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Enhanced biodiesel production via esterification of palm fatty acid distillate (PFAD) using rice husk ash (NiSO₄)/SiO₂ catalyst

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Abstract

Waste or low-cost feedstock utilization for preparing renewable energy is a noble effort towards a greener environment. In this work, palm fatty acid distillate (PFAD), which is usually transacted at a concession rate versus crude palm oil, is esterified to methyl esters. Conventional catalysts are not feasible in the process since PFAD consists of a significant amount of free fatty acids. As such, nickel sulfate supported on waste rice husk ash is utilized to catalyse the reaction under moderate reaction conditions of 15 wt.% catalyst, 5:1 methanol: PFAD (molar ratio) for 7 h, that produces 93% of methyl esters. The prepared catalyst was characterized for thermal stability (TGA), acid strength, surface analysis and compositional analysis via XPS, XRD and FTIR. The esterification of PFAD with NiSO₄/SiO₂ under the optimized reaction conditions of 15 wt.% catalyst, 5:1 methanol to PFAD molar ratio and 7 h reaction time gave the highest methyl esters conversion of 93%. The utilization of low-cost feedstock and waste utilization in catalyst preparation readily implies merits in term of environmental gains and lower cost biodiesel preparation.

Keywords Palm fatty acid distillate · Nickel sulfate · Rice husk ash · Esterification · Biodiesel

Introduction

Undoubtedly, climate change is a natural phenomenon. Most of the models that predict global climate change and the impairments have been quite accurate (Buis 2020). Numerous efforts have been taken to mitigate the adverse effects of climate variation, including the use of renewable energy (Hajjari et al. 2017; Dadak et al. 2016; Aghbashlo et al. 2015), switching to more efficient power sources (Silva and Santos 2019; Backlund et al. 2012), turn to low-carbon sources (Kumar et al. 2019; Roadmap 2011; Bhuyar et al.

2019a). Apart from mitigation, adaptation is crucial in tackling the global issue, yet the impacts are felt locally. As for renewable energy, biodiesel is one of the options which has been successfully implemented in many regions (Mahlia et al. 2020; Jayakumar et al. 2021; Manmai et al. 2020a, b).

Biodiesel has the potential to replace fossil-based fuels and contribute to the mitigation of GHGs emission (Lin et al. 2011; Bhuyar et al. 2019b). Biodiesel from soy oil gives a 57% reduction (on average) in greenhouse gases than fossil diesel, and biodiesel produced from waste grease results in about 86% reduction (EPA 2010). The credibility of biodiesel as a source of low-carbon energy that delivers greenhouse gas savings compared with fossil fuels is a crucial driver of many countries efforts to set standards worldwide for lowering emissions in the future (Saengsawang et al. 2020; Whangchai et al. 2021). Europe demand that 1 in 10 vehicles in their region fuelled with biofuels to cut GHG emission by one-fifth by 2020 and the USA 28% by 2020 (Buckley 2015; Bhuyar et al. 2021). To realize the role of biodiesel in the broader scope, the feedstock and the catalyst cost need to be lowered as much as possible (Nguyen et al. 2020).

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On the other hand, PFAD brownish in colour is produced from the refining process of crude palm oil (CPO). The amount of readily available PFAD is significant, and about 820 360 tonnes of PFAD were produced in Malaysia in the year 2019 as a by-product of palm refining, which processing out 19 516 141 tonnes of CPO annually (MPOB 2019). The greater the amount of CPO is processed, the greater the volume of PFAD is generated. Several researchers have succeeded in esterifying PFA at significantly high conversion (above 90%) (Akinfalabi et al. 2017; Syazwani et al. 2017; Soltani et al. 2017).

Alumina, silica, montmorillonite, organic polymer, and zeolite are some of the supports or precursors used for solid catalysts. These materials have a porous structure and a large surface area (100–1000 m²/g). Any active catalyst must have a large surface area for reactants and products to pass mass quickly and have robust and active phase dispersion (Mansir et al. 2017; Singh and Patel 2014). Due to its ease of handling, abundance, low-cost, and non-corrosive nature, silica is one of the most commonly used cases (Shirini et al. 2013). Amorphous silica has been successfully used as a help in the biodiesel sector in numerous studies. Lin and Radu (2006) patented the use of sulfonic acid aided by mesoporous silica as a concentrated solid acid in a transesterification reaction using tetraethoxysilane (TEOS) silica precursor. Shao and co-authors (Shao et al. 2013) used the sol–gel method to investigate the efficiency of sulphated titania assisted with silica. In terms of cost, current research favours agricultural wastes, specifically rice husk ash (RHA), as a source of silica.

Rice husk ash (RHA) is primarily made up of silica (87–99%) and a small number of inorganic salts (Prasetyoko et al. 2006). RHA was collected during the milling process after the rice husk (outer cover of rice grain) was burned in the air, resulting in agricultural waste. RHA contains a high percentage of silica (87–99%) and cellulose, hemicellulose, lignin, and a small amount of inorganic salt (Hindryawati et al. 2014; Chakraborty et al. 2011). RHA can be an economically viable support for the preparation of silica-based solid acids catalyst because of its high pozzolanic activity and a large amount of silica content (Malek et al. 2021; Feng et al. 2004; Chen et al. 2015). Present study aimed to esterify the methyl esters from Palm fatty acid distillate (PFAD) as a feedstock in the presence of NiSO₄ loaded on RHA-based SiO₂ as a catalyst for the enhanced biodiesel production.

Materials and methods

Material collection

A local palm refinery provided palm fatty acid distillate (PFAD) (Felda Vegetable Oil Products Sdn. Bhd, Pahang,

Malaysia). Our previous paper (Embong et al. 2016) defined the fatty acid profile of PFAD. Rice husk ash (RHA) was obtained from rice mills in Kedah, Malaysia, and used as a source of silica. Bendosen Laboratory Chemicals provided methanol, heptane, sulfuric acid, Hammett indicator (crystal violet, bromophenol blue, and methyl red), and analytical grade hexane (Norway). Sigma-Aldrich (Switzerland) provided the chromatographic grade internal standard (methyl heptadecanoate) NiSO₄·6H₂O, and RM Marketing (Essex) provided the analytical grade titanium dioxide (UK).

Preparation and characterization of catalyst

Preparation of RHA as a silica source

The SiO₂ from RHA was obtained using a method previously published (Hindryawati et al. 2014). The rice husk was washed and heated in a furnace for 4 h at 900 degrees Fahrenheit. The ash was macerated into a fine powder using porcelain mortar. Before washing with 60 mL of 0.1 M HCl for an hour, about 10 g of RHA powder was weighed. The powder was then neutralized (pH7) with deionized water and dried in an oven at 110 °C overnight. The filtered powder (SiO₂) was ready to use in the catalyst as a supporter.

Preparation NiSO₄/SiO₂ catalyst

NiSO₄/SiO₂ was made by impregnating RHA support with an aqueous solution of NiSO₄·6H₂O to achieve a 20% active metal loading. To stimulate the acidity of catalyst and complete dissolution of NiSO₄·6H₂O is attained by adding a suitable amount of 0.2 N H₂SO₄ was added. The metal (salt) and silica slurry were then refluxed for about 3 h (90 °C), dried for 1 day at 110 °C, and calcined for 3 h at 300, 900, and 500 °C (Kim et al. 2013).

Esterification of PFAD using NiSO₄/SiO₂ catalyst

The PFAD was first heated in the range 60–70 °C to be liquefied from its solid state at room temperature. The esterification and transesterification reaction were carried out in a round-bottom flask with the constituent of 3 g of PFAD and varying amount of solid acid catalyst, NiSO₄/SiO₂ with desired oil to methanol molar ratio at a constant temperature with a specific reaction time. The reaction temperature is set up at 110 °C. The esterification reaction was performed with a condenser immersed in an oil bath. Then, the reaction mixture was centrifuged to separate the solid catalysts from the reaction after the stipulated reaction time. *n*-Hexane was used to extract the supernatant. The supernatant could settle down to separate into three layers (*n*-hexane, oil phase consisted of methyl esters, and the aqueous phase contained water, unreacted methanol, and glycerol) and then subjected

to place in a fume hood to remove *n*-hexane. The methyl esters content in the final product is quantified using GC-FID (Agilent 7890A). The methyl ester was determined as stipulated in EN 14103, and the content was quantified as followed by Eq. (1):

$$\text{Methyl ester conversion (\%)} = \frac{A_{\text{total}} - A_{\text{ISTD}}}{A_{\text{ISTD}}} \times \frac{C_{\text{ISTD}} \times V_{\text{ISTD}}}{W_{\text{sample}}} \times 100\% \quad (1)$$

Where A_{total} is the total peak area of methyl esters from C_{12} – C_{18} , A_{ISTD} is the area of methyl heptadecanoate, V_{ISTD} is the volume of methyl heptadecanoate in mL, C_{ISTD} is the concentration of methyl heptadecanoate in mg/mL, W_{Sample} is the weight of sample in mg.

Reusability and leachability test

The reusability of $\text{NiSO}_4/\text{SiO}_2$ catalyst was studied by collecting the remaining solid after each reaction without post-treatment and refluxed with PFAD and methanol for 3 h with stirring. About 3 g catalyst was used for the first run reaction. The catalyst was reused four times while maintaining catalyst amount of 15 wt.%, 15:1 methanol to PFAD and 110 °C of reaction temperature. A leachability test of $\text{NiSO}_4/\text{SiO}_2$ was performed to determine the heterogeneity of the catalyst in the reaction mixture. The $\text{NiSO}_4/\text{SiO}_2$ catalyst (15 wt.%) was refluxed with methanol (15:1 methanol to PFAD molar ratio) without the presence of PFAD. After that, the

liquid was added to 2 g of PFAD and refluxed for 7 h with stirring. The remaining solid catalyst was added to PFAD and refluxed for 7 h.

Results and discussion

Characteristic of PFAD

FFA content and an acid value of PFAD are found to be 91.63% and 183.25 mg KOH/g, respectively. The fatty acids compositions of the PFAD are shown in Table 1. Palmitic acid was the major fatty acid for PFAD. PFAD was found to contain 55.12% saturated fatty acids and 44.88% unsaturated fatty acids. Malaysian PFAD was said to have more than 88% FFA content, as reported by Bonnie and Mohtar (2009). Over the years, intensive research has been done to convert PFAD to biodiesel (Ibrahim et al. 2020; Hidayat 2015; Cho et al. 2012). A breakthrough happened in October 2009 when the world's first continuous large-scale 200 MT/day PFAD biodiesel plant (in Sumatra, Indonesia) had successfully operated by a large Asian-based multinational palm oil group, in which fresh PFAD from the refineries is sent directly to the PFAD biodiesel plant for conversion to biodiesel. In addition, biodiesel made from PFAD was found to meet the European Standards specifications for biodiesel (Cheah et al. 2010).

Characteristic of $\text{NiSO}_4/\text{SiO}_2$ catalyst

Three weight-loss steps were discovered for $\text{NiSO}_4/\text{SiO}_2$ catalyst calcined at 300 °C but only two weight loss when calcined at 500 and 700 °C as illustrated in Fig. 1. The first weight loss was below 100 °C, attributed to water evaporation in the catalyst sample. Weight loss ranging from 300 to 350 °C is due to the preliminary release of sulphur from the catalyst, and the subsequent weight loss ranging from 710 to 780 °C is due to the evolution of SO_3 decomposed from nickel sulphate (Hua et al. 2000). According to the Hammett test, $\text{NiSO}_4/\text{SiO}_2$ was firmly lying in the acidic form ($1.8 < H_0 < 3$) as depicted by Table 2. The FTIR spectra (Fig. 2) for the three-calcination temperature shows the existence of bidentate sulphate ion coordinated to metal like Si^{4+} at the bands around 985 cm^{-1} , 1093 cm^{-1} , 1150 cm^{-1} , 1200 cm^{-1} . However, these bands tend to be overlapped with the characteristic's bands of SiO_2 in the region of $1300\text{--}900 \text{ cm}^{-1}$ (Sohn et al. 2006). Besides, all the catalysts show broad peaks around 3300 cm^{-1} coupled with bands at 1630 cm^{-1} , confirming the existence of adsorbed water. The adsorbed water contributes to the Brønsted acidity after being acidified by the neighbouring cationic Lewis acid site (Gu et al. 2013). The $\text{NiSO}_4/\text{SiO}_2$ calcined at 300 °C has a larger pore size of 177.62 Å compared to

Table 1 Fatty acid composition of PFAD

Fatty acid	Composition (%)		
	This work	(Chang et al. 2016)	(Lokman et al. 2015)
Saturated			
Tridecylic ($C_{13:0}$)	0.13	–	–
Myristic ($C_{14:0}$)	1.13	0.42	1.9
Palmitic ($C_{16:0}$)	48.23	41.25	45.7
Stearic ($C_{18:0}$)	2.5	7.29	4.3
Arachidic ($C_{20:0}$)	–	0.27	–
Docosanoic ($C_{22:0}$)	1.69	0.07	–
Tetracosanoic ($C_{24:0}$)	1.44	0.05	–
Sub total	55.12	49.35	51.9
Unsaturated			
Palmitoleic ($C_{16:1}$)	0.25	–	–
Oleic ($C_{18:1}$)	36.52	41.58	40.2
Linoleic ($C_{18:2}$)	8.11	8.95	7.9
Eicosenoic ($C_{20:1}$)	–	0.04	–
Sub total	44.88	50.57	48.1
Total	100	99.92	100

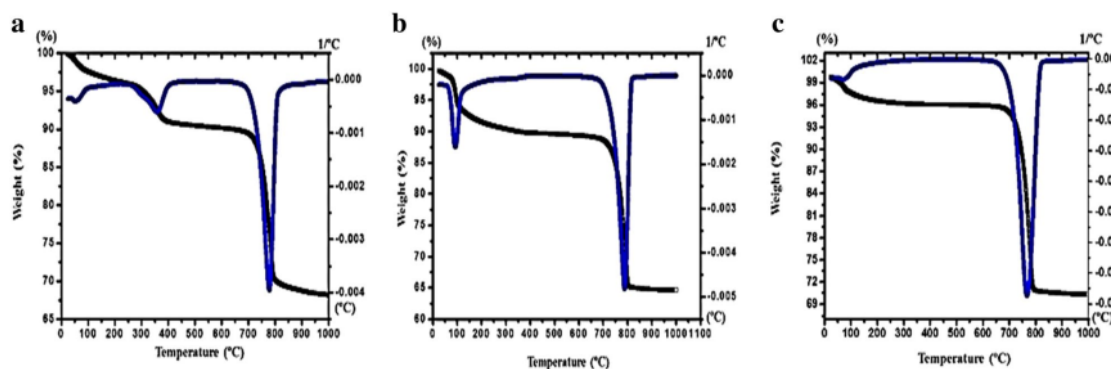


Fig. 1 Thermogram of $\text{NiSO}_4\text{-SiO}_2$: **a** NS300; **b** NS500; **c** NS700

Table 2 Acidic strength of $\text{NiSO}_4/\text{SiO}_2$

Indicator	pH range	Acidic form	Colour change		
			NS300	NS500	NS700
Methyl red	4.2–6.2 Red–Yellow	Red (< 4.2)	Red	Red	Red
Bromophenol blue	3.0–4.6 Yellow–Purple	Yellow (< 3.0)	Yellow	Yellow	Yellow
Crystal violet	0.0–1.8 Yellow–Purple	Yellow (< 0.0); Purple (< 1.8)	Purple	Purple	Purple

Fig. 2 FTIR spectra of NS300, NS500 and NS700

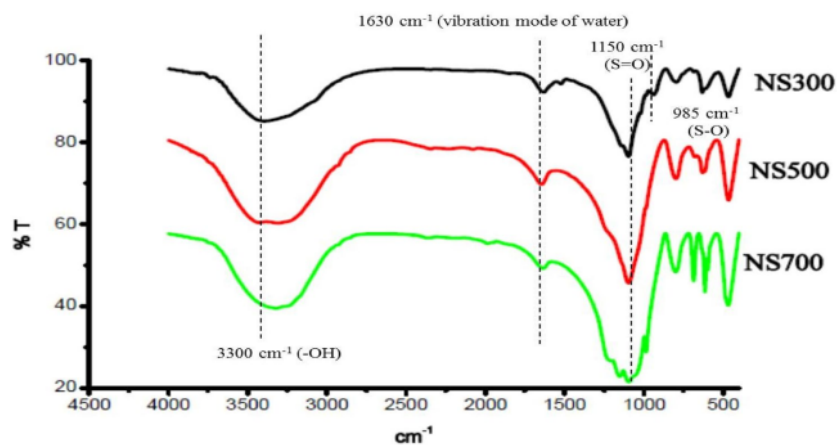


Table 3 Surface area and pore structure analysis of RHA300, NS300, NS500 and NS700

Parameters	RHA300	NS300	NS500	NS700
BET surface area ($\text{m}^2 \text{g}^{-1}$)	14.1997	10.1919	15.6018	12.5449
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.082999	0.045257	0.056779	0.027121
Average pore size (Å)	226.7181	177.6170	145.5708	86.4782

145.57 and 86.4782 Å at 500 and 700 °C (Table 3). The polynucleation of the sulphate species and their condensation on the outer face pores may be the product of calcination at a higher temperature. However, calcination at 500 °C results in a significant increase in pore volume and surface area (Table 2). As the broad sulphate anions are easily deposited on the pore mouth area (Lei et al. 2000), nickel sulphate species are required to decompose to Ni^{2+} and SO_4^{2-} , enhancing

nickel species dispersion by pushing them to pass into inner pores, causing pore deepening.

Jacquin and his co-authors (2008) studied pore structure as a primary requirement for an ideal solid catalyst for biodiesel production because a typical triglyceride molecule has a pore diameter of approximately 58 Å. Furthermore, mesopores (2–50 nm) are favourable to a macromolecule such as oleic acid and palmitic acid diffusing in and out the interior of the catalyst (Shu et al. 2010). The result showed that NiSO₄/SiO₂ cannot stand at higher temperature as at 500 °C above cubic phase of nickel oxide (NiO) appeared (Fig. 3). The XPS spectrum (Fig. 4) indicates Ni, S, Si and O entities in and on the support.

As a result of NiSO₄ species accumulation on the support surface, deceitful agglomeration of support particles to bulky aggregates is depicted in Fig. 5. (RHA). Calcination of NS500 shows that the accumulation of NiSO₄ causes the bulky aggregates to dissociate into agglomerates of small particles. Further calcination of the NiSO₄-SiO₂ catalyst at 700 °C (NS700) results in creating larger particles that appear to be uniformly distributed and result from sulphate polynucleation on the surface as well as nickel crystallite growth. Therefore, the NiSO₄/SiO₂ calcined at 300 °C was selected for the esterification of PFAD in this study.

Fig. 3 XRD patterns of NS300, NS500 and NS700.: NiSO₄ (orthorhombic):NiO (cubic)

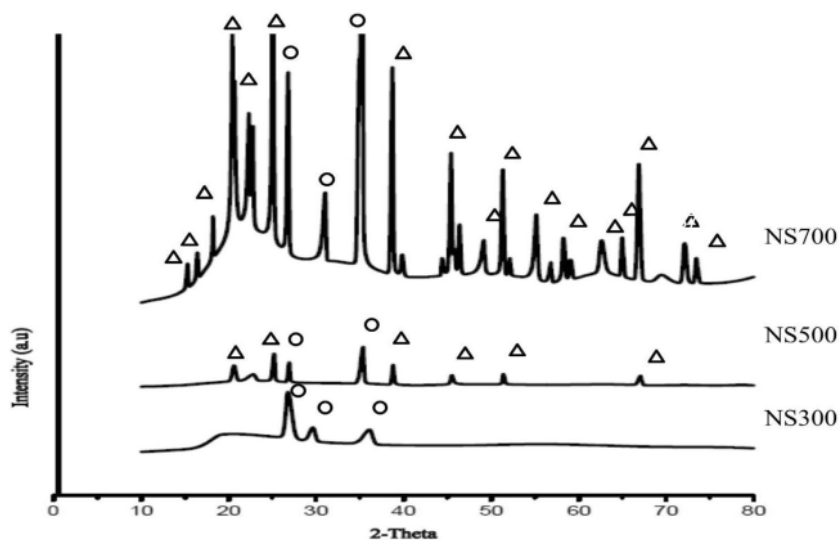
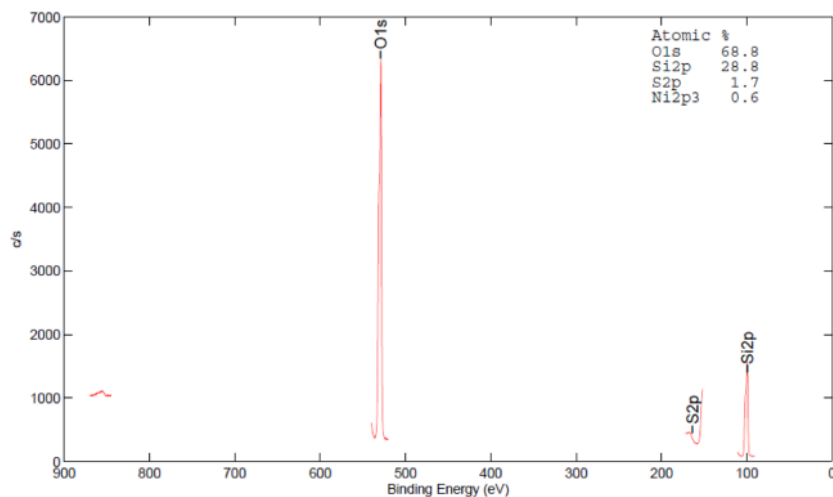


Fig. 4 XPS spectra of NiSO₄-SiO₂



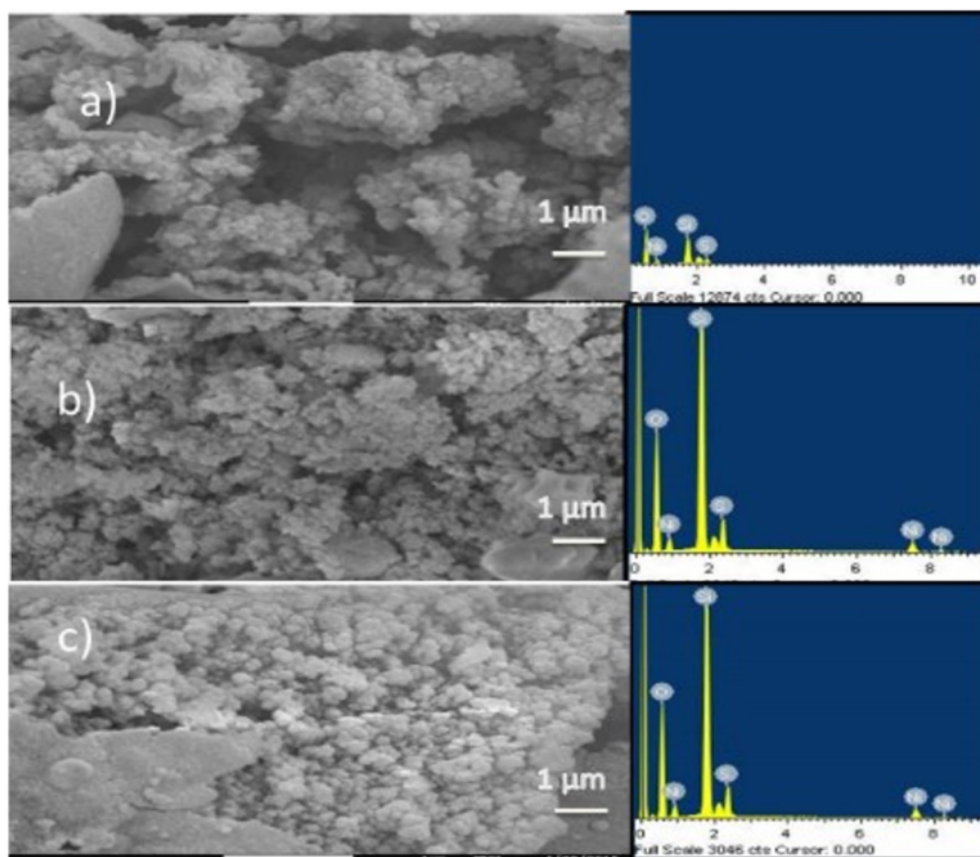


Fig. 5 FESEM-EDX images analysis of **a** NS300, **b** NS500 and **c** NS700

9

Effect of methanol molar ratio on methyl esters conversion

The methyl ester conversion increased with increasing methanol to PFAD molar ratio (Fig. 6). At 15 wt.% NiSO₄/RHA and reaction temperature of 110 ± 5 °C, the results suggest that the ME conversion increase when the MeOH/PFAD molar ratio increase until the conversion rate attained a plateau. In this work, the molar ratio of 5:1 has the highest ME content (83–93%), and the molar ratio of 7:1 has the lowest ME content (77–79%). The higher methanol molar ratio in 5:1 was not efficient to improve the conversion rate. The effect of water formation during the esterification of FFA and a small amount of water already existed in the commercially grade methanol may have influenced the sustainability of the FFA conversion to methyl ester (Nakpong and Wootthikanokkhan 2010; Malek et al. 2020). Hence, the methanol to PFAD molar ratio of 5:1 was selected as the optimum methanol molar ratio in this reaction.

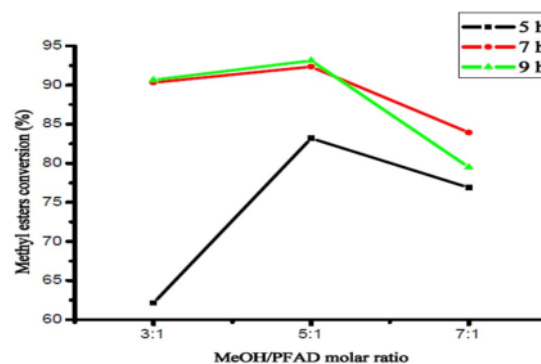


Fig. 6 Effect of MeOH/PFAD molar ratio on methyl esters conversion at 15 wt.% catalyst amount and 110 °C

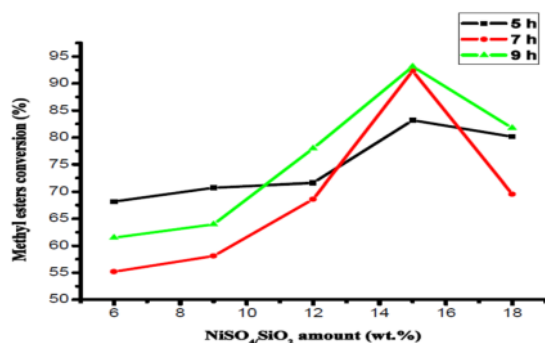


Fig. 7 Effect of catalyst amount on methyl ester conversion conducted at 110 °C with a molar ratio of methanol/PFAD of 5:1

Effect of catalyst amount on methyl ester conversion

Weight ratios of 6–18 wt. % NiSO₄/SiO₂ catalyst to PFAD were analysed in reactions performed at 110 °C with a molar ratio of methanol/PFAD of 5:1 as shown in Fig. 7 to investigate the effect of catalyst number conversion efficiency. When the volume of catalyst was increased, the methyl ester conversion increased until it reached equilibrium. Beyond the equilibrium state, the methyl ester conversion dropped no matter how long the reaction takes place. In this study, the highest methyl ester conversion obtained at 15 wt.% catalyst. If the dosage was surpassed, the reaction equilibrium phenomenon avoided any rise in the overall amount of available catalyst active sites. In this case, the extra dose of solid catalyst affects the stirring effectiveness, disturbing the mixing of reactant (methanol and PFAD), thus lowering the esterification reaction rate. Besides that, too much catalyst provides different active sites to attract the methyl esters produced attached to them. Consequently, lower methyl esters conversions were recorded with a higher amount of catalyst.

Effect of reaction time on methyl ester conversion

The times of reaction duration were varied (5, 7 and 9 h) under the fixed conditions of methanol/PFAD of 5:1, 15 wt.% of catalyst and at the temperature of 110 °C (Fig. 8). The results show that methyl esters yield increased as increasing reaction time. However, once the reaction time exceeded 7 h, the methyl esters did not increase substantially. Therefore, it can be assumed that the FFA conversion to methyl esters as biodiesel accomplished in 7 h with 93% conversion.

Reusability and leachability of catalysts

NiSO₄/SiO₂ catalyst can be reused twice while maintaining methyl esters at about 80% (drop from 90.14% in first

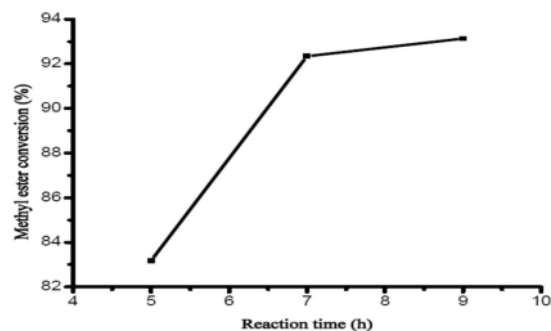


Fig. 8 Effect of reaction time on methyl ester conversion at fix condition of MeOH/PFAD molar ratio 5:1, 15 wt.% and 110 °C

use to 79.85%). The obvious dropped could be due to the leachability of Ni and S, which reduce the number of active sites and, in turn, the reactivity of the catalyst (Ahmad et al. 2021). The ICP-MS results of the methanol sample after separated the catalyst, which undergoes a reaction process (leachability test as prepared in Sect. 2.2), showed that about 2121 ppm (0.2121%) of Ni and 43 ppm (0.0043%) of S leached. To increase the catalyst's recyclability, more study on the active ingredient stability (the anchoring strength of Ni and S on the support) is needed.

Conclusion

The esterification of PFAD with NiSO₄/SiO₂ under the optimized reaction conditions of 15 wt.% catalyst, 5:1 methanol to PFAD molar ratio and 7 h reaction time gave the highest methyl esters conversion of 93%. The prepared catalyst was well characterized and performed well with significantly higher conversion that implies that the catalyst having a significant number of active sites for esterification to takes place. However, more effort is needed in improving the reusability of it beyond two cycles of reusable, by enhancing the stability of Ni and S on the support material. Nevertheless, the production of biodiesel from low-cost PFAD and waste-derived catalyst support is a noble effort towards a greener environment.

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Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

- Aghbashlo M, Tabatabaei M, Mohammadi P, Pourvosoughi N, Nikbakht AM, Goli SAH (2015) Improving exergetic and sustainability parameters of a DI diesel engine using polymer waste dissolved in biodiesel as a novel diesel additive. *Energy Conv Manage* 105:328–337
- Ahmad MS, Cheng CK, Bhuyar P, Atabani AE, Pugazhendhi A, Chi NTL, Juan JC (2021) Effect of reaction conditions on the lifetime of SAPO-34 catalysts in methanol to olefins process—A review. *Fuel* 283:118851
- Akinfalabi SI, Rashid U, Yunus R, Taufiq-Yap YH (2017) Synthesis of biodiesel from palm fatty acid distillate using sulfonated palm seed cake catalyst. *Renew Energy* 111:611–619
- Backlund S, Thollander P, Palm J, Ottosson M (2012) Extending the energy efficiency gap. *Energy Policy* 51:392–396
- Bhuyar P, Rahim MHA, Yusoff MM, Maniam GP, Govindan N (2019a) A selective microalgae strain for biodiesel production in relation to higher lipid profile. *Maejo Int J Energy Environ Commu* 1(1):8–14
- Bhuyar P, Sundararaju S, Rahim MHA, Ramaraj R, Maniam GP, Govindan N (2019b) Microalgae cultivation using palm oil mill effluent as growth medium for lipid production with the effect of CO₂ supply and light intensity. *Biomass Conv Bioref*. <https://doi.org/10.1007/s13399-019-00548-5>
- Bhuyar P, Sundararaju S, Rahim MHA, Maniam GP, Govindan N (2021) Enhanced productivity of lipid extraction by urea stress conditions on marine microalgae *Coelastrum* sp. for improved biodiesel production. *Bioresour Technol Rep* 15:100696
- Board MPO (2019) Refinery: monthly production of selected processed palm oil for the month of december 2019
- Bonnie TYB, Mohtar Y (2009) Characteristics and properties of fatty acid distillates from palm oil. *Oil Palm Bull* 59:5–11
- Buis A (2020) Study confirms climate models are getting future warming projections right. NASA's Jet Propulsion Laboratory
- Chakraborty S, Chowdhury S, Saha PD (2011) Adsorption of Crystal Violet from aqueous solution onto NaOH-modified rice husk. *Carbohydr Polym* 86(4):1533–1541
- Chang AS, Sherazi STH, Kandhro AA, Mahesar SA, Chang F, Shah SN, Panhwar T (2016) Characterization of palm fatty acid distillate of different oil processing industries of Pakistan. *J Oleo Sci*. <https://doi.org/10.5650/jos.ess16073>
- Cheah KY, Toh TS, Koh PM (2010) Palm fatty acid distillate biodiesel. *Int News Fats Oils Relat Mater* 21(5):264–266
- Chen GY, Shan R, Shi JF, Yan BB (2015) Transesterification of palm oil to biodiesel using rice husk ash-based catalysts. *Fuel Process Technol* 133:8–13
- Cho HJ, Kim JK, Hong SW, Yeo YK (2012) Development of a novel process for biodiesel production from palm fatty acid distillate (PFAD). *Fuel Process Technol* 104:271–280
- Buckley C (2015) China pledges to halt growth of carbon emissions in climate plan. *The New York Times*
- da Silva GVA, dos Santos FJM (2019) Energy management system ISO 50001: 2011 and energy management for sustainable development. *Energy Policy* 133:110868
- Dadak A, Aghbashlo M, Tabatabaei M, Younesi H, Najafpour G (2016) Exergy-based sustainability assessment of continuous photobiological hydrogen production using anaerobic bacterium *Rhodospirillum rubrum*. *J Clean Prod* 139:157–166
- Embong NH, Maniam GP, Rahim MHA, Lee KT, Huisingh D (2016) Utilization of palm fatty acid distillate in methyl esters preparation using SO₄²⁻/TiO₂-SiO₂ as a solid acid catalyst. *J Clean Prod* 116:244–248
- EPA (2010) Part II: Environmental Protection Agency 40 CFR. Part 80. Regulation of fuels and fuel additives: changes to renewable fuel standard program. Final Rule 75(58):14669–15320
- Feng Q, Yamamichi H, Shoya M, Sugita S (2004) Study on the pozzolanic properties of rice husk ash by hydrochloric acid pretreatment. *Cem Concr Res* 34(3):521–526
- Gu Y, Liu S, Li C, Cui Q (2013) Selective conversion of glycerol to acrolein over supported nickel sulfate catalysts. *J Catal* 301:93–102
- Hajjari M, Tabatabaei M, Aghbashlo M, Ghanavati H (2017) A review on the prospects of sustainable biodiesel production: a global scenario with an emphasis on waste-oil biodiesel utilization. *Renew Sustain Energy Rev* 72:445–464
- Hidayat A, Rochmadi, Wijaya K, Nurdawati A, Kurniawan W, Hinode H, Yoshikawa K, Budiman A (2015) Esterification of palm fatty acid distillate with high amount of free fatty acids using coconut shell char-based catalyst. *Energy Procedia* 75:969–974
- Hindryawati N, Maniam GP, Karim MR, Chong KF (2014) Transesterification of used cooking oil over alkali metal (Li, Na, K) supported rice husk silica as potential solid base catalyst. *Eng Sci Technol Int J* 17(2):95–103
- Hua W, Xia Y, Yue Y, Gao Z (2000) Promoting effect of Al on SO₂—/MxOy (M=Zr, Ti, Fe) catalysts. *J Catal* 196(1):104–114
- Ibrahim SF, Asikin-Mijan N, Ibrahim ML, Abdulkareem-Alsultan G, Izham SM, Taufiq-Yap YH (2020) Sulfonated functionalization of carbon derived corncob residue via hydrothermal synthesis route for esterification of palm fatty acid distillate. *Energy Conv Manage* 210:112698
- Jacobson K, Gopinath R, Meher LC, Dalai AK (2008) Solid acid catalyzed biodiesel production from waste cooking oil. *Appl Catal B* 85(1):86–91
- Jayakumar S, Bhuyar P, Pugazhendhi A, Rahim MHA, Maniam GP, Govindan N (2021) Effects of light intensity and nutrients on the lipid content of marine microalgae (diatom) *Amphiprora* sp. for promising biodiesel production. *Sci Total Environ* 768:145471
- Kim HJ, Hilger H, Bae S (2013) NiSO₄/SiO₂ catalyst for biodiesel production from free fatty acids in brown grease. *J Energy Eng* 139(1):35–40
- Kumar S, Rawat MK, Gupta S (2019) An evaluation of current status of renewable energy sources in India. *Int J Innov Technol Explor Eng* 8(10):124–1239
- Lei T, Xu JS, Hua WM, Gao Z (2000) New solid superacid catalysts for n-butane isomerization: γ -Al₂O₃ or SiO₂ supported sulfated zirconia. *Appl Catal A* 192(2):181–188
- Lin VSY, Radu DR (2006) U.S. Patent No. 7,122,688. U.S. Patent and Trademark Office, Washington, DC
- Lin L, Zhou C, Saritporn V, Shen X, Dong M (2011) Opportunities and challenges for biodiesel fuel. *Appl Energy* 88(4):1020–1031
- Lokman IM, Rashid U, Taufiq-Yap YH, Yunus R (2015) Methyl ester production from palm fatty acid distillate using sulfonated glucose-derived acid catalyst. *Renew Energy* 81:347–354
- Mahlia TMI, Syazmi ZAHS, Mofijur M, Abas AP, Bilad MR, Ong HC, Silitonga AS (2020) Patent landscape review on biodiesel production: technology updates. *Renew Sustain Energy Rev* 118:109526
- Malek MNFA, Hussin NM, Embong NH, Bhuyar P, Rahim MHA, Govindan N, Maniam GP (2020) Ultrasonication: a process intensification tool for methyl ester synthesis: a mini review. *Biomass Conv Bioref*. <https://doi.org/10.1007/s13399-020-01100-6>
- Malek MNFA, Pushparaja L, Hussin NM, Embong NH, Bhuyar P, Rahim MHA, Maniam GP (2021) Exploration of efficiency of nano calcium oxide (CaO) as catalyst for enhancement of biodiesel production. *J Microbiol Biotechnol Food Sci*. <https://doi.org/10.15414/jmbfs.3935>
- Manmai N, Unpaprom Y, Ramaraj R (2020a) Bioethanol production from sunflower stalk: application of chemical and biological pretreatments by response surface methodology (RSM). *Biomass Conv Bioref*. <https://doi.org/10.1007/s13399-020-00602-7>

- Manmai N, Unpaprom Y, Ponnusamy VK, Ramaraj R (2020b) Bioethanol production from the comparison between optimization of sorghum stalk and sugarcane leaf for sugar production by chemical pretreatment and enzymatic degradation. *Fuel* 278:118262
- Mansir N, Taufiq-Yap YH, Rashid U, Lokman IM (2017) Investigation of heterogeneous solid acid catalyst performance on low grade feedstocks for biodiesel production: a review. *Energy Conv Manage* 141:171–182
- Nakpong P, Wootthikanokkhan S (2010) High free fatty acid coconut oil as a potential feedstock for biodiesel production in Thailand. *Renew Energy* 35(8):1682–1687
- Nguyen TVT, Unpaprom Y, Manmai N, Whangchai K, Ramaraj R (2020) Impact and significance of pretreatment on the fermentable sugar production from low-grade longan fruit wastes for bioethanol production. *Biomass Conv Bioref* 1–13
- Prasetyoko D, Ramli Z, Endud S, Hamdan H, Sulikowski B (2006) Conversion of rice husk ash to zeolite beta. *Waste Manage* 26(10):1173–1179
- Roadmap E (2011) 2050 impact assessment and scenario analysis. European Commission, Brussels 15
- Saengsawang B, Bhuyar P, Manmai N, Ponnusamy VK, Ramaraj R, Unpaprom Y (2020) The optimization of oil extraction from macroalgae, *Rhizoclonium* sp. by chemical methods for efficient conversion into biodiesel. *Fuel* 274:117841
- Shao GN, Sheikh R, Hilonga A, Lee JE, Park YH, Kim HT (2013) Biodiesel production by sulfated mesoporous titania–silica catalysts synthesized by the sol–gel process from less expensive precursors. *Chem Eng J* 215:600–607
- Shirini F, Mamaghani M, Seddighi M (2013) Sulfonated rice husk ash (RHA-SO₃H): A highly powerful and efficient solid acid catalyst for the chemoselective preparation and deprotection of 1,1-diacetates. *Catal Commun* 36:31–37
- Shu Q, Gao J, Nawaz Z, Liao Y, Wang D, Wang J (2010) Synthesis of biodiesel from waste vegetable oil with large amounts of free fatty acids using a carbon-based solid acid catalyst. *Appl Energy* 87(8):2589–2596
- Singh S, Patel A (2014) 12-Tungstoposphoric acid supported on mesoporous molecular material: synthesis, characterization and performance in biodiesel production. *J Clean Prod* 72:46–56
- Sohn JR, Park WC, Shin DC (2006) Characterization of nickel sulfate supported on SiO₂ for ethylene dimerization and promoting effect of Al₂O₃ on catalytic activity. *J Mol Catal A Chem* 256(1):156–163
- Soltani S, Rashid U, Nehdi IA, Al-Resayes SI, Ala'a H (2017) Sulfonated mesoporous zinc aluminate catalyst for biodiesel production from high free fatty acid feedstock using microwave heating system. *J Taiwan Inst Chem Eng* 70:219–228
- Syazwani ON, Ibrahim ML, Kanda H, Goto M, Taufiq-Yap YH (2017) Esterification of high free fatty acids in supercritical methanol using sulfated angel wing shells as catalyst. *J Supercrit Fluids* 124:1–9
- Whangchai K, Inta W, Unpaprom Y, Bhuyar P, Adoonsook D, Ramaraj R (2021) Comparative analysis of fresh and dry free-floating aquatic plant *Pistia stratiotes* via chemical pretreatment for second-generation (2G) bioethanol production. *Bioresour Technol Rep* 14:100651

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