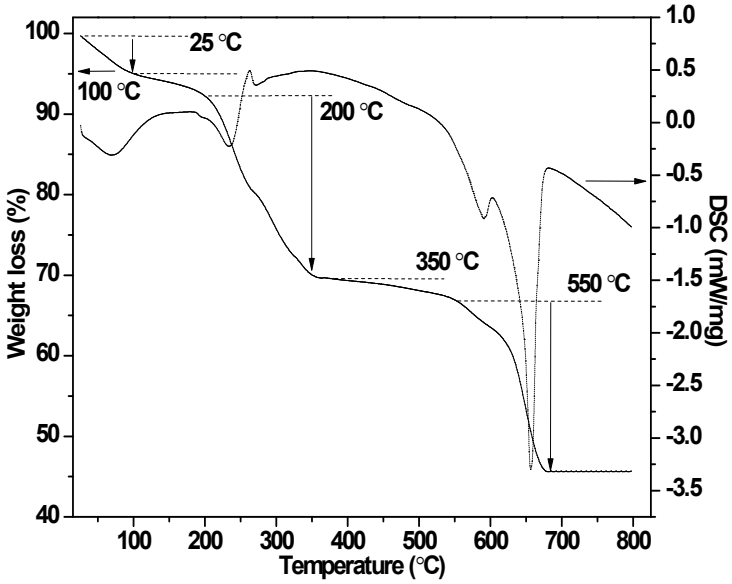

Fig. S2. Thermogravimetric analysis of 2Sr:Zr precursor.

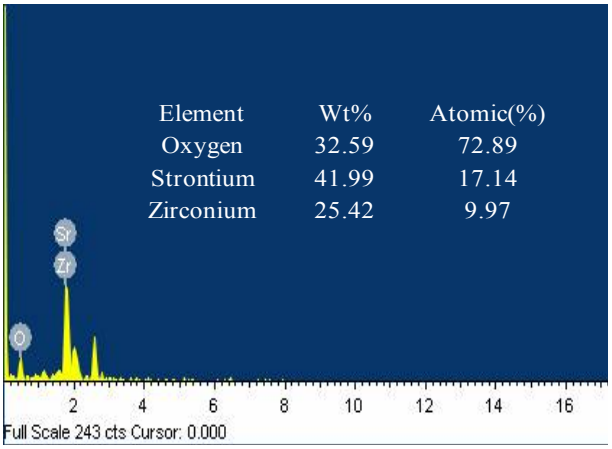

Fig. S3. EDX analysis of 2Sr:Zr-650.

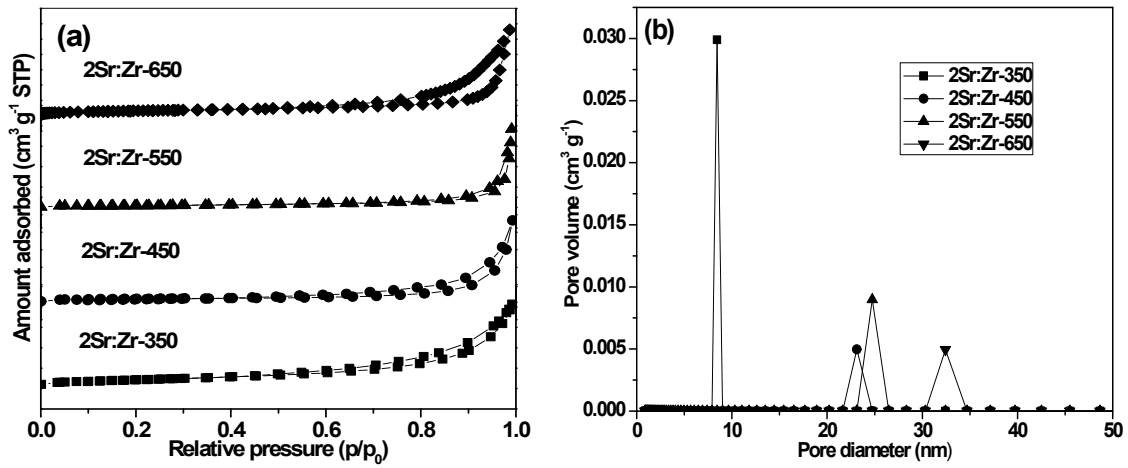

Fig. S4. (a) N_2 adsorption-desorption isotherms and (b) Pore size distribution curve for 2Sr:Zr catalyst at different calcination temperature.

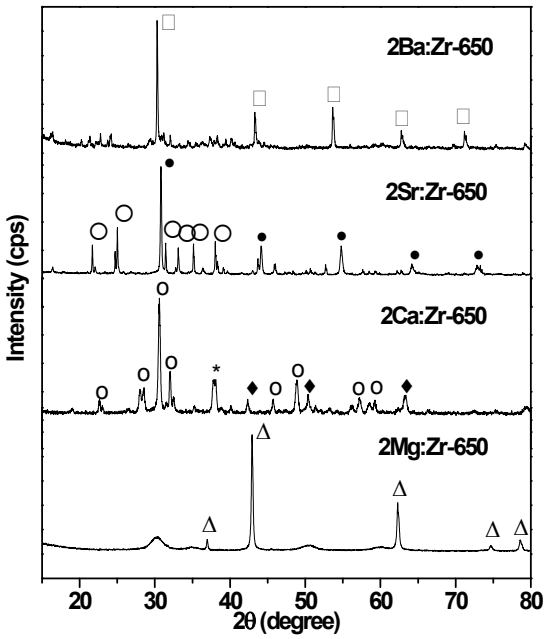

Fig. S5. XRD pattern of varying metal to zirconia atomic ratio (• = $SrZrO_3$, 🕘 = SrO, ♦= m-ZrO_2, o = $CaZrO_3$, * = CaO, Δ = MgO, □ = $BaZrO_3$).

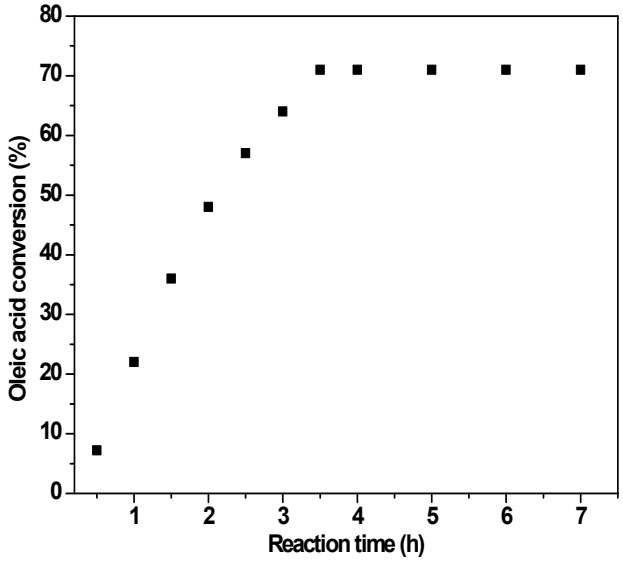

Fig. S6. Esterification of oleic acid with ethanol (**Reaction conditions:-** Ethanol to oleic acid ratio 12:1 in presence of 75 °C reaction temperature in presence of 5 wt% of catalyst with respect to oleic acid).

Optimization of reaction parameters

The effect of stirring speed on the reaction rate was examined to establish the stirring speed at which the mass transfer limitations are minimal during Sr:Zr catalyzed transesterification reaction. As could be seen from Fig. S7(a), initially the reaction rate increases with the increase in stirring speed and at ≥ 400 rpm the reaction rate become maximum and constant. Thus all experiments in present study were carried out at a stirring speed of 400 rpm to exclude the effect of mass transfer phenomenon on reaction rate.

In order to find the optimum catalyst concentration, a series of transesterification reactions of WO with ethanol were performed in presence of 1–6 wt% (with respect to oil) of 2Sr:Zr-650. The FAEE yield was found to increases as the catalyst concentration was increased from 1 to 5 wt% as shown in Fig. S7(b). A 5 wt% catalyst concentration required 7 h for the complete conversion of WO into FAEE (> 99% yield). A further increase in catalyst loading (≥ 5 wt%) was not found to enhance the reaction rate to significant extent. This may be due to the higher mass transfer resistance in liquid–liquid–solid system at higher catalyst loading.[1]

Stoichiometrically, the ethanolysis of oil requires three moles of ethanol for each mole of VO. Since the transesterification of triglycerides is reversible reaction, excess ethanol shifts the equilibrium towards the direction of ester formation. The use of excess alcohol not only promotes the transesterification rate but also removes product molecules from the catalyst surface and thus, regenerates the catalytic sites.[2] To determine the optimum ethanol/oil molar ratio for 2Sr:Zr-650, the reactions were performed by varying the ethanol/oil molar ratio from 3:1 to 15:1. The FAEE yield as well as reaction rate were found to increase on increasing the ethanol/oil molar ratios up to 12:1 and no significant gain in reaction rate was observed on increasing the molar ratio beyond 12, as shown in Fig. S7(c).

Literature reported heterogeneous catalysts for the ethanolysis reaction have been reported to work at high reaction temperature and high pressure, owing to the low reactivity of ethanol in comparison to methanol. Same reaction conditions demand the costlier and complicated reactor design which lead to increase the biodiesel production cost.[3] The optimum reaction temperature for 2Sr:Zr-650 catalyst was determined by performing the transesterification of WO in the temperature range of 35–85 ºC and at ≥ 75 ºC, maximum reaction rate was observed (Fig. S7(d)).

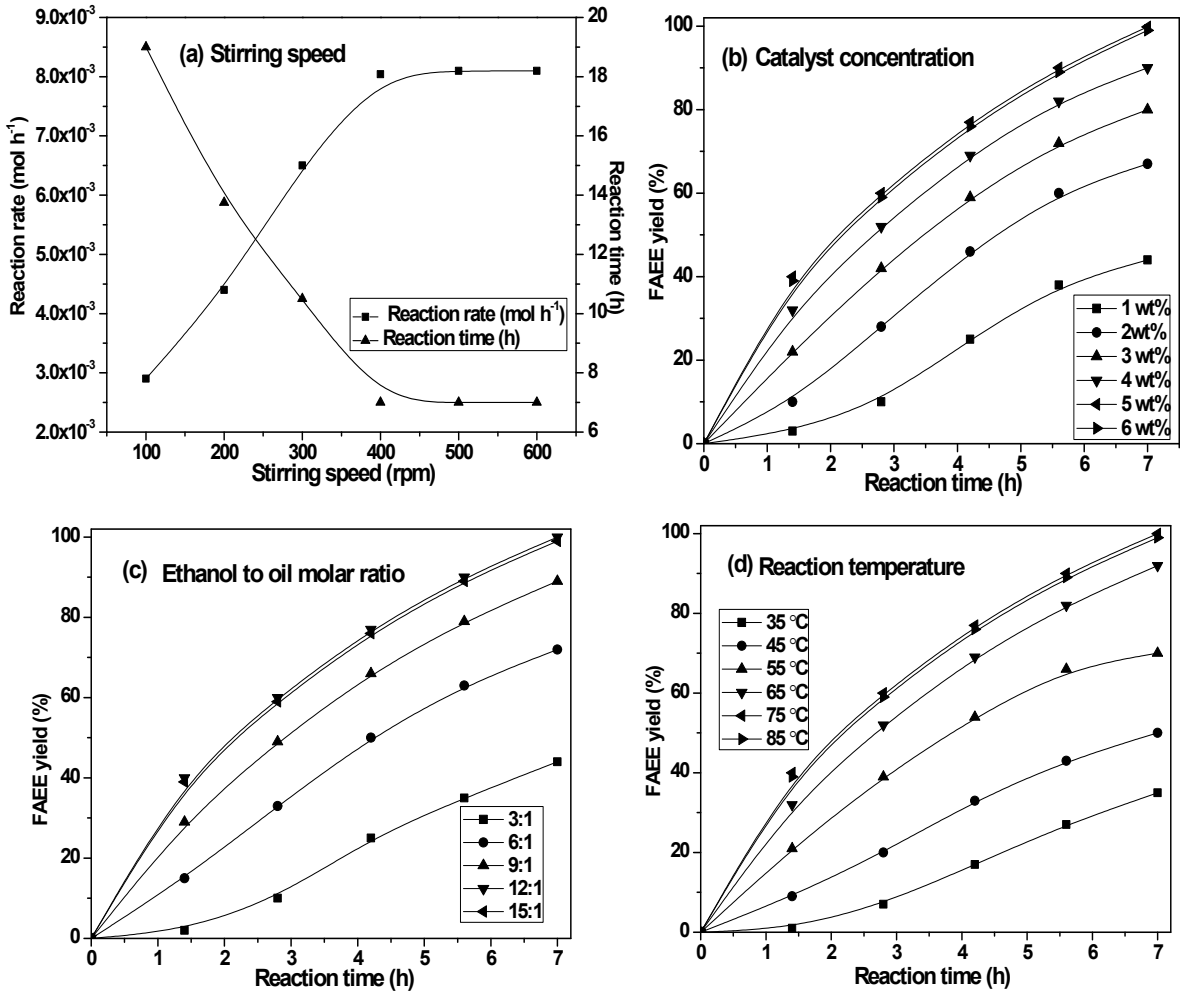

Fig. S7. Effect of reaction conditions on 2Sr:Zr-650 catalyzed transesterification of WO. **Reaction conditions:-** (a) ethanol to oil molar ratio of 12:1 at 75 ºC reaction temperature in presence of 5 wt% of catalyst with respect to oil. (b) ethanol to oil molar ratio of 12:1 at 75 ºC reaction temperature (c) Reaction temperature at 75 ºC, in presence of 5 wt% of catalyst with respect to oil (d) ethanol to oil molar ratio of 12:1 in presence of 5 wt% of catalyst with respect to oil.

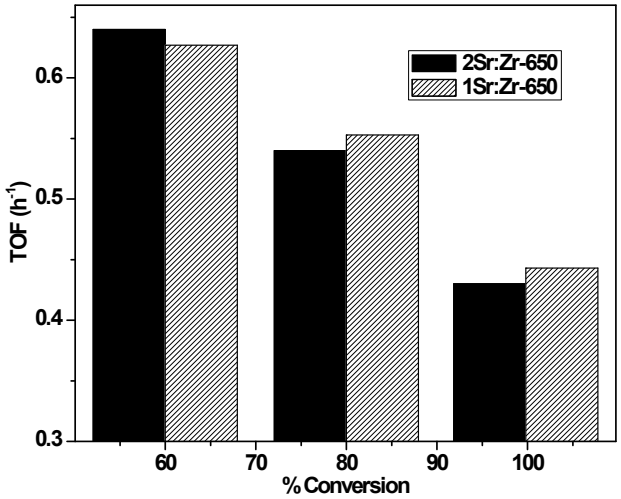

Fig. S8. A plot of TOF *vs* % conversion for the 1Sr:Zr-650 and 2Sr:Zr-650 catalyzed ethanolysis of WO. **Reaction conditions:** ethanol to oil molar ratio; 12:1 at 75 °C and catalyst concentration; either 5 wt% of 2Sr:Zr-650 or 6 wt% of 1Sr:Zr-650.

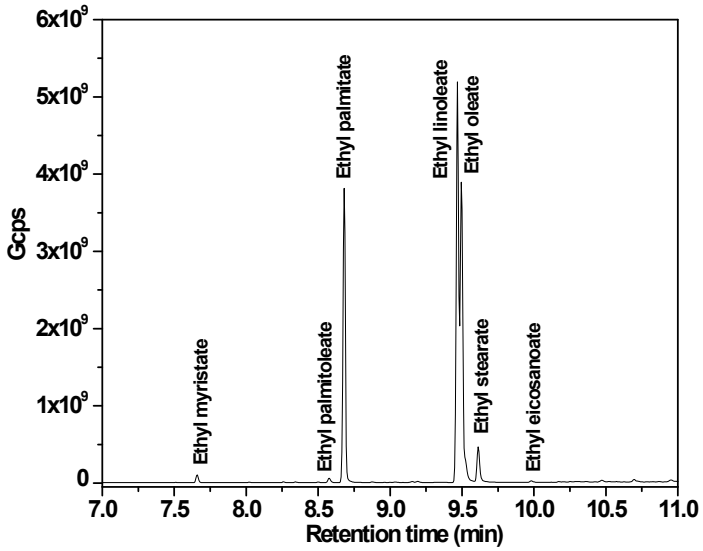

Fig. S9. Gas chromatogram of FAEE.

Table S1. The chemical analysis of the vegetable oils employed as feedstock in the present study.

Feedstock	Free fatty acid value (wt%)	Moisture content (wt%)	Saponification value (mg of KOH/g of sample)	Iodine value (mg of I_2/g of sample)
CO	0.3	0.24	181.4	88.2
WO	4.7	0.27	192.3	94.3
JO	8.8	0.36	186.2	98.2
KO	18.1	0.30	194.1	103.5

Table S2. Surface properties of the catalysts at different calcination temperature.

Catalyst	Surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
2Sr:Zr-350	15.10	9.02	0.0298
2Sr:Zr-450	0.66	23.14	0.0049
2Sr:Zr-550	0.87	24.74	0.0093
2Sr:Zr-650	0.55	32.58	0.0043

References

1. R. Song, D. Tong, J. Tang and C. Hu, *Energy Fuel*, 2011, **25**, 2679.
2. S. Yan, H. Lu and B. Liang, *Energy Fuel*, 2008, **22**, 646.
3. Q. Liu, B. Wang, C. Wang, Z. Tian, W. Qu, H. Ma and R. Xu, *Green Chem*., 2014, **16**, 2604.