CHEMICAL ENGINEERING TRANSACTIONS
VOL. 98, 2023
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Sauro Pierucci, Carlo Pirola

ISBN 978-88-95608-97-6; **ISSN** 2283-9216
DOI: 10.3303/CET2398048

Effects of Ethanol Purity and Ethanol-to-Oleic Acid Ratio on the Esterification of Oleic Acid Using 13X Zeolite Heterogeneous Catalyst

Shahd I. Jurmot, Ammar S. Abbas

Chemical Engineering Department, College of Engineering, University of Baghdad, Baghdad. Iraq
ammarabbas@coeng.uobaghdad.edu.iq

The effects of ethanol-to-oleic acid molar ratio and ethanol purity on the yield of biodiesel production were investigated for the esterification of oleic acid. The esterification reaction was conducted in a batch system utilizing 13X zeolite as a catalyst. The molar ratio of ethanol to oleic was studied in a range of 1:1 to 12:1, and the ethanol purity ranged from 80 to 100%. The reaction was conducted at 70 ºC up to 120 min with catalyst loads of 5 wt.%. The yield of ethyl oleate increased from 9.56 % at the 1:1 ethanol-to-oleic molar ratio to 11.13% at the 3:1, then decreased as the ethanol-to-oleic molar ratios increased. The reported water yield was 20.56% at 1:1 and higher values of water yield (roughly, 26 to 27 %) were recorded when higher molar ratios of ethanol-to-oleic molar ratios were used. The results showed that the best ethyl oleate yield was 13.90% achieved at a 3:1 ethanol to oleic acid molar ratio and 100% ethanol purity, and the use of excess ethanol encourages a forward reaction. The conversion of oleic acid was enhanced by increasing the ethanol purity and optimizing the molar ratio of ethanol to oleic acid. The maximum oleic acid conversion was 55.60%, attained at 100% ethanol purity and a 3:1 molar ratio of ethanol to oleic acid. In addition, the kinetic model revealed that the values of the reaction rate constant were 0.00270 and 0.00108 L/mol. min at 70 ºC for the forward and backward reactions, respectively. Moreover, the obtained results of the kinetic model were consistent with the experimental results.

1. Introduction

Global population growth drives an increase in energy demand. The global energy demand is expected to increase by 53% in 2030 compared to 2001 (Jayakumar et al., 2021). Therefore, the use of fossil fuels must be controlled because of their scarcity and environmental consequences. Accordingly, the transition toward sustainable technology has become a requirement (Kumar et al., 2020). Hydropower, wind power, solar power, geothermal power, hydrogen power, nuclear power, and biomass are all viable alternatives to fossil fuels (Hossain et al., 2010,Abbas et al., 2019) Furthermore, several conversion methods are available for fuels made from biomass, including vegetable oil extraction followed by esterification to make biodiesel, conversion of sugar-rich crops to ethanol by fermentation, wood pyrolysis, and hydrothermal upgrading of wet biomass (Demirbas, 2008) In 2017, global biodiesel production was approximately 36 billion litres, and the current yearly biodiesel production in the European Union and the United States is estimated to be 13.5 and 6.9 billion litres, separately (Ewunie et al., 2021).

Notably, the main advantage of using biodiesel is sustainability. The CO_2 emitted during burning is reused by nature for feedstock preparation, which is known as the "Closed Carbon Cycle" or "Carbon Neutral Cycle (Zulqarnain et al., 2021). Biodiesel is known for being biodegradable, renewable, easier to handle because of the higher flashpoint, having lower exhaust emissions, and being a lubricant (Alshahidy et al., 2021,Macawile et al., 2022) . Biodiesel, the alkyl ester of long chain fatty acids (Sahu et al., 2018), is produced through esterification, transesterification, or both processes using an alcohol-based feedstock and catalyst (Krishnan et al., 2022, Wadood et al., 2016, Chuah et al., 2021). Generally, biodiesel is produced in the presence of short-chain alcohols (regularly methanol, ethanol, or butanol) (Casa et al., 2021), vegetable oils, or animal fats, and a catalyst (homogeneous or heterogeneous) (Alismaeel et al., 2018, Tan et al., 2021, Okolie et al., 2022). Homogeneous catalysts are not favored, owing to their slow reaction rate, higher costs for food-grade oils,

Paper Received: 31 October 2022; Revised: 12 January 2023; Accepted: 20 April 2023
Please cite this article as: Jurmot S.I., Abbas A.S., 2023, Effects of Ethanol Purity and Ethanol-to-Oleic Acid Ratio on the Esterification of Oleic Acid Using 13X Zeolite Heterogeneous Catalyst, Chemical Engineering Transactions, 98, 285-290 DOI:10.3303/CET2398048

separation issues, and environmental pollution (Hamza et al., 2021). Heterogenous reaction systems are diphasic, and the recovery of the catalyst only requires a few washing reactions (Narasimhan et al., 2021) بلقيس. Reaction parameters significantly impact biodiesel yields, such as the alcohol-to-oil mole ratio, catalyst load, reaction pressure, temperature, and time (Singh et al., 2021). An excess amount of alcohol is typically added to enhance the forward reaction of the esterification reactions to produce more biodiesel (Neumann et al., 2016, Abbas et al., 2013). Later, the excess alcohol added must be recovered from products to reutilize and purify biodiesel, usually through distillation. However, the separation processes increase energy consumption and the operation cost of biodiesel production (Mohammed et al., 2015). Previous studies of the esterification of oleic acid with a different type of zeolite have used a range of ethanol to oleic acid molar ratios (EOM), from 3:1 to 30:1 (Abbas et al., 2013, Sun et al., 2015, Doyle et al., 2016, Jurmot et al., 2022).

The present work studies the effects of the ethanol purity (EP) and EOM on esterification reactions using 13X zeolite and discusses their influence on biodiesel yield. The impact of water in the reactant mixture is also discussed. This work considers the reaction kinetics and determines the optimal EP and EOM.

2. Materials and methods

The esterification of oleic acid was performed with ethanol and 13X zeolite with a 4.3:1 ratio of silica to alumina, Na content of 6.81 wt.%, surface area of 551.2 m^2/g, and pore volume of 0.25 mL/g. The experiment procedure, apparatus, and measurement details were described previously (Jurmot et al., 2022) and shown in Figure1. First, 150 mL (0.475 mol) of oleic acid and a stochiometric amount of 90% EP (27.6 mL), to have the initial molar ratio of 1:1 for ethanol to oleic acid, were added to the reactor. The experiment was conducted at EOMs of 3:1 to 12:1 with 90% EP, and at an EOM while varying the EP from 80 to 100 wt.%. In addition, 5 wt.% of 13X zeolite was used in all experiments, and the reaction was conducted at 70 °C for up to 120 minutes. The conversion of oleic acid was determined by the acid value (AV), which was calculated using Eq (1) and (2).

$$AV = \frac{mL\ of\ KOH \times N \times 56.1}{weight\ of\ sample} \tag{1}$$

$$X_{oleic\ acid}, \% = \frac{AV_o - AV_t}{AV_o} \times 100 \tag{2}$$

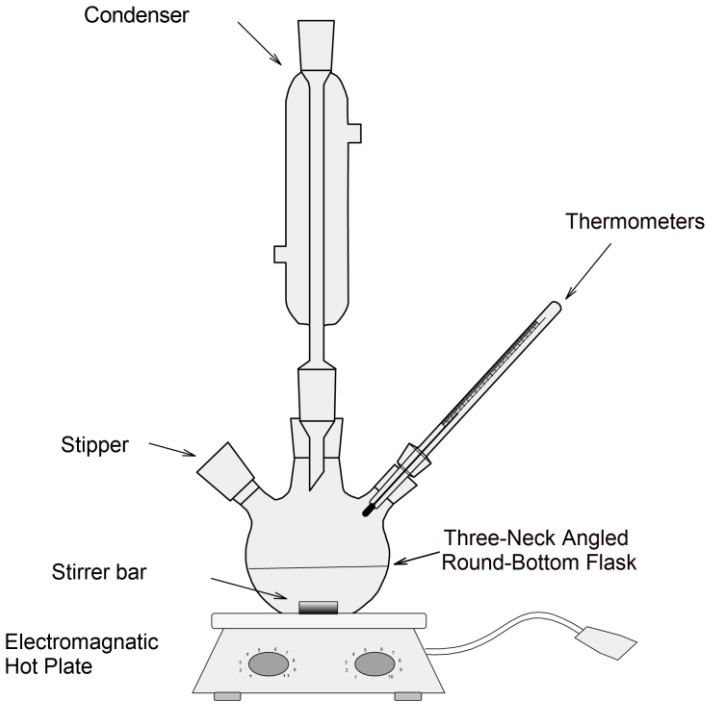

Figure 1: Setup diagram of the batch reactor

The AV is assessed at time t, and AV_0 is the initial acid value (198.66 mL KOH/g for oleic acid) and N is the normality of KOH solution. The concentrations of the reactants (oleic acid and ethanol) and products (ethyl oleate and water) were calculated based on the stoichiometric coefficients (Eq (3)) and the oleic acid conversion (Eq (4) to Eq (7)).

$$Oelic\ acid + Ethanol \leftrightarrow Ethyl\ oleate + Water \tag{3}$$

$$C_{oleic\ acid} = C_{\ initial\ oleic}\left(1 - X_{oleic\ acid}\right) \tag{4}$$

$$C_{ethanol} = C_{\ ethanol}\left(1 - X_{oleic\ acid}\, C_{initial\ oleic}\right) \tag{5}$$

$$C_{ethayl\ \ oleate} = C_{\ initial\ ethayl\ oleate} + X_{oleic\ acid}\, C_{initial\ oleic} \tag{6}$$

$$C_{water} = C_{initial\ water} + X_{oleic\ acid}\, C_{initial\ oleic} \tag{7}$$

Ethyl oleate and water are the products, and their yields can be determined using Eq (8) and Eq (9).

$$Ethayl\ oleate\ yield, \% = \frac{C_{ethyl\ oleate}}{C_{initial\ oleic}} \tag{8}$$

$$Water\ \ yield, \% = \frac{C_{water}}{C_{initial\ oleic}} \tag{9}$$

3. Results and Discussion

3.1 Effect of EOM on esterification reaction

The esterification of oleic acid was conducted at different EOMs and 90% EP. The product analysis was conducted for each molar ratio, summarized in Table 1.

Table 1: The effect of on the esterification reaction products at 90% ethanol purity

EOM	Oleic acid conversion, %	Oleic acid, mol	Ethanol, mol	Ethyl oleate, mol	Water, mol	Ethyl oleate yield, %	Water yield, %
1/1	19.12	0.81	0.59	0.19	0.41	9.56	20.56
3/1	43.42	0.57	1.87	0.43	1.03	11.13	26.52
6/1	61.34	0.39	4.07	0.61	1.94	8.75	27.72
9/1	61.34	0.31	6.31	0.69	2.69	6.88	26.88
12/1	71.77	0.28	8.48	0.72	3.42	5.56	26.49

The product analysis shows that, at stoichiometric amounts of ethanol and oleic acid, the yield of ethyl oleate was 9.56%, which increased to 11.13% at 3:1. After that, the yield decreased to 5.56% with increasing EOM, and the oleic acid conversion was increasing with increasing EOM. The reduction in ethyl oleate yield was caused by the excess amount of ethanol, which was unreacted in the final product, but the excess amount of ethanol positively affected oleic acid conversion (71% at 12:1 ethanol to oleic acid). At the same time the water yield increased at a 3:1 mol ratio to 26.53% and is still close to that value at a 6,9,12 :1 ratio, while it was 20.56% with using stichometry amount of ethanol to oleic acid.

The esterification process is a reversible-reactions, and the chemical equilibrium state could change by subject stress, such as subjecting heat, or changing the volume, causes the reaction to shift toward keeping the equilibrium state of the system. So, the addition of alcohol affects the reaction to make more products according to the principle known principle of Le Châtelier (Mortimer, 2000). Although the highest conversion of oleic acid was obtained at the 12:1 EOM, the highest ethyl oleate yield (11.13%) was achieved at the 3:1 EOM.

3.2 Effect of EP on esterification reaction products

The esterification reaction of oleic acid was conducted using a range of EP (80–100 wt.%) and at 3:1 EOM. The results revealed increased ethyl oleate yield with increasing ethanol purity. At 80% ethanol purity, the yield of ethyl oleate was 8.58%, which increased gradually with increased ethanol purity, with a yield of 13.90% at 100% ethanol purity. Furthermore, the oleic acid conversion simultaneously increased with ethanol purity. The low EP

implies the presence of water in the reactants, which can have adverse effects on the reaction medium. A rapid contact between the water and the catalyst could result in deactivation, and because the esterification reaction is an equilibrium reaction, having a product at the start of the reaction can shift the reactions toward the reactants, reducing the final conversion (Marchetti et al., 2008). The highest yield of ethyl oleate was 13.90%, and the highest conversion was 55.60%, which were both obtained at 100% ethanol purity, and the yield of produced water was reduced with increasing ethanol purity. The results are summarized in Table 2.

Table 2: The effect of EP on the esterification reaction products at 3:1 EOM

Ethanol purity, %	Oleic acid conversion, %	Oleic acid, mol	Ethanol, mol	Ethyl oleate, mol	Water, mol	Ethyl oleate yield, %	Water yield, %
80	34.41	0.66	1.50	0.34	1.51	8.58	37.76
85	38.77	0.61	1.69	0.39	1.33	9.64	33.03
90	43.62	0.56	1.90	0.44	1.10	10.91	27.41
95	49.57	0.50	2.18	0.50	0.86	12.27	21.18
100	55.60	0.44	2.44	0.56	0.56	13.90	13.90

The results indicated that the best condition for the esterification reaction of oleic acid involves extremely pure alcohol (100% ethanol) and a mole ratio of 3:1.

3.3 Kinetics model

The esterification reaction was conducted under the optimal EOM of 3:1 and EP of 100%. The concentration of reactants and products was calculated experimentally using Eq(4) to Eq(7) and Eq (2), and the results were plotted versus time, as shown in Figure 2. The oleic acid concentration starts at 1 mol and ethanol starts at 3 mol. Their concentrations decrease with time, and the ethyl oleate and water appear. The final concentration for oleic acid and ethyl oleate was 0.44 and 2.44 mol, respectively. The final concertation of products was 0.55 mol. A pseudo-homogeneous bimolecular reversible reaction was proposed to characterize the reaction rate. Furthermore, the noncatalyzed reaction rates were neglected. The reaction rate is expressed in Eq (10).

$$-r_{oleic\ acid} = -\frac{d\,C_{oleic\ acid}}{dt} = k_1 [C_{oleic\ acid}]\,[C_{ethanol}] - k_2 [C_{ethyl\ oleate}]\,[C_{water}] \quad (10)$$

$C_{oleic\ acid}$, $C_{ethanol}$, $C_{ethyl\ oleate}$, and C_{water} denote the concentrations of oleic acid, ethanol, ethyl oleate, and water and k_1 and k_2 refer to the reaction rate constants for the forward and backward reactions. k_1 and k_2 were calculated mathematically as 0.00270 and 0.00108 L/mol.min at 70 ºC, respectively. The kinetic model equation (Eq (10)) was applied to predict the concentration of reactants and products, and the predicted and experimental results were compared, as shown in Figure 2.

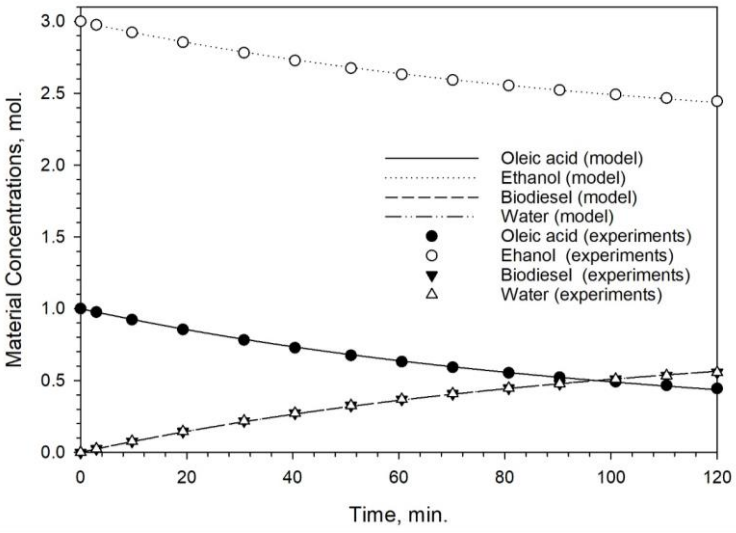

Figure 2: The concentration distribution of the materials with time at 3:1 ethanol to the EOM using ethanol EP of 100% at 70 ºC and 120 min

Figure 2 shows that the results predicted by the kinetic model matched the experimental results, and the kinetic model was solved accurately. In addition, the correlation coefficient and variance were 0.9998 and 1.0095, respectively.

4. Conclusions

The impacts of the EOM and EP on biodiesel production were investigated for the esterification reaction of oleic acid. The study was conducted at 70 ºC for up to 120 min using 5 wt.% of 13X zeolite with EOMs ranging from 1:1 to 12:1 and ethanol purities of 80–100%. The product analysis showed that the yield of ethyl oleate was 9.56% at the 1:1 EOM and increased to 11.13% at the 3:1 EOM, then decreased with increasing EOMs. The water yield was 20.56% for the EOM of 1:1 and higher values were reported when higher values of EOM were used. Overall, there was an optimal EOM for maximizing the product yield in the esterification reaction. Moreover, the ethyl oleate yield, water content, and conversion of oleic acid increase with increasing ethanol purity. The highest yield of ethyl oleate was 13.90%, and the highest oleic acid conversion was 55.60%, which were both obtained at 100% EP with a 3:1 EOM. The yield of ethyl oleate is higher when EP is closer to 100%, which implies no water content in the initial mixture of reactants. Therefore, the optimal EOM and EP for obtaining the highest yield of biodiesel was 3:1 and 100%. The kinetic model of the esterification reaction at 70ºC for 120 min using 5 wt.% of the catalyst at a 3:1 EOM mole ratio with 100% EP was solved. The values of the rate constants were 0.00270 and 0.00108 L/mol.min for the forward and backward reactions, respectively.

Nomenclature
$C_{ethanol}$ – concentration of ethanol, mol
$C_{ethyl\ oleate}$ – concentration of ethyl oleate, mol
$C_{initial\ ethanol}$ – initial concentration of ethanol, mol
$C_{initial\ ethyl\ oleate}$ – initial concentration of ethyl oleate, mol
$C_{initial\ oleic}$ – initial concentration of oleic acid, mol
$C_{initial\ water}$ – initial concentration of water, mol
$C_{oleic\ acid}$ – concentration of oleic acid, mol
C_{water} – concentration of water, mol
k_1 – forward reaction rate constant, L/mol.min
k_2 – backward reaction rate constant, L/mol.min
t – time, minutes
$X_{initial\ oleic}$ – initial conversion amount of oleic acid, -
$X_{oleic\ acid}$ – conversion amount of oleic acid, -

References

Abbas, A. S.; Abbas, R. N. Kinetic Study and Simulation of Oleic Acid Esterification in Different Type of Reactors, *Iraqi Journal of Chemical and Petroleum Engineering*, v.14, p.13–20, 2013.

Abbas, A. S.; Hussein, M. Y.; Mohammed, H. J. Preparation of solid catalyst suitable for biodiesel production,*Plant Archives*, v.19, p.3853–3861, 2019.

Casa, M.; Prizio, C.; Miccio, M. Biodiesel production from tomato seed by transesterification with Alkaline and 'Green' catalysts: Simulation and discussion, *Chemical Engineering Transactions*, v.87, p.451–456, 2021.

Alismaeel, Z. T.; Abbas, A. S.; Albayati, T. M.; Doyle, A. M. Biodiesel from batch and continuous oleic acid esterification using zeolite catalysts,*Fuel*, v.234, p.170–176, 2018.

Alshahidy, B. A.; Abbas, A. S. Comparative study on the catalytic performance of a 13X zeolite and its dealuminated derivative for biodiesel production,*Bulletin of Chemical Reaction Engineering & Catalysis*, v.16, p.763–772, 2021.

Chuah, L. F.; Klemeš, J. J.; Bokhari, A.; Asif, S. A Review of Biodiesel Production from Renewable Resources: Chemical Reactions,*Chemical Engineering Transactions*, v.88, p.943–948, 2021.

Demirbas, A. *Biodiesel: A realistic fuel alternative for diesel engines*, *Biodiesel: A Realistic Fuel Alternative for Diesel Engines*. Springer-Verlag London Limited Apart, 2008.

Doyle, A. M.; Albayati, T. M.; Abbas, A. S.; Alismaeel, Z. T. Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin, *Renewable Energy*, v.97, p.19–23, 2016.

Ewunie, G. A.; Morken, J.; Lekang, O. I.; Yigezu, Z. D. Factors affecting the potential of Jatropha curcas for sustainable biodiesel production: A critical review, *Renewable and Sustainable Energy Reviews*, v.137, p.110500, , 2021.

Hamza, M.; Ayoub, M.; Shamsuddin, R. Bin; Mukhtar, A.; Saqib, S.; Zahid, I.; Ameen, M.; Ullah, S.; Al-Sehemi, A. G.; Ibrahim, M. A review on the waste biomass derived catalysts for biodiesel production, *Environmental Technology and Innovation*, v.21, p.101200, 2021.

Hossain, A. B. M. S.; Boyce, A. N.; Salleh, A.; Chandran, S. Impacts of alcohol type, ratio and stirring time on the biodiesel production from waste canola oil,*African Journal of Agricultural Research*, v.**5**, p.1851–1859, 2010.

Jayakumar, M.; Karmegam, N.; Gundupalli, M. P.; Bizuneh Gebeyehu, K.; Tessema Asfaw, B.; Chang, S. W.; Ravindran, B.; Kumar Awasthi, M. Heterogeneous base catalysts: Synthesis and application for biodiesel production – A review, *Bioresource Technology*, v.331, 2021.

Jurmot, S. I.; Abbas, A. S. Kinetics and Activation Complex Thermodynamic Study of the Acidity Removal of Oleic Acid via Esterification Reaction on Commercial 13X Zeolite,*Iraqi Journal of Chemical and Petroleum Engineering*, v.**23**, p.43–49, 2022.

Krishnan, S. G.; Pua, F. L.; Tan, E. S. Synthesis of Magnetic Catalyst Derived from Oil Palm Empty Fruit Bunch for Esterification of Oleic Acid : An Optimization Study,*Bulletin of Chemical Reaction Engineering & Catalysis*, v.**17**, p.65–77, 2022.

Kumar, G.; Lay, C. H.; Kim, S. H.; Ponnusamy, V. K. Recent developments on alternative fuels, energy and environment for sustainability,*Bioresource Technology*, p.124010, 2020.

Li Voti, M.; Bax, C.; Marzocchi, M.; Sironi, S.; Capelli, L. Testing procedure for performance evaluation of electronic noses for environmental odour monitoring,*Chemical Engineering Transactions*, v.**68**, p.277–282, 2018.

Macawile, M. C.; Durian, A.; Rubi, R. V.; Quitain, A.; Kida, T.; Tan, R.; Razon, L.; Auresenia, J. Green Synthesis, Characterization, and Catalytic Activity of Amine-multiwalled Carbon Nanotube for Biodiesel Production, *Bulletin of Chemical Reaction Engineering & Catalysis*, v.17, p.286–303, 2022.

Marchetti, J. M.; Errazu, A. F. Comparison of different heterogeneous catalysts and different alcohols for the esterification reaction of oleic acid, *Fuel*, v.87, p.3477–3480, 2008.

Mohammed, W. T.; Jabbar, M. F. A. Esterification of Free Fatty Acid with High Chain Alcohol for Biodiesel Production Using Semi-Batch Reactive Distillation,*Iraqi Journal of Chemical and Petroleum Engineering*, v.**16**, p.11–19, 2015.

Mortimer, R. G. *Physical Chemistry*,*Chemical Physics Letters*. Academic Press, 2000.

Narasimhan, M.; Chandrasekaran, M.; Govindasamy, S.; Aravamudhan, A. Heterogeneous nanocatalysts for sustainable biodiesel production: A review, *Journal of Environmental Chemical Engineering*, v.9, p.104876, 2021.

Neumann, K.; Werth, K.; Martín, A.; Górak, A. Biodiesel production from waste cooking oils through esterification: Catalyst screening, chemical equilibrium and reaction kinetics, *Chemical Engineering Research and Design*, v.107, p.52–62, 2016.

Okolie, J. A.; Ivan Escobar, J.; Umenweke, G.; Khanday, W.; Okoye, P. U. Continuous biodiesel production: A review of advances in catalysis, microfluidic and cavitation reactors, *Fuel*, v.307, p.121821, 2022.

Sahu, G.; Gupta, N. K.; Kotha, A.; Saha, S.; Datta, S.; Chavan, P.; Kumari, N.; Dutta, P. A Review on Biodiesel Production through Heterogeneous Catalysis Route, *ChemBioEng Reviews*, v.5, p.231–252, 2018.

Singh, D.; Sharma, D.; Soni, S. L.; Inda, C. S.; Sharma, S.; Sharma, P. K.; Jhalani, A. A comprehensive review of biodiesel production from waste cooking oil and its use as fuel in compression ignition engines: 3rd generation cleaner feedstock, *Journal of Cleaner Production*, v.307, p.127299, 2021.

Sun, K.; Lu, J.; Ma, L.; Han, Y.; Fu, Z.; Ding, J. A comparative study on the catalytic performance of different types of zeolites for biodiesel production, *Fuel*, v.158, p.848–854, 2015.

Tan, W. T.; Jusoh, M.; Zakaria, Z. Y.Starch-derived Solid Acid Catalyst for Biodiesel Production: A Mini Review,*Chemical Engineering Transactions*, v.89, p.487–492, 2021.

Wadood, P.; Mohammed, T. Zirconium Sulfate as Catalyst for Biodiesel Production by Using Reactive Distillation, *Journal of Engineering*, v.22, p.68–82, 2016.

Zulqarnain; Ayoub, M.; Yusoff, M. H. M.; Nazir, M. H.; Zahid, I.; Ameen, M.; Sher, F.; Floresyona, D.; Budi Nursanto, E. A comprehensive review on oil extraction and biodiesel production technologies, *Sustainability (Switzerland)*, v.13, p.1–28, 2021.