

Transesterification of Jatropha Oil over Ceria-Impregnated ZSM-5 for the Production of Bio-Diesel

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In this study transesterification of Triglycerides (TG) from *Jatropha curcas* oil (JCO) with methanol for production of biodiesel was investigated over cerium impregnated ZSM-5 catalysts. NaZSM-5 was synthesized in an alkaline medium and impregnated with cerium oxide by wet method using cerium nitrate as a source for cerium. They were characterized by X-ray diffraction (XRD), Thermogravimetric analysis (TGA), CO₂-temperature programmed desorption, and N₂ adsorption/desorption analysis. XRD analysis showed decrease in intensity of the patterns with the increase in the ceria loading but crystallization of ceria to larger size is an evident for 10 and 15% loading. The optimal yield of transesterification process was found to be 90% under the following conditions: oil to methanol molar ratio: 1:12; temperature: 60 °C; time: 1 h; catalyst: 5 wt %. Here the yield of fatty acid methyl ester (FAME) was calculated through ¹H NMR analysis. The investigation on catalyst loading, temperature, time and reusability illustrated that these ceria impregnated NaZSM-5's were found to be selective, recyclable and could yield biodiesel at low temperature with low methanol to oil ratio due to the presence of both Lewis and Bronsted basicity. Hence, from the above study it is concluded that ceria impregnated ZSM-5 could be recognized as a potential catalysts for biodiesel production in industrial processes.

Key Words : Biodiesel, Transesterification, *Jatropha curcas* oil, NaZSM-5, Cerium oxide

Introduction

Zero net carbon dioxide emission is the recent task of every researcher all over the world. Hence the quest for renewable fuels and chemical feed stocks to maintain sustainable development resulted in conversion of oils and fats to biodiesel by transesterification with alcohols. Biodiesel synthesis through transesterification of triglycerides (oil sources) using alcohol is believed to be typically progressed under an acid, base or enzyme catalyst.¹ The resulting alkyl esters (*i.e.*, fatty acid alkyl esters) with various alkyl groups are utilized as biodiesel in the industry. Reports on the solid acid catalyst such as mesoporous Ta₂O₅/SiO₂-[H₃PW₁₂O₄₀/R] hybrid catalysts, sulfated zirconia, sulfated carbon-base catalysts and ZnO-La₂O₃ catalysts²⁻⁵ illustrated that high reaction temperature, high alcohol to oil ratios and longer reaction time for complete conversion to biodiesel. Whereas, the solid base catalysts in homogeneous state is fast and needs less methanol (5-15:1 methanol/oil ratio) and a lower reaction temperature (60-75 °C, around the reflux temperature of methanol). Near complete conversion (90%) is usually achieved within 2-6 h depending on the catalyst. Despite the extraordinary efficiency, generally, homogeneous catalysts suffers corrosion and separation problem and could be reused. Hence the heterogeneous catalysts are recommended in many processes.

Various heterogeneous catalysts have been proposed for transesterification of oil.⁶⁻¹² It has been reported that dehyd-

rated Al-Mg mixed oxides, which exhibit Bronsted basic sites show excellent selectivity to monoglycerides in transesterification of fatty acid methyl esters (FAME).¹³ While, there is also report on Lewis base catalyst Al-Li mixed oxide for transesterification. Hence presence of both the Bronsted and Lewis basicity is required for transesterification and is not easy to evaluate their relative importance in the reaction.

Since, zeolites are recognized to have versatile catalyst property based on its controlled the basicity and ability to undergo ion exchange with alkali metal ions and confinement of metal ions or metal oxides inside the micropores of zeolite,¹⁴⁻¹⁹ it is planned to impregnate Lewis base transition metal oxide CeO₂ over ZSM-5 and to investigate for activity of transesterification. When compared to the basicity of alkali and alkaline metal oxides, transition metal and rare earth metal oxides basicity are advantageous for transesterification.²⁰

Until now only few report are available on cerium oxide impregnated NaZSM-5 and it is very hard to find report on transesterification with cerium oxide impregnated ZSM-5. As mentioned by Helwani *et al.*,²¹ to avoid dramatic increase in the price of some food items due to food biodiesel demand competition, the *jatropha curcas* oil has been chosen as a raw material, as it comprises a non-edible oil, coming from a perennial plant, with high oil content in the seed,^{22,23} for transesterification to biodiesel. It is also reported that *jatropha* has an added advantage over other non-edible oil sources due to its drought-resistant plant capable of surviv-

ing in tropical and unsown agricultural land.²⁴ Further, oil content of jatropha seeds varies from 28% to 40%. The oil contains 21% saturated fatty acids and 79% unsaturated fatty acids and these jatropha oil could be most appropriate feedstock for producing biodiesel substituting petroleum diesel.^{25,26} Therefore, the potential of using *Jatropha* as a feedstock for biodiesel production has attracted much attention. Hence in this study transesterification of Triglycerides (TG) from *Jatropha curcas* oil was carried out over cerium oxide impregnated on ZSM-5.

Materials and Methods

Materials. Tetrapropyl ammonium bromide, TPABr (98%), Tetraethyl orthosilicate, TEOS (98%), aluminum sulphate $\text{Al}_2\text{SO}_4 \cdot 18\text{H}_2\text{O}$ (98%), sulfuric acid (98%), sodium hydroxide (98%), and cerium nitrate (98%) were obtained from Fisher Scientific and used without further purification for synthesis. *Jatropha curcas* seeds are used for extraction of oil for further transesterification

Synthesis of NaZSM-5 and Ceria Impregnated ZSM-5. Typically, Na form of ZSM-5 was synthesized by dissolving 19.19 g TEOS in 65 g of deionized water and adjusted to pH 1 with few drops of sulfuric acid and the mixture was vigorously stirred for 20 h at 30 °C. Then 2.39 g TPABr and 1.35 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were added to the above mixture and continued stirring for another 30 mins, the hydrogel was obtained at pH of 10 by adding 1.62 g NaOH. The final gel composition was $8.8\text{Na}_2\text{O}:40\text{SiO}_2:1\text{Al}_2\text{O}_3:3.9\text{TPABr}:1600\text{H}_2\text{O}$. The crystallization was carried out at 180 °C for 3 days in the static oven. The crystallized product was recovered by filtration, washed repeatedly with water, dried at 100 °C and calcined at 500 °C in air. The obtained material is designated as NaZSM-5. The ceria impregnated ZSM-5's with varying ceria loading were prepared by wet impregnation of 5g of NaZSM-5 with ethanol solution of cerium nitrate (5, 10 and 20 wt %). The mixture was stirred and vacuum dried to remove ethanol. The obtained material is finally calcined in air at 550 °C for 10 h. Thereafter product is designated as X%Ce-ZSM-5 (Where X=5, 10 and 20).

Catalyst Characterization. Powder X-ray diffraction pattern (XRD) were recorded using a Rigaku Miniflex diffractometer with Cu-K α radiation ($\lambda = 1.54$ nm). The diffraction data was recorded in the 2θ range 5–40° at 0.02° step size and a 1s step time. The nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 100 °C under vacuum ($p < 10^{-5}$ mbar) in the degas port. The surface area was determined from the linear part of the Brunauer, Emmett and Teller (BET) equation. The pore volume was calculated using the BET plot from the amount of nitrogen gas adsorbed at the last adsorption point ($p/p_0 = 0.95$). TGA analyses were carried out in N_2 atmosphere at a flow rate of 20 mL/min on SCINCO thermal gravimeter N-1000 Thermo gravimetric analyzer, by heating 10 mg of the sample from 25 to 700 °C in steps of 10 °C/min. The CO_2 -

TPD study was performed on a BELCAT-M catalyst analyzer. The sample cell was loaded with ca. 200 mg of the synthesized material and then heated in flowing helium at 500 °C for 2 h. After it was cooled to 25 °C, CO_2 (diluted in He gas) at a flow rate of 30 mL/min was introduced to the sample cell for CO_2 adsorption for 60 min. Afterwards the TPD experiment was carried out by purging helium with a rate of 80 mL/min from 25 to 500 °C with a temperature ramp of 10, 15 and 25 °C min⁻¹.

Transesterification of Jatropha Oil for Production of Biodiesel. Transesterification of jatropha oil with methanol was carried out in liquid phase. Jatropha oil (1 mole), methanol (3–15 mole), 5 wt % of Ce-ZSM-5 catalyst, were taken in a 25 mL round-bottomed flask fitted with a reflux condenser. The flask with its content was heated at a constant temperature (75, 100 and 120 °C) in an oil bath with simultaneous stirring magnetically. In order to monitor the progress of the reaction, aliquots of the hot mixture was withdrawn at the end of every one hour and the samples were centrifuged and analysed on Mayura gas chromatograph equipped with Varian CP Sil 5 CB (column length 30 m; diameter 0.25 mm) and FID detector. Nitrogen was used as the carrier gas at a flow rate of 30 ml per minute. After completion of each reaction, the catalyst was regenerated for reuse by washing several times with methanol and subsequent drying at 200 °C in air. The characterization of biodiesel was carried out by ¹H NMR technique on Bruker AV-III FT-NMR instrument using CDCl_3 as solvent at 500 MHz. The conversion of TG to methyl ester for few samples was also calculated from ¹H NMR data that depends on A_{ME} and $A_{\alpha\text{-CH}_2}$.²⁷ The TG conversion was calculated using following Eq.

$$\text{Conversion\%} = \frac{100 \times 2A_{\text{ME}}}{3A_{\alpha\text{-CH}_2}}$$

Where, A_{ME} is integration value of the protons of the methyl esters, and $A_{\alpha\text{-CH}_2}$ is the integration value of the methylene protons.

Results and Discussion

Catalyst Characterization. The powder diffraction patterns of the NaZSM-5 and the ceria impregnated samples are presented in Figure 1. The XRD pattern of ZSM-5 clearly indicates that the synthesized samples are crystalline and the characteristic peak resembles as that of previous works.²⁸ The intensity of the patterns decreased with the increase in the ceria loading which evidenced pore filling of ZSM-5 with ceria, but crystallization of ceria to larger size is evident for 10 and 15% loading. Ceria impregnated ZSM-5 catalysts exhibits peaks at $2\theta = 28^\circ$ which corresponds to (111) lattice plane of fcc CeO_2 and also confirmed from the JCPDS files for ceria (JCPDS 34-394).²⁹

N_2 adsorption and desorption isotherms exhibits type 1 curve (figure not shown) confirming the characteristic microporosity nature of the ZSM-5. The surface area and the pore volume are tabulated in Table 1. The results illustrate decrease

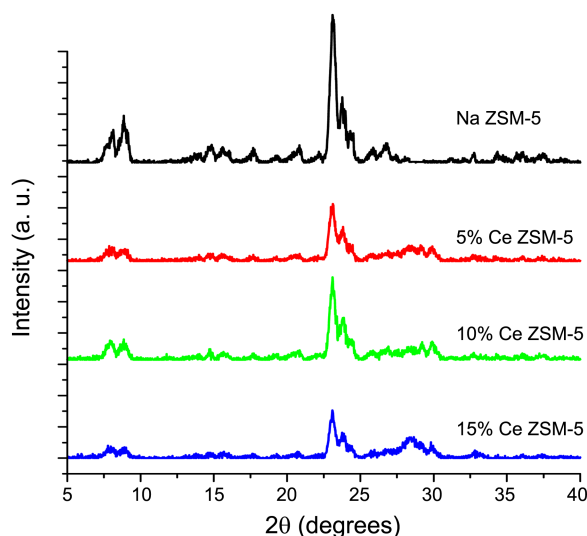


Figure 1. XRD patterns of NaZSM-5 and Ce-impregnated ZSM-5.

Table 1. Surface area and pore volume of NaZSM-5 and Ce-impregnated ZSM-5

Catalysts	Surface area by BET (m ² /g)	Pore volume (cm ³ /g)
Na-ZSM-5	430	0.28
5% Ce-ZSM-5	377	0.26
10% Ce-ZSM-5	344	0.21
15% Ce-ZSM-5	342	0.21

in the surface area and pore volume with increase upon ceria loading. The decrease might be attributed to filling of ZSM-5 pores with ceria as reported elsewhere.²⁹

The thermograms of as-synthesized NaZSM-5, 10% Ce-ZSM-5 and 15% Ce-ZSM-5 are shown in Figure 2. The weight loss due to desorption of water and template TPABr locked inside the pores was observed for as synthesized Na-ZSM-5 catalysts at 100 and 400–450 °C. Whereas in Ce-impregnated ZSM-5, exhibited sharp weight loss around 200 °C, which reveals the oxidative decomposition of nitrate.

Figure 3 shows the CO₂ TPD profiles of ceria impregnated NaZSM-5 catalysts which illustrated the both Bronsted and

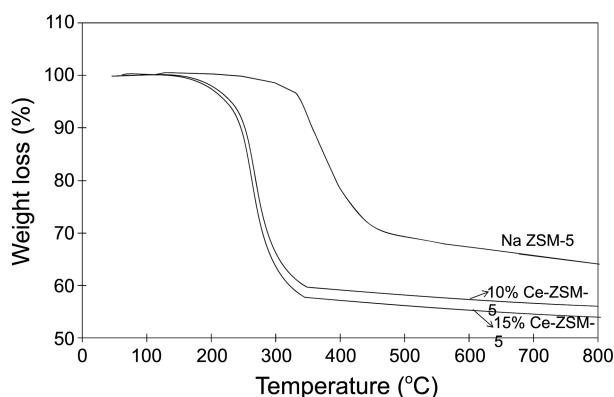


Figure 2. Thermogram of NaZSM-5 and Ce-impregnated ZSM-5.

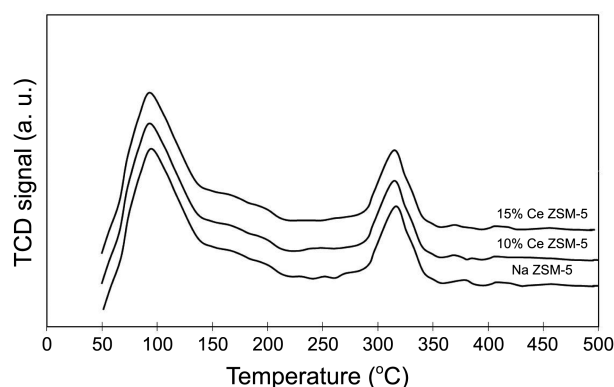


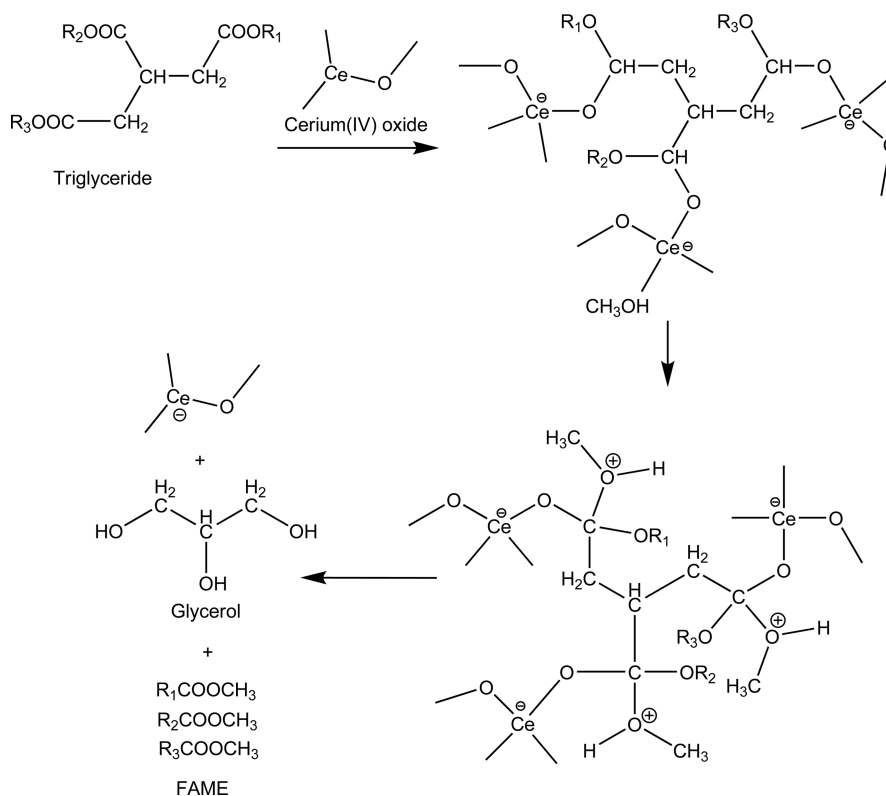
Figure 3. CO₂ TPD of NaZSM-5 and Ce-impregnated ZSM-5.

Lewis basicity. All materials exhibits two main desorption peaks at around 150 and 300 °C which corresponds to both medium and strong sites, related respectively to the oxygen of Ce–O₂ ion pairs and isolated O^{2–} anions (250–350 °C), that can be expected to possess Lewis base character.³⁰

Biodiesel Production. Transesterification of jatropha oil with methanol over pristine and cerium oxide impregnated ZSM-5 (0.1 g) catalysts was studied in the liquid phase at 75 °C, 100 °C and 120 °C. The feed ratio of jatropha oil with methanol was kept at 1:6 and the aliquots of the reaction mixture were withdrawn for analysis at the end of every 1 h up to 3 h in order to monitor the progress of esterification using GC. Figure 4 shows that the biodiesel yield increases with increase in temperature and almost 93% over 15% Ce-ZSM-5 at 75 °C. The higher yield of the methyl ester over ceria impregnated ZSM-5 is mainly catalyzed by the Lewis base ceria and also to some extent by Bronsted base ZSM-5 as shown in the Scheme 1.

The carbonyl group of triglycerides is adsorbed over the ceria which results in polarization of C=O group and more positive charge is created over the carbonyl carbon. Thereafter methanol could make nucleophilic attack over the carbonyl carbon and its corresponding proton is removed by the oxidic sites of ceria. The acid catalyst transesterification reported Yan *et al.*³¹ also suggested the same mechanism. Recently, Masazumi *et al.*,³² reported that mechanism of transesterification based on *in situ* species analysis by IR and kinetic results. It is examined that transesterification occurs through following steps (1) dissociative adsorption of ester to adsorbed carboxylate species, (2) dissociative adsorption of alcohol to alkoxide species assisted by the base sites of CeO₂ and (3) nucleophilic substitution reaction of alkoxide species to carboxylate species and desorption of the corresponding esters. The mechanism proposed in our studies is also exactly same to the reported one but which is performed by the CeO₂ dispersed over the microporous solid support. Such dispersion of ceria over the solid support with higher surface area results in spreading of active ceria sites through the catalyst which enhances the conversion of reactant to product.

Thus reaction is catalyzed by ceria and hence maximum yield of 93% over 15% Ce-ZSM-5 might be due to the



Scheme 1. Transesterification mechanism of jatropha oil with methanol.

availability more ceria for transesterification. The yield of methyl ester increases with increase in time and also with increase in temperature. Yu *et al.* also reported the activity of CeO-CaO mixed oxide catalyst is enhanced by the presence of CeO, and yield of biodiesel of 91%, similarly from this study CeO enhanced the similar yield was obtained with 5% of catalyst weight. It has been reported that the acido-basic characteristics of CeO plays a vital role as potent catalyst for esterification reactions.³³ It has been reported that Lewis acid/surfactant cerium trisdodecylsulfate shows highest catalytic activity for transesterification.³⁴ Similarly, as a basic counterpart the ceria impregnated ZSM-5 catalysts shows higher conversion of triglyceride to methyl ester. In fact, it is reported that CeO₂ is of higher oxidation state, shows much less basicity and less catalytic activity towards transesteri-

fication,³⁵ but when CeO₂ is dispersed over the ZSM-5 the final catalyst is found to possess both Lewis and Bronsted basicity, this synergetic effect makes the ceria impregnated ZSM-5 to give higher yield of methyl esters at 75 °C. Cannilla *et al.* has also reported that combination of Mn and Ce oxide shows higher yield of methyl ester than their individual performance.³⁰

As shown in the Figure 4 the yield of methyl ester increased with increase in reaction time up to 2 h and no further change in conversion beyond 2 h was observed. A rapid formation of biodiesel was observed within the initial 2 h and attains steady state (93%) at 3 h. Here, equilibrium is established even at the end of 2 h reaction period suggesting that basic strength as well as density of basic sites of the catalysts is important parameters to speed up transesterification and to attain equilibrium. Thus, with more basic 15% Ce-ZSM-5, equilibrium is attained at 2 h. The effect of temperature on transesterification of TG with methanol over Ce impregnated ZSM-5 is also shown in the Figure 4. It is observed that increase of temperature beyond 75 °C shows no significant increase in the yield of methyl ester. Thus the results obtained, the optimum temperature and time for transesterification of jatropha oil is 75 °C and 2 h which is same as those reported for the acid catalyzed La/ZSM-5 catalysts.³⁶ It is concluded that Further, high ceria loading are more active than other catalysts. In order to detect any leaching of ceria from the support, a portion of the reaction mixture after 12 h was tested by ICP-MS which proved absence of ceria leaching.

The effect of oil to methanol ratio is an important para-

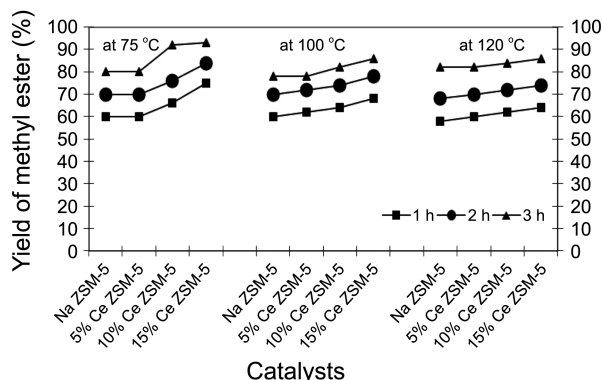


Figure 4. Transesterification of jatropha oil with methanol over NaZSM-5 and Ce-impregnated ZSM-5.

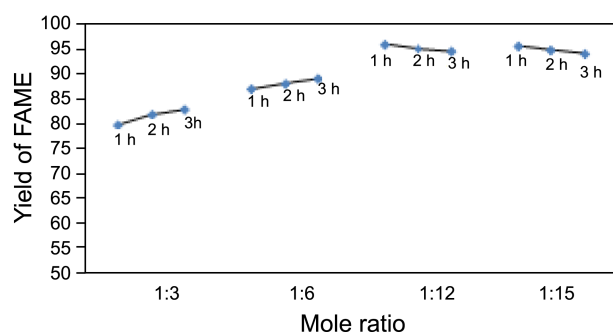


Figure 5. Effect of mole ratio on the yield of FAME over 15% Ce ZSM-5 (0.1 g) at 100 °C.

meter in the transesterification process for production of biodiesel. The stoichiometric ratio of oil: methanol is 1:3, however, higher molar ratio is encouraged to enhance the rate of esterification, yield of esters and also for completion of reaction.³⁷ Figure 5 shows effects of methanol to oil molar ratio on biodiesel yield. When the ratio was increased from 1:3 to 1:15, the yield of methyl esters and observed considerably from 75 to 95.7 wt %. An optimum yield was achieved with the molar ratio 1:12 and further increase shows no significant change in yield. Hence the optimum molar ratio is identified as 1:12.

The effect of catalyst weight was studied with 15% Ce-ZSM-5 at 75 °C with a feed ratio 1:12. The results are shown in Table 2. The conversion slightly increases from 94% to 96% when increasing catalysts weight from 0.1 to 0.2 g of the catalyst. While more amount of catalysts employed in the reaction, the reactants are more exposed to the active basic sites of the catalysts and hence the yield increase with catalyst weight.

Effect of reusability (figure not shown) of ceria impregnated NaZSM-5 for transesterification of jatropha oil was also studied by reusing the catalyst after rinsing with methanol. It is observed that the yield of methyl ester is nearly 95% at end of 10 cycles which is nearly same as that of initial activity. This clearly suggested that the ceria impregnated NaZSM-5 are reusable which is the essential requirement in industrial processes.

Figure 6 shows the ¹H NMR spectrum of methyl ester obtained on transesterification of jatropha oil with methanol over Ce-ZSM-5 catalyst. It exhibits a peak at 3.30 ppm which is attributed to protons of O-CH₃ groups as reported elsewhere.²⁷ Biodiesel produced by this method was tested to ensure its fuel property and results are shown in the Table

Table 2. Effect of catalyst weight on yield of FAME

Catalyst weight (g)	Yield of FAME (%)		
	1 h	2 h	3 h
0.1	94.2	94.8	95.7
0.15	94	94.6	95.8
0.2	94.8	95.2	96.2

Temperature: 100 °C; Catalyst: 15% Ce ZSM-5; Mole ratio; 1:12

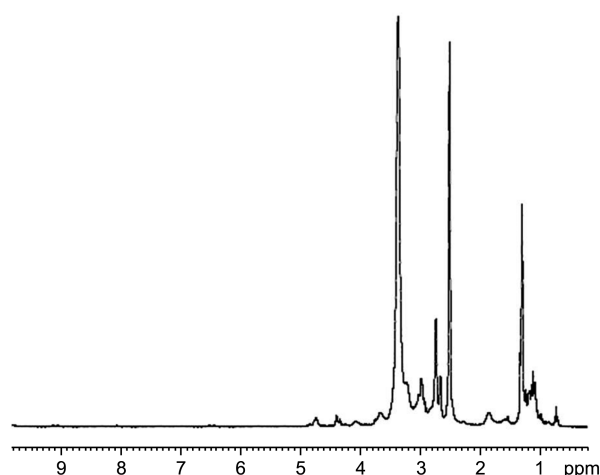


Figure 6. ¹H NMR of FAME obtained on transesterification of jatropha oil with methanol over Ce ZSM-5.

Table 3. Fuel property of FAME obtained on transesterification of jatropha oil over Ce-ZSM-5 catalysts

Properties	Units	Method	Limits	FAME
Specific gravity	–	ASTM D4052	–	0.868
Flash point	°C	ASTM D93	130 min	144
Cloud point	°C	ASTM D2500	Report	12
Viscosity @40 °C	mm ² s ⁻¹	ASTM D445	1.9-6	5.1
Acid number	mgKOHg ⁻¹	ASTM D664	0.05 max	0.04
Cetane Number	–	ASTM D613	47 min	54
Water & sediments	% volume	ASTM D2709	0.05 max	0.04
Carbon residue	% mass	ASTM D4530	0.05 max	0.03

3. The estimated values of biodiesel quality are in line with the ASTM D 6751 standards.

Recent report on CeO₂ catalysts for transesterification shows that pure CeO₂ could yield 97% ester at 160 °C under the solvent-free conditions. In our present study, the attempt to impregnated CeO₂ over ecofriendly solid support shows the minimum usage of CeO₂ for higher yield of FAME (93%). The higher yield of FAME with minimum metal oxide over impregnation on solid support might be due to increased surface area (~300 m²/g) compared to pure CeO₂ (surface area ~81 m²/g).³² In general, CeO₂ is stable due to its high lattice enthalpy (–4850 kJ mol⁻¹)³⁸ hence these CeO₂ impregnated ZSM-5 could also be used at high temperature. Further, isoelectric point of CeO₂ is pH = ~7.5³⁹ hence CeO₂ is less soluble than CaO or MgO under an acidic solution. Thus, based on the above discussions when CeO₂ is impregnated over solid supports is the most effective catalyst for transesterification in terms of activity, leaching-resistance and reusability.

Conclusion

NaZSM-5 was synthesized in an alkaline medium and impregnated with cerium oxide by wet method, and investigated for transesterification of *Jatropha curcas* oil (JCO)

with methanol for production of biodiesel. The characteristics of cerium impregnated ZSM-5 catalysts were verified by XRD, TGA, TPD and BET. XRD analysis showed decrease in intensity of the patterns for 10 and 15% ceria loading, which evidenced pore filling of ZSM-5 with ceria. This was further verified by BET results which show decrease in surface area and pore volume due to filling of ceria. CO₂ TPD signals illustrated the presence of two different basic sites (medium and strong) of cerium impregnated ZSM-5. The yield of methyl esters was calculated from the GC results and also verified with ¹H NMR analysis. The optimum reaction parameters, temperature, oil to methanol molar ratio and catalyst weight were found to be 75 °C; 1:12; 0.1 g. Further, high ceria loading are more active than other catalysts. Since these ceria impregnated NaZSM-5's possess anticipated catalytic properties, could be effectively used as a potential catalysts for biodiesel production in industrial processes.

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