Biomass Conversion and Biorefinery
https://doi.org/10.1007/s13399-021-02082-9

ORIGINAL ARTICLE

Solid sulfonated silica acid catalyst for epoxidation of *podocarpus falcatus* seed oil

Yigezu Mekonnen Bayisa[1] · Werku Aweke Teso[1]

Received: 31 August 2021 / Revised: 24 October 2021 / Accepted: 1 November 2021

Abstract

This study presents epoxidizing *podocarpus falcatus* seed oil through epoxidation reaction by using synthesized solid sulfonated silica catalyst from locally available sugarcane bagasse ash. The prepared sulfonated solid acid silica catalyst was characterized using bulk density, porosity, surface area, thermogravimetric, powder X-ray diffractometer, and FT-IR (Fourier-transform infrared spectroscopy). Thus, synthesized sulfonated silica catalyst works successfully for epoxidation of *podocarpus falcatus* seed oil. The epoxidation reaction was analyzed by design expert software Box-Behnken with four factors three-level: reaction temperatures, the molar ratio of hydrogen peroxide to the podocarpus falcatus seed oil double bond, reaction times, and catalyst loading. From the experimental results, the maximum relative conversion of oxirane of 84.75% was obtained using a temperature of 70 °C, hydrogen to carbon carbon double bond molar ratio of 2.5:1, using catalyst 5 (% w/w), and at 4-h reaction time. The product of epoxidized podocarpus falcatus oil was characterized by identifying the functional group, and composition of podocarpus falcatus seed oil, in comparison to epoxidized podocarpus falcatus oil, using Fourier-transform infrared spectroscopy and proton nuclear magnetic resonance spectroscopy. The produced epoxidizing *podocarpus falcatus* seed oil can be substitutes for petrochemical resources because of its sustainable, renewable, and environment-friendly nature.

Keywords Epoxidation · Sugarcane bagasse · Podocarpus falcatus seed oil · Sulfonated solid acid silica catalyst

1 Introduction

Nowadays, the key element and stimulates of searching alternative renewable material that hinders both exhaustion of natural petroleum assets and increased environmental concerns are seeking and fulfilling increasing epoxides from easily available renewable material that help as prime and intercedes chemicals in many manufacturing industries [1, 2]. The derivation of epoxide oil is either from related natural petroleum or vegetable oil sources. Hence, the sustainability and degradability of petroleum epoxy products rising problems like the depletion of natural fossil fuel and instability of oil price [2, 3].

The fabrication sources of plant oil-based vegetable oil for the production of epoxide play a major role in many industries that utilize as a primary source because of its sustainable raw material and eco-environment friendly nature [4, 5]. Thus, most epoxide oil from natural renewable polyunsaturated vegetable oils is edible oil since they have high oil content and are grown in many regions [2]. Besides this, *podocarpus falcatus* seed which is underutilized for any application in industry as well as not used for the production of edible oil commercially can be a strong renewable crop seed feedstock of novel oil-based for industrial since it contains high amount of unsaturation in this seed oil and can convert into epoxide through epoxidation reaction by using catalyst [6–8].

In the industry for epoxidation reaction, most of the homogeneous catalysts with a per carboxylic acid by oxidation with hydrogen peroxide are using for the synthesis of epoxy oil from bio plant vegetable oils [9]. However, most of the problems associated with using this homogeneous catalyst are toxic residues released, causing environmental issues, and separation of the desired product and the catalyst [10]. Therefore, nowadays replacement of homogeneous by heterogeneous catalysts is being investigated by different

✉ Yigezu Mekonnen Bayisa
yigezu338@gmail.com

[1] School of Chemical Engineering, Jimma Institute of Technology, Jimma University, Jimma, Oromia, Ethiopia

scholars for solving the above-raised problem because of its being environmentally friendly and efficient [11].

Despite this advantage, the silica-based sulfonated catalyst is not widely used especially for epoxidation reactions [12]. Therefore, biomass-based material from sugarcane bagasse ash treated as waste can be synthesis silica-based sulfonated catalyst to reduce serious environmental problems.

Therefore, in this study sugarcane bagasse is used for the production of silica-based sulfonated catalyst for epoxidation of *podocarpus falcatus* seed oil.

2 Material and methods

2.1 Materials

Podocarpus falcatus oil was extracted from its seed acquired from Backo Agricultural Research Centre, West Showa area. Once the oil is extracted using organic solvents, n-hexane, purification was carried out using standard procedures [6] and characterized with different techniques. Analytical grade hydrogen peroxide and glacial acetic acid were purchased from Sigma-Aldrich Chemical Company.

2.2 Equipment

Powder X-Ray Diffractometer (XRD-7000) and Thermo-Gravimetric Analyzer (TGA- 4000) were used in Material Science and Engineering laboratory for the synthesis of sulfonated silica catalyst. Fourier-transform infrared spectroscopy analysis was performed on a Nicolet model Protégé 460 Magna IR spectrometer. The analysis of the sulfonated silica catalyst, *podocarpus falcatus* oil, epoxidized *podocarpus falcatus* oil was carried out with analytical grade KBr pellets using the transmission mode. C-NMR spectra were recorded on a 400 MHz Bruker 400 Ultra-Shield spectrometer.

2.3 Synthesis of silica gel and sulfonated silica catalyst

The sugarcane bagasse physical impurities were removed, cleaned, and dried to get rid of the remaining moisture contents. The dried sugarcane bagasse was placed in a muffle furnace at 700 °C for 6 h using crucibles to produce sugarcane bagasse ash. The obtained ash was washed by distilled water and filtered and again dried for 2 h at 100 °C. The dried sugarcane bagasse ash and 200 ml of 1 M NaOH were introduced into a vessel equipped with a stirrer boiling for 1 h. The solution was left overnight and filtered followed by neutralization by dropwise addition of 0.6 M HCl resulting in pH of 7.0, and then allowed to stand for 1 day to form hydrogel. A 30 ml of distilled water was slowly added into the gel under stirring for 10 min. The gel was then parted and dried in oven at 100 °C for 6 h, and the resulted in solid silica was ground into powder. Finally, the sulfonated silica catalyst was prepared according to the procedure reported in [13]. The sulfonated silica catalyst was prepared by sulfonation of silica gel with H_2SO_4. Forty grams of slurry of silica gel was placed in 500 ml beaker. Then, 200 ml of diethyl ether was added into the sample holder beaker. Then, 12 ml of H_2SO_4 was slowly added to the mixture and covered with aluminum foil. The solution was shaken well for 5 min to distribute the H_2SO_4 in whole surface of the silica gel by the help of diethyl ether. Then, the sample mixture was placed on water bath that operated at 36 °C. The diethyl ether was slowly evaporated from the solution mixture. The remained sample was allowed to dry at atmospheric condition.

2.4 Characterization of sulfonated silica catalyst

The prepared catalyst was characterized by using an X-ray diffractometer (XRD), thermogravimetric analyzer, and a Fourier-transform infrared (FTIR) spectroscopy. The acid density, porosity, and specific area of the sulfonated silica catalyst were determined.

2.5 Epoxidation experiments

Epoxidation of *podocarpus falcatus* seed oil was carried out in a 100 ml three-neck glass reactor equipped with MSH-D hotplate magnetic stirrer, time controller, and thermometer. The epoxidation experiment was carried out by adding the mixture of *podocarpus falcatus* seed oil, acetic acid (peroxy acid), and sulfonated silica catalyst. To start the epoxidation, hydrogen peroxide solution was gradually changed into the mixture within 30 min and stirred at a constant stirring speed of 1200 rpm for all test runs. The experiments were planned to investigate the optimum conditions for conversion of oil to epoxy and to study the effects of the variables on the reactions, such as hydrogen peroxide to oil ratios, reaction temperature, reaction time, and catalyst loading. Then, analysis of physicochemical properties of epoxidized p. falcatus seed oil (formed product) such as functional group by FT-IR test and C-NMR spectroscopy was studied.

2.6 Analytical methods

The overall values of produced epoxidized *p. falcatus* seed oil were analyzed by calculating the relative conversion to oxirane of the samples. The relative conversion to oxirane implies that the total amount of desired epoxidized oil formed per total amount of limiting reactant consumed. It was calculated as follows;

Journal : Large 13399 | Article No : 2082 | Pages : 9 | MS Code : 2082 | Dispatch : 17-11-2021

Table 1 Independent variables and levels used for the epoxidized oil production

Variables	Temperature (°C)	Time (h)	Hydrogen peroxide to oil ratio (mole/mole)	Catalyst loading Wt%
Levels	60	2	1:1	2
	80	6	4:1	8

Table 2 Physical properties of silica gel and sulfonated silica catalyst

Properties	Silica gel	Sulfonated silica
Porosity	0.52 ± 0.02	0.49 ± 0.01
Bulk density(g/ml)	0.54 ± 0.01	0.57 ± 0.01
Specific surface area (m^2/g)	352 ± 0.92	337 ± 0.85
Total acid density (millmole/g)		0.59 ± 0.05

$$conversion \text{ to oxirane, COC,} = \frac{OO_C}{OO_{th}}$$

where OO_C is oxirane oxygen content of the epoxidized oil determined by experiment and OOC_{th} is the theoretical value of oxirane oxygen content of the oil; their values were determined according to the method reported in [8].

2.7 Experimental design

Response surface methodology was used to determine the effects of parameters on the epoxidation of *podocarpus falcatus* seed oil. A Box-Behnken design with three numerical factors on four levels was used (Table 1).

3 Result and discussion

3.1 Physical property synthesized sulfonated silica catalyst from sugarcane bagasse

Physical properties: porosity, density, and specific surface area of silica gel and SS catalyst were determined.

As indicated from Table 2, the density of silica gel was lower than that of sulfonated silica catalyst, but porosity was higher than the porosity of sulfonated silica catalyst. This indicates that after the modification of silica gel with H_2SO_4, some pore space of catalyst was reduced by attachment of particles; this was due to the introduced sulfonic group.

The specific surface area of silica gel was 352.01 m^2/g that was in the range value (350–450) m^2/g of silica gel specification. However, the specific surface area of the sulfonated silica catalyst was 337.42 m^2/g that was lower than that of silica gel. This indicates that some portion of porous media was reduced by attachment of the particles. The catalysts with a small specific surface area are good in the epoxidation reaction of epoxide production. As the result of total acid density in solid acid catalysts indicated in Table 2, the concentration of proton or hydrogen ion distributed on the surface of the catalyst has high catalytic activity. The epoxidation reaction becomes faster when catalysts have high acid density [12]. The total acid density of sulfonated silica catalyst in this work indicates a good catalytic feature of the catalyst.

3.2 Functional groups found in silica gel and sulfonated silica catalyst

The functional groups' silica gel and catalyst were determined by FTIR spectroscopy as shown in Fig. 1. From this result, the major peaks of silica gel were Si–O vibration modes, Si—O—Si stretching bands, OH stretching and OH bending vibration with absorption band at 1000–1100 1000–1200, 1643.5, and 3400–3600 cm^{-1} respectively. In FTIR spectra of silica sulfonated at 1100–1230, absorption band indicates that overlap of Si–O stretching and O = S = O stretching modes. In FTIR spectra of SS at 1100–1230, absorption band indicates that overlap of Si–O stretching and O = S = O stretching modes. In addition, the absorption at 2356.1 shows sulfonic group attached on silica sulfonated catalyst. This confirmed the presence of sulfonic group on the surface of sulfonated silica catalyst. The FTIR spectra of sulfonated silica catalyst demonstrated a similar feature with the literature reported [14].

3.3 Structural analysis of synthesized sulfonated silica catalyst

Structural analysis of synthesized sulfonated silica catalyst powder was performed by XRD pattern. XRD patterns of SS and silica gel are shown in Fig. 2. In XRD patterns, there was a broad band peak in two-theta (22.5 degrees) that conformed amorphous nature of the silica gel and SS catalyst. The XRD pattern similarity of SS with that of silica gel shows that the amorphous nature of the catalyst was not alerted after the introduction of a sulfonic group [15].

3.4 Thermo-gravimetric synthesized sulfonated silica catalyst

The prepared sulfonated silica catalyst was subjected to thermal stability analyses by thermogravimetric analysis (TGA). Thermal degradation and percent weight loss of the catalyst are shown in Fig. 3. It represents the thermal degradation of sulfonated silica catalyst with increasing temperature with three stages of weight loss of catalyst that is 100, 100–200, and 200–400 °C. The initial sample weight was slowly degraded with increasing temperature [16].

Journal : Large 13399 | Article No : 2082 | Pages : 9 | MS Code : 2082 | Dispatch : 17-11-2021

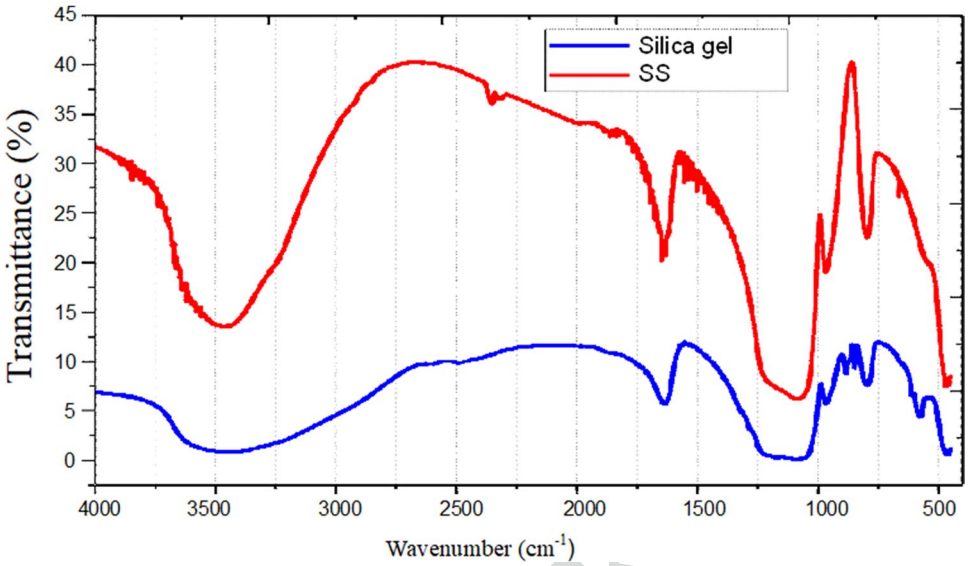

Fig. 1 FTIR spectra of fresh silica gel and sulfonated silica catalyst

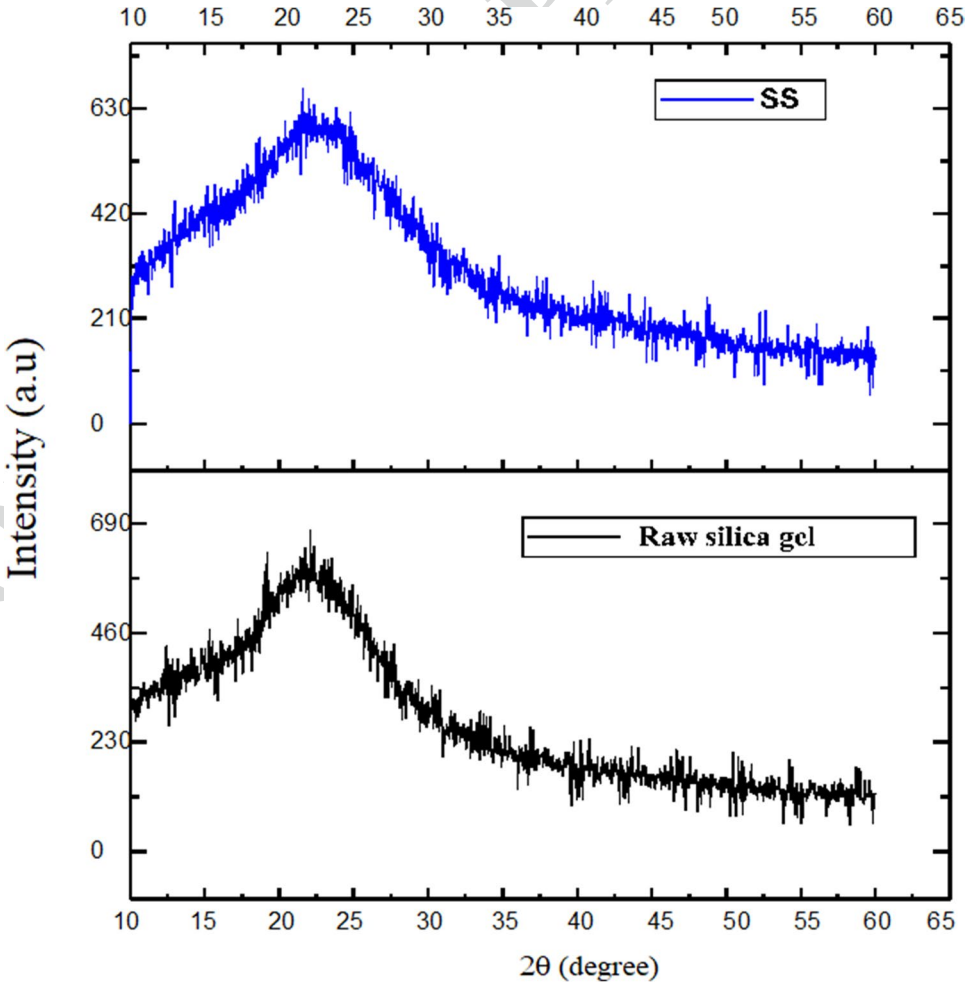

Fig. 2 Powder XRD patterns of silica gel and sulfonated silica catalyst

As it is shown in Fig. 3 until the sulfonated silica catalyst reached a temperature almost at 100 °C, there was only 2.63% of weight loss due to removal of moisture from the catalyst sample. In another way starting from the temperature of 200 to 400 °C, there was rapid weight loss and evolution of SO_2 and OH due to the removal of remaining

Journal : Large 13399 | Article No : 2082 | Pages : 9 | MS Code : 2082 | Dispatch : 17-11-2021

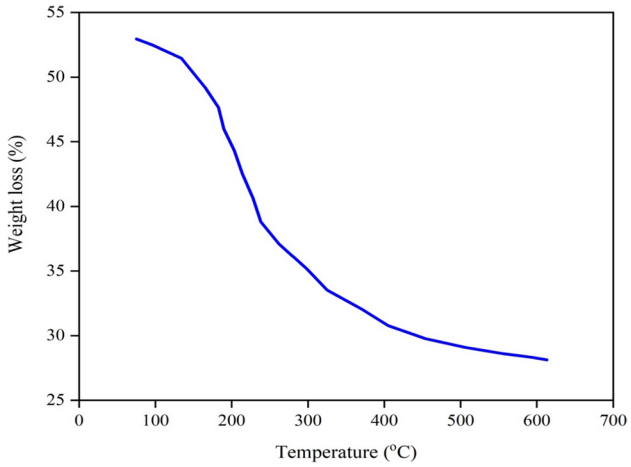

Fig. 3 TGA profile of the sulfonated silica catalyst

moisture, volatile matter, and decomposition of the sulfonic group ($-SO_3H$) [17]. The catalyst weight loss was almost constant beyond 400 °C. The maximum weight loss of the catalyst about 47.58% was illustrated at 647 °C.

3.5 Statistical analysis

The effects of process variables such as reaction temperature, H_2O_2 to $-C=C$-ratio, catalyst load, and epoxidation time were examined as factors to investigate percentage conversion of oxirane of epoxy oil. The complete experiment variables value and experimental responses are presented in Table 3. The ANOVA was carried out to investigate the model terms, select a suitable model, and detect the model equation's significances.

Table 4 shows the models and their significant coefficients of the responses, where all the models are significant at a level of less than 0.0001. The statistical analyses show that quadratic models fit very well into the data for the response and the response was highly significant ($p < 0.0001$). The Model F value of 133.71 implies the model is significant

Table 3 Box-Behnken design experimental results

Run	Temperature (°C)	H_2O_2 to -C=C-ratio (mole/mole)	Catalyst load (Wt%)	Epoxidation time (h)	Conversion to oxirane (%)
1	60.00	1.00	5.00	4.00	75.32
2	80.00	1.00	5.00	4.00	63.93
3	60.00	4.00	5.00	4.00	83.05
4	80.00	4.00	5.00	4.00	66.12
5	70.00	2.50	2.00	2.00	71.1
6	70.00	2.50	8.00	2.00	83.27
7	70.00	2.50	2.00	6.00	83.51
8	70.00	2.50	8.00	6.00	76.12
9	60.00	2.50	5.00	2.00	69.72
10	80.00	2.50	5.00	2.00	66.43
11	60.00	2.50	5.00	6.00	82.71
12	80.00	2.50	5.00	6.00	56.68
13	70.00	1.00	2.00	4.00	78.37
14	70.00	4.00	2.00	4.00	84.16
15	70.00	1.00	8.00	4.00	83.3
16	70.00	4.00	8.00	4.00	82.11
17	60.00	2.50	2.00	4.00	73.84
18	80.00	2.50	2.00	4.00	67.5
19	60.00	2.50	8.00	4.00	81.79
20	80.00	2.50	8.00	4.00	62.4
21	70.00	1.00	5.00	2.00	75.32
22	70.00	4.00	5.00	2.00	82.55
23	70.00	1.00	5.00	6.00	79.695
24	70.00	4.00	5.00	6.00	78.64
25	70.00	2.50	5.00	4.00	83.41
26	70.00	2.50	5.00	4.00	84.75
27	70.00	2.50	5.00	4.00	83.1

Journal : Large 13399 | Article No : 2082 | Pages : 9 | MS Code : 2082 | Dispatch : 17-11-2021

Table 4 Analysis of variance for response surface quadratic model of elative conversion to oxirane of epoxidation reaction of podocarpus falcatus seed oil

Source	Sum of squares	df	Mean square	*F*-value	*p*-value
Model	1667.69	14	119.12	133.71	0.0001
A-Temperature	579.21	1	579.21	650.15	0.0001
B-H_2O_2 to -C=C-ratio	35.69	1	35.69	40.06	0.0001
C-Catalyst	9.21	1	9.21	10.33	0.0074
D-Epoxidation time	6.70	1	6.70	7.52	0.0179
AB	7.67	1	7.67	8.61	0.0125
AC	42.58	1	42.58	47.79	0.0001
AD	129.28	1	129.28	145.11	0.0001
BC	12.18	1	12.18	13.67	0.0030
BD	17.16	1	17.16	19.26	0.0009
CD	95.65	1	95.65	107.36	0.0001
A^2	646.34	1	646.34	725.49	0.0001
B^2	2.08	1	2.08	2.33	0.1526
C^2	8.48	1	8.48	9.52	0.0094
D^2	84.34	1	84.34	94.67	0.0001
Residual	10.69	12	0.8909		
Lack of fit	9.15	10	0.9153	1.19	0.5401
Cor total	1678.38	26			

for conversion of epoxidized podocarpus falcatus seed oil. In this case A, B, C, D, AB, AC, AD, BC, BD, CD, A^2, C^2, and D^2 were found to significantly affect the relative conversion to oxirane of epoxidation reaction of podocarpus falcatus seed oil, while B^2 was not significant as is shown in Table 4. The analysis of variance for the lack of fit test did not show the inadequacy of the model concerning them. Relative conversion to oxirane of epoxidation reaction of *podocarpus falcatus* seed oil ($p > 0.05$), indicating that the model could adequately fit the experimental data.

3.6 Effect of variables on percentage relative conversion to oxirane of epoxy oil

The relative conversion to oxirane of epoxidation reaction of *podocarpus falcatus* seed oil was carried out by varying four process variables namely temperature, the molar ratio of hydrogen peroxide to carbon double of podocarpus falcatus seed oil, catalyst loading, and time where the reaction is conducted with the sulfonated silica catalyst which was prepared from silica gel extracted from sugarcane bagasse ash by sol–gel method and sulfuric acid.

As shown in Fig. 4 (a), the percentage of conversion is significantly affected by the reaction temperature. It can be seen from the figure that with increasing reaction temperature, 60 to70 °C favors increasing relative conversion to oxirane of epoxidation reaction of podocarpus falcatus seed oil until it reaches the maximum temperature. The reason was that the formation of peroxyacetic acid favored when temperatures of epoxidation reaction were at maximum. This resulted in a more rapid epoxidation rate, but also in a higher rate of hydrolysis (oxirane cleavage) of the product which is reactions at lower temperatures had lower rates but gave a more stable oxirane ring [7, 17].

The effect of the H_2O_2 to carbon double mole ratio of *podocarpus falcatus* seed oil on the percentage yield of epoxy was studied in the ratio range 1:1 to 4:1 in Fig. 4 (a) shows that the epoxidation rate increased as the concentration of H_2O_2 in the system increased. This was due to the degradation of the double bond in podocarpus falcatus oil, and the stability of the oxirane ring was very poor using a higher concentration of hydrogen peroxide [18]. Although the maximum conversion was obtained for a mole ratio of 2.5:1, the conversion increased as H_2O_2 increased as it can be observed from the figure which means that hydrogen peroxide to oil molar ratio has a positive effect on the percentage yield.

As it can be seen from Fig. 4 (b), at shorter reaction time the conversion of epoxy oil was increased as catalyst loading increased but as reaction time increases, an increase of catalyst amount leads to minimum epoxy conversion because of the occurrence of side reaction through elongation of reaction and hydrolysis time [9]. In this study, as the reaction time and temperature increase, the conversion decreases with increasing the amount of catalyst. That is when the reaction temperature is above 70 ℃ and when the reaction time exceeds 4 h, the oxirane ring cleavage will occur and the conversion will decrease and this result agrees with the reported work of [1, 19].

Journal : Large 13399 | Article No : 2082 | Pages : 9 | MS Code : 2082 | Dispatch : 17-11-2021

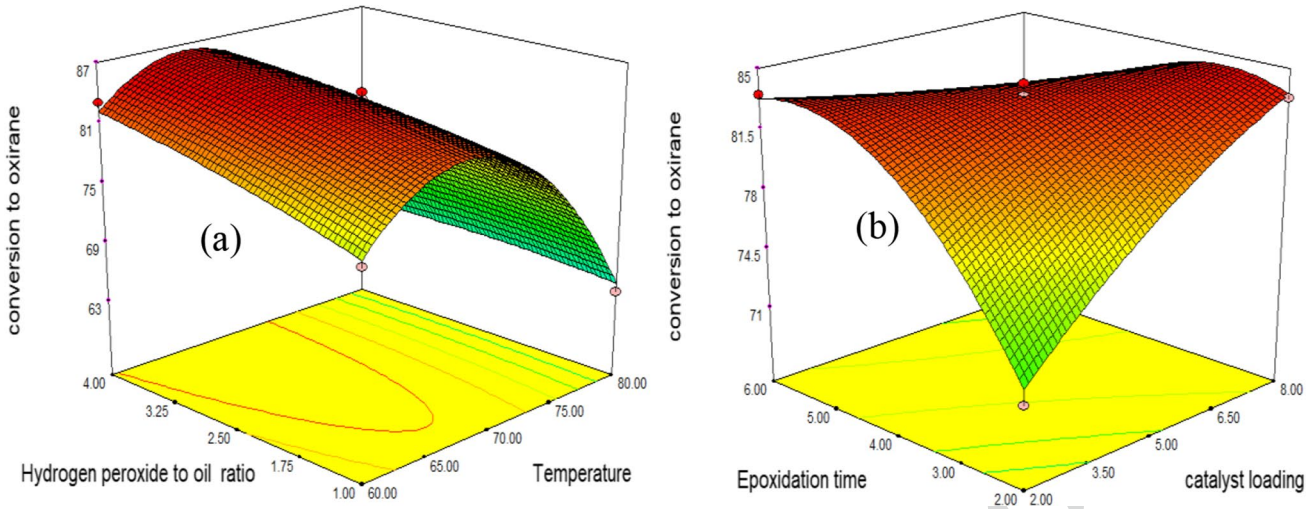

Fig. 4 Percentage of conversion of oxirane versus (**a**) temperature (°C) and hydrogen peroxide to oil ratio (mole/mole), (**b**) epoxidation time (h) and catalyst loading (w/w)

3.6.1 Characterization of epoxidized *p. falcatus* seed oil

3.6.2 FTIR analysis for epoxidized Podo Carpus Falcatus seed oil

The production and characterization of epoxidized podocarpus falcatus oil were analyzed in this study with a special focus on the characterization of the desired product at optimum condition by FTIR (Fourier-transform infrared spectrometry) spectrum analysis. As it is shown in Fig. 5, it is investigated by using FTIR by observing the existence of new peaks and the presence of a new peak in the FTIR spectra of epoxidized podocarpus falcatus seed oil at 823.4 cm^{-1}, attributed to the epoxy group, corroborated the conclusion that is the success of the epoxidation reaction of podocarpus falcatus seed oil. The epoxy groups were found in epoxidized podocarpus falcatus seed oil (doublet at 823 cm^{-1} and 843 cm^{-1}) indicating that nearly all of the carbon double bonds turned into epoxy groups [20] reporting the presence of epoxy groups at 822–833 cm^{-1}, which agrees well with this study.

3.6.3 C-NMR spectrum analysis of epoxidized *podocarpus falcatus* seed oil

The new signal peaks appeared in epoxidized *p. falcatus* oil were assigned at 57.35–57.07 ppm and 54.99–54.38 ppm

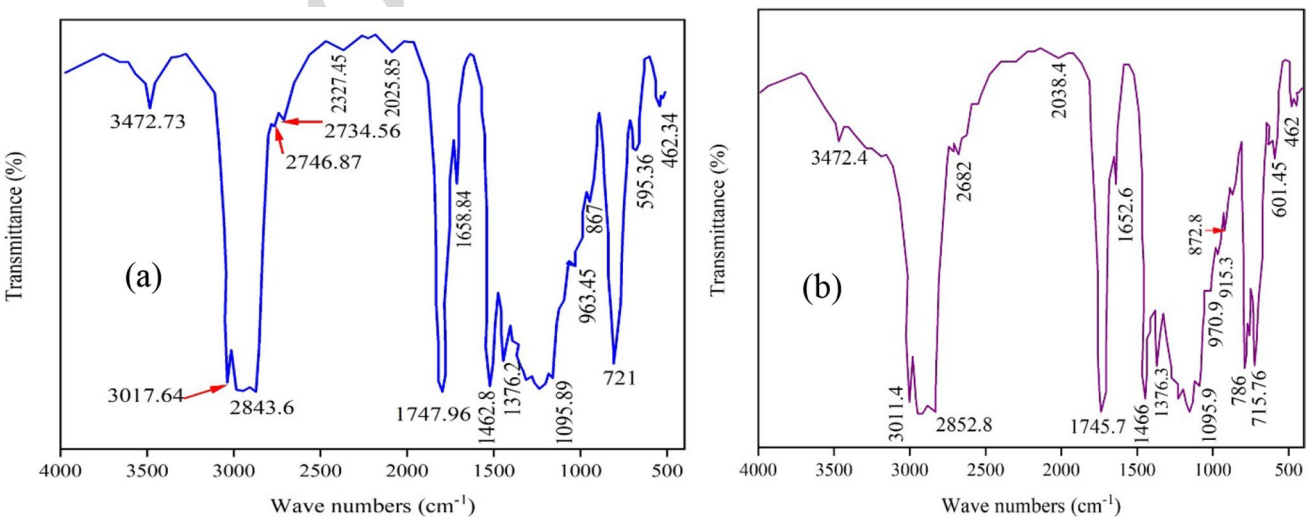

Fig. 5 FTIR spectrum of (**a**) podocarpus falcatus seed oil, (**b**) epoxidized podocarpus falcatus seed oil

Journal : Large 13399 | Article No : 2082 | Pages : 9 | MS Code : 2082 | Dispatch : 17-11-2021

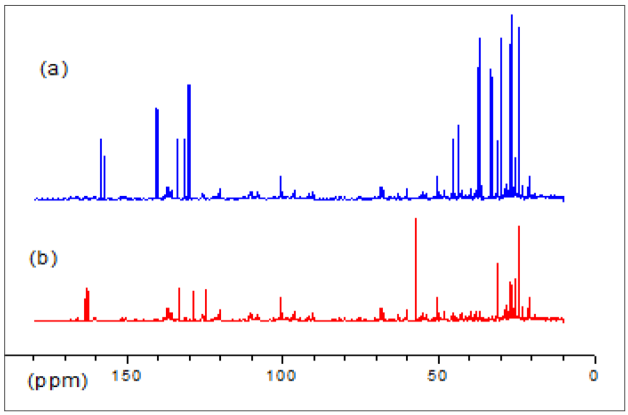

Fig. 6 Spectrum C-NMR for (**a**) *Podocarpus falcatus* oil, (**b**) epoxidized *podocarpus falcatus* oil

whereas the peaks at 133.24–132.41 ppm, 130.28–129.70 ppm, and 128.51–127.32 ppm are representing the double bond in *p. falcatus* oil as is shown in Figure 6 (b) and (a) respectively. As observed in Figure 6 between the regions of 163.64 and 162.76 ppm, the emergence of many carbons of new ester groups has occurred; meanwhile short peak at 133.51–124.09 ppm (corresponding to carbon carbon double bond) also indicates the conversion of the double bond in epoxidized podocarpus falcatus oil compare with the podocarpus falcatus oil spectrum [21]. The C-NMR spectrum analysis was confirmed that epoxy groups were found in epoxidized podocarpus falcatus seed oil [22].

4 Conclusion

In this research, epoxidized vegetable oil was produced from podocarpus falcatus seed oil by using an epoxidation reaction. The reaction was carried out with peroxyacetic acid in the presence of sulfonated silica as a heterogeneous solid acid catalyst converting the original double bond into a three-membered epoxide (oxirane) ring. The effect of process variables such as reaction temperature, the molar ratio of hydrogen peroxide to carbon double bond of oil, catalyst loading, and reaction time on the yield of epoxidized p. falcatus oil based on iodine value was investigated.

The main objective of this research was to produce and characterize epoxidized podocarpus falcatus seed oil by new synthesized sulfonated silica catalysts from sugarcane bagasse ash that have high activities on epoxidation. Synthesized catalysts were physically and chemically characterized considering bulk density, acid density, TGA, XRD, and using Fourier-transform infrared spectroscopy (FTIR).

From the experimental results, the maximum epoxy conversion of 84.75% was obtained using the temperature of 70 °C, hydrogen peroxide to oil molar ratio of 2.5:1, using catalyst 5 (%w/w) at 4-h reaction time. In addition, FTIR and C-NMR spectrum analysis characterization of produced epoxy oil confirmed that of standard IR spectra.

Acknowledgements We would like to acknowledge the XRD and FT-IR platform at the Faculty of Material Science and Engineering, Jimma University, for support in the FT-IR spectroscopy.

Declarations

Conflict of interest The authors declare no competing interests.

Credit author statement Yigezu Mekonnen is responsible for writing — review and editing, supervision, and ensuring that the descriptions are accurate and agreed by all authors. Werku Aweke for investigation, Software and Methodology agreed by all authors.

References

1. Mungroo R, Pradhan NC, Goud VV, Dalai AK (2008) Epoxidation of canola oil with hydrogen peroxide catalyzed by acidic ion exchange resin. JAOCS, J Am Oil Chem Soc 85(9):887–896
2. Campanella A, Baltanás MA (2005) Degradation of the oxirane ring of epoxidized vegetable oils in liquid-liquid systems : ii. Reactivity with solvated acetic and peracetic acids 216:211–216
3. Samarth NB, Mahanwar PA, Samarth NB, Mahanwar PA, Appl A, Res S. Available online a t www.scholarsresearchlibrary.com Scholars Research Library Scholars Research Library 2016;8(4):1–7.
4. Anggoro DD, Kumoro AC. Waste cooking oil utilisation as bioplasticiser through epoxidation using inorganic acids as homogeneous catalysts. 2017;56:1861–6
5. Malarczyk-matusiak K, Milchert E. Optimization of selective epoxidation of canola oil with in situ generated peracetic acid. 2018;21(1).
6. Feleke S, Haile F, Alemu A, Abebe S. Characteristics of seed kernel oil from podocarpus. 2012;24(4):512–6
7. Gupta NK, Yadav PKS, Eadara R, Singh RP. Synthesis of epoxy resin from waste ricebran oil. 2015;7(1):21–32
8. Mekonnen Y (2021) Epoxidation of Podocarpus falcatus oil by sulphuric acid catalyst : process optimization and physio-chemical characterization. Am J Chem Eng 9(4):84–90
9. Biermann U, Bornscheuer U, Meier MAR, Metzger JO, Schäfer HJ. Renewable raw materials oils and fats as renewable raw materials in Chemistry Angewandte. 2011;3854–71.
10. Chem JM, Robertson J. Heterogeneous catalysis model of growth mechanisms of carbon nanotubes , graphene and silicon nanowires. 2012;1(1):19858–62
11. Shagufta, Ahmad I, Dhar R (2017) Sulfonic acid-functionalized solid acid catalyst in esterification and transesterification reactions. Catal Surv from Asia. 21(2):53–69
12. Silva VF, Batista LN, Cunha VS, Costa MAS (2017) Production of catalyst to vegetable oil epoxidation from toxic biomass residue. Waste and Biomass Valorization 8(4):1265–1271
13. Sharghi H, Shiri P, Aberi M (2018) An overview on recent advances in the synthesis of sulfonated organic materials, sulfonated silica materials, and sulfonated carbon materials and their catalytic applications in chemical processes. Beilstein J Org Chem 14:2745–2770
14. Thompson AE, Dierig DA, Kleiman R. Characterization of Vernonia galamensis germplasm for seed oil content, fatty acid composition, seed weight, and chromosome number. Ind Crops Prod

[Internet]. 1994;2(4):299–305. Available from: http://www.sciencedirect.com/science/article/pii/092666909490121X
15. Campanella A, Baltan MA. Degradation of the oxirane ring of epoxidized vegetable oils in a liquid – liquid – solid heterogeneous reaction system. 2007;46:210–21.
16. Guo Y, Xiao L, Li P, Zou W, Zhang W, Hou L (2019) Binuclear molybdenum Schi ff -base complex : an e ffi cient catalyst for the epoxidation of alkenes. Mol Catal 475(June):1–7
17. Bakthavachalam A, Beyene SD, Gopal V (2018) Industrial crops & products green epoxy synthesized from Perilla frutescens : a study on epoxidation and oxirane cleavage kinetics of high-linolenic oil. Ind Crop Prod 123(February):25–34
18. Epoksida P, Neopentil D, Sebagai G, Perantara B. Synthesis and characterization of epoxidized neopenthyl glycol diolete as an intermidiate of biolubricant. 2016;20(6):1329–37
19. Performik A, Hong LK, Yusop RM, Salih N, Salimon J. Optimization of the in situ epoxidation of linoleic acid of Jatropha curcas oil with performic acid (pengoptimuman tindakbalas pengepoksidaan in situ asid linoleik minyak jatropha curcas. 2015;19(1):144–54.
20. Petrovic ZS. Optimization of the Chemoenzymatic Epoxidation of Soybean Oil. 2006;83(3).
21. Xia W, Budge SM, Lumsden MD. New ^{1}H-NMR-based technique to determine epoxide concentrations in oxidized oil. 2015;
22. Salih AM, Ahmad M Bin, Ibrahim NA. Synthesis of radiation curable palm oil–based epoxy acrylate: NMR and FTIR spectroscopic investigations. 2015;14191–211.

Journal:	**13399**
Article:	**2082**

Author Query Form

Please ensure you fill out your response to the queries raised below and return this form along with your corrections

Dear Author

During the process of typesetting your article, the following queries have arisen. Please check your typeset proof carefully against the queries listed below and mark the necessary changes either directly on the proof/online grid or in the 'Author's response' area provided below

Query	Details Required	Author's Response
AQ1	Please check "Credit author statement" is captured and presented correctly.	