COMPARATIVE EVALUATION OF HOMOGENEOUS AND HETEROGENOUS CATALYSTS IN THE ESTERIFICATION OF WASTE COOKING OIL

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ABSTRACT

Waste cooking oil is a potential raw material for biodiesel production, yet its reuse poses health and environmental risks due to the presence of carcinogenic compounds and high peroxide values. This study aimed to convert waste cooking oil into biodiesel through the transesterification process using different catalysts—acid (HCl), base (NaOH), and heterogeneous (MgO)—combined with pretreatment methods (untreated, bleaching earth, and banana peel adsorption). The reactions were carried out using ethanol as alcohol, followed by homogenization, heating at 60°C for 1 hour, and settling for 24 hours. The results showed that HCl produced the highest biodiesel yield (up to 3.1792 with bleaching earth treatment), followed by MgO and NaOH. Glycerol was obtained as the main by-product, with the highest values also associated with HCl catalysis. Residues were only formed in reactions involving NaOH and MgO due to their heterogeneous and insoluble nature, whereas no residue was found in HCl-based reactions. Pretreatment with bleaching earth significantly improved biodiesel yield compared to banana peel or untreated samples. In conclusion, acid-catalyzed transesterification of pretreated waste cooking oil, particularly with bleaching earth treatment, provides the most effective route for biodiesel production while also generating glycerol as a valuable by-product.

KEYWORDS Catalyst, Esterification, Waste Cooking Oil

INTRODUCTION

Used cooking oil, also known as waste frying oil, contains carcinogenic compounds. Continuous use of waste cooking oil can endanger human health, causing

cancer, fat accumulation in blood vessels, and ultimately reduce cognitive performance. Oxidation occurs, leading to the conversion of unsaturated fatty acids with a cis structure into a trans. Based on peroxide value analysis, there is a correlation between frying frequency and peroxide value; the more frequently oil is used, the higher its peroxide value. Moreover, the peroxide value of repeatedly used oil is significantly higher (Alamsyah et al., 2017).

There are many ways to reduce the risks posed by waste cooking oil, one of which is adsorption, which can restore the oil to a clearer state without diminishing its quality. This process is referred to as regeneration and is considered relatively low cost, effective, and economical. The method of refining used cooking oil using adsorbents and zeolites and moringa seeds, the refined oil shows a fairly good level of purity (Alamsyah et al., 2017).

A conservative solution is to improve the quality of used cooking oil through a purification process using adsorbents such as bleaching earth, charcoal, and coconut shell. The adsorption method is chosen because it is effective, economical, simple, and allows the adsorbent to be regenerated. This process is carried out by adding the adsorbent to the used cooking oil, stirring it, and then filtering it to separate impurities. Through this method, used cooking oil that was initially cloudy can become clearer and suitable for reuse (Ardhani et al., 2024).

In this study, bleaching earth and banana peel were used as adsorbents. Bleaching earth is a natural zeolite-based adsorbent in the form of bleaching clay, where temperature, the amount of bleaching earth, and stirring speed influence its (Ardhani et al., 2024). Banana peels, which are abundantly available in Indonesia, can also be utilized as an adsorbent for waste cooking oil due to their large pore structure, which allows for more effective absorption of undesirable substances in the oil.

Free fatty acids (FFA) in used cooking oil are formed through hydrolysis during frying at temperatures of 160–200°C. Steam generated in the frying process triggers the breakdown of triglycerides into free fatty acids, diglycerides, monoglycerides, and glycerol, which can be identified by an increase in the acid value. Triglycerides, the main lipid component, are fatty acid esters of glycerol. Natural triglycerides from vegetable oils are the primary source for biodiesel production. In general, catalysts used in biodiesel production through transesterification include homogeneous, heterogeneous, and enzymatic catalysts (Ardhani et al., 2024).

Biodiesel is a type of fuel produced from vegetable oils or animal fats through transesterification or esterification with the aid of alcohol and catalysts. Transesterification is a chemical process that converts large, branched triglyceride molecules from vegetable oils and fats into smaller, straight-chain molecules that are structurally like diesel fuel molecules (Hadrah et al., 2018).

In biodiesel production, a pretreatment step is necessary to reduce the free fatty acid (FFA) content of waste cooking oil. A high acid value reduces biodiesel yield because it complicates the separation of glycerol from biodiesel. Key requirements for this process include a minimum ester content of 96.5% and a maximum acid value of 0.5 mg KOH/g. Biodiesel production technologies have advanced rapidly and can be classified into single-step (transesterification) and two-step (esterification–transesterification) processes. The two-step process is recommended when the FFA content in waste cooking oil exceeds 1%, as high FFA levels lead to soap formation, which hinders biodiesel separation (Hadrah et al., 2018).

Transesterification is the chemical conversion of large, branched triglyceride molecules from vegetable oils or fats into smaller, straight-chain molecules that closely resemble diesel fuel molecules. Typically, vegetable oils or fats react with an alcohol

(commonly methanol) in the presence of a catalyst (base), producing alkyl esters (e.g., methyl esters) as biodiesel.

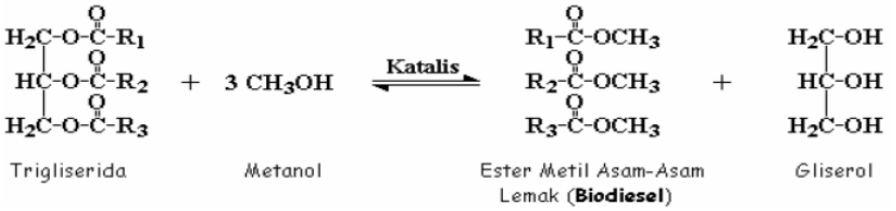

Figure 1. Transesterification reaction of triglycerides into methyl esters

Current biodiesel production technologies are classified into one-step processes (transesterification) and two-step processes (esterification followed by transesterification). Used cooking oil, which typically has a free fatty acid (FFA) content above 1%, is best processed using the two-step method. High FFA levels can lead to soap formation, creating emulsions that make biodiesel separation difficult. Continuous heating during cooking increases the FFA content in the oil, making esterification necessary as the first step to reduce FFA levels. This prevents excessive soap formation and improves biodiesel yield, followed by transesterification to convert triglycerides into biodiesel. The transesterification process employs catalysts to accelerate the reaction rate. The most used catalysts are bases, although heterogeneous catalysts may also be applied. The transesterification reaction proceeds in three stages (Hadrah et al., 2018).

Biodiesel is a renewable, biodegradable, non-toxic, and carbon-neutral alternative fuel for diesel engines. It is primarily composed of mono-alkyl esters of long-chain fatty acids, usually in the form of methyl esters, and is produced from plant oils, animal fats, or waste cooking oils through a transesterification process using methanol. This reaction can be catalyzed by acids, bases, or enzymes. Recently, heterogeneous catalysts have gained significant attention due to their potential advantages in biodiesel production. This paper reviews the use of heterogeneous catalysts in the biodiesel manufacturing process (Basumatary, 2013). Homogeneous catalysts are those that exist in the same phase as the reactants, whereas heterogeneous catalysts are in a different phase from the reactants. Commonly used homogeneous catalysts include acids such as HCl, H2SO4, and HNO3, while zeolite is an example of a heterogeneous catalyst (Mohandass et al., 2016).

The transesterification process used for biodiesel production also generates by-products. One of the main by-products is glycerol, as shown in the reaction scheme above. Glycerol, also known as glycerin in oleochemistry, is a simple trihydric alcohol that exists as a clear, viscous liquid. It is odorless, sweet-tasting, hygroscopic, and typically produced in yields ranging from 9% to 13.5% during transesterification. However, glycerol derived as a by-product of transesterification contains impurities and therefore requires further purification to obtain a clearer sample (Fitri et al., 2019).

In the cooking oil industry, the refining process is closely associated with the use of bleaching earth. Bleaching earth, also known as bleaching clay or bentonite, is a type of clay primarily composed of SiO_2, Al_2O_3, bound water, as well as Ca^{2+} ions, MgO, and Fe_2O_3. The ability of bleaching earth to whiten and purify oil comes from the presence of Al^{3+} ions on the surface of the adsorbent particles. The effectiveness of the refining process is highly influenced by the ratio of Al_2O_3 to SiO_2 in the bleaching earth (Pujiastuti et al., 2022).

RESEARCH METHOD

The used cooking oil employed in this study was first purified using two different methods, namely bleaching earth and banana peel. In the purification method using bleaching earth, 1000 mL of used cooking oil was heated on a hotplate to a temperature of 70°C. Subsequently, 20 g of bleaching earth (2% of the total oil) was weighed and added to the hot oil. The mixture was then cooled, filtered using filter paper to separate the solids, and the purified oil was stored in a closed container (Atikah, 2017).

In the purification method using banana peel, fresh banana peels were cut into small pieces, squeezed to reduce water content, and then dried in an oven at 150°C for 1 hour until completely dry. A 30 g sample of the dried peel was weighed and mixed with 300 mL of used cooking oil (1:10 ratio) in a closed container. The mixture was stirred and left to stand for four days to allow the active compounds in the banana peel to interact with the oil (Aminullah et al., 2018).

Biodiesel production was carried out using the esterification method with homogeneous catalysts (HCl, NaOH) and a heterogeneous catalyst (MgO). For the HCl treatment, 10 mL of 96% ethanol was mixed with 25.3 mL of HCl, then added into a beaker containing the used cooking oil sample. The mixture was homogenized, transferred into a test tube, and heated at 60°C for 1 hour. After being left to stand for 24 hours, separate phases of biodiesel, glycerol, and by-products were obtained (Wang et al., 2023).

For the NaOH treatment, 10 mL of 96% ethanol was mixed with 0.09 g of solid NaOH and then added to the used cooking oil. The subsequent procedure was the same: homogenization, heating at 60°C for 1 hour, and standing for 24 hours until phase separation occurred (Elliyanti et al., 2017).

For the MgO treatment, 10 mL of 96% ethanol was mixed with 0.09 g of MgO, then added to the used cooking oil. The process continued with homogenization, heating at 60°C for 1 hour, and standing for 24 hours to separate the biodiesel and glycerol products.

RESULT AND DISCUSSION

Based on the results of the study, the biodiesel production process from used cooking oil samples using an acid catalyst (HCl), a base catalyst (NaOH), and a heterogeneous catalyst (MgO) yielded the following data:

Table 1. Results of the esterification reaction of used cooking oil

Treatment Waste Cooking Oil	Catalyst	Biodiesel (mL)	Glycerol (mL)	By-Product (mL)
Without	HCl	1,59	12,72	-
	NaOH	0,35	10,06	1,06
	MgO	0,88	10,95	0,88
Bleaching earth	HCl	3,18	9,54	-
	NaOH	0,53	9,54	0,88
	MgO	0,88	11,13	1,06
Banana Peel	HCl	1,59	11,13	-
	NaOH	0,35	7,42	0,53
	MgO	0,18	11,3	1,06

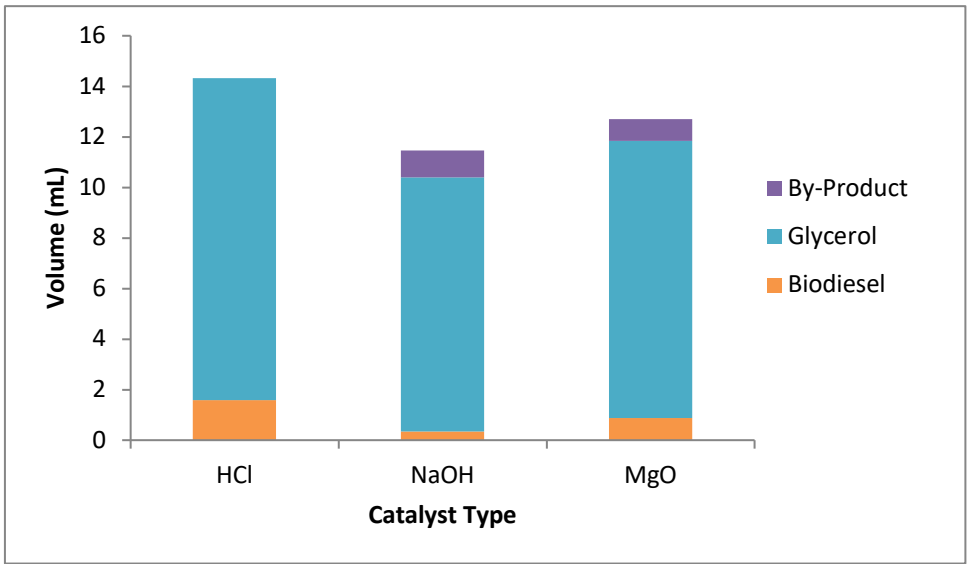

Figure 2. Comparison of product volume using catalyst type with waste cooking oil treated without treatment

Based on Figure 2, three main components were obtained—biodiesel, glycerol, and residue—from the untreated used cooking oil samples processed with three different catalysts: an acid catalyst (HCl), a base catalyst (NaOH), and a heterogeneous catalyst (MgO). From the diagram, the highest biodiesel yield was obtained using HCl at 1.59, followed by MgO at 0.883, and the lowest yield was produced using NaOH at 0.353. This indicates that HCl is more effective in converting used cooking oil into biodiesel compared to base and heterogeneous catalysts. For the glycerol layer, the highest yield was also achieved with HCl at 12.717, followed by MgO at 10.95 and NaOH at 10.066. This suggests that HCl catalysis proceeds more optimally, not only in biodiesel formation but also in producing glycerol as a by-product. Meanwhile, residue was only formed when using NaOH and MgO, with values of 1.06 and 0.883, respectively. The formation of residue occurs because NaOH and MgO are solid catalysts that are insoluble in the sample. In contrast, no residue was observed in the case of HCl, as it is a liquid catalyst and soluble in the reaction medium (Sumarlan dan Mentari, 2020).

In the used cooking oil samples treated with bleaching earth (Figure 3), the biodiesel yield obtained after allowing the samples to settle for one day was 3.1792 with HCl as the catalyst, 0.883 with MgO, and 0.5298 with NaOH. Alongside biodiesel, glycerol was also produced as a by-product. The glycerol yields were 9.5376 for HCl, 11.1258 for MgO, and 9.5364 for NaOH. In addition to these two products, residue was also formed: 1.0596 with MgO and 0.883 with NaOH. The presence of residue as one of the products of the transesterification process is likely due to the use of heterogeneous catalysts, which are not completely soluble in the reaction medium. In contrast, no residue was observed in the sample treated with HCl, as this homogeneous catalyst dissolves fully in the reaction system.

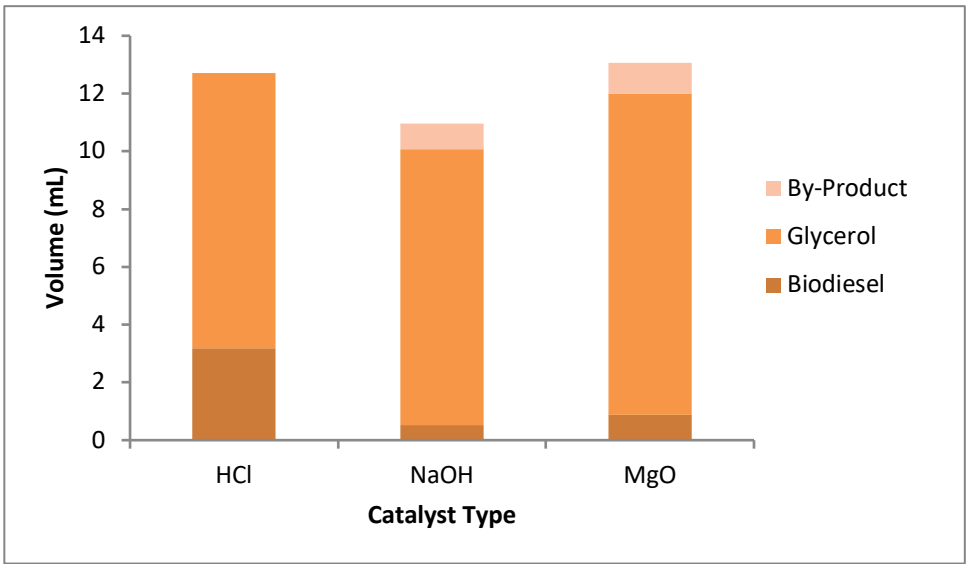

Figure 3. Comparison of product volume using catalyst type with waste cooking oil treated with Bleaching Earth

In the used cooking oil samples treated with banana peel (Figure 4), the biodiesel yield obtained after one day of settling was 1.5896 with HCl as the catalyst, 0.1766 with MgO, and 0.3532 with NaOH. Along with biodiesel, glycerol was also produced as a by-product. The glycerol yields were 11.1272 for HCl, 11.3024 for MgO, and 7.4172 for NaOH. In addition to these products, residues were also observed: 1.0596 with MgO and 0.5298 with NaOH. The presence of residue as one of the products of the transesterification process is likely due to the use of heterogeneous catalysts, which are not completely soluble in the reaction medium. In contrast, no residue was formed in the sample treated with HCl, as this homogeneous catalyst dissolves fully in the system.

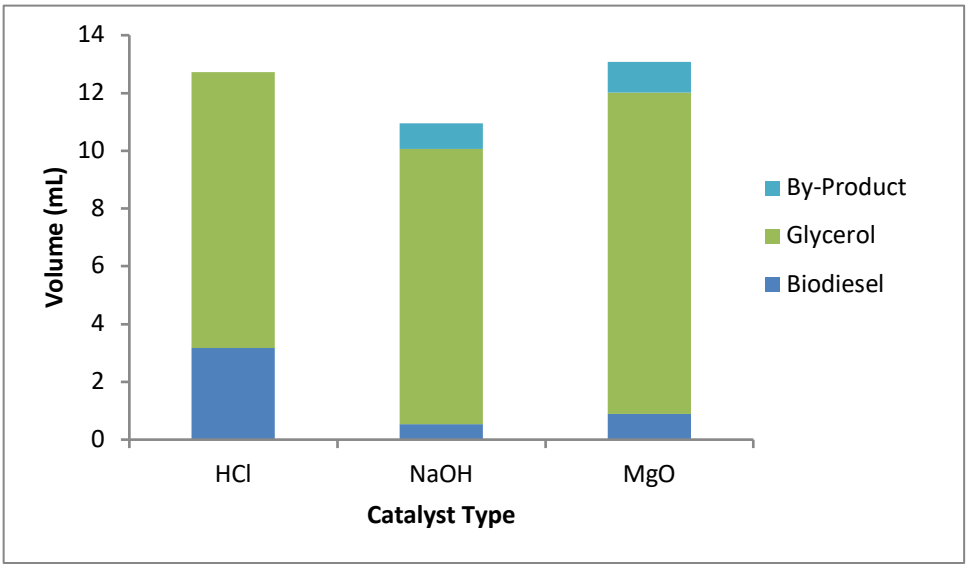

Figure 4. Comparison of product volume using catalyst type with waste cooking oil treated with banana peel

In a previous study (Prasetyo, 2018), biodiesel production was carried out through the transesterification method using a base catalyst (NaOH) and alcohol (ethanol) as the

triglyceride reactant. The NaOH catalyst used had a normality of 2N, with volumes of 10, 25, 40, 55, and 70 mL, and excess ethanol ranging from 0, 25, 50, 75, and 100%. The transesterification process was conducted at 80°C for 3 hours with continuous homogenization. Using 200 mL of waste cooking oil as the sample, the optimum condition was achieved with 10 mL of 2N NaOH and 100 mL of ethanol (0% excess), producing 196.64 g/mL of biodiesel and 79.79 mL of glycerol.

In contrast, in the present experiment, the process was carried out using 9 mL of waste cooking oil, 10 mL of 96% ethanol, and 0.09 g of solid NaOH catalyst (0.1N). The transesterification results were as follows: biodiesel yield of 0.3532, glycerol yield of 10.0662, and residue of 1.0596 from untreated samples; biodiesel yield of 0.5298, glycerol yield of 9.5364, and residue of 0.883 from bleaching earth–treated samples; and biodiesel yield of 0.3532, glycerol yield of 7.4172, and residue of 0.5298 from banana peel–treated samples.

CONCLUSION

The study demonstrated that waste cooking oil can be successfully converted into biodiesel through the transesterification process using different types of catalysts and pretreatment methods. Among the catalysts tested, HCl (acid catalyst) consistently produced the highest biodiesel yields compared to NaOH (base catalyst) and MgO (heterogeneous catalyst), indicating its superior effectiveness in facilitating the conversion process. Furthermore, glycerol was obtained as a major by-product, with the highest values also associated with HCl, confirming the optimal performance of this catalyst.

Pretreatment methods were also shown to influence the overall yield. Samples treated with bleaching earth produced higher biodiesel yields compared to banana peel treatment or untreated samples, highlighting the effectiveness of bleaching earth as an adsorbent in improving oil quality prior to conversion. Meanwhile, residue formation was observed only in reactions involving NaOH and MgO due to their heterogeneous and partially insoluble nature, whereas no residue was produced with HCl because of its homogeneity in the reaction medium.

Overall, the findings suggest that acid-catalyzed transesterification of pretreated waste cooking oil, particularly with bleaching earth, offers the most efficient pathway for biodiesel production, while simultaneously generating glycerol as a valuable by-product.

REFERENCES

Alamsyah, M., Kalla, R., & La Ifa, L. I. (2017). Pemurnian Minyak Jelantah Dengan Proses Adsorbsi. *Journal Of Chemical Process Engineering*, *2*(2), 22. https://doi.org/10.33536/jcpe.v2i2.162

Aminullah, A., Suhartani, R., & Novidahlia, N. (2018). Penggunaan Bubuk Kulit Pisang Kepok (Musa paradisiaca) Sebagai Adsorben Terhadap Sifat Fisikokimia Minyak Jelantah. *Jurnal Agroindustri Halal*, *4*(2), 162–171. https://doi.org/10.30997/jah.v4i2.1289

Ardhani, K., Pratiwi, N., Puspita, S. N., Amalia, R., Muna, M. C., Febiola, F., Alimawati, Q. C., & Wulandari, H. H. (2024). Analisis Perbandingan Hasil Pemurnian Minyak Jelantah Menggunakan Adsorben Bleaching Earth, Tempurung Kelapa, dan Arang. *Jurnal Majemuk*, *3*(2), 196–205. http://jurnalilmiah.org/journal/index.php/majemuk

Atikah. (2017). Penurunan Bilangan Peroksida Pada Minyak Goreng Bekas Menggunakan Adsorben Ca Bentonit. *Distilasi*, *2*(1), 35–45.

Basumatary, S. (2013). Transesterification with heterogeneous catalyst in production of biodiesel: A review. *Journal of Chemical and Pharmaceutical Research*, *5*(1), 1–7.

Elliyanti, A., Zahiroh, N., & Ayu, P. (2017). Pengaruh Katalis Homogen dan Heterogen pada Proses Reaksi Transesterifikasi. *Chemistry ITS*, *12*(1), 1–4. https://www.researchgate.net/publication/322036904_REVIEW_Pengaruh_Katalis_Homogen_dan_Heterogen_Pada_Proses_Reaksi_Transesterifikasi

Fitri, P. N., Nurjanah, S., & Widyasanti, A. (2019). Pemurnian Dan Karakterisasi Gliserol Hasil Samping Produksi Biodiesel Kemiri Sunan. *Prosiding Simposium Nasional Multidisiplin (SinaMu)*, *1*. https://doi.org/10.31000/sinamu.v1i0.2145

Hadrah, H., Kasman, M., & Sari, F. M. (2018). Analisis Minyak Jelantah Sebagai Bahan Bakar Biodiesel dengan Proses Transesterifikasi. *Jurnal Daur Lingkungan*, *1*(1), 16. https://doi.org/10.33087/daurling.v1i1.4

Mohandass, R. A., Selvaraju, A., & S. Rajagopan. (2016). Homogeneous Catalysts used in Biodiesel Production: A Review. *International Journal of Engineering Research And*, *V5*(05), 264–268. https://doi.org/10.17577/ijertv5is050381

Pujiastuti, C., Ketut Sumada, Meriana Armidianti, & Adinda Rimarsya Bahita Ahmad. (2022). Bleaching Earth Recovery from Waste to Purify Cooking Oil by Extraction–Activation Method. *Journal of Research and Technology*, *8*(2), 169–177. https://doi.org/10.55732/jrt.v8i2.401

Sumarlan, I., & Mentari, R. B. (2020). Esterification of Waste Cooking Oil using Heterogeneous Catalyst from Pearl Shell. *Jurnal Akademika Kimia*, *9*(3), 183–190. https://doi.org/10.22487/j24775185.2020.v9.i3.pp183-190

Wang, B., Wang, B., Shukla, S. K., & Wang, R. (2023). Enabling Catalysts for Biodiesel Production. *Catalysts*, *13*(April 2023), 1–23.