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Application of biosynthesized nano-catalyst for biodiesel synthesis and impact assessment of factors influencing the yield

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This study presents a green process to synthesize biodiesel using biosynthesized nano-catalyst and a novel methodology for analyzing the impact of influencing factors – methanol/oil ratio, the concentration of nano-catalyst, temperature, and time of reactions- on the yield of biodiesel obtained by heterogeneous nano-catalyst-based transesterification reaction. Nano-calcium oxide (nano-CaO) was obtained as a heterogeneous nano-catalyst using waste eggshells. Waste cooking oil was treated with methanol and nano-catalyst at varying methanol: oil ratios (4 – 14:1), nano-catalyst concentration (0.5 – 2 %), time of reaction (3 – 4.5 hrs), and temperature (50 – 65 °C). The superiority and effectiveness of the proposed transesterification indices were accomplished making use of Deluca and Termini fuzzy entropy weighted indexes to obtain optimal reaction conditions with 95.49 % biodiesel yield.

Keywords: nano-catalyst, biodiesel, transesterification, fuzzy entropy, neutrosophic entropy.

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1. Introduction

Worldwide consumption of energy is progressing especially in the transportation sector which is solely dependent upon petroleum-based non-renewable resources of energy [1]. These resources are the primary source of increasing environmental pollution due to the emission of carbon dioxide from vehicular exhausts in addition to the greenhouse effect [2]. The resulting environmental degradation and the expected energy depletion require the continuous search for alternative energy resources if the quality of the environment must be maintained [3]. Consideration of the energy policy review indicates that India and several nations of the world are facing great challenges towards alternative and sustainable energy resources that are eco-friendly, less expensive, biodegradable, and easily available [4]. Consequently, the search for biofuels such as biogas, hydrogen cells, and biodiesel has attracted intense research interest because of the potential of green chemistry usage [5]. Biodiesel has emerged as a sulfur-free, bio-degradable, cost-effective, non-toxic, and more reliable option among the alternative sustainable fuels [6]. It is miscible in diesel at all proportions and is favored as a blending constituent of automotive fuel due to its very high cetane value and high lubricity [7]. It can be obtained as fatty acid alkyl esters employing transesterification of cheap resources viz oils and fat with alcohols (ethanol/methanol) or alkoxides and homogeneous or heterogeneous catalyst with the production of glycerol as a by-product [8]. Vegetable oil is commonly obtained from oil crops such as coconut, sunflower, canola, palm, mustard, soybean, flax, rapeseed, jatropha, hemp, and rice bran, etc. India has a great potential for production of biodiesel with vast production of oil crops in the wasteland and forest area. In the global society, efforts are ongoing toward reducing dependency on fossil fuels and reducing production costs for biodiesel by opting for low-cost and easy to obtain feedstock and catalysts [9]. Many researchers have used vegetable oils in the form of raw, non-edible and waste oils obtained from various oil processing units as well as from household and locally available food ventures [10].

It has been found that heterogeneous catalysts exhibit better performance compared to homogeneous catalysts. The major factor includes the high production cost during industrial production on large scale due to the involvement of the multistep purification process and difficulties to remove the byproducts such as glycerol formed during the reaction. Treatment of the effluent resulted from this process also adds to the cost [11]. Further, all the conventional feedstock including non-edible oils with high content of fatty acids can not be used in the homogeneous esterification due to the possibility of soap formation that leads to loss of yield and adds to the separation issue of byproducts. Hence, researchers are seeking economically viable and alternative methods for the production of biodiesel [12]. However, the greatest advantage of heterogeneous catalysts is the ease of separation while the disadvantage is limited activity and selectivity. Heterogeneous (solid) catalyst-based transesterification offers future hope to current challenges because solid catalysts are required in a lesser amount compared to conventional catalysts and can be easily separated and be re-used. Also, the solid catalyst can be fabricated and tailored as per the requirement to increase the catalytic properties.

Various solid catalysts including metal oxide and alumina/silica supported metal oxide catalysts have been explored by researchers [13]. Several reports are available with usage of CaO as a heterogeneous nano-catalyst. Animal eggshells are a rich source of calcium carbonate that can be easily converted to nano-CaO. Throughout the world, eggshells of chicken, duck, and snails are discarded as waste and their improper disposal leads to environmental pollution that results in various health hazards. Hence, the use of waste eggshells for the generation of nano-CaO as a heterogeneous nano-catalyst is an eco-friendly step [14]. Likewise, edible oil is processed in various food processing units especially in the kitchen and restaurants for frying purposes. After frying, edible oil becomes unfit for consumption and is discarded and is known as waste cooking oil (WCO). This oil is rich in free fatty acids and may be successfully employed to obtain biodiesel using nano-CaO based heterogeneous transesterification [15].

Production of biodiesel is dependent upon many factors including methanol/oil ratio, temperature, the concentration of nano-catalyst, time of reaction, extent of stirring, etc. [16]. Subsequently, Yi et al. approached the enduring Karl's Pearson's coefficient formula and designed the optimal reaction conditions responsible for transesterification reaction [17]. However, the correlation coefficient formula has some limitations as it can be only used for studying interrelation and thus leads to a non-significant curvilinear relationship between two variables. The fuzzy set theory proposed by Zadeh has been proven as an indispensable tool for optimizing energy-related problems [18]. Ovchinnikov elaborated many impressions of fuzzy sets (FSs), one of which corresponds to the representation of membership degree or grade of the underlying FS [19]. Since then, FSs have been extended into a variety of equivalents and more quantified information is provided by the neutrosophic set (NS) contribute in comparison with the existing fuzzy set theory [20]. Moreover, the NS theory has the potential of predicting optimal reaction conditions under heterogeneous catalyzed transesterification reactions. To handle and solve these problematic issues, an effort is accomplished in this pathway by establishing a novel neutrosophic entropy-based methodology which can play a crucial role for the classification of influencing factors (i) methanol/oil ratio (ii) concentration of nano-catalyst (iii) temperature and (iv) time of reactions, responsible for optimal biodiesel yield, obtained by heterogeneous nano-catalyst-based transesterification reaction. The underlying neutrosophic entropy-based methodology provides remarkable yield information confirming the optimum parameters. The results of this underlying study are superseded as below.

Section 2 provides the details of the materials and procedures employed in performing the reaction. Section 3 introduces the projected methodology for constructing fuzzy entropy weighted waste cooking oil transesterification index (FCOTI), single-valued neutrosophic entropy weighted waste cooking oil transesterification index (SCOTI), and Deluca and Termini fuzzy entropy-based weighted waste cooking oil transesterification index (ECOTI) respectively. Section 4 provides the details for the characterization of the prepared nano-catalyst and biodiesel. It also provides the applicability and remarkability of the underlying methodology by identifying the most influencing reaction set, responsible for the optimum biodiesel yield whereas Section 5 finally summarizes the study. The basic terminology of fuzzy and neutrosophic entropy measures, required for the successive progress of the underlying study has been given in supplementary information.

2. Materials and methods

2.1. Materials

WCO, procured from the resident food vendors, was utilized as resource material for the reaction. Waste chicken eggshells, collected from the local food junctions, were used to develop the heterogeneous nano-catalyst. All the chemicals of analytical grade were acquired from Merck, Mumbai, and were utilized without any additional processing or purification.

2.2. Collection of reaction sets

A heterogeneous nano-catalyst based on waste eggshells was developed by the procedure given in literature [21]. Methanol has been used as a solvent and co-reactant. After washing, drying, and grinding, the eggshells were calcined to obtain nano-CaO as a nano-catalyst. The nano-catalyst was characterized by FTIR (Model Perkin Elmer Spectrum 400 FT-IR Spectrometer) operating with a resolution of 2 cm^{-1} (range 4000 – 400 cm^{-1}) and XRD (Model PANalytical X'Pert Pro) operating at a voltage of 45 kV with a current of 35 mA using Cu-Kα radiation ($K = 1.5406$ Å) and 2θ ranging from 20 – 80° at a continuous speed of 0.045° per min. Waste cooking oil was subjected to filtration for the removal of any insoluble impurities and was pre-treated with anhydrous sodium sulfate before heating at 100 °C. The reaction was executed in a batch reactor supported with a thermostatic water bath and magnetic stirrer by varying methanol: oil ratio (4 – 14:1), nano-catalyst concentration (0.5 – 2 %), time of reaction (3 – 4.5 hrs.), and temperature (50 – 65 °C) as per reaction sets and a constant stirring was maintained.

After the separation of glycerol, the by-product, the % yield of biodiesel was determined using the standard equation [22]. The biodiesel so obtained was characterized by FTIR (Model Perkin Elmer Spectrum 400 FT-IR

Spectrometer) and GC-MS analysis (Model THERMO Scientific Trace 1300GC) operating at conditions as shown in Table 1.

TABLE 1. GC-MS Conditions for the analysis of essential oils

GC Condition		
Injection Temperature	280 °C	
Injection Mode	Split	
Column Flow (Helium)	1.21 mL/min	
Split Ratio	5	
Injection Volume	1 μL	
MS Conditions (EI mode at 70 eV)		
Ion Source Temperature	200 °C	
Interface Temperature	280 °C	
Solvent Cut Time	2.2 min	
Start Time	2.5 min	
End Time	55 min	
Start m/z	40	
End m/z	700	
Oven Temperature Program		
Rate (°C/min)	Temperature (°C)	Hold Time (min)
	60	1
5	220	2
5	280	8

3. Normalization of monitored biodiesel yield

Suppose the number of parameters (influencing factors) under study is denoted by "n". Let the number of reaction sets to be optimized is denoted by "m". Let r_{ji} denote the monitored biodiesel yield of the j^{th} influencing factor at i^{th} reaction set. To diminish the errors created by the various influencing factor, it becomes essential for us to normalize each monitored biodiesel yield. If V_{ji} denotes the normalization construction function for a typical j^{th} influencing factor at a particular i^{th} reaction set, then:

$$V_{ji} = \frac{r_{ji} - \min r_{ji}}{\max r_{ji} - \min r_{ji}}, \tag{1}$$

where j runs over 1 to n and i over 1 to m.

3.1. Determination of fuzzy and neutrosophic entropy weights

In the existing literature of Information theory, many fuzzy entropy (FE) measures have been investigated and characterized by researchers, but with some faults and limitations. De Luca and Termini suggested the first non-additive FE measure as follows [23]:

$$H_F^d\left(C_{FS}^b\right) = -\frac{1}{\log m}\sum_{j=1}^{n}\Big[\tilde{\mu}_{C^b}(p_j)\log\tilde{\mu}_{C^b}(p_j) + (1-\tilde{\mu}_{C^b}(p_j))\log\left(1-\tilde{\mu}_{C^b}(p_j)\right)\Big], \tag{2}$$

where m is a fixed natural number.

The fuzzy entropy $H_F^d\left(C_{FS}^b\right)$ has been found capable of optimizing the uncertainty problems associated with various aspects of the environment, pollution, and energy-saving resources. Unfortunately, the FE measure is facing a major drawback with assumption $0 \times \log 0 = 0$. Due to this reason, this fuzzy entropy faced intrinsic conflicts and hence indicated uncertainty and elusiveness in the quality evaluation. To overcome this problematic situation and to meet the exigency, we have been able to establish Neutrosophic fuzzy entropy (NTFE) and applied it for identifying

the most influencing reaction sets responsible for the optimal bio-diesel yield. Let T_{ji} denote the amount of fuzziness (concentration) based on the truth membership degree of j^{th} persuading factor at the i^{th} reaction set. Then:

$$T_{ji} = \frac{V_{ji}}{\sum_{j=1}^{n} V_{ji}}, \tag{3}$$

where j runs over 1 to n and i over 1 to m.

(a) The weights W_{ji}^{1} of j^{th} influencing factors at i^{th} reaction set can be determined as follows. Let m be the number of reaction sets, then:

$$W_{ji}^{1} = \frac{1 - H_{ji}^{1}}{\sum_{j=1}^{n} H_{ji}^{1}}, \tag{4}$$

where

$$H_{ji}^{1} = -\frac{1}{\log m} \sum_{j=1}^{n} \Big[T_{ji} \log T_{ji} + (1 - T_{ji}) \log (1 - T_{ji}) \Big]. \tag{5}$$

(b) The weights W_{ji}^{2} of j^{th} influencing factors at i^{th} reaction set employing the proposed trigonometric FE measure (1) can be determined as follows. Let m be the number of reaction sets, then:

$$W_{ji}^{2} = \frac{1 - H_{ji}^{2}}{\sum_{j=1}^{n} H_{ji}^{2}}, \tag{6}$$

where

$$H_{ji}^{2} = -\tan\left(\frac{1}{m}\right) \sum_{j=1}^{n} \left[\tan\left(\frac{2}{\sqrt{2} + \sqrt{T_{ji}} + \sqrt{(1 - T_{ji})}} \right) - \tan\left(\frac{2}{\sqrt{2} + 1} \right) \right].$$

(c) Let $F_{ji} = 1 - V_{ji}$ and $I_{ji} = 1 - V_{ji} - F_{ji}$ denote the amount of fuzziness (concentration) based on falsity and indeterminacy membership degree of j^{th} influencing factor at i^{th} reaction set respectively. Then, the weights $W_{ji}^{(3)}$ of j^{th} influencing factors at i^{th} reaction set employing the proposed Single Valued Neutrosophic Entropy (SVNE) measure can be determined as follows. Let m be the number of reaction sets, then:

$$W_{ji}^{(3)} = \frac{1 - H_{ji}^{3}}{\sum_{j=1}^{n} H_{ji}^{3}}, \tag{7}$$

where

$$\begin{aligned} H_{ji}^{3} = \tan\left(\frac{1}{m}\right) \sum_{j=1}^{n} \Bigg[& 3 \tan\left(\frac{2}{\sqrt{2} + 1} \right) - \tan\left(\frac{2}{\sqrt{2} + \sqrt{I_{ji}} + \sqrt{1 - I_{ji}}} \right) \\ & - \left(\frac{2 + V_{ji} + F_{ji}}{3} \right) \tan\left(\frac{1 + V_{ji} + F_{ji}}{\sqrt{2} + \left(\sqrt{V_{ji}} + \sqrt{F_{ji}}\right) \left(\sqrt{V_{ji} + F_{ji}}\right)} \right) \\ & - \left(\frac{4 - V_{ji} - F_{ji}}{3} \right) \tan\left(\frac{3 - V_{ji} - F_{ji}}{\sqrt{2} + \left(\sqrt{1 - V_{ji}} + \sqrt{1 - F_{ji}}\right) \left(\sqrt{2 - V_{ji} - F_{ji}}\right)} \right) \Bigg]. \end{aligned} \tag{8}$$

3.2. Calculation of relative sub-indices of each influencing factor at various reaction sets

Two types of sub-indices, absolute and relative, are being used by eminent researchers. Since absolute (or relative) sub-indexing approaches are fully independent (or dependent) on quality standards, the relative sub-indexing approach has been empowered in this study.

Let Q_{ji} = The relative sub-indices, S_{ji} = The maximum monitored biodiesel yield, and c_{ji} =The monitored biodiesel yield of the j^{th} influencing factor at i^{th} reaction set consecutively. Then, the relative sub-indexing of each influencing factor concerning various reaction sets in this study has been assigned by:

$$Q_{ji} = \frac{c_{ji}}{S_{ji}} \times 100, \tag{9}$$

where j runs over 1 to n and i over 1 to m.

3.3. Constructions of ECOTI, FCOTI and SCOTI

The existing Deluca–Termini fuzzy entropy, proposed fuzzy trigonometric entropy and SVNE weighted waste cooking oil transesterification indices (ECOTI, FCOTI and SCOTI) can be computed employing the following equations:

$$\text{ECOTI at } i^{th} \text{ reaction set} = \sum_{j=1}^{n} W_{ji}^{1} Q_{ji}, \tag{10}$$

$$\text{FCOTI at } i^{th} \text{ reaction set} = \sum_{j=1}^{n} W_{ji}^{2} Q_{ji}, \tag{11}$$

$$\text{SCOTI at } i^{th} \text{ reaction set} = \sum_{j=1}^{n} W_{ji}^{3} Q_{ji}. \tag{12}$$

The maximum ECOTI, FCOTI, or SCOTI score for a typical influencing factor at a particular reaction set is designated as the most influencing reaction set.

4. Results and discussion

4.1. Characterization of nano-catalyst

The X-ray diffraction patterns of nano-CaO have been plotted in Fig. 1. The narrow and intense peaks in the patterns can be attributed to the crystalline nature (calcite) of nano-CaO [24]. The diffraction patterns clearly show that the nano-catalyst showed characteristic peaks for CaO at 2θ equal to 31.5, 37.5, 46.4, 51.1, 52.3, 55.2, and 58.1° [25]. The prepared nano-catalyst was also characterized using FTIR analysis as shown in Fig. 2. A band at 3267.67 cm^{-1} corresponded to the O-H stretching while two bands around 1439.41 and 438.43 cm^{-1} were attributed to Ca–O bending [26]. The FTIR features shown by the nano-catalyst in our study are consistent with the already reported data in the literature [27].

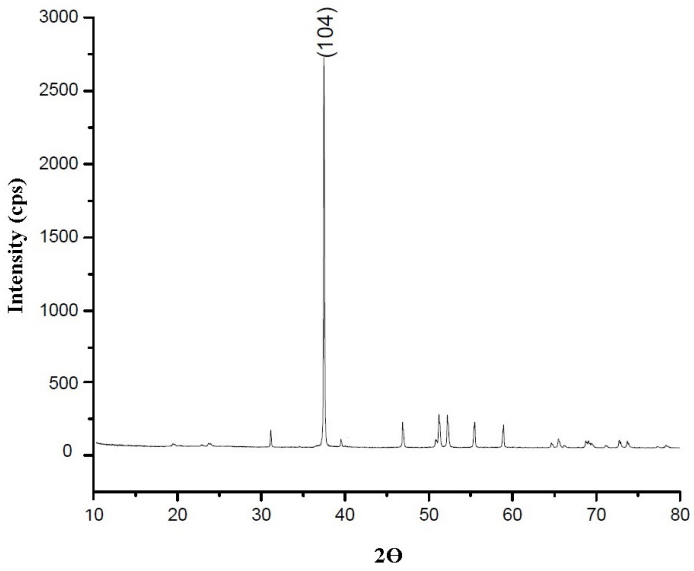

FIG. 1. X-ray Diffraction pattern for nano-CaO

4.2. Characterization of biodiesel

The biodiesel composition in terms of fatty acid methyl esters was identified by a pattern of mass fragmentation and the retention time of GCMS analysis. Fig. 3 shows the composition of the biodiesel produced under optimized conditions and confirms the completion of the transesterification reaction. The results found were consistent with previously reported results [28].

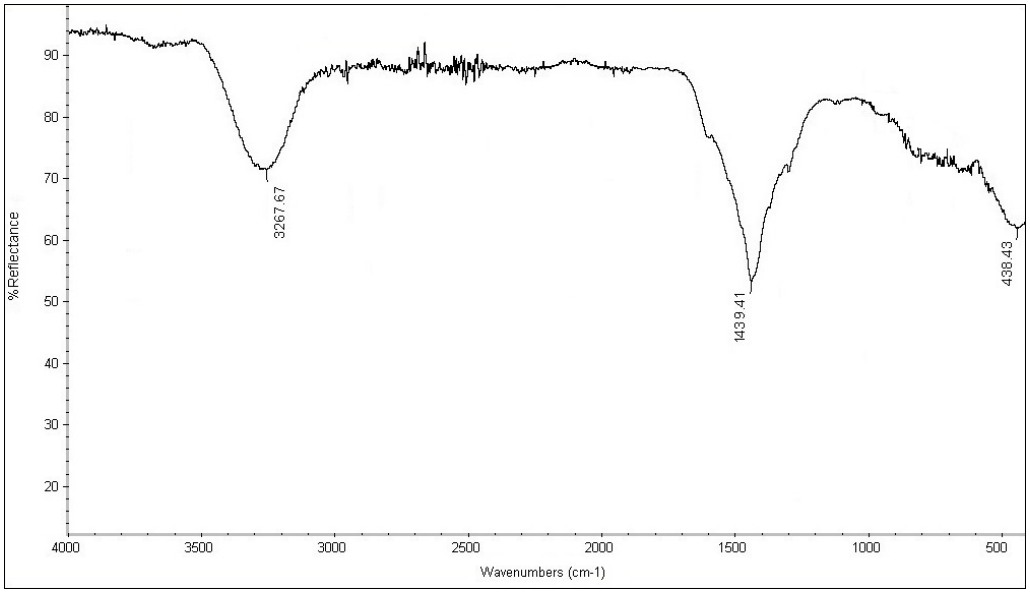

FIG. 2. FTIR spectrum for nano-CaO

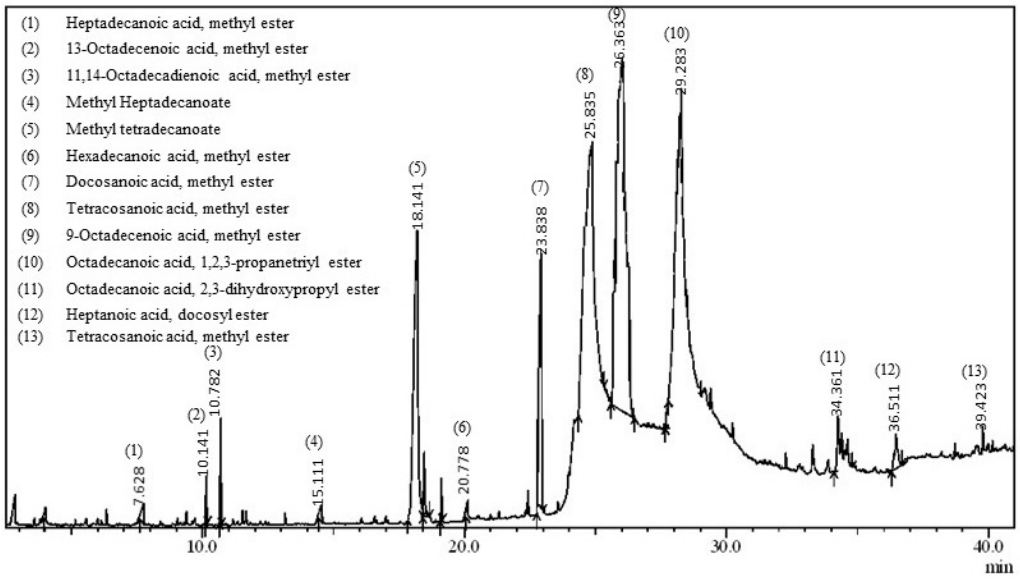

FIG. 3. GCMS for biodiesel

Functional group analysis of biodiesel was explored by FTIR as represented in Fig. 4. The most intense peak at 1755.96 cm^{-1} was assigned to CO stretching in esters [29, 30]. The absorption bands corresponding to the asymmetric bending of methyl groups of esters in the biodiesel were observed at 1639.41 cm^{-1} while that for stretching vibrations of methoxy groups were observed at 1239.85 cm^{-1} [31, 32]. The axial deformation of CH_2 bond was indicated by absorption bands at 2911.66 cm^{-1} [28, 33]. The absorption band at 2407.14, and 2170.60 cm^{-1} corresponded to stretching vibrations of C–O while O–H stretching vibration was observed as a weak absorption band at 3400.91 cm^{-1} [34]. The absorption bands at 628.59 cm^{-1} corresponded to CH_2 and CH_3 bending vibrations [28].

4.3. Identification of most influencing reaction set through ECOTI, FCOTI, and SCOTI

To predict the most influencing reaction set responsible for the optimum bio-diesel yield employing the proposed methodology has already been explained. The number of influencing factors in this study is four $(n = 4)$ and the number of transesterification reaction sets is eleven $(m = 11)$ for the concentration of nano-catalyst, temperature, and time of reaction, and ten $(m = 10)$ for methanol/oil ratio. We have been able to evaluate Deluca and Termini [23] fuzzy

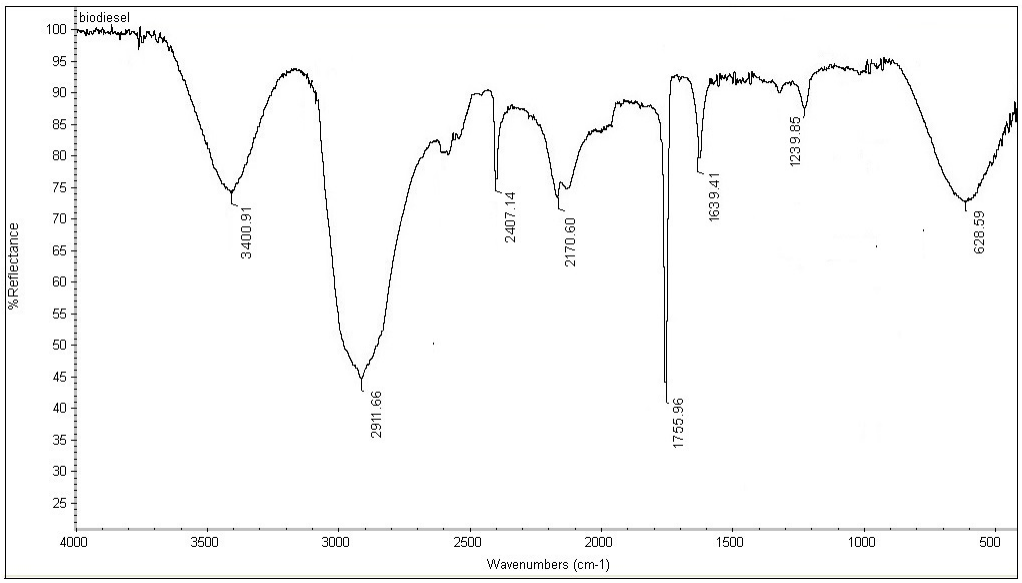

FIG. 4. FTIR spectrum for biodiesel

entropy-based weighted waste cooking oil transesterification index (ECOTI) employing equation (11) concerning each influencing factor at various reaction sets as summarized in Table 2. A careful analysis of the results depicted in Table 2 along with Fig. 5(a) reveals that, like the proposed fuzzy and SVNE measures, for the variation of (i) concentration of nano-catalyst (ii) temperature (iii) time of reaction and (iv) methanol:oil ratio, the reaction sets RS_8, RS_{19}, RS_{30}, RS_{35} were found to be the most influencing ones owing to their maximum ECOTI scores. The desired TFE weighted waste cooking oil transesterification index (FCOTI) can be evaluated employing equation (12). The results have been depicted in Table 2 along with Fig. 5(b), revealing that for the variation of concentration of nano-catalyst, temperature, time of reaction, and methanol: oil ratio, the reaction sets RS_8, RS_{19}, RS_{30}, RS_{35} were found to be the most promising ones owing to their maximum FCOTI scores. Following the proposed methodology and resulting equation (13), the desired trigonometric SVNE weighted waste cooking oil transesterification index (SCOTI) concerning each influencing factor at various reaction sets is summarized in Table 2. The subsequent analysis of the results depicted in Table 2 along with Fig. 5(c) reveals that for the variation of concentration of nano-catalyst, temperature, time of reaction, and methanol: oil ratio, the reaction sets RS_8, RS_{19}, RS_{30}, RS_{35} were found to be the most influencing ones owing to their maximum ECOTI scores.

The previous discussion reveals that for the variation in methanol: oil ratio with variation in concentration of nano-catalyst from 0.5 – 2 %, the reaction set RS_8 was found to be most influencing, owing to its maximum ECOTI, FCOTI, and SCOTI scores. Similarly, for the variation in methanol: oil ratio with variation in temperature of transesterification from 50 – 65 °C, the reaction set RS_{19} was found to be most effective owing to its maximum ECOTI, FCOTI, and SCOTI scores. Also, for the variation in methanol: oil ratio with variation in time of esterification from 3 – 4.5 hrs., the reaction set RS_{30} was found to be most effective owing to its maximum ECOTI, FCOTI, and SCOTI scores. These reaction sets involve the use of methanol: oil ratio as 11:1 which means that the optimized methanol: oil ratio for best yield of biodiesel is 11:1.

During the study of the effect of nano-catalyst concentration, temperature, and time of reactions at constant methanol: oil ratio, it was observed that the reaction set corresponding to the nano-catalyst concentration as 1 %, reaction temperature as 60 °C, and reaction time as 4.5 hrs., was found to be most effective, owing to its maximum ECOTI, FCOTI, and SCOTI scores resulting in 95.49 % biodiesel yield. It is therefore concluded that during the optimization analysis, the methanol: oil ratio has been the most influencing factor. This is due to the reason that for transesterification reaction, excess methanol is required for obtaining maximum yield (methanol being the co-reactant for the reaction). For a particular methanol: oil ratio, the temperature is the most influencing factor followed by nano-catalyst concentration and time of reaction owing to their highest ECOTI, FCOTI, and SCOTI scores. However, for the optimized value of nano-catalyst concentration and time of reaction, a slight decrease of reaction temperature 55 °C was observed followed by an increase of reaction temperature 65 °C indicating that at the optimized value of nano-catalyst concentration and reaction time, temperature change can be afforded. However, all four factors are interdependent and can be suitably varied at particular methanol: oil ratios to obtain the best yield of biodiesel.

TABLE 2. FCOTI, SCOTI and ECOTI Score for (i) Methanol: Oil Ratio (MR) with the variation of nano-catalyst (Cat), temperature (Temp.) and time of reactions

FCOTI Score							
RSs	Nano-catalyst	RSs	Temp.	RSs	Time	RSs	MR
RS_1	0.0000	RS_{12}	0.0000	RS_{23}	0.0000	RS_{34}	357.83
RS_2	305.80	RS_{13}	307.83	RS_{24}	294.78	RS_{35}	367.57
RS_3	312.72	RS_{14}	316.63	RS_{25}	302.84	RS_{36}	361.33
RS_4	320.19	RS_{15}	324.50	RS_{26}	310.46	RS_{37}	360.21
RS_5	327.81	RS_{16}	331.51	RS_{27}	316.71	RS_{38}	357.39
RS_6	342.00	RS_{17}	343.71	RS_{28}	330.05	RS_{39}	364.27
RS_7	350.00	RS_{18}	350.09	RS_{29}	337.19	RS_{40}	364.15
RS_8	359.44	RS_{19}	359.58	RS_{30}	347.12	RS_{41}	0.0000
RS_9	356.95	RS_{20}	358.13	RS_{31}	345.09	RS_{42}	347.07
RS_{10}	354.30	RS_{21}	356.35	RS_{32}	341.65	RS_{43}	359.97
RS_{11}	352.80	RS_{22}	354.67	RS_{33}	339.19		
SCOTI Score							
RSs	Nano-catalyst	RSs	Temp.	RSs	Time	RSs	MR
RS_1	0	RS_{12}	0	RS_{23}	0	RS_{34}	358.73
RS_2	305.8	RS_{13}	307.82	RS_{24}	294.78	RS_{35}	367.57
RS_3	312.73	RS_{14}	316.63	RS_{25}	302.84	RS_{36}	362.71
RS_4	320.21	RS_{15}	324.5	RS_{26}	310.47	RS_{37}	360.64
RS_5	327.83	RS_{16}	331.51	RS_{27}	316.73	RS_{38}	356.22
RS_6	342.06	RS_{17}	343.72	RS_{28}	330.11	RS_{39}	365.22
RS_7	349.99	RS_{18}	350.07	RS_{29}	337.2	RS_{40}	363.09
RS_8	359.44	RS_{19}	359.58	RS_{30}	347.12	RS_{41}	0
RS_9	357.3	RS_{20}	358.28	RS_{31}	345.83	RS_{42}	347.22
RS_{10}	354.52	RS_{21}	356.37	RS_{32}	342.35	RS_{43}	360.55
RS_{11}	353.01	RS_{22}	354.71	RS_{33}	340.02		
ECOTI Score							
RSs	Nano-catalyst	RSs	Temp.	RSs	Time	RSs	MR
RS_1	0.0000	RS_{12}	0	RS_{23}	0.0000	RS_{34}	357.51
RS_2	305.78	RS_{13}	307.82	RS_{24}	294.79	RS_{35}	367.57
RS_3	312.68	RS_{14}	316.63	RS_{25}	302.82	RS_{36}	360.97
RS_4	320.15	RS_{15}	324.5	RS_{26}	310.44	RS_{37}	360.13
RS_5	327.78	RS_{16}	331.51	RS_{27}	316.68	RS_{38}	357.70
RS_6	341.97	RS_{17}	343.71	RS_{28}	330.03	RS_{39}	364.36
RS_7	350.00	RS_{18}	350.09	RS_{29}	337.19	RS_{40}	364.09
RS_8	359.44	RS_{19}	359.58	RS_{30}	347.12	RS_{41}	0.0000
RS_9	356.95	RS_{20}	358.13	RS_{31}	345.08	RS_{42}	346.96
RS_{10}	354.29	RS_{21}	356.35	RS_{32}	341.61	RS_{43}	359.86
RS_{11}	352.79	RS_{22}	354.67	RS_{33}	339.11		

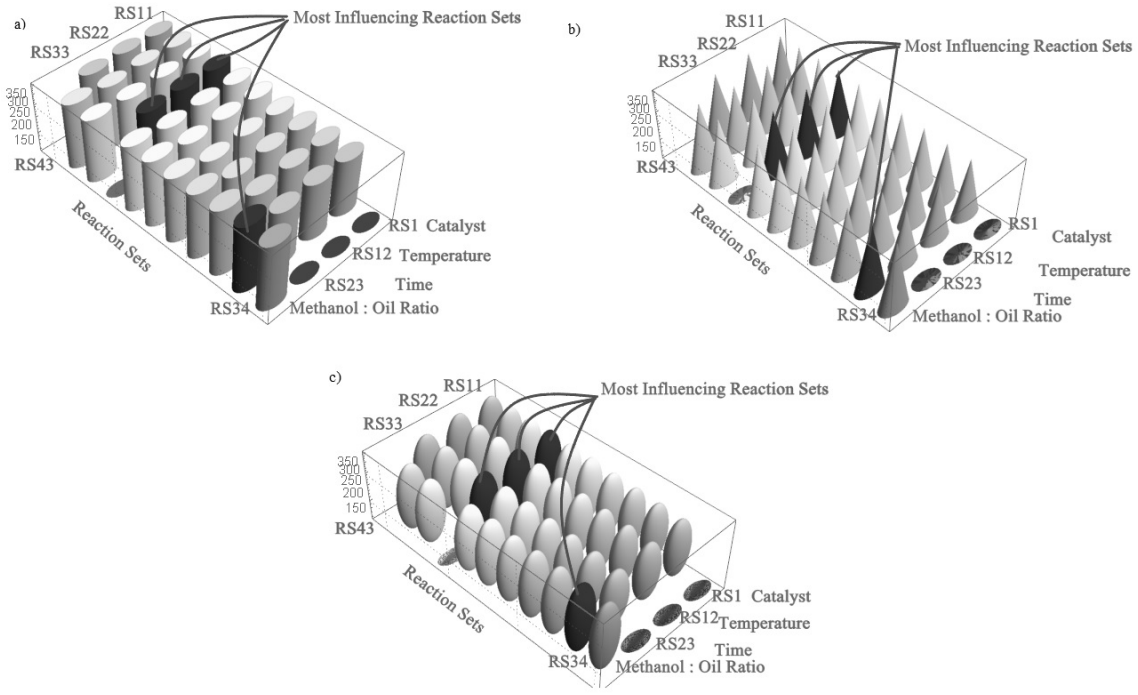

FIG. 5. Identification of Most Influencing Reaction Sets Employing a) ECOTI; b) FCOTI; c) SCOTI

5. Conclusion

This study investigates the synthesis of biodiesel using bio-synthesized nano-CaO as a nano-catalyst and employs a novel trigonometric fuzzy and SVNE-based methodology for evaluating the impact of various influencing factors (i) methanol/oil ratio (ii) concentration of nano-catalyst (iii) temperature and (iv) time of reaction on the biodiesel yield obtained through a heterogeneous nano-catalyst-based transesterification reaction. The proposed trigonometric entropy measures are deployed for constructing fuzzy entropy weighted waste cooking oil transesterification index (FCOTI) and SVNE weighted waste cooking oil transesterification index (SCOTI) respectively. The maximum FCOTI or SCOTI score concerning each influencing factor at various reaction sets indicated that the optimum methanol: oil ratio under the variation of nano-catalyst concentration from 0.5 – 2 % and the temperature variation from 50 – 65 °C comes out to be 11:1 to provide the maximum yield of biodiesel. Further, out of the next three parameters, the effect of temperature is more prominent to obtain the best yield of biodiesel followed by nano-catalyst and time of reaction. If nano-catalyst and time are suitably controlled within the range of optimum values, the reaction temperature doesn't significantly affect the reaction yield. The classification of various influencing factors obtained through the proposed FCOTI and SCOTI coincides with the existing Deluca and Termini fuzzy entropy-based weighted waste cooking oil transesterification index (ECOTI). This confirms that the optimum parameters are nano-catalyst concentration value of 1 %, reaction temperature as 60 °C, methanol: oil ratio as 11:1, and reaction time as 4.5 hrs.

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