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Heterogeneous Transesterification of *Garcenia gummi gutta* Oil Using t-ZrO_2: A Novel Feedstock for Biodiesel Synthesis and Fuel Property Evaluation

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Zirconium dioxide catalyst was prepared from $ZrOCl_2 \cdot 8H_2O$ by sol-gel method using ammonium hydroxide as hydrolyzing agent and calcined at 500 °C for 5 h. The catalyst basicity was analyzed by Hammet-indicator method and its thermal stability, crystalline phase, surface morphology, surface area, porosity characterizations were obtained respectively by TGA, XRD, SEM and BET techniques. The yield of 90.9 % was achieved under the optimal conditions; 20 wt % catalyst, time 10 h, methanol:oil molar ratio, 1:18 at temperature 70 °C at high stirring rate of 1400 (± 20) rpm. The application of commercial ZrO_2 was also tested under optimal conditions and got a yield of 19.4. The biodiesel properties of *Garcenia gummi gutta* (L. Robson) oil were evaluated as per the Bureau of Indian Standards and the oil was found to be a novel biodiesel feedstock.

Keywords: *Garcenia gummi gutta*, Diffusion, Zirconium oxide, Biofuels.

INTRODUCTION

Biodiesel is the best alternative fuel as it is renewable, biodegradable, non-toxic, ecofriendly, possess higher flash point, high cetane number, burns completely when blended with petrodiesel, better ignition quality on account of 10 % inbuilt oxygen, free of sulphur and aromatics [1-3] and offers better lubricity when blended with petrodiesel [4]. The high viscosity, higher cloud point and more emission of NO_x [1-4] are the worrying factors. Transesterification is a simple and economical method of overcoming the problems related to the vegetable oils. The prime focus of the present work is biodiesel synthesis from-*Garcenia gummi gutta* oil (GGO) a novel feedstock using synthesized zirconium oxide as heterogeneous base catalyst. Through structural modifications with respect to surface area, pore volume, basicity and phase, probably undoped zirconium oxide would become a better catalyst for transesterification process. The *Garcinia gummi gutta* (in kannada - *uppage*) of *Guttiferae* family, is a tropical tree, geographically confined to the rainforests of Western Ghats of southern India and globally they are more endemic to India and Srilanka. In Karnataka state, the density of *Garcenia gummi gutta* trees is more confined to Uttara Kannada district as it is covered by 79 % of the forest area. The tree grows up to a distance of 18 to 20 m, with a trunk diameter of 70 cm. The unripe green fruit weighs about 75 g and becomes deep yellow or brown colour on ripening and the flowering season starts in the month of February and the dry fruits are available till the end of June. The pulp, also known as *'kokum'*, is covered by a very hard and sticky rind, is rich in antioxidants hence offer better antiseptic properties and traditionally used in curing skin diseases. The fleshy fruits bear five to seven seeds and on an average the seeds are of length 23.31 mm, breadth 11.90 mm, thickness 23.31 mm and weighs about 1.15 g [5,6] and the dry seeds of *Garcenia gummi gutta* possess an oil content of 30-40 %.

EXPERIMENTAL

The solvents methanol (99 %), ammonium hydroxide (25 %, 0.91 sp.gr - S.D.Fine), absolute ethanol (99.9 % - S.D. Fine), petroleum-ether (60-80 °C - Finar Chemical Ltd.) and sulphuric acid (98 % - S.D. Fine) were purchased from a local chemical vendor, Bengaluru. Potassium hydroxide, zirconium oxy chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) and ZrO_2 (99 %) of AR grade were purchased from S.D. Fine chemicals limited.

Oil extraction: The *Garcenia gummi gutta* (L. Robson) fruits were sun dried, removed the outer hard rind to get the brown coloured seed kernel, water washed 3-4 times to remove adhered sand particles and oven dried at 110 °C for 60 min.

The dried seeds showed in Fig. 1, were crushed mechanically to 1/4th size for better surface area and extraction. The oil was extracted through soxhlet apparatus using *n*-hexane as solvent for 6 h [7]. The separated oil from solvent using rotary evaporator (Buchi make) was heated at 110 °C for 30 min to eliminate water content and stored in an air tight bottle.

Fig. 1. Dried seeds of *Garcenia gummi gutta*

Characterization of oil: The fatty acid composition of *Garcenia gummi gutta* (L. Robson) oil (GGO) was evaluated by GC technique (DB-Wax - 0.25 × 30 m) using helium as carrier gas and FID detector. The acid value was estimated by titration method with KOH in ethanol, using phenolphthalein indicator and was calculated using eqn. 1. The evaluation of density, kinematic viscosity and high heating values were based on procedures approved by Bureau of Indian Standards. Further the iodine number, saponification value were obtained by simple titration methods reported [8].

$$\text{Acid value} = \frac{N_{KOH} \times V_{KOH} \times 56.11}{\text{Weight of oil (g)}} \quad (1)$$

Synthesis of catalyst: The zirconium oxychloride precursor was subjected to sol-gel method in which, the precursor solution was slowly added to an excess amount of aqueous 5 M ammonium hydroxide solution, which resulted in a gelatinous precipitate of zirconium hydroxide. During the entire precipitation, basic medium was maintained and an initial pH of 11.5 (± 0.05) decreased to 10 as monitored using calibrated pH meter fixed with combined glass electrode. The gelatinous precipitate of zirconium hydroxide formed, was left digested for 48 h in basic medium [9] at 80 °C, filtered and tested for any chloride content by silver nitrate test. At 110 °C the precipitate was dried for 12 h and calcined at 500 °C for 5 h in a muffle furnace at an increment of 5 °C/min.

Characterization of catalyst: Qualitatively basicity of the catalyst was estimated using acidic Hammet indicators [10] and quantitative basicity was obtained by benzoic acid titration method [11]. The surface area was obtained by BET (Brunauer Emmett & Teller) method (NOVA-1000 version-3.70 using N_2 gas). For the crystalline phase, X-ray powder diffraction measurements were taken (Cu-K_α radiation, 1.5406 Å, Bruker-D8 advance instrument, IISc, Bengaluru - 2θ from 20° to 70°). The surface morphology was obtained with the help of SEM (SEM, IISc, Bengaluru, India). The thermo gravimetric analysis was performed using TGA (Mettler-Toledo, Department of High energy physics, IISc, Bengaluru, India) in Nitrogen atmosphere with a rise of 10 °C/min.

Transesterification process: Since the free fatty acid content of *Garcenia gummi gutta* was found to be 2.64 %, a two step transesterification procedure was followed to reduce free fatty acid content < 1 %, added pre-calculated mixture of H_2SO_4 and methanol [12] and the decrease in free fatty acid value was ascertained by repeating the titration procedure and also from the eqn. 2. Transesterification process was performed in a two necked 100 mL R.B. flask, fitted with a PID controller (Selec-TC544, with pt100 thermocouple) to monitor temperature. To a known amount of oil, added pre calculated amounts of methanol and the synthesized zirconium oxide catalyst at a fixed high stirring rate of 1400 (± 20) rpm for better interaction between reaction components. The experimental conditions maintained were; methanol:oil molar ratio- 1:6 to 1:24, time-2 to 20 h catalyst wt %-5 to 30wt % and reaction temperature 50 to 80 °C. Also under the optimal conditions, the transesterification of *Garcenia gummi gutta* was conducted using commercial ZrO_2 to the efficiencies of both commercial and synthesized ZrO_2. After transesterification process, the biodiesel was isolated using methanol and petroleum ether combination, taken the weights of unreacted oil, biodiesel and glycerol and finally calculated the biodiesel % yield [13].

$$\text{Free fatty acid conversion} = \frac{FFA_{initial} - FFA_{final}}{FFA_{initial}} \times 100 \quad (2)$$

Characterization of biodiesel: The biodiesel properties of *Garcenia gummi gutta* methyl ester were evaluated as per Bureau of Indian standards and for comparison heating value was also calculated theoretically from the viscosity data using eqn. 3 [14].

$$HHV = 0{:}4625VS + 39.450 \quad (3)$$

Cetane number was empirically calculated from estimated saponification value (SV) and iodine value (IV), using the eqn. 4 [15].

$$CN = 46.\ 3 + 5458/SV - 0.225 \times IV \quad (4)$$

RESULTS AND DISCUSSION

Properties of oil: The chemical composition of *Garcenia gummi gutta* is given in Table-1, shows the rich stearic acid (18:0) and oleic acid (18:1contents. The high percentage of oleic acid (18:1-56.89 %) provides a high oxidation stability and thus facilitates ease of processing [16]. The density of *Garcenia gummi gutta* oil is higher than that of mineral diesel and kinematic viscosity was 42.13cSt at 40 °C. Acid value was found to be 5.28 mg KOH/g with an free fatty acid value of 2.64 % and all the properties of *Garcenia gummi gutta* oil are mentioned in Table-2.

Catalyst properties

Basicity: The zirconia catalyst was tested for its basicity using acidic Hammet-indicators; phenolphthalein (pK_{BH^+}: 8.2-9.6), nile blue (pK_{BH^+}: 10.1-11.1) and tropaeolin (pK_{BH^+}: 11.1-

TABLE-1
FATTY ACID COMPOSITION OF *Garcenia gummi gutta* OIL

Fatty acid	*Garcenia gummi gutta* oil	m.f.	m.w.
Palmitic acid (C16:0)	3.94	$C_{16}H_{32}O_2$	256.42
Stearic acid (C18:0)	34.81	$C_{18}H_{36}O_2$	284.48
Lignoceric acid (C24:0)	1.73	$C_{24}H_{48}O_2$	368.63
Oleic acid (C18:1)	56.89	$C_{18}H_{34}O_2$	282.46
Linoleic acid (C18:2)	1.56	$C_{18}H_{32}O_2$	280.45
Saturation	40.48		
Monounsaturation	56.89		
Polyunsaturation	1.56		

TABLE-2
PHYSICAL PROPERTIES OF *Garcenia gummi gutta* OIL

Property	Test result
Molecular weight (g/mol)	887.47[a]
Density (Kg/m^3) at 40 °C	883
Kinematic viscosity @ 40 °C cSt	42.13
Acid value (mg KOH/g)	5.28
Free fatty acid (%)	2.64
IV (g/100 g of oil)	52.07 (54)[*]
Saponification value	194.11 (195)[*]
Higher heating value (MJ/Kg)	39.78
Colour of the oil	Brown
Oil content (wt %)	30-40
Titre (°C)[b]	37-41

[*]Values in the parenthesis are calculated.
[a]Based on the fatty acids % content of oil.
[b]The temperature at which fat becomes oil.

12.7) indicators. From Hammet indicator test the basicity of the catalyst was designated as 9.6 < H < 11.1, as the catalyst showed colour change with nile blue and failed further with tropaeolin confirming considerably good basicity of the synthesized zirconia catalyst.

BET analysis: The specific surface area and porosity data were obtained by BET analysis and are mentioned in Table-3. A better surface area of 40.6 m^2/g and the average pore diameter of 111.415 Å of the catalyst were the consequences of longer digestion time at higher temperature of gelatinous zirconium hydroxide precipitate [9]. The mesoporous distribution is attributed to the polymerization of hydrous zirconia which forms a highly porous three-dimensional structure; $[ZrO_x(OH)_{4-2x,y}H_2O]_n$ [17] and the porosity distribution is shown in Fig. 2.

TABLE-3
BASICITY AND SURFACE AREA DATA OF SYNTHESIZED ZrO_2

Method	Catalyst - $5ZrO_2$500	
Basicity	Hammet - indicator basicity	9.6 < H < 11.1
	Basicity (benzoic acid titration) mmol/g	0.201
BET	Specific surface area (m^2/g)	40.6
	Total Pore volume (cc/g)	0.1034
	Average pore diameter (Å)	111.415

The nitrogen adsorption - desorption isotherm is drawn in the Fig. 3, in which the strong uptake of nitrogen was on account of capillary condensation at higher relative pressure (P/P_o) greater than 0.45, continued further and no plateau was observed indicating the high mesoporous distribution in the catalyst.

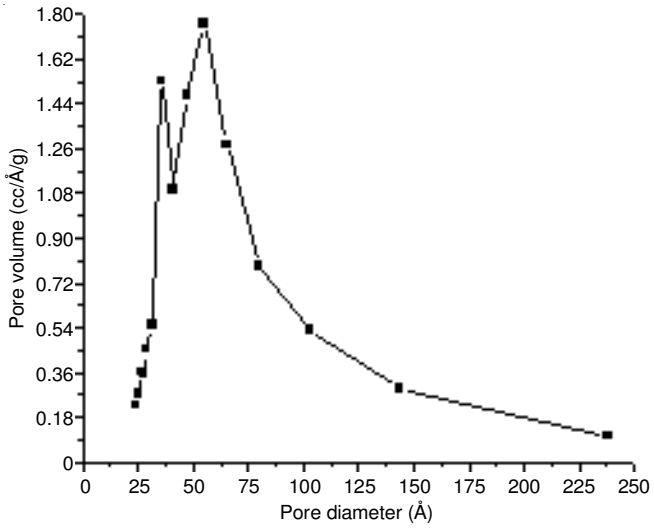

Fig. 2. Pore size distribution

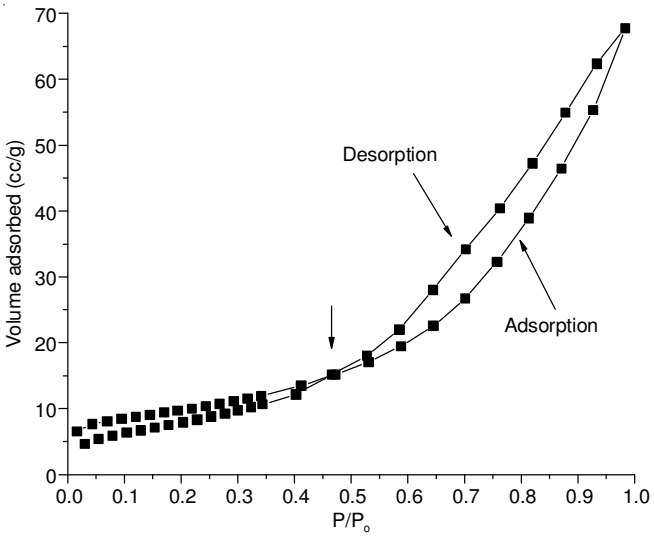

Fig. 3. Nitrogen adsorption–desorption isotherm

SEM analysis: The SEM images were taken for surface morphology of the zirconia catalyst and the images are shown in Fig. 4. From the SEM images shows that the catalyst is porous and the size of the particles ranges from 2 to 10 μm, which supports the porosity distribution in the catalyst.

X-ray diffraction: The XRD profile is shown in the Fig. 5 and the most intense peak (101) is at 2θ = 30.2°, with lattice parameters; a = b = 3.592 Å and c = 5.183 Å which represents the characteristic peak of the tetragonal phase (JCPDS# 800965). The other peaks observed are at 2θ; 30.3° (110), 50.2° (112) and 60.2° (211).

TGA analysis: The TGA analysis confirms good thermal stability of the catalyst and the Fig. 6 explains the thermal behaviour of the zirconia catalyst. A weight loss of 8.5 % between 80-100 °C and the second weight loss of 3.8 % was noticed between 515 to 650 °C, with a total weight loss of 12.3 %.

Effect of parameters on biodiesel yield

Effect of catalyst wt %: The increase of fatty acid methyl ester (FAME) yield was observed with the amount of catalyst and the highest FAME yield obtained was 90.9 % at 20 wt %

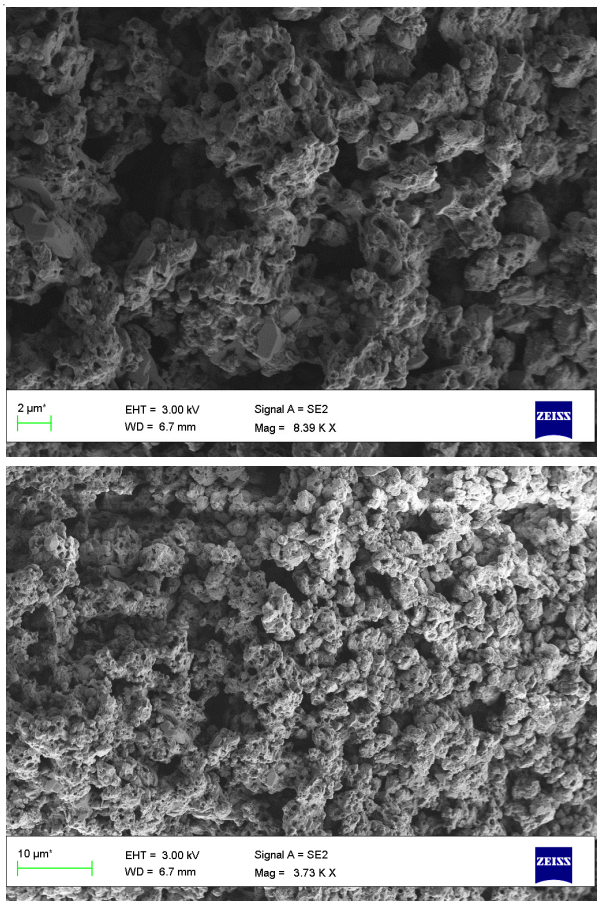

Fig. 4. SEM image

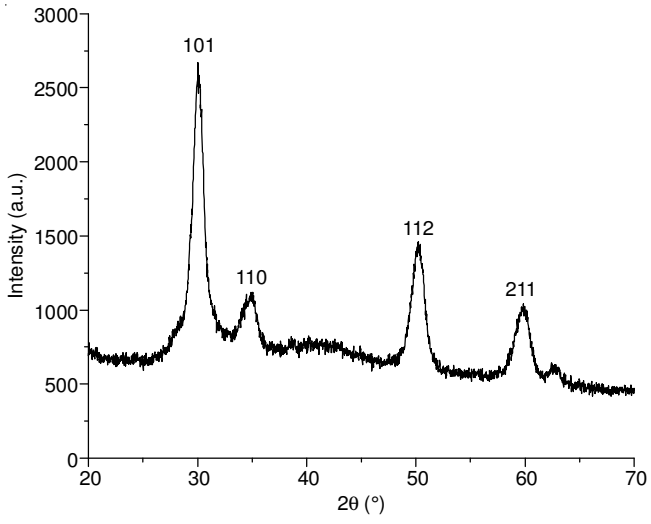

Fig. 5. XRD of ZrO_2

of catalyst when other parameters were constant. This was due to the availability of more number of basic sites with the increase in the catalyst amount. The presence of more non-bridging hydroxyl groups on t-zirconia phase, formed upon dissociative adsorption of water, could be potential basic sites (Bronsted acid sites) which led to an enhanced transesterification reaction by dissociating methanol into RO^- and H^+ [19]. The decrease in biodiesel yield thereafter shown in Fig. 7 is attributed to diffusion limitations on account of blockage of pores and also high viscosity factor that could have raised [20].

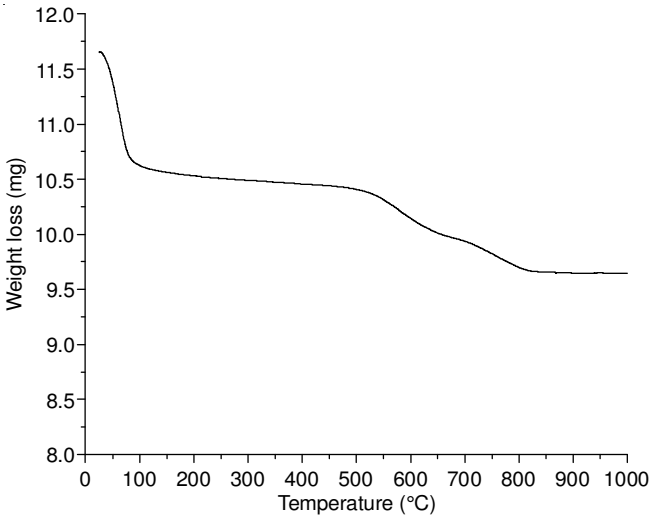

Fig. 6. Thermogram of ZrO_2

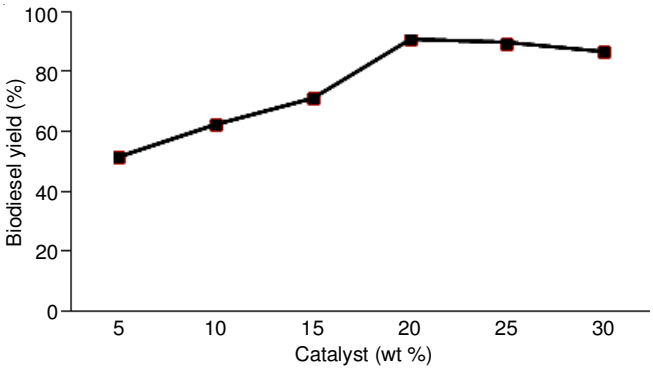

Fig. 7. Effect of ZrO_2 catalyst wt %

Effect of time: The solid catalysts require much longer time for the reaction compared to homogeneous catalysts due to heterogeneity with the increase in time, the % biodiesel yield was increased and at 10 h duration maximum yield was obtained, after which no much influence was observed indicating a nearly equilibrium conversion reaction. The effect of the time on biodiesel % yield is shown in Fig. 8.

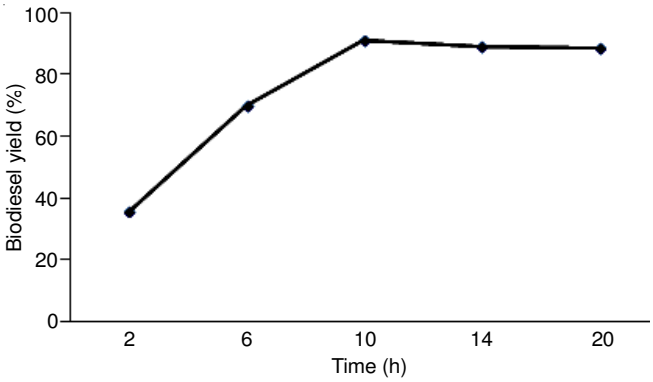

Fig. 8. Effect of reaction time

Effect of methanol:oil molar ratio: Molar ratio is a critical parameter for better biodiesel yield in transesterification process and an excess methanol is always significant to achieve better methyl ester yield. An optimal molar ratio of 1:18 showed a maximum yield of biodiesel of *Garcenia gummi gutta* and

further methanol content would dissolve the byproducts, glycerol making separation process difficult leading to decrease in the biodiesel yield as shown in Fig. 9.

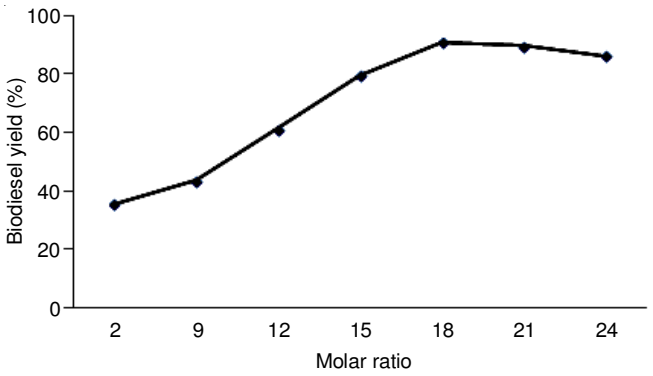

Fig. 9. Effect of methanol:oil molar ratio

Effect of temperature: Higher the temperature, higher would be the rate of reaction and 70 °C was the optimum temperature value which produced maximum yield. Further temperature rise decreased biodiesel yield due to the severe bubble formation and high volatility of methanol causing the quick equilibrium attainment also could be one of the reasons at higher temperature value. A high stirring rate of 1400 (± 20) along with temperature was an additional factor for better results. The variation in the biodiesel yield of *Garcenia gummi gutta* with temperature is mentioned in the Fig. 10.

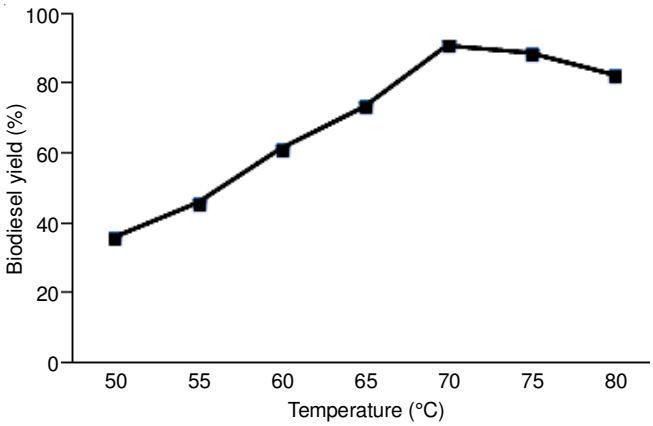

Fig. 10. Effect of reaction temperature

Reusability of catalyst: The catalyst reusability was performed by feeding fresh *Garcenia gummi gutta* (L. Robson) seed oil under the optimal experimental conditions using zirconium oxide with and without pretreatment and no conversion was observed with untreated ZrO_2. A yield of 29.8 % was obtained using ZrO_2, which was washed with methanol and calcined at 500 °C for 3 h. This poor yield indicated the complexity of the catalyst deactivation. On the other hand, the commercial ZrO_2 catalyst under the optimal conditions resulted in 19.4 % biodiesel yield.

Properties of biodiesel: The viscosity value of *Garcenia gummi gutta* biodiesel was found to be 4.61cSt, greater than that of petrodiesel which could mainly because of slight increase in the polarity of biodiesel due to the electronegative oxygen atom [16]. But the value lies in the biodiesel range defined by D6751, hence would be a better alternate fuel with good combustion properties. Density of the biodiesel is 876 kg/m^3 well within in the specifications. An increase in the HHV from 39.78 to 41.25 MJ/Kg was observed after transesterification. This could be due to the higher oxygen content which in turn induces higher energy and efficiency of biodiesel produced. The lower sulphur content keeps environment safe and increases engine life [21] and the sulphur content of *Garcenia gummi gutta* biodiesel is 0.007 % mass. The interdependency of iodine value and cetane number is significant, accounts to the polyunsaturation content.

Conclusion

The fatty acid composition is very conducive for biodiesel synthesis and high oleic acid (18:1) content offers high oxidation stability, facilitating the use of *Garcenia gummi gutta* biodiesel at high temperatures. The properties of the *Garcenia gummi gutta* biodiesel are within the standard specifications and hence *Garcenia gummi gutta* (L. Robson) is a novel biodiesel feedstock. The lab synthesized zirconia catalyst with modified properties was tested and achieved better results compare to commercial ZrO_2. The digestion of the zirconium hydroxide gel for 48 h time length definitely influenced the formation of tetragonal phase of the catalyst. The addition of precursor solution to 5 M NH_4OH, led to the formation of good basic zirconium oxide catalyst. The combination of, crystal phase, basicity, surface area and porosity were crucial during transesterification.

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TABLE-4
PROPERTIES OF *Garcenia gummi gutta* BIODIESEL AND COMPARISON WITH STANDARDS [Ref. 18]

Property	Test value	Bureau of Indian Standards	ASTM – Standards		
			Diesel - D975	Biodiesel - D6751	
Viscosity (cSt)	4.61	IS-1448-1976 - P-25 (Ref. 2002)	1.9 - 4.1	1.9 - 6.0	D-445
Density (Kg/m^3)	876	IS-1448 1992 - P-32 (Ref. 2003)	850	880	–
HHV (MJ/Kg)	41.25 (41.58)*	IS-1448-1984 P-6	–	–	–
Acid value (mg KOH/g)	0.15	–	–	0.5-0.8	D-664
Sulphur content (mass %)	0.007	IS-1448 - 1991 P-33 (Ref. 2003)	–	0.05	D-5453
Cetane Number	62**	–	40-55	Min. 47	D-613

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