

## Article

# Comparison of Water-Removal Efficiency of Molecular Sieves Vibrating by Rotary Shaking and Electromagnetic Stirring from Feedstock Oil for Biofuel Production

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**Abstract:** Adequate water-removal techniques are requisite to remain superior biofuel quality. The effects of vibrating types and operating time on the water-removal efficiency of molecular sieves were experimentally studied. Molecular sieves of 3 Å pore size own excellent hydrophilic characteristics and hardly absorb molecules other than water. Molecular sieves of 3 Å accompanied by two different vibrating types, rotary shaking and electromagnetic stirring, were used to remove initial water from the reactant mixture of feedstock oil in order to prevent excessive growth or breeding of microorganisms in the biofuel product. The physical structure of about 66% molecular sieves was significantly damaged due to shattered collision between the magnetic bar and molecular sieves during electromagnetic stirring for 1 h. The molecular sieves vibrated by the rotary shaker appeared to have relatively higher water-removal efficiency than those by the electromagnetic stirrer and by keeping the reactant mixture motionless by 6 and 5 wt.%, respectively. The structure of the molecular sieves vibrated by an electromagnetic stirrer and thereafter being dehydrated appeared much more irregular and damaged, and the weight loss accounted for as high as 19 wt.%. In contrast, the structure of the molecular sieves vibrated by a rotary shaker almost remained original ball-shaped, and the weight loss was much less after regenerative treatment for those molecular sieves. As a consequence, the water-removal process using molecular sieves vibrated by the rotary shaker is considered a competitive method during the biofuel production reaction to achieve a superior quality of biofuels.

**Keywords:** molecular sieve; water removal; rotary shaking; electromagnetic stirring; biofuel



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## 1. Introduction

The mesocarp of palm accounting for 45–60 wt.% of whole palm fruit is the major contribution of palm oil. Palm oil is primarily composed of free fatty acids (FFA) and triglycerides consisting of glycerol and three fatty acids. Palm oil is the largest feedstock oil provider for food, biochemical, and biofuels due to its highest ratio of oil yield/production area and lowest production cost among terrestrial plants [1]. The oil yield of palm oil is 5.5 t/ha in comparison with 0.5 t/ha and 2 t/ha of soybean and rapeseed oils, respectively. The production cost of palm oil is 300 USD/t, which is much lower than 700 and 800 USD/t for rapeseed and soybean oils [2]. Global palm oil consumption is increasing rapidly from 61.6 million tons in 2016 to 71.5 million tons in 2020 [3]. Widespread use of various vegetable oils for biofuel production is considered one of the significant measures to mitigate the effects of greenhouse gases and acute climate change [4].

The preservation extent of vegetable oil quality partly depends on the water concentration in the oil. The existence of water in the palm oil might facilitate the oxidation rate, leading to the deterioration of oxidation stability and increase in peroxidation value. Further, fatty acids are hydrolyzed by water in lipids to form free fatty acids, which react with the alkaline compounds to cause saponification and produce more water in the

compounds [5]. The rate of hydrolysis reaction is further accelerated with higher water concentration [6], leading to the deterioration of biofuel quality.

Water in vegetable oil frequently causes metallic corrosion of the oil storage tank and might even break down the oil feeding system, including the high-pressure injection pump. The water in vegetable oil also facilitates the growth and breeding of microorganisms such as bacteria and fungi ascribed to accelerating biodegradability characteristics of vegetable oils, resulting in worsening biofuel properties and damage to the flavors and nutrients in the food oils. Water content in biofuel might be increased with its intensity of microbial activity [7]. Hence, the lowest possible water content in biofuels is suggested [8].

Sebastian et al. [8] observed that the presence of water and free fatty acids in tallow feedstock oil inhibited the extent of transesterification reaction. Further, Ma and Hanna [9] suggested that the water content, acid value, and free fatty acids (FFA) are less than 0.06 wt.%, 1 mg KOH/g, and 0.5 wt.%, respectively, to prevent saponification reaction. Eze et al. [10] found that the conversion rate of transesterification was only 50 wt.% when the raw oil contained 5.6 wt.% FFA and 0.2 wt.% water. Hence, the separation of water from feedstock oil is considered a requisite to improve biofuel properties [11]. The frequently applied techniques of separating a liquid from adhered liquid include electrolytic dissociation, extractive distillation [12], vapor permeation [13], ion exchange adsorption [14], and absorbent selection [15].

Some water-separating processes involve heating liquid mixtures to reach their boiling points and thus require higher energy consumption. Here, the output energy to input energy ratio of the whole production process may be less than 1 and, therefore, is less economical in terms of energy requirement. The membrane separation method, which requires high vacuum pressure at the permeation side of the mixture and regular cleaning of its membrane structure, may not be an adequate choice for water separation during biofuel production. Distillation by heating is the most often applied water-removal method in the current transesterification with a strong alkaline catalyst [16]. Nevertheless, the fuel properties of biofuel products might deteriorate with continuous heating under high temperatures. Continuous or intermittent vacuum distillation was carried out by Lawrence and Jiang [17] for separating water from biofuel. The vacuum pressure and operating temperature were controlled under 2.6 kPa and 105–110 °C. Likewise, some other more efficient water-removal processes continue to be proposed and investigated. For example, aluminum silica materials have many tiny pores on the surface for absorbing compounds that are smaller than those pores' sizes, and those compounds can be stored within them [18]. The volume of the pore material may not change obviously with the stored compounds from the surrounding. The function of the pore material after absorbing water could be regenerated by heating under a high temperature and low humidity environment.

A few materials have been applied to those water-removal techniques, such as activated carbon, silica gel, activated aluminum oxide, and molecular sieve. Khalil et al. [19] used activated carbon to remove nitrate and phosphate from water. Hybrid membranes produced from activated carbon and whey protein fibrils were used to remove mercury and chromium in water [20]. In addition, solid silica gel (SiO<sub>2</sub>) was applied to enhance the oxidative transformation of caffeine in water [21]. Among those, a molecular sieve composed of alkaline metal aluminosilicate is a constructive crystalline material possessing precise uni-pore size. A molecular sieve with a pore diameter less than 2 nm (i.e., 20 Å) is referred to as microporous material. Molecular sieves are frequently used as desiccants or catalytic applications, including fluid catalytic cracking or hydrocracking [22]. In particular, molecular sieves of precise pore size can be used to absorb materials of the corresponding size. Only sufficiently smaller compounds than the pore size can enter these pores and be adsorbed by the molecular sieves. Chemical compounds whose molecular diameter is larger than the corresponding pore size of the molecular sieves are hardly adsorbed [23]. Further, a molecular sieve has extremely high hydrophilic characteristics so that even under an ultra-low humid environment, its superior water absorption and storage properties are retained [24]. The characteristics of the molecular sieves also include excellent crushing

resistance, convenient regeneration capability, and swift adsorption rate [25]. The pore sizes of commercialized molecular sieves are generally in the range of 3 and 10 Å. Zeolite molecular sieve beds of 4 Å pore size were observed to successfully absorb water from humid natural gas [26]. The carbon molecular sieve membrane was evaluated to be a highly cost-effective method for separating CH<sub>4</sub> from CO<sub>2</sub> to upgrade biogas characteristics [27]. A total of 4 Å zeolite molecular sieves synthesized from attapulgite were also applied to remove hydrogen sulfide (H<sub>2</sub>S) in gaseous fuels. The removal rate of H<sub>2</sub>S might reach nearly 100% [28]. The molecular sieve of 3 Å pore size has excellent water-absorption capacity and hardly absorbs molecules other than water [29]. Highly hygroscopic material such as molecular sieve might absorb a large amount of water several times of its own weight, while it is difficult to extrude out the absorbed water from the material.

The long-chained molecules of high-hygroscopicity material appear as a twisted and curled structure before they absorb water. After water absorption, the twisted structure of the molecular sieve swiftly expands to become cross-linked cubes full of water molecules [30]. Water content in feedstock oil might retard the transesterification reaction, leading to deteriorated fuel characteristics of the biofuel product [31]. The water-removal process is hence a necessity to enhance the reaction process for biofuel production. Although high water-absorbing materials have been widely applied in industrial practices, no study used those materials for water absorption during transesterification from feedstock oil or alcohol. Moreover, there is no study reporting the investigation of the effects of highly hygroscopic material accompanied by vibrating motion on the extent of water removal from raw oil or alcohol during transesterification. Hence, the effects of vibration modes and operating time of molecular sieves on the fraction of water removal from palm oil and ethanol and the extent of structural damage of the water-absorbing material after the process were experimentally investigated in this study. Molecular sieves accompanied by two different kinds of vibrating motions, including electromagnetic stirring and rotary shaking, were used to absorb water from the reactant mixture of transesterification. The efficiency and rate of water removal and appearance and weight loss of molecular sieves were observed and compared to find the optimum water-removal technique and thus improve the fuel characteristics of biofuel.

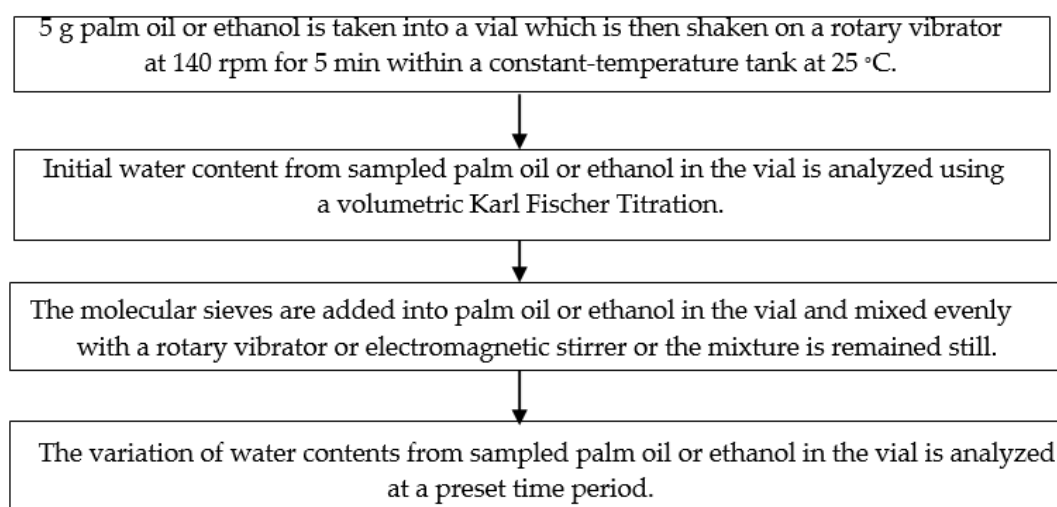
## 2. Materials and Methods

### 2.1. Experimental Materials

Molecular sieves were used to absorb water from palm oil or ethanol, which are the reactants of the transesterification for biofuel production. Palm oil was procured from Formosa Oilseed Processing Co., Ltd. in Taichung City, Taiwan. Molecular sieves of 3 Å pore size were provided by Eikme International Ltd. in Hsinchu County, Taiwan. The water-absorption capability of 3 Å pore size has been found to be superior among those commercialized molecular sieves of pore sizes in the range of 3 to 10 Å. One gram of the 3 Å molecular sieve is able to absorb as high as 0.83 g water [32]. The bulk density of the molecular sieve is 0.63 g/mL. The molecular sieves of 3 Å are also used for the desiccation of petroleum-cracking alkenes and gas [33].

### 2.2. Experimental Methods

Palm oil or ethanol has the disposition to absorb moisture from the environment [34]. Five grams of palm oil or ethanol was poured into a vial and sealed. The vial was placed within a constant-temperature tank (Model LE-509D, Yih Der Ltd. in Taichung City, Taiwan) at 25 °C. An internal circulating fan was operated to keep an even temperature distribution in the tank. The vial was vibrated by a rotary shaker (Model TS-520D, Yih Der Ltd. in Taichung City, Taiwan) within the tank for 5 min to mix the compound with 0.09 wt.% initial water uniformly in the vial. The vibration frequency of the rotary shaker was set at 140 rpm. A volumetric Karl Fischer Titrator (Model DL-31, Mettler Toledo Ltd. in Greifensee, Switzerland) was used to measure the water content of palm oil or ethanol stored in the vial. The experimental procedures are illustrated in Figure 1.



**Figure 1.** The experimental procedures for removing water from palm oil or ethanol by molecular sieves under different vibrating modes.

Molecular sieves of equal weight (5 g) to ethanol or palm oil were then added into the vial containing palm oil or ethanol. The vial at a constant temperature of 25 °C was then vibrated either by an electromagnetic stirrer or a rotary shaker for 1 h. The vial containing the oil or ethanol sample after removing water using the molecular sieves was then moved out from the constant-temperature tank to measure their water contents by a volumetric Karl Fischer Titration. After absorbing water from palm oil or ethanol under various operating conditions, the molecular sieves were collected and heated in a high-temperature furnace (Model DF 404, Deng Yng Ltd. in New Taipei City, Taiwan) at a constant temperature of 300 °C for 5 h for their dehydration and drying. The photographs of molecular sieves before and after dehydration processes were taken for comparison. The weights of the molecular sieves before and after dehydration were measured by a precise electronic balance (Model 210 g, Mettler Toledo Ltd. in Greifensee, Switzerland) to calculate weight loss of the molecular sieves during the water-removal process from palm oil or ethanol under different vibration modes.

At every consecutive 0.5 h of operating time period from 0 to 6 h for comparing the water-removal efficiencies between vibrating motions of electromagnetic stirring and rotary shaking, the water contents in the mixture of molecular sieves and palm oil or ethanol in the vial before and after the water-absorption processes were measured by a volumetric Karl Fischer Titration. When the water-removal efficiencies between ethanol and palm oil were compared, the water contents before and after the water-removal process at every consecutive 5 min of operating time from 0 to 60 min were measured. The water-removal efficiency from palm oil or ethanol by molecular sieves under rotary shaking and electromagnetic stirring was defined as shown in Equation (1):

$$\text{Water-removal efficiency (\%)} = \frac{(\text{water content prior to water removal (wt.\%)}) - (\text{water content after water removal (wt.\%)})}{(\text{water content prior to water removal (wt.\%)})} \times 100\% \quad (1)$$

The results of water-removal efficiencies between different vibrating motions or absorbents were thus be calculated and plotted. The water-removal rate, defined as the amount of water-removal per unit time, was also calculated for evaluating the effectiveness of potential water-removal techniques. The rate of water removal is formulated as shown in Equation (2):

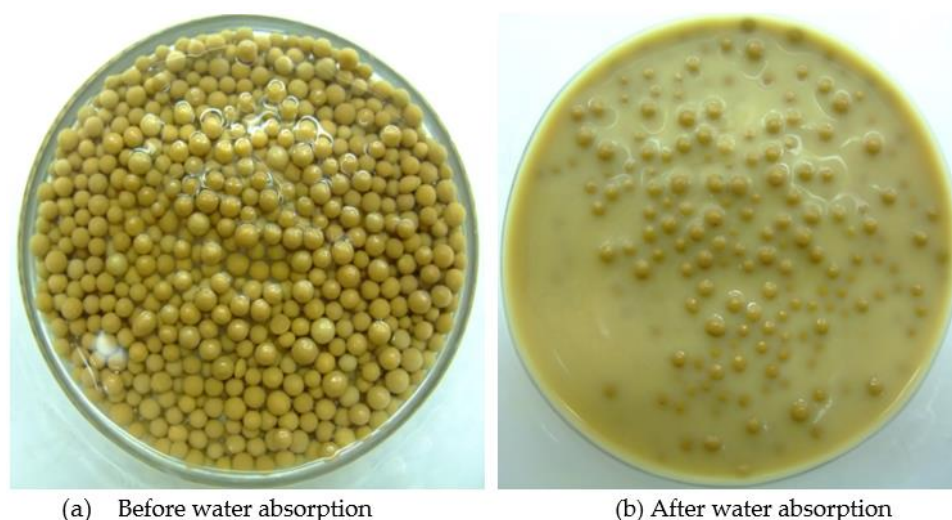
$$\text{Rate of water-removal (wt.\%/min)} = \frac{(\text{water content prior to water removal (wt.\%)}) - (\text{water content after water removal (wt.\%)})}{\text{water-removal time (min)}} \quad (2)$$

### 3. Results and Discussion

The effects of vibration modes and operating time on the water-removal efficiency were experimentally investigated in this study. At least three repetitions were carried out to obtain the mean values of the experimental data. The experimental uncertainties of the water-removal efficiency by electromagnetic stirring, rotary shaking, and being kept motionless were  $\pm 2.72\%$ ,  $\pm 4.36\%$ , and  $\pm 1.84\%$ , respectively; the uncertainty of the water-removal rate was  $\pm 3.35\%$ . The experimental results were explained and discussed as follows.

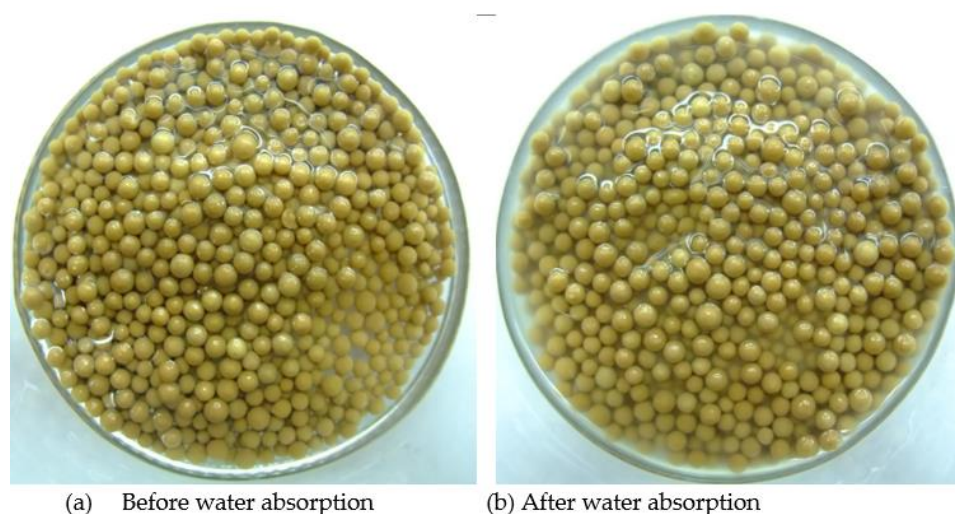
#### 3.1. Effect of Vibration Modes on Water-Removal Efficiency

The sample oil, molecular sieves, and a magnetic bar were kept in a vial to be vibrated by an electromagnetic stirrer. The magnetic bar began stirring the mixture of the sample oil and molecular sieves after triggering the electromagnetic stirrer. However, the magnetic bar was prone to collide with the molecular sieves, causing structural damage to the molecular sieves during the vibration of the vial. Part of the molecular sieves was even shattered to become powder after the vial's vibration, leading to fast deterioration of the water-absorption capability of the molecular sieves. The appearance of molecular sieves before and after the water-removal process vibrated by an electromagnetic stirrer is shown in Figure 2. Around 66% of the molecular sieves were subjected to structural damage ascribed to collision and friction between the molecular sieves and magnetic bar during electromagnetic stirring for 1 h. This caused the scaling-off of the surface material from the molecular sieves to mix with surrounding palm oil, resulting in a turbid palm oil liquid mixed with molecular sieve material. In contrast, under rotary shaking, most of the molecular sieves, after absorbing water content from palm oil or ethanol, appeared to be in original shape, with only a slight scale-off from the molecular sieves' surface. The comparative appearance of molecular sieves before and after water-removal processes under the vibration effect of the rotary shaker is shown in Figure 3. It was shown that after water removal by molecular sieves, palm oil appeared as only mildly turbid because of little damage to the molecular sieves by rotary shaking, and the shapes of molecular sieves remained almost integrated. Almost 100% structure of the molecular sieves after water-removal process by rotary shaking for 1 h remained but suffered only slight collision. Herold and Mokhtab [35] found that zeolite molecular sieves of 3 Å pore size are capable of selectively removing water from liquid aliphatic alcohol. The vibrating motion could help molecular sieves in promoting their rate of water adsorption from aliphatic alcohol.



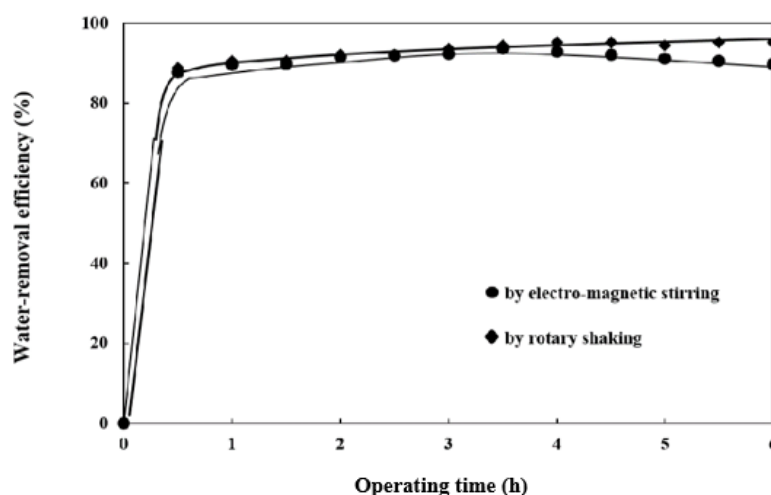
**Figure 2.** A comparison of the appearance of molecular sieves (a) before water absorption and (b) after water absorption from palm oil accompanied by electromagnetic stirring.





**Figure 3.** Comparison of the appearance of molecular sieves (a) before water absorption and (b) after water absorption from palm oil accompanied by rotary shaking.

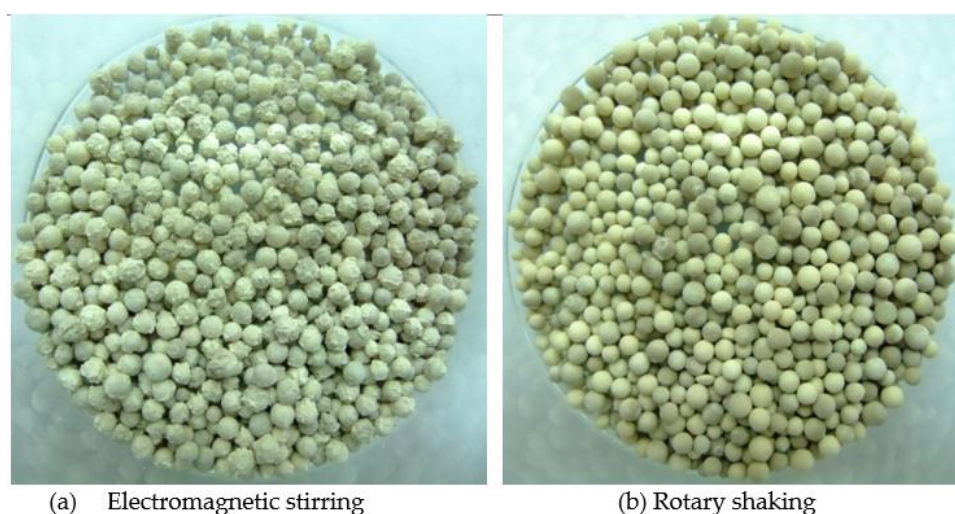
The water-removal efficiency, as defined in Equation (1), was found to decrease with the operating time due to the broken structure and thus partial water-adsorption function loss of the molecular sieves after 3 h of absorbing water from ethanol accompanied by electromagnetic stirring in Figure 4. After 6 h of water absorption, part of the water absorbed by the molecular sieves accompanied by electromagnetic stirring released back to ethanol liquid, indicating that its water-removal efficiency decreased after 3 h of water absorption, as shown in Figure 4. In contrast, the water-removal efficiency steadily increased after 30 min of fast water absorption from ethanol by molecular sieves accompanied by the vibration effect of rotary shaking (Figure 4). The water-removal efficiency of the molecular sieves vibrated by rotary shaking for 6 h was observed to be higher than that of electromagnetic stirring by 6% for the same time, as shown in Figure 4. Molecular sieves are considered more efficient than other desiccants such as activated charcoal, silica gel, and alumina for dehydration in that they are small-pore adsorbents and with less possibility of co-adsorption of hydrocarbons [36]. Lad and Makkawi [37], after comparing the adsorption efficiency of methyl chloride among activated carbon, silica, and molecular sieves, found that the adsorption capability increased with the increase in adsorbent surface area. The molecular sieves vibrated by rotary shaking were found to have superior water-absorption efficiency due to its less damage by collision and higher complete adsorption surface area in turn in comparison with that by electromagnetic stirring.



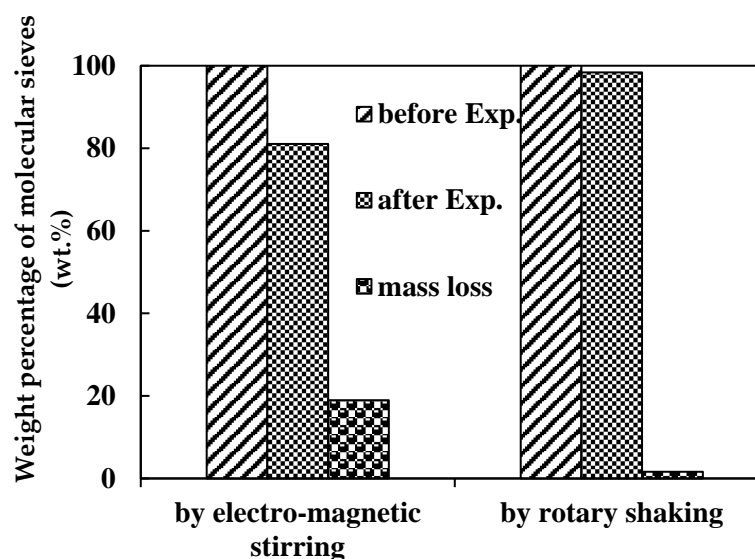
**Figure 4.** Effects of vibrating motion on water-removal efficiency of molecular sieves from ethanol.

The molecular sieves, after 6 h-water absorption under two different vibrating modes, were dehydrated, and their appearance was compared (Figure 5). The surface shapes of the dehydrated molecular sieves under electromagnetic stirring in Figure 5a appeared to be more irregular and broken than those under rotary shaking, as shown in Figure 5b, which were considerably glossier and mostly retained their original ball-shapes. The extent of damage caused to molecular sieves varied under different vibrating modes. When electromagnetic stirring was used to vibrate the mixture of molecular sieves and ethanol, a magnetic bar stirred the mixture under the effect of an electromagnetic field. Molecular sieves, being less hard than the magnetic bar, were prone to apparent damage due to the collision of the magnetic bar. In contrast, under rotary shaking action, direct collision among the molecular sieves with the same structure hardness rendered relatively less damage to the molecular sieves. The variation of total weight percentages of molecular sieves before and after water absorption under different vibrating modes are presented in Figure 6. Jemil et al. [38] found that increasing concentration of molecular sieves caused the gradual reduction in water in the reaction system. The vibration motion could decrease the concentration of molecular sieves required to reduce the same amount of water in the reaction system. Particularly, the molecular sieves suffered significantly larger weight loss under electromagnetic stirring treatment than rotary shaking action. The weight loss of molecular sieves under electromagnetic stirring accounted for as high as 19 wt.%, compared with less than 2 wt.% by rotary shaking after 6 h of water absorption. This indicated nearly 10-times higher weight loss after electromagnetic stirring than that after rotary shaking. This considerable weight loss of molecular sieves under electromagnetic stirring can also be judged by their indented and shrank surfaces, as shown in Figure 5a. Wang et al. [39] studied the effects of electromagnetic stirring (EMS) on mechanical properties and microstructure of Incoloy825 superalloy. They found that both the ultimate tensile strength and elongation rate of the superalloy increased with the application of electromagnetic stirring.

Based on the above-mentioned results, rotary shaking is suggested to be a more efficient vibrating mode to remove water from feedstock oil mixture during transesterification reaction. Further, rotary shaking causes considerably less structural damage to the adsorbent molecular sieves compared with electromagnetic stirring. The rotary shaking motion could also enhance the extent of fluidity [40] between the oil sample and adsorbent through the vibration of the rotary platform. The mixing extent of various reactants could also be raised by rotary shaking under an adequate rotary speed to facilitate a chemical reaction [41].



**Figure 5.** Surface of dehydrated molecular sieves after water-removal processes vibrated by (a) electromagnetic stirring and (b) rotary shaking.



**Figure 6.** Comparison of weight percentages of molecular sieves before and after water-removal experiments vibrated by electromagnetic stirring and rotary shaking.

### 3.2. Effects of Rotary Shaking and Motionless Treatment on Water Absorbency

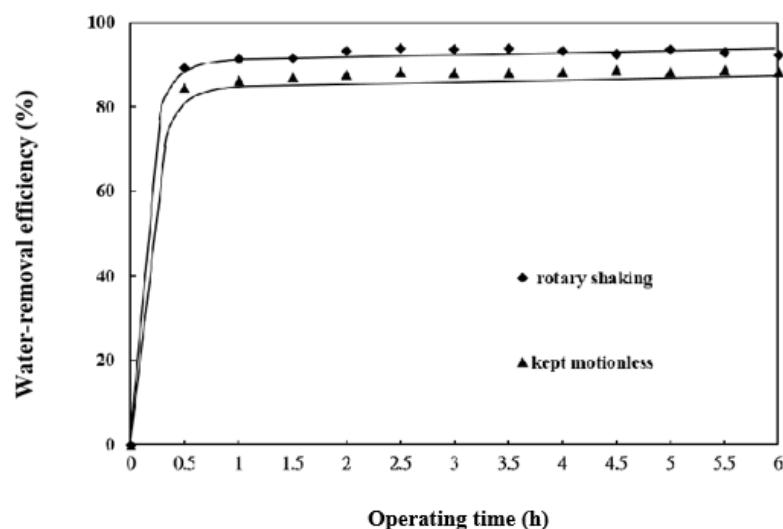
Rotary shaking was shown to have significantly higher water-removal efficiency than keeping the mixture of oil sample and molecular sieves motionless, as shown in Figure 7. After 30 min of water absorption from ethanol, the water-removal efficiency of rotary shaking was higher than that of the motionless mixture by 5%. The water-removal efficiencies of those two cases appeared to slightly increase with the operating time after 1 h of operation. This is attributed to the increase in the contact area and frequency of interaction between molecular sieves and ethanol under the rotary shaking motion at 140 rpm speed, resulting in superior water-absorption capacity of molecular sieves than keeping the mixture motionless. Tiadi et al. [42] found that higher adsorbent dosage, agitation speed, and contact time caused faster adsorption rates after comparing three different adsorbents. The increase in rotary shaking speed and reactant temperature was also observed to facilitate the activity of the chemical reaction and catalyst [43]. Raviadaran et al. [44] suggested that the increase in the absorption rate of contaminants by molecular sieves may be ascribed to more available adsorption sites provided by a higher adsorbent dosage or increased contact frequency between adsorbent and contaminants. Hence, the molecular sieves vibrated by rotary shaking were observed to remove more water from ethanol compared to other keeping motionless processes.

### 3.3. Effects of Water-Absorption Time

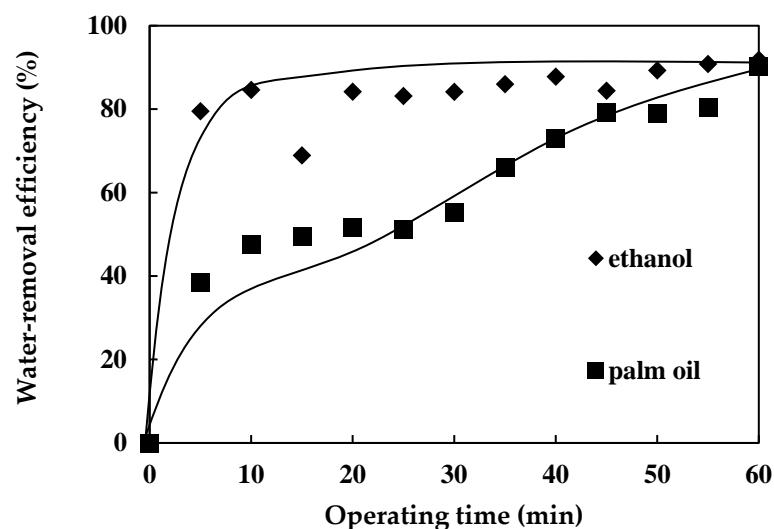
In the initial 5 min of water absorption by rotary shaking, the efficiency of water-removal from ethanol was considerably higher than that of palm oil (Figure 8). The water-removal efficiency of ethanol remained almost unchanged at nearly 85% after 10 min of water absorption. After 60 min of the absorption process, the water-removal efficiency of palm oil achieved that of ethanol, as shown in Figure 8. It is possible because ethanol is a polar solvent with low viscosity. Water molecules are thus prone to be absorbed and mixed with ethanol. The molecular structure of ethanol sustains its superior miscibility with both polar and nonpolar compounds. In particular, ethanol is rather hydroscopic to readily absorb water molecules from the environment [45]. Likewise, water can also be easily adsorbed out from ethanol by molecular sieves. In contrast, under rotary shaking, palm oil mixed with water tended to form a partial emulsion of water droplets-in-oil, resulting in the formation of many water droplets enveloped by the outer oil layer [46]. Palm oil is primarily composed of fatty acids, which are esterified with glycerol. The saturated fatty acids of palm oil could reach as high as 50 wt.% [47]. Hence, palm oil is considerably



more viscous and heavier than ethanol, makes it relatively difficult to adsorb water out from the emulsion of palm oil by the molecular sieves. Hence, a milder increasing curve of water-removal efficiency with the operating time for palm oil appeared as, as observed in Figure 8.



**Figure 7.** Comparison of water-removal efficiency of molecular sieves from ethanol under motionless and rotary shaking conditions.



**Figure 8.** Comparison of the changes in water-removal efficiency with operating time between palm oil and ethanol by molecular sieves with rotary shaking.

Under rotary shaking motion, the water-removal efficiency of molecular sieves from ethanol soon reached 80% within 5 min of initiation. The water absorbency of molecular sieves for ethanol tended to reach saturation in the initial 10 min and thereafter appeared unvaried with the operating time while the water-removal efficiency for palm oil steadily increased and reached that of ethanol (at nearly 90%) after 60 min of operation. Water molecules were found to be more prone to be squeezed out from ethanol-water matrix under rotary shaking motion of the molecular sieves than from palm oil-water structure [48]. Superior water-absorbent materials such as molecular sieves provide high water-absorption function and excellent water retention performance [49]. Fluid and burning characteristics of biofuel products such as kinematic viscosity, cold filter plugging point (CFPP), and acid value are influenced by the water content in the reactant mixture [50]. The water-removal

rate in terms of wt.%/min as formulated in Equation (2) is defined as the amount of water removal (wt.%) per unit time (min). The water-removal rate of the molecular sieves for ethanol and palm oil under rotary shaking motion in the first 5 min was 1.005 and 0.476 wt.%/min, respectively. This indicates that the water-removal rate of ethanol was considerably faster than the palm oil by nearly two-fold. After 60 min of operation, the water-removal rate from both the analytes reached the same at 0.097 wt.%/min.

#### 4. Conclusions

In this study, molecular sieves accompanied by two different vibration modes, including rotary shaking and electromagnetic stirring, were used to remove initial water from feedstock palm oil or ethanol. The water-removal efficiency and water-removal rate from ethanol or palm oil at various operating times were analyzed. The major results of this study are summarized as follows:

1. The magnetic bar was prone to collide with the molecular sieves in the vial to cause structural damage of the latter during electromagnetic stirring. The shape and structure of about 66% of molecular sieves were obviously damaged due to frequent collision and friction between the molecular sieves and magnetic bar under the effect of the electromagnetic field. It resulted in fast deterioration of water-absorption capability of the molecular sieves and a slight decrease in water-removal efficiency due to the release back of absorbed water from the molecular sieves;
2. The surface shapes of all the molecular sieves were nearly intact and only scaled off slightly from their surfaces after water removal from ethanol by rotary shaking motion for 6 h. The water-removing capability of the molecular sieves is almost sustained after the process accompanied by rotary shaking;
3. The water-removal efficiency of the molecular sieves vibrated by a rotary shaker was higher by 6% than that by an electromagnetic stirrer after 6 h water absorption from ethanol. The electromagnetic stirring motion caused an obvious loss of water-absorption capability of the molecular sieves due to severe structural damage during the water-removal process;
4. The shapes of molecular sieves were much more irregular and broken after being used for 6 h water-removal from ethanol under electromagnetic stirring than those by rotary shaking. In contrast, the molecular sieves under rotary shaking remained almost like original, ball-shaped, and much glossier. The extent of structural damage of the molecular sieves resulted in the accompanied loss of their water-adsorption capability;
5. The water-absorbing process by molecular sieves vibrated by electromagnetic stirring for 6 h caused significantly larger weight loss of the molecular sieves, which accounted for 19 wt.%, nearly 10 times, than that by rotary shaking, which was less than 2 wt.%. The rotary shaking motion is considered a much more adequate agitation method to increase contact frequency and area among the reactant mixtures of feedstock oil, water, and alcohol. This results in a higher reaction rate and faster water-removal efficiency;
6. The water-removal efficiency of molecular sieves vibrated by a rotary shaker is higher than that of the remaining motionless mixture of molecular sieves and ethanol by 5% after 30 min of the water-absorption process. The vibrating motion could facilitate the fluidity and mixing extents of the reactant mixture and thus accelerate the chemical reaction;
7. The water-removal efficiency from ethanol was considerably higher than that from palm oil by molecular sieves vibrated by a rotary shaker. The water-absorbing capability of the molecular sieves from ethanol reached saturation and steady-state after 10 min while the water-removal efficiency from palm oil increased with time and reached that of ethanol (90%) after 60 min of operation. Ethanol is highly hydroscopic and readily absorbs or desorbs water molecules than palm oil, composed of complex fatty acids and glycerol with much higher viscosity;

8. The water-removal rate of the molecular sieves from ethanol by rotary shaking motion in the first 5 min of the operation period was significantly higher and nearly twice that from palm oil in the same period of operation. The molecular structure of ethanol assures its superior miscibility with water molecules and higher water-removal rate.

**Author Contributions:** Conceptualization, C.-Y.L.; methodology, C.-Y.L.; validation, C.-Y.L.; formal analysis, C.-Y.L. and L.M.; investigation, C.-Y.L. and L.M.; resources, C.-Y.L.; data curation, L.M.; writing—original draft preparation, C.-Y.L. and L.M.; writing—review and editing, C.-Y.L.; visualization, L.M. supervision, C.-Y.L.; project administration, C.-Y.L.; funding acquisition, C.-Y.L. Both authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Masudi, A.; Muraza, O. Vegetable oil to biolubricants: Review on advanced porous catalysts. *Energy Fuel* **2018**, *32*, 10295–10310. [CrossRef]
2. Zimmer, Y. Competitiveness of rapeseed, soybeans and palm oil. *J. Oilseed Brassica* **2016**, *1*, 84–90.
3. Statista Inc. Available online: <https://www.statista.com/> (accessed on 11 May 2021).
4. Lin, C.Y.; Lu, C. Development perspectives of promising lignocellulose feedstocks for production of advanced generation biofuels: A review. *Renew. Sust. Energy Rev.* **2021**, *136*, 110445. [CrossRef]
5. Oliverira, E.D.C.; Silva, P.R.D.; Ramos, A.P.; Aranda, D.A.G.; Freire, D.M.G. Study of soybean oil hydrolysis catalyzed by *Thermomyces lanuginosus* lipase and its application to biodiesel production via hydroesterification. *Enzym. Res.* **2011**, *2011*, 1–8. [CrossRef] [PubMed]
6. Porfyrus, A.; Vasilakos, S.; Zotiadi, C.; Papaspyrides, C.; Moser, K.; Van Der Schueren, L.; Vouyiouka, S. Accelerated ageing and hydrolytic stabilization of poly (lactic acid) (PLA) under humidity and temperature conditioning. *Polym. Test.* **2018**, *68*, 315–332. [CrossRef]
7. Carrillo, L.; Bilason, L.; Loveres, S.F.; Paurillo, J.E.; Sacobo, C.J.; Sakay, C.; Espinosa, K.; Vergara, J. Utilization of vegetable oil refinery activated carbon-bleaching earth as an additive to the production of low-density facing bricks. *E&ES* **2020**, *463*, 012092.
8. Sebastian, J.; Muraleedharan, C.; Santhiagu, A. Enzyme catalyzed biodiesel production from rubber seed oil containing high free fatty acid. *Int. J. Green Energy* **2017**, *14*, 687–693. [CrossRef]
9. Ma, F.; Hanna, M.A. Biodiesel production: A review. *Bioresour. Technol.* **1999**, *70*, 1–15. [CrossRef]
10. Eze, V.C.; Phan, A.N.; Harvey, A.P. Intensified one-step biodiesel production from high water and free fatty acid waste cooking oils. *Fuel* **2018**, *220*, 567–574. [CrossRef]
11. Gil, I.D.; Uyazán, A.M.; Agular, J.L.; Rodríguez, G.; Caicedo, L.A. Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: Process simulation. *Braz. J. Chem. Eng.* **2008**, *25*, 207–215. [CrossRef]
12. Bui, D.T.; Nida, A.; Ng, K.C.; Chua, K.J. Water vapor permeation and dehumidification performance of poly (vinyl alcohol)/lithium chloride composite membranes. *J. Membr. Sci.* **2016**, *498*, 254–262. [CrossRef]
13. Fang, Z.; He, C.; Li, Y.; Chung, K.H.; Xu, C.; Shi, Q. Fractionation and characterization of dissolved organic matter (DOM) in refinery wastewater by revised phase retention and ion-exchange adsorption solid phase extraction followed by ESI FT-ICR MS. *Talanta* **2017**, *162*, 466–473. [CrossRef] [PubMed]
14. Moreno, D.; Ferro, V.R.; De Riva, J.; Santiago, R.; Moya, C.; Larriba, M.; Palomar, J. Absorption refrigeration cycles based on ionic liquids: Refrigerant/absorbent selection by thermodynamic and process analysis. *Appl. Energy* **2018**, *213*, 179–194. [CrossRef]
15. Karmakar, A.; Karmakar, S.; Mukherjee, S. Properties of various plants and animals feedstocks for biodiesel production. *Bioresour. Technol.* **2010**, *101*, 7201–7210. [CrossRef] [PubMed]
16. Zhou, H.; Zuo, G. Discussion on the production technology of biodiesel reaching BD100 standard. *China Oil Fat* **2009**, *34*, 59–62.
17. Lawrence, M.; Jiang, Y. Porosity, pore size distribution, micro-structure. In *Bio-Aggregates Based Building Materials*; Springer: Dordrecht, The Netherlands, 2017; pp. 39–71.

18. Besnardiere, J.; Ma, B.; Torres-Pardo, A.; Wallez, G.; Kabbour, H.; González-Calbet, J.M.; Von Bardeleben, H.J.; Fleury, F.; Buissette, V.; Sanchez, C.; et al. Structure and electrochromism of two-dimensional octahedral molecular sieve h'-WO<sub>3</sub>. *Nat. Commun.* **2019**, *10*, 1–9. [CrossRef]
19. Khalil, A.M.; Eljamal, O.; Amen, T.W.; Sugihara, Y.; Matsunaga, N. Optimized nano-scale zero-valent iron supported on treated activated carbon for enhanced nitrate and phosphate removal from water. *Chem. Eng. J.* **2017**, *309*, 349–365. [CrossRef]
20. Ramírez-Rodríguez, L.C.; Díaz Barrera, L.E.; Quintanilla-Carvajal, M.X.; Mendoza-Castillo, D.I.; Bonilla-Petriciolet, A.; Jiménez-Junca, C. Preparation of a hybrid membrane from whey protein fibrils and activated carbon to remove mercury and chromium from water. *Membranes* **2020**, *10*, 386. [CrossRef]
21. Manoli, K.; Nakhla, G.; Feng, M.; Sharma, V.K.; Ray, A.K. Silica gel-enhanced oxidation of caffeine by ferrate (VI). *Chem. Eng. J.* **2017**, *330*, 987–994. [CrossRef]
22. Li, X.; Chen, G.; Liu, C.; Ma, W.; Yan, B.; Zhang, J. Hydrodeoxygenation of lignin-derived bio-oil using molecular sieves supported metal catalysts: A critical review. *Renew. Sust. Energy Rev.* **2017**, *71*, 296–308. [CrossRef]
23. Atyakshcheva, L.F.; Kasyanov, I.A.; Ivanova, I.I. Adsorptive Immobilization of proteins on mesoporous molecular sieves and zeolites. *Petrol. Chem.* **2019**, *59*, 327–337. [CrossRef]
24. Tasharrofi, S.; Golchoobi, A.; Fesahat, H.; Taghdisian, H.; Hosseinnia, A. Effects of water content on so<sub>2</sub>/n<sub>2</sub> binary adsorption capacities of 13x and 5a molecular sieve, experiment, simulation, and modeling. *J. Petrol. Sci. Technol.* **2019**, *9*, 30–45.
25. Garcia, L.; Rodriguez, G.; Orjuela, A. Study of the pilot-scale pan granulation of zeolite-based molecular sieves. *Braz. J. Chem. Eng.* **2021**, *38*, 165–175. [CrossRef]
26. Santos, M.G.; Correia, L.M.; de Medeiros, J.L.; Ofélia de Queiroz, F.A. Natural gas dehydration by molecular sieve in offshore plants: Impact of increasing carbon dioxide content. *Energy Convers. Manag.* **2017**, *149*, 760–773. [CrossRef]
27. He, X.; Chu, Y.; Lindbråthen, A.; Hillestad, M.; Hägg, M.B. Carbon molecular sieve membranes for biogas upgrading: Techno-economic feasibility analysis. *J. Clean. Prod.* **2018**, *194*, 584–593. [CrossRef]
28. Liu, X.; Wang, R. Effective removal of hydrogen sulfide using 4A molecular sieve zeolite synthesized from attapulgite. *J. Hazard. Mater.* **2017**, *326*, 157–164. [CrossRef]
29. Xia, Z.; Ying, L.; Fang, J.; Du, Y.Y.; Zhang, W.M.; Guo, X.; Yin, J. Preparation of covalently cross-linked sulfonated polybenzimidazole membranes for vanadium redox flow battery applications. *J. Membr. Sci.* **2017**, *525*, 229–239. [CrossRef]
30. Lin, C.Y.; Ma, L. Influences of water content in feedstock oil on burning characteristics of fatty acid methyl esters. *Processes* **2020**, *8*, 1130. [CrossRef]
31. Pahl, C.; Pasel, C.; Luckas, M.; Bathen, D. Adsorptive water removal from organic solvents in the ppm-region. *Chem. Ing. Tech.* **2011**, *83*, 177–182. [CrossRef]
32. Xu, Y.M.; Tang, Y.P.; Chung, T.S.; Weber, M.; Maletzko, C. Polyarylether membranes for dehydration of ethanol and methanol via pervaporation. *Sep. Purif. Technol.* **2018**, *193*, 165–174. [CrossRef]
33. Salam, M.A.; Ahmed, K.; Hossain, T.; Habib, M.S.; Uddin, M.S.; Papri, N. Prospect of molecular sieves production using rice husk in bangladesh: A review. *Int. J. Chem. Math. Phys.* **2019**, *3*, 105–134. [CrossRef]
34. Gabruś, E.; Witkiewicz, K.; Nastaj, J. Modeling of regeneration stage of 3A and 4A zeolite molecular sieves in TSA process used for dewatering of aliphatic alcohols. *Chem. Eng. J.* **2018**, *337*, 416–427. [CrossRef]
35. Herold, R.H.M.; Mokhatab, S. Optimal Design and Operation of Molecular Sieve Gas Dehydration Units—Part 1. Gas Processing & LNG. 2017. Available online: <http://www.gasprocessingnews.com/features/201708/optimal-design-and-operation-of-molecular-sieve-gas-dehydration-units%E2%80%94part-1.aspx> (accessed on 25 July 2021).
36. Wang, H.; Jia, C.; Xia, X.; Karangwa, E.; Zhang, X. Enzymatic synthesis of phytosteryl lipoate and its antioxidant properties. *Food Chem.* **2018**, *240*, 736–742. [CrossRef]
37. Lad, J.B.; Makkawi, Y.T. Adsorption of methyl chloride on molecular sieves, silica gels, and activated carbon. *Chem. Eng. Technol.* **2020**, *43*, 436–446. [CrossRef]
38. Jemil, N.; Hmidet, N.; Ayed, H.B.; Nasri, M. Physicochemical characterization of Enterobacter cloacae C3 lipopeptides and their applications in enhancing diesel oil biodegradation. *Process. Saf. Environ.* **2018**, *117*, 399–407. [CrossRef]
39. Wang, F.; Wang, E.; Zhang, L.; Jia, P.; Wang, T. Influence of electromagnetic stirring (EMS) on the microstructure and mechanical property of Incoloy825 superalloy. *J. Manuf. Process.* **2017**, *26*, 364–371. [CrossRef]
40. Saremnia, B.; Esmaeili, A.; Sohrabi, M.R. Removal of total petroleum hydrocarbons from oil refinery waste using granulated NaA zeolite nanoparticles modified with hexadecyltrimethylammonium bromide. *Can. J. Chem.* **2016**, *94*, 163–169. [CrossRef]
41. Van Thuoc, D.; My, D.N.; Loan, T.T.; Sudesh, K. Utilization of waste fish oil and glycerol as carbon sources for polyhydroxyalkanoate production by *Salinivibrio* sp. M318. *Int. J. Biol. Macromol.* **2019**, *141*, 885–892. [CrossRef] [PubMed]
42. Tiadi, N.; Dash, R.R.; Mohanty, C.R.; Patel, A.M. Comparative studies of adsorption of chromium (VI) ions onto different industrial wastes. *J. Hazard Toxic Radioact. Waste* **2020**, *24*, 04020021. [CrossRef]
43. Dey, S.; Mehta, N.S. To optimized various parameters of Hopcalite catalysts in the synthetic processes for low temperature CO oxidation. *Appl. Energy Combust. Sci* **2021**, *6*, 100031.
44. Raviadaran, R.; Ng, M.H.; Manickam, S.; Chandran, D. Ultrasound-assisted water-in-palm oil nano-emulsion: Influence of polyglycerol polyricinoleate and NaCl on its stability. *Ultrason. Sonochem.* **2019**, *52*, 353–363. [CrossRef] [PubMed]
45. Davis, G.W. Addressing concerns related to the use of ethanol-blended fuels in marine vehicles. *J. Sustain. Dev. Energy Water Environ. Syst.* **2017**, *5*, 546–559. [CrossRef]



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46. Anand, V.; Juvekar, V.A.; Thaokar, R.M. Coalescence, partial coalescence, and noncoalescence of an aqueous drop at an oil–water interface under an electric field. *Langmuir* **2020**, *36*, 6051–6060. [[CrossRef](#)] [[PubMed](#)]
  47. Purnama, K.O.; Setyaningsih, D.; Hambali, E.; Taniwiryono, D. Processing, characteristics, and potential application of red palm oil—A review. *Int. J. Oil Palm* **2020**, *3*, 40–55. [[CrossRef](#)]
  48. Zhu, Z.; Hu, D.; Liu, Y.; Xu, Y.; Zeng, G.; Wang, W.; Cui, F. Three-component mixed matrix organic/inorganic hybrid membranes for pervaporation separation of ethanol–water mixture. *J. Appl. Polym. Sci.* **2017**, *134*. [[CrossRef](#)]
  49. Ai, F.; Yin, X.; Hu, R.; Ma, H.; Liu, W. Research into the super-absorbent polymers on agricultural water. *Agric. Water Manag.* **2021**, *245*, 106513. [[CrossRef](#)]
  50. Lin, C.Y.; Ma, L. Fluid characteristics of biodiesel produced from palm oil with various initial water contents. *Processes* **2021**, *9*, 309. [[CrossRef](#)]