Abstract: In this work, the beads and powder potassium hydroxide (KOH) and potassium carbonate (K$_2$CO$_3$) supported on alumina oxide (Al$_2$O$_3$) were successfully prepared via incipient wetness impregnation technique. Herein, the perforated hydrophilic materials (PHM) made from low-density polyethylene (LDPE) was used as the catalyst reactor bed. The prepared catalysts were investigated using TGA, XRD, BET, SEM-EDX, TPD, FTIR while spent catalysts were analyzed using XRF and ICP-AES to study its deactivation mechanism. The catalytic performance of beads and powder KOH/Al$_2$O$_3$ and K$_2$CO$_3$/Al$_2$O$_3$ catalysts were evaluated via transesterification of waste cooking oil (WCO) to biodiesel. It was found that the optimum conditions for transesterification reaction were 1:12 of oil-to-methanol molar ratio and 5 wt.% of catalyst at 65 °C. As a result, the mesoporous size of beads KOH/Al$_2$O$_3$ and K$_2$CO$_3$/Al$_2$O$_3$ catalysts yielded 86.8% and 77.3% at 2 h’ reaction time of fatty acids methyl ester (FAME), respectively. It was revealed that the utilization of PHM for beads K$_2$CO$_3$/Al$_2$O$_3$ increase the reusability of the catalyst up to 7 cycles. Furthermore, the FAME produced was confirmed by the gas chromatography-mass spectroscopic technique. From this finding, beads KOH/Al$_2$O$_3$ and K$_2$CO$_3$/Al$_2$O$_3$ catalysts showed a promising performance to convert WCO to FAME or known as biodiesel.

Keywords: biodiesel; waste cooking oil; transesterification; K$_2$CO$_3$/Al$_2$O$_3$; KOH/Al$_2$O$_3$

1. Introduction

One of the most promising and safest means to overcome the global environmental issue is by replacing conventional diesel with biodiesel generated from edible and non-edible plant oils or animal fats [1,2]. Theoretically, biodiesel has low sulfur content than petrol diesel and could reduce hazardous gas emissions, such as SO$_2$, NO$_2$, CO$_2$ and particulate matter, generally produced by diesel engines [3]. Nowadays, scientists believed that the utilization of WCO as the biodiesel feedstock could reduce environmental pollutions.

Esterification and transesterification processes are the common techniques to produce biodiesel. Both techniques generally assist by heterogeneous or homogeneous catalyst either acidic or basic. The homogeneous catalytic reaction is defined as the catalyst that has the same phase as a solvent and is found to have several drawbacks, such as (i) corrosion of container pipelines [4], (ii) wastewater pollutions, and (iii) weak catalyst
recovery [5]. The heterogeneous catalyst was introduced because of easy preparation, affordability and promising high biodiesel conversion. The chemical characteristic of the catalyst can be acidic or basic depending on the method used. Example of acid catalysts used are such as sulfonated D-glucose [6], MF-SO$_3$H [7], and SiO$_2$(CH$_2$)$_3$NHSO$_3$H [8]; while, for basic catalyst used such as KOH/NaY [9], Ca/Ba/Al$_2$O$_3$ [10], MgO/Al$_2$O$_3$ [11], and K$_3$PO$_4$/Ac [12]. The chemical characteristic of the catalyst is important to know to match with the feedstock used.

Recently, the powdered heterogeneous catalysts such as RHC/K$_2$O/Fe [13] and KOH/Al$_2$O$_3$ [14] have been utilized in conversion of biodiesel from WCO. However, the powder catalyst has drawbacks such as easy deactivation of catalyst upon exposure to the reaction medium [15], incompatibility with the large batch of the reactor [16], and weak catalyst recovery that leads to difficulties in recycling the catalyst [17]. The use of heterogeneous beads catalysts has been considered. The beads catalyst has an advantage in terms of its different geometrical shapes that create various pores, allowing the optimum hydrodynamic and contact between reactant, catalyst, and solvent to increasing the catalyst’s performance [18].

Several heterogeneous beads catalysts are reported compatible with biodiesel production [19,20], such as K$_2$CO$_3$/Al$_2$O$_3$ and KOH/Al$_2$O$_3$ due to their simple preparation, low cost, and high-yield capacity of biodiesel production [21,22]. The reversible chemisorption on both K$_2$CO$_3$/Al$_2$O$_3$ and KOH/Al$_2$O$_3$ was reported to be stable at higher temperature and pressure [23–25], making the essential salt suitable as a catalyst for the reactions. The alkaline-catalyzed transesterification process is generally adopted for biodiesel production because alkaline metal alkoxides and hydroxides are the most effective transesterification catalysts compared to the acid catalysts. However, for economic reasons, hydroxides are more often used.

This research aims to improve and study the binding strength between K$_2$CO$_3$ and KOH onto Al$_2$O$_3$ beads support and Al$_2$O$_3$ powder with a simple, environmental-friendly, and green preparation technique by using perforated hydrophilic material (PHM) as reactor container for beads catalyst. To the best of our knowledge, this is the first reported paper to discuss the utilization of PHM reactor for the protection and stability of the catalyst. This study also focused on the effect of alumina beads-supported K$_2$CO$_3$ and KOH catalysts on the transesterification of WCO with low free fatty acid (FFA) numbers. Besides, the PHM reactor made from low-density polyethylene (LDPE) for reactor container was introduced to reduce the catalyst damage and deactivation due to physical contact with the stirrer. The PHM reactor was designed as a porous catalyst container that helps the catalyst maintain its shape before and after the reaction. The solution can easily pass through the container via a tiny hole. The effects of the catalyst preparation, reaction conditions, catalyst performance, and catalyst reusability, were also investigated and discussed in this paper.

2. Results and Discussion

2.1. Thermogravimetric Analysis

In this work, to determine the optimum calcination temperature for the catalyst, the thermal gravimetric analysis (TGA) was carried out; thus, both powdered and beads K$_2$CO$_3$/Al$_2$O$_3$ and KOH/Al$_2$O$_3$ catalysts were analyzed. As shown in Figure 1, results of all prepared catalysts ranging between 32 and 1000 ºC showed four stages of decomposition phase, which are: (1) Evaporation of water molecules for all catalyst in between 32 ºC and 100 ºC [14,26]; (2) commencement of dehydroxylation of OH$^-$ molecules [27]; and (3) observation of broadband of K$_2$CO$_3$/Al$_2$O$_3$ catalyst, indicating the decomposition of KHCO$_3$ [28].

At stage 3, the 25% decomposition of KAl(CO$_3$)(OH)$_2$ occurred for beads K$_2$CO$_3$/Al$_2$O$_3$ ranging from 300 to 400 ºC [29]. While the last decomposition phase at stage 4, represents the successful activation of the catalyst as a result of the formation of K$_2$O and K$_2$O$_3$ has been reported in XRD (Figure 2). The optimum calcination temperature of 700 ºC was chosen based on the average of 850 ºC and 650 ºC, the temperatures at which for both
powder and beads Al₂O₃ treated with KOH showed the formation of K₂O₂ (4KOH + O₂ → 2K₂O₂ + 2H₂O) and additional active species for K₂CO₃ showed the formation of K₂O (2K₂CO₃ + O₂ → 2CO₂ + O₂ + K₂O) species on the Al₂O₃ [18]. For the K₂CO₃/Al₂O₃ powder catalyst (Figure 1c), the desorption peak is very small because the layer is compressed in one thermogram. The effect of decomposition rate between powder and beads catalyst is not much different, so the decomposition of K₂CO₃/Al₂O₃ powder catalyst can be referred to K₂CO₃/Al₂O₃ beads catalyst. A study from Sharikh et al. [30] also stated that by using K₂CO₃ catalyst, the suitable calcination temperature was at 700 °C because of the activation of the catalyst in the range of 680 °C to 1000 °C. Meanwhile, starting from 700 °C, the powder and beads Al₂O₃ treated with K₂CO₃ showed the formation of K₂O with the simultaneous loss of carbon dioxide [31]. The catalyst studied showed good strength and stability at high temperatures making the hydrophobic characteristic of the catalyst more efficient toward biodiesel production.

Figure 1. TGA thermogram of (a) powder KOH/Al₂O₃, (b) beads KOH/Al₂O₃, (c) powder K₂CO₃/Al₂O₃, and (d) beads K₂CO₃/Al₂O₃.
2.3. Catalyst Surface Characteristics

Pore size distribution curves and nitrogen adsorption-desorption isotherm graph for powder Al₂O₃, beads Al₂O₃, powder KOH/Al₂O₃, beads KOH/Al₂O₃, powder K₂CO₃/Al₂O₃, and beads K₂CO₃/Al₂O₃ catalysts are shown in Figure 3. The BET surface area, total pore volume and average pore diameter are shown in Table 1. It was observed that the BET surface area of all catalysts decreases as compared to Al₂O₃ powder and beads support. Surface area for powder KOH/Al₂O₃ and K₂CO₃/Al₂O₃ decrease from 2.45 m²/g to 2.36 m²/g and 1.51 m²/g, respectively. For beads catalyst, surface area for KOH/Al₂O₃ and K₂CO₃/Al₂O₃ decrease from 282.10 m²/g to 133.37 m²/g and 199.94 m²/g, respectively. It was suspected that the surface of catalyst support was covered by potassium compounds, and the pore of the catalyst was blocked [32]. M.A Mohammed et al. [33] also stated that the reduction of the

Figure 2. XRD patterns for (a) powder Al₂O₃, (b) beads Al₂O₃, (c) powder KOH/Al₂O₃, (d) beads KOH/Al₂O₃, (e) powder K₂CO₃/Al₂O₃, and (f) beads K₂CO₃/Al₂O₃.

2.2. XRD Analysis of K₂O₂/Al₂O₃ and K₂O/Al₂O₃ Catalysts

The crystallinity and phase transition of powder Al₂O₃, beads Al₂O₃, powder KOH/Al₂O₃, beads KOH/Al₂O₃, powder K₂CO₃/Al₂O₃, and beads K₂CO₃/Al₂O₃ samples were studied by using XRD. As shown in Figure 2, there are ten peaks observed at 2θ = 26°, 35°, 38°, 44°, 53°, 58°, 62°, 67°, 69°, and 78° which corresponded to the Al₂O₃ (JCPDS file 51-0769). The intensity of the support (beads and powder) increase after KOH and K₂CO₃ are deposited onto the surface of the support. In general, all catalysts possessed high crystallinity, indicated by the high intensity and sharp peaks. Based on (Figure 2c,f), all catalysts show same plot for the presence of K₂O at 2θ = 31°, 33°, and 34° (JCPDS file 50-05241) except for K₂CO₃/Al₂O₃ beads (Figure 2f) which show additional K₂O₂ spotted at 2θ = 43° (JCPDS file 50-05241). For K₂O, it was found that the species spotted at 2θ = 22°, 39°, 40°, 41°, and 42° for KOH/Al₂O₃ powder (Figure 2c) and another K₂O spotted at 2θ = 47°, 48°, 49°, and 50° for K₂CO₃/Al₂O₃ beads (Figure 2f) (JCPDS file 50–1327). The intensity peaks of beads KOH/Al₂O₃ and powder K₂CO₃/Al₂O₃ seem to decrease compared to others due to the hindrance of the higher amount of K disperse on the surface of the catalyst [29]. In this study, powder KOH/Al₂O₃ and beads K₂CO₃/Al₂O₃ catalyst was successfully converted to desired species (K₂O₂ and K₂O) for the reaction.
surface area might be due to the sintering effect that led to particle growth and crystallization. On the other hand, the pore sized of KOH/Al₂O₃ and K₂CO₃/Al₂O₃ catalyst increased, as observed in Figure 3.

Figure 3. N₂ adsorption-desorption equilibrium and BJH pore size distribution of (a) powder Al₂O₃, (b) beads Al₂O₃, (c) powder KOH/Al₂O₃, (d) beads KOH/Al₂O₃, (e) powder K₂CO₃/Al₂O₃, and (f) beads K₂CO₃/Al₂O₃ catalyst.
Table 1. Physical properties of alumina-based $\text{K}_2\text{CO}_3$ and KOH catalyst with its mass content and density of active sites.

| Catalyst               | Physical Properties | Mass of Element (%) | Density of Active Site (mmol/g) |
|------------------------|---------------------|---------------------|---------------------------------|
|                        | Surface Area (m$^2$/g) | Pore Volume (cm$^3$/g) | Pore Size (nm) | Weak (<160 °C) | Moderate (160–400 °C) | Strong (>400 °C) |
| Al$_2$O$_3$ powder     | 2.50                | 0.01                | 5.03            | 0.00           | 0.00                 | 99.98            | 2.36 - -          |
| Al$_2$O$_3$ beads      | 282.10              | 0.44                | 6.24            | 0.00           | 0.00                 | 99.98            | 0.34 0.20 0.45   |
| KOH/Al$_2$O$_3$ powder | 2.40                | 0.01                | 5.16            | 22.50          | 45.26                | 32.24            | N/A N/A N/A      |
| KOH/Al$_2$O$_3$ beads  | 133.40              | 0.35                | 7.09            | 25.37          | 41.48                | 33.15            | 0.15 0.08 2.38   |
| $\text{K}_2\text{CO}_3$/Al$_2$O$_3$ powder | 1.506              | 0.0069              | 5.437           | 18.96          | 43.27                | 37.77            | N/A N/A N/A      |
| $\text{K}_2\text{CO}_3$/Al$_2$O$_3$ beads | 199.94             | 0.474               | 6.512           | 28.41          | 45.44                | 26.15            | 0.00 0.17 3.94   |

1 BET surface area; 2 estimated from Barrett, Joyner, and Halenda (BJH) model.

All four catalysts and supports that have narrow pore size distribution with diameter in between ~5 and ~7 nm are displayed in Figure 4c–f and summarized in Table 1. Pore sizes for Al$_2$O$_3$ powder and beads support were 5.03 and 6.24 nm, respectively and the broad peak of pore distribution is displayed in Figure 3a,b. When KOH and $\text{K}_2\text{CO}_3$ are immobilized onto the surface of the Al$_2$O$_3$ powder support, the pore size increases to 5.15 nm and 5.44 nm, with both catalysts seem to have similar pore distribution with Al$_2$O$_3$ powder support (Figure 3c,e). For Al$_2$O$_3$ beads support, the better pore distribution was spotted after KOH and $\text{K}_2\text{CO}_3$ were immobilized onto the surface of the Al$_2$O$_3$ beads support (Figure 3d,f). Beads KOH/Al$_2$O$_3$ and $\text{K}_2\text{CO}_3$/Al$_2$O$_3$ seem to have wider pore distribution and better pore size making the catalyst much effective and efficient. As shown in Figure 3 all catalyst displayed type V (based on IUPAC classification) isotherms for the typical $H_3$ hysteresis loop for powder catalyst and $H_4$ hysteresis loop for beads catalyst, validating the existence of mesoporous characteristics (2–50 nm based on IUPAC) [34] in the channel. Based on the isotherm plot in Figure 3, if the adsorption-desorption reaction occurs in relative pressure ($p/p^\circ$) of 0.4 to 0.6 is generally attributed to small pores [35]. The KOH/Al$_2$O$_3$ powder, KOH/Al$_2$O$_3$ beads, $\text{K}_2\text{CO}_3$/Al$_2$O$_3$ powder, and $\text{K}_2\text{CO}_3$/Al$_2$O$_3$ beads samples show a hysteresis effect in the 0.4 to 0.6 relative pressure region, which is characteristic of small pore texture. Powder catalyst has small pore texture and small surface area while beads catalyst shows smaller pore texture and large surface area based on the hysteresis loop [36]. Beads catalysts seem to be the best catalyst as the surface area, pore size, and pore distribution are better than powder catalysts.
Saba et al. [28] stated that the strong basic properties of the catalyst of K$_2$CO$_3$/Al$_2$O$_3$ have a high potential to absorb moisture resulting from particle agglomeration.

Figure 4. Cont.
Figure 4. SEM images and EDX mapping for (a) powder Al₂O₃, (b) beads Al₂O₃, (c) powder KOH/Al₂O₃, (d) beads KOH/Al₂O₃, (e) powder K₂CO₃/Al₂O₃, and (f) beads K₂CO₃/Al₂O₃.

2.4. Scanning Electron Microscope—Energy Dispersive X-ray Analysis

Figure 4 shows the SEM images of Al₂O₃, KOH/Al₂O₃, and K₂CO₃/Al₂O₃ catalyst with the EDX mapping of potassium (K) and oxygen (O). It was observed that the morphology of alumina-based K₂CO₃ and KOH catalysts exhibited a relatively tight irregular plate structure. For powder K₂CO₃/Al₂O₃ (Figure 4e), the appearance of a large oval shape-like fibrous plate on the surface is due to the agglomeration of the catalyst in addition to the exfoliation of its surface. Compared to the beads catalyst (Figure 4d,f), the irregular plate image can be clearly observed and showed a good morphological structure with higher surface area as recorded by BET data in Table 2.

Table 2. The reusability study for beads catalyst with and without PHM.

| Catalyst            | Reusability |
|---------------------|-------------|
|                     | 1st | 2nd | 3rd | 4th | 5th | 6th | 7th | 8th |
| K₂CO₃/Al₂O₃ (PHM)   | 77.4 | 70.2 | 66.7 | 55.7 | 43.6 | 40.2 | 19.5 | 0   |
| K₂CO₃/Al₂O₃         | 72.1 | 0    | 0    | 0    | 0    | 0    | 0    | 0   |
| KOH/Al₂O₃ (PHM)     | 86.8 | 70.6 | 0    | 0    | 0    | 0    | 0    | 0   |
| KOH/Al₂O₃           | 73.5 | 0    | 0    | 0    | 0    | 0    | 0    | 0   |
Saba et al. [28] stated that the strong basic properties of the catalyst of \( \text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3 \) have a high potential to absorb moisture resulting from particle agglomeration.

This observation is consistent with the data in Table 1, where the structure is mesoporous with a high surface area. Based on the mapping images of the EDX, the distribution of elements K and O revealed significant dispersion on the surface of the \( \text{Al}_2\text{O}_3 \) support material. It was observed that the distribution of K and O on the \( \text{Al}_2\text{O}_3 \) has better uniformity as compared to powder catalyst. This finding is in good agreement with the research reported by A. Islam et al. [34] where they reported that the potassium element has good dispersion on the surface of the \( \text{Al}_2\text{O}_3 \) catalyst.

2.5. Temperature Programmed Desorption-Carbon Dioxide Analysis

The strength and proportion of the different basic sites of the catalyst need to be evaluated by thermal desorption of \( \text{CO}_2 \) (\( \text{CO}_2\)-TPD). Figure 5 shows the TPD-CO\(_2\) profile of calcined material for beads \( \text{Al}_2\text{O}_3 \), \( \text{KOH}/\text{Al}_2\text{O}_3 \), and \( \text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3 \) with the amount of \( \text{CO}_2 \) desorbed (mV) as a function of the \( \text{CO}_2 \) desorption temperature (°C). The higher \( \text{CO}_2 \) desorption peak indicates the highest catalyst basicity because the strength of the surface bond reflects the temperature at which the \( \text{CO}_2 \) is desorbed, resulting in peaks that can be correlated to three different types of active sites. The three different types of strength active sites reported by Junior et al. and Shan et al. [18,37] were weak sites (\( \text{CO}_2 \) desorbed <160 °C), medium sites (\( \text{CO}_2 \) desorbed 160 °C < x < 400 °C), and strong site (\( \text{CO}_2 \) desorbed >400 °C). Then, according to the attained desorption temperature, beads \( \text{Al}_2\text{O}_3 \) show medium desorption peak range 90 °C to 384 °C (higheast peak at 270 °C). The peak was assigned by the presence of SiO\(_2\), where it was used as the binder to keep the sphere structure of supports and enhanced basic properties of catalyst [38]. For beads, \( \text{KOH}/\text{Al}_2\text{O}_3 \) catalyst shows a strong and broad desorption peak range 350 °C to 800 °C (peak at 536 °C). This broadband indicated the presence of covalent bonding between \( \text{CO}_2 \) and K/\( \text{Al}_2\text{O}_3 \) [32]. However, the \( \text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3 \) has broad peaks from 350 °C to 850 °C, peaked at 764 °C with two small shoulders at 524 °C and 630 °C. Within that range, between 350 and 580 indicates low strength, in between 580 and 697 indicates medium strength, and 700 and 860 indicates high strength [39–41]. Furthermore, it was observed that \( \text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3 \) has 3.94 mmol/g of basic sites, and \( \text{KOH}/\text{Al}_2\text{O}_3 \) has 2.38 mmol/g of basic sites. From this data, \( \text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3 \) has higher basic sites and is predicted to be a high performance of catalyst for biodiesel production. TPD-CO\(_2\) findings were in agreement with BET data in Table 2 in regards to the increased basicity due to the higher surface area (higher active sites) [41]. Despite the similarity between the physical properties of beads and powder catalysts, beads catalyst remains a better choice.
2.6. Transesterification Reaction

Further analysis on the sample was conducted by using GC-MS to calculate the actual pure FAME content from the impure biodiesel collected from transesterification reaction where the percentage of ester content was obtained. Methyl heptadecanoate (C17) was used as the internal standard in the analysis to calculate the ester content based on the peak area of FAME species in the sample relative to the standard [42]. The ester content was calculated using formula (2) as mentioned in Section 2.6 (EN14103). Sample from beads K2CO3/Al2O3 catalyst at 1 h reaction time was tested for GCMS qualitative analysis, and from the result in Figure 6, eight peaks were observed for the entire compound present in the biodiesel, of which only seven corresponded to the methyl ester group [43]. The identified FAME was analyzed against the standard peak from pure biodiesel sample (internal standard) of myristate methyl ester, palmitate methyl ester, stearate methyl ester, oleate methyl ester, linoleate methyl ester, linolenate methyl ester, and heptadecanoic acid methyl ester. All peaks that appeared (except for 9-hexadecanoic acid) were verified against different esters and confirmed using the mass spectroscopy (MS) library programmed. Furthermore, a standard sample (100% pure biodiesel) was tested and used as a benchmark for the selection of the right peaks to calculate the ester contained in the collected biodiesel [42].

The results of biodiesel yield are shown in Figure 7. The experiments were carried out using a catalyst containing 30% KOH/70% Al2O3 and 30% K2CO3/70% Al2O3. The optimum condition for the transesterification reaction was 1:12 of oil to methanol ratio, 5 wt% of catalyst loading, 65 °C of reaction temperature, and 1 to 4 h reaction time. According to the results, powder KOH/Al2O3 catalyst shows 66.7% biodiesel yield at 3 h reaction time, and powder K2CO3/Al2O3 catalyst shows 72.28% biodiesel yield at 4 h reaction time. In comparison, beads catalyst exhibited the highest biodiesel yield which beads KOH/Al2O3 catalyst shows 86.8% biodiesel yield at 2 h reaction time and powder K2CO3/Al2O3 catalyst shows 77.3% biodiesel yield at 2 h reaction time. This result is coherent with BET and TPD results where beads catalyst provides larger surface area (refer to Table 1) that increases many active sites deposited on the surface and increasing the basicity of the catalyst. The lack of performance of powder catalyst can be divided into two, which are either the catalyst is easily coated by glycerol as the catalyst and glycerol at the bottom of the container or direct contact between the catalyst and magnetic stirrer resulting in deactivation of the catalyst [44,45]. Moreover, a study from [34] stated that increasing the reaction time will ultimately increase the effect of the leaching of the powder catalyst.

Figure 5. TPD-CO2 profile of calcined material for beads Al2O3, beads KOH/Al2O3, and beads K2CO3/Al2O3.
catalyst. The catalyst that can produce biodiesel more than 70% can be considered a good catalyst, as industrial production in Malaysia using homogeneous catalysts can produce biodiesel up to 65% to 85% per batch. Beads catalysts for both K$_2$CO$_3$ and KOH remain a better choice for increased biodiesel production compared to the powder catalyst. In comparison, research studied by Shan et al. [37], produce biodiesel from palm oil catalyzed by palygorskite-supported K$_2$CO$_3$ resulting in 75–85% biodiesel yield at 2 h reaction time.

### Table 1

| Standard peak | Sample peak | Compound name                          |
|---------------|------------|----------------------------------------|
| 12.236        | 12.231     | Mynriste methyl ester                   |
| 13.320        | 13.330     | Palmitate methyl ester                  |
| -             | 13.576     | 9-Hexadecenic acid                      |
| 13.829        | 13.827     | Heptadecanoic methyl ester (IS)         |
| 14.321        | 14.331     | Stearate methyl ester                   |
| 14.544        | 14.548     | Oleate methyl ester                     |
| 14.911        | 14.897     | Linoleate methyl ester                  |
| 15.357        | 15.327     | Linolenate methyl ester                 |

**Figure 6.** Example of GC-MS intensity peak area and compound of each peak for K$_2$CO$_3$/Al$_2$O$_3$ beads catalyst. * (IS) Internal Standard.

**Figure 7.** Percentage yield of pure biodiesel.
2.7. Reusability Testing for Beads KOH/Al₂O₃ and K₂CO₃/Al₂O₃

K₂CO₃/Al₂O₃ and KOH/Al₂O₃ (beads and powder) catalysts that reveal the highest yield in Section 2.6 then underwent reusability testing to obtain the stability information of the catalyst after a few cycles of reaction. Beads formed of both catalysts were proceed at 2 h reaction time while for powder K₂CO₃/Al₂O₃ catalyst at 4 h reaction time and KOH/Al₂O₃ catalyst at 3 h reaction time. The catalyst recovered after the reaction was washed and reactivated at 700 °C for 2 h. By washing and reactivating the catalyst, the impurities that remained on the catalyst’s surface were removed, and the active sites were exposed for another reaction. The reusability testing was performed up to the 7th cycle for K₂CO₃/Al₂O₃ beads catalyst and 2nd cycle for KOH/Al₂O₃ beads catalyst by maintaining the amount of catalyst for every cycle in order to cover up the loss of the catalyst amount during the separation and reactivation process. From the experiment, the mass for the spent catalyst remains unchanged and Figure 8 reveals that there was a slight decrease in the pattern in the biodiesel yield. However, the conversions were still considered as high until the second cycle. For KOH/Al₂O₃ beads and powder catalyst, the reusability of the catalyst stops at the third cycle because the catalyst becomes soggy and ruptures due to the hygroscopic characteristic of the material [14,46]. The K₂CO₃/Al₂O₃ catalyst shows tremendous performance in converting the biodiesel. The strong and stable structure makes the catalyst very useful until the last cycle. In the end, the reason for declining biodiesel conversion might be due to the leaching of K₂O₂ and K₂O from Al₂O₃, resulting in the loss of active sites from the surface of the catalyst [47,48].

![Figure 8. Reusability testing for K₂CO₃/Al₂O₃ and KOH/Al₂O₃ catalyst.](image-url)
previous study conducted by [31] used K$_3$PO$_4$ supported-alumina beads and revealed that the reusability of the catalyst was up to the 2nd cycle, as leaching effect resulting from the crushed beads catalyst becomes apparent at the 3rd cycle.

2.8. Identification of Post-Reaction Compounds on the Catalyst Surface Using Fourier-Transform Infrared Spectroscopy

The beads K$_2$CO$_3$/Al$_2$O$_3$ and beads KOH/Al$_2$O$_3$ catalysts were chosen and favored over others due to their high biodiesel production and reusability. Thus, further investigation was carried out to identify the compounds present in the spent catalyst using FTIR and compared with fresh beads K$_2$CO$_3$/Al$_2$O$_3$ and KOH/Al$_2$O$_3$ catalysts. The catalysts showed sample adsorption of wavelength, with the observation of higher adsorption intensity of beads KOH/Al$_2$O$_3$ catalyst compared to beads K$_2$CO$_3$/Al$_2$O$_3$ catalyst. This implies that the catalyst can easily degenerate after yielding low biodiesel for few consecutive cycles and then become unrecyclable. This may be attributed to the presence of an undesired compound on the surface of the catalyst after the reaction. The compound probably binds permanently to the surface of the catalyst and inhibit the performance of active sites. The catalyst may also be leached out from the support, thereby reducing the catalyst performance.

Figure 9 shows the FTIR spectrum of the fresh and spent catalyst after 2nd cycle for KOH/Al$_2$O$_3$ and 7th consecutive cycle for K$_2$CO$_3$/Al$_2$O$_3$, resulting in the degeneration of the potential catalyst. From the FTIR spectrum, the fresh catalyst for KOH/Al$_2$O$_3$ and K$_2$CO$_3$/Al$_2$O$_3$ shows straight lines indicating that there is no species/impurities found on the surface of the catalyst compared to the spent catalyst. For the spent catalyst, it was presented that the strong hydroxyl (υ-OH) stretching vibration of the surface of the hydroxyl group that attached to the catalyst can be observed at the wavelength range of 3500 to 3200 cm$^{-1}$ [44]. For sp$^3$ and sp$^3$ aliphatic hydrocarbon chain (υ-CH) for stretching vibration can be observed at a wavelength of 3000 to 2820 cm$^{-1}$ and 2750 cm$^{-1}$, respectively [49,50]. The carbonyl group (υ-C=O) stretching vibration of 1735 cm$^{-1}$ and continue adsorption at wavelength of 1600 cm$^{-1}$ due to aliphatic alkene structure (υ-C=C) were caused by fatty acids methyl ester [51,52]. The hydroxyl (υ-OH) bending vibration occurs at 1550 caused by H$_2$O adsorbed from the air [44]. The vibration of a cyclic compound such as benzene rings (υ-C=C) and the major absorption peak at the wavenumber of 1407 cm$^{-1}$ can be assigned to the asymmetric stretching of carbonate (υ-CO$_2^+$) group observed in the K$_2$CO$_3$ calcined at 700 °C. The resonance of the carbon bond atom with an oxygen atom (υ-CO, υ-C=C, and υ-COC) can be observed at a range of 1600 to 1200 cm$^{-1}$ and continue at a range of 1100 to 1000 cm$^{-1}$, respectively [53–55]. The lower frequency basically shows the properties of the metal oxide where the range 1000 to 700 cm$^{-1}$ indicates the strong bending of a carbonyl compound with metal ions (υ-C-O-X$^+$) where X represents the potassium ion (K) [37,56].

As shown in Figure 9, the spent catalyst shows the formation of a new peak that might be coming from the impurities or side product at the end of the reaction. Surprisingly, as can be seen from the catalyst’s figure, the potential beads catalyst retains its shape and can overcome the mass loss problem from the catalyst caused by cracking or flushing away of the catalyst together with the reagent used in the reaction. This statement is supported by the TGA result in Figure 1, where the catalyst shows good stability even calcined at higher temperatures. The next observation found was the catalyst changes its color from white to dark orange gradually in every cycle. The spent catalyst changes its color because of the poisoning effect by the side product of the reaction [27,57,58], which is glycerol. During the separation process, glycerol has a dark red color and the side product was located at the bottom of the flask mixed with beads catalyst [59] through the PHM. At the end of 7th catalytic cycle, the physical appearance of the catalyst shows a crack layer for some beads due to the vibration and collision with a magnetic stirrer which reduces the catalyst’s performance [60]. Moreover, the K$_2$O and K$_2$O$_2$ have difficulties from water molecules (H$_2$O) during the reaction because the catalyst reacts with sorbed water from the sample by physical adsorption [34] and causes the bending of OH radical (>1650 cm$^{-1}$) and formation of glycerol carbonate (1800–1000 cm$^{-1}$) [14].
2.9. XRF and ICP-AES Analysis

Spent beads $K_2CO_3/Al_2O_3$ catalyst were chemically analyzed by means of X-ray fluorescent spectrometry (XRF) as mentioned in Table 3. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) was carried out to study the element present in the biodiesel liquid, and the data are shown in Table 4. The XRF and ICP-AES data were obtained only for 1st, 4th, and 8th cycles. According to the results of analyses, it was detected that the leaching happens on the surface of the catalyst—the number of elements that leach out from the surface does not exceed 7%. The previous study also reported that using potassium-based catalyst resulted in the lowest percent of leaching [61] and is easy to recover as the catalyst has defined shape and is larger in size. These data have an agreement with ICP-AES where the catalyst performance starts to drop at the 8th cycle.

Table 3. XRF analysis results of used beads $K_2CO_3/Al_2O_3$ catalyst in the transesterification process.

| Element Analyzed | Fresh (%) | 1st Cycle (%) | 4th Cycle (%) | 8th Cycle (%) |
|------------------|-----------|---------------|---------------|---------------|
| Potassium, (K)   | 0.21      | 0.97          | 4.3           | 6.3           |
| Aluminum, (Al)   | 0.00      | 0.02          | 0.05          | 2.4           |
| Others           | 0.03      | 1.03          | 1.52          | 2.0           |
Table 4. Chemical analysis by ICP-AES of biodiesel liquid sample by using beads K$_2$CO$_3$/Al$_2$O$_3$ catalyst in the transesterification process.

| Element Analyzed | 1st Cycle (%) | 4th Cycle (%) | 8th Cycle (%) |
|------------------|---------------|---------------|---------------|
| Potassium, (K)   | 1.0           | 3.3           | 6.4           |
| Aluminum, (Al)   | 0.0           | 0.1           | 1.5           |

3. Materials and Methods

3.1. Materials

The WCO was obtained from Pasir Gudang, Johor, Malaysia. The pre-treated process started when the WCO bottle was heated first on a hot water bath to dissolve all saturated fat that was deposited at the bottom of the bottle. After that, WCO was filtered to remove traces such as suspended solids and WCO was transferred to the beaker and it was heated at 100 °C on a hotplate for 1 h to remove traces of water, followed by preliminary analysis; acid value (AV) (ASTM D664/D8045-17e1), saponification value (SV) (ASTM D94), free fatty acids content (FFA) (ASTM D5555-95), viscosity (ASTM D445/D446), and moisture content (ASTM D5556-19). Meanwhile, the beads alumina oxide (Al$_2$O$_3$) (particle size < 5 mm), and powder Al$_2$O$_3$ (particle size < 1mm), the analytical grade (AR) methanol (CH$_3$OH, purity 99%), phenolphthalein (C$_{20}$H$_{14}$O$_4$, purity 99%), and methyl heptadecanoate (C$_{18}$H$_{36}$O$_2$, purity 99%) as the internal standard for biodiesel were purchased from Sigma-Aldrich (Selangor, Malaysia). The potassium carbonate (K$_2$CO$_3$, purity 99%), potassium hydroxide (KOH, purity 99%), sodium hydroxide (NaOH, purity 99%), and hydrochloric acid (HCl) (32% concentration, purity 97%) were obtained from Merck (Selangor, Malaysia) chemical company. Meanwhile, the container for the catalyst in the reaction medium (Figure 10) was made from low-density polyethylene (LDPE) of perforated hydrophilic materials (PHM).

Figure 10. Schematic design of the open-system reactor for the transesterification process with the application of the fabricated PHM porous catalyst container.
3.2. Preparation of K$_2$CO$_3$ and KOH/Al$_2$O$_3$ Catalysts

In this work, both beads and powder catalysts were prepared by incipient wetness impregnation technique. Briefly, K$_2$CO$_3$ and KOH salt solutions were added dropwise to water suspension containing powder-Al$_2$O$_3$ in the separate beaker. The mixture was stirred and heated at 100 °C for 5 h, followed by the ageing process at 90 °C for 24 h, and calcined at 700 °C for 3 h with ramping 15 °C min$^{-1}$ to produce powdered K$_2$CO$_3$/Al$_2$O$_3$ and KOH/Al$_2$O$_3$ catalysts. The same procedure was applied to prepare K$_2$CO$_3$/Al$_2$O$_3$ and KOH/Al$_2$O$_3$ catalysts using beads Al$_2$O$_3$ as support.

3.3. Catalyst Characterization of K$_2$CO$_3$/Al$_2$O$_3$ and KOH/Al$_2$O$_3$ Catalysts

The TGA-Pyris 2012 thermogravimetric analysis assisted by thermal gas detector GSA7 from Perkin Elmer (Selangor, Malaysia) was used to determine the thermal decomposition of the prepared catalyst. The analysis was carried out in a static air atmosphere at a heating rate of 15 °C min$^{-1}$. The weight lost and the derivative thermogravimetry (DTG) of the sample against the temperature was plotted.

While the LabX XRD-6100 PANalytical, X-ray diffraction (XRD) analyzer was used for the identification and characterization of the internal structure, bulk phase, and the composition crystallinity phases of the catalyst, the analysis was carried out utilizing XPert PRO Theta from PANalytical diffracted beam monochromator, using step scan mode with range 0°–90° of theta (θ) with the scan rate of 2° min$^{-1}$.

For the quantity, distribution, and strength of the catalyst’s active sites, the prepared catalysts were examined using Thermo Finnigan (Selangor, Malaysia), TPDRO 1100 series of carbon dioxide-temperature programmed desorption CO$_2$-TPD. The sample was first treated with N$_2$ and heated up to 150 °C for 1 h to remove all the particulates and moisture, followed by the absorption of CO$_2$ gas at 10 cc min$^{-1}$ for 1 h at ambient temperature. The second treatment of the sample was done to remove excess CO$_2$ gas by flowing the N$_2$ gas through the samples for another 1 h. Finally, the sample is ready for analysis, and was heated from 50 °C to 1000 °C with a heating rate at 10 °C min$^{-1}$, and the He gas was flowed through the system to carry the CO$_2$ gas detached from the sample before being detected by the thermal conductivity detector. Finally, the intensity of detected gas molecules was plotted versus the temperature.

N$_2$ adsorption/desorption isotherm analysis was performed using Micro metrics ASAP 2010 (Selangor, Malaysia) to determine the catalyst surface area, average pore sizes, pore type, and total pore volumes. Prior to the analysis, the sample was degassed and heated for 24 h at 120 °C to remove moisture and other particulate matter. The N$_2$ gas was allowed to enter the sample reactor to fill the tube with N$_2$ molecules. The reactor containing catalyst was a dip into the liquid N$_2$ to ensure the physisorption attachment of the molecules on the surface of the catalyst. The data isotherms were recorded against the pressure detected to determine the pore volume and surface area of the K$_2$CO$_3$ and KOH/Al$_2$O$_3$ catalysts.

For the morphological and elemental composition analyses, the TESCAN VEGA3 scanning electron microscopy (SEM), Novatiq scientific Singapore (Selangor, Malaysia) equipped with energy-dispersive X-ray spectroscopy (EDX) was utilized. Before analysis, the sample powder was placed on the sample holder and coated with Au using a TESCAN coater.

To study the stability and the strength of catalyst structure, the spent catalyst was analyzed by Fourier transform infrared spectroscopy (FTIR) model Nicolet Is5 from Thermo Fisher (Selangor, Malaysia). It was used to record the remaining active species present on the catalyst after few cycles of the reaction. The spent catalyst was analyzed by Supermini bench-top sequential wavelength dispersive X-ray fluorescence (XRF) spectrometer in helium (He) atmosphere. Normalized contents of a dominant element were used as a reference and compared to samples recovered after transesterification reaction. The contents were calculated from XRD intensities and analytical apparatus factory calibration data for certain elements. All samples before XRF analysis were ground, sieved to particle size (x < 0.011 mm), and dried at 250° for 6 h. The contents of the main components
on the biodiesel liquid were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The ICP-AES measurements were performed on a Prodigy 7 (Selangor, Malaysia) spectrometer and carried out under optimized experimental conditions.

3.4. Transesterification Reaction of WCO

The transesterification process was adapted with slight modification from previous research reported by Abdullah et al. [25]. About 10 g of the WCO was added to a 50 mL two-necked round bottom flask, heated to 65 °C and subsequently added with 4.32 g methanol with oil to methanol molar ratio of 1:12. Later, 30 wt.% of beads catalyst was added to the PHM before the reaction started. Figure 10 showed a schematic image for the open-system reactor, which was used in this experiment.

The mixture of the product was separated by the centrifugation process to recover the spent catalyst. The final product was observed as three layers with the top layer containing biodiesel, the middle layer containing glycerol, and the bottom layer was the catalyst. For the beads catalyst, after the reaction ended, the catalyst was separated by removing PHM, followed by centrifugation process. As the top layer found was biodiesel, the biodiesel needs to wash up by hot water by using a separating funnel several time to remove impurities such as excess glycerol and methanol. After that, the biodiesel was transferred into the beaker and heated up at 100 °C for 2 to 5 min to remove excess water from the washing process. Finally, the biodiesel was collected for the determination of FAME yield using 7860B Agilent gas chromatography-mass spectroscopy (GC-MS). The injector and detector temperature were programmed at 240 °C. Helium was used as the carrier gas with a flow rate of 19.2 mL min⁻¹. The Agilent J&W (Selangor, Malaysia) column temperature was set at 150 °C with ramping rate 15 °C min⁻¹.

3.5. Determination of Ester Content

Table 5 shows the formula to calculate the biodiesel from the conversion until the pure result, and Equation (1) shows the classical technique to calculate biodiesel where A refers to the mass of the product obtained divided by the mass of the WCO [62]. However, due to the presence of impurities stated in Section 2.5, this formula cannot reflect the true estimate of the collected biodiesel [63]. Hence, Equations (2)–(4) suggested the most accurate formula to determine the exact amount of FAME in the product.

Therefore, to obtain the actual mass of the pure biodiesel, the GC peaks area of FAME present in the product was determined by adding the internal standard of methyl heptadecanoate and comparing with the biodiesel standard. Thus, the FAME yield or percentage of ester content was determined based on Equations (2)–(4) as indicated by Agilent standard method EN14103. Where c refers to the ester content in biodiesel sample, TA for the total area, AEI for the area of internal standard, CEI for the concentration (mg mL⁻¹) of methyl heptadecanoate solution, VEI for the volume (mL) of methyl heptadecanoate solution, and m for the mass of the sample.

| Formula | Equation | Nr. |
|---------|----------|-----|
| Conversion (%) * | \[ d = \frac{A}{\text{Mass of WCO}} \times 100\% \] | (1) |
| Ester content (%) From EN 14103 | \[ c = \frac{\text{TA} - \text{AEI}}{\text{AEI}} \times \frac{\text{CEI} \times \text{VEI}}{m} \times 100 \] | (2) |
| Mass of pure biodiesel from biodiesel conversion (g) | | |
| Pure biodiesel yield (%) | \[ \text{FAME yield, \%} = \frac{Y(g)}{\text{mass WCO (g)}} \times 100\% \] | (3) |

* Conventional technique to estimate the biodiesel conversion.
4. Conclusions

K$_2$CO$_3$ and KOH supported onto Al$_2$O$_3$ beads and powder successfully converted a waste cooking oil to biodiesel via transesterification process. With an optimum reaction condition of catalyst concentration of 30%, oil to methanol ratio of 1:12, catalyst loading of 5 wt%, and reaction temperature of 65 °C, the following yields of pure biodiesel were obtained: 86.8% for beads KOH/Al$_2$O$_3$ catalyst at 2 h reaction time, 77.4% for beads K$_2$CO$_3$/Al$_2$O$_3$ catalyst at 2 h, 66.7% for powder KOH/Al$_2$O$_3$ catalyst at 3 h, and 72.3% for powder K$_2$CO$_3$/Al$_2$O$_3$ catalyst at 4 h. In terms of biodiesel yield, KOH/Al$_2$O$_3$ catalyst shows the highest biodiesel yield collected, but K$_2$CO$_3$/Al$_2$O$_3$ catalyst offers better reusability (up to 6 times for K$_2$CO$_3$/Al$_2$O$_3$ powder catalyst and 7 times for K$_2$CO$_3$/Al$_2$O$_3$ beads catalyst) by using PHM as the reactor container. Based on the result, in between powder and beads catalysts, beads catalyst can be considered a better alternative to powder heterogeneous and normal homogeneous catalyst for biodiesel production as it can be easily recovered, can be reuse back without mass loss of the catalyst, and proved suitable for an industrial-scale application. Overall, beads K$_2$CO$_3$/Al$_2$O$_3$ catalyst shows better performance and PHM was suitable as the reaction container in the transesterification process, as it maintains the original shape and mass of beads catalyst.

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References

1. Sadaf, S.; Iqbal, J.; Ullah, I.; Bhatti, H.N.; Nouren, S.; Nisar, J.; Iqbal, M. Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel. Sustain. Cities Soc. 2018, 41, 220–226. [CrossRef]

2. Tredja, M.; Nurwita, A.; Kryszak, D. Synthesis of solid acid catalysts for esterification with the assistance of elevated pressure. Microporous Mesoporous Mater. 2019, 278, 115–120. [CrossRef]

3. Ganesan, S.; Arunkumar, T.; Munuswamy, D.; Appavu, P.; Devarajan, Y. Effect of egr & nanoparticles on performance and emission characteristics of a diesel engine fuelled with palm biodiesel and diesel blends. J. Oil Palm. Res. 2019, 31, 130–137. [CrossRef]

4. Mohd Shohaimi, N.A.; Wan Abu Bakar, W.A.; Jaafar, J. The catalytic deacidification of acidic crude oil using Cu-doped alkaline earth metal oxide catalysts. Pet. Sci. Technol. 2017, 35, 1097–1103. [CrossRef]

5. Mohadesi, M.; Aghel, B.; Maleki, M.; Ansari, A. The use of KOH/Clinoptilolite catalyst in pilot of microreactor for biodiesel production from waste cooking oil. Fuel 2019, 116659. [CrossRef]

6. Lokman, I.M.; Rashid, U.; Taufiq-Yap, Y.H.; Yunus, R. Methyl ester production from palm fatty acid distillate using sulfonated glucose-derived acid catalyst. Renew. Energy 2015, 81, 347–354. [CrossRef]

7. Liu, F.; Ma, X.; Li, H.; Wang, Y.; Cui, P.; Guo, M.; Xayin, H.; Lu, W.; Zhou, S.; Yu, M. Dilute sulfonic acid post functionalized metal organic framework as a heterogeneus acid catalyst for esterification to produce biodiesel. Fuel 2020, 266, 111749. [CrossRef]

8. Khodamorady, M.; Sohрабnejad, S.; Bahrami, K. Efficient one-pot synthetic methods for the preparation of 3,4-dihydropyrimidinones and 1,4-dihydropyridine derivatives using BNP@SO2(CH2)3NH2SO3H as a ligand and metal free acidic heterogeneous nano-catalyst. Polyhedron 2020, 178, 114340. [CrossRef]

9. Niroj, K.; Intarapong, P.; Luengnaruemitchai, A.; Jai-In, S. A comparative study of KOH/Al$_2$O$_3$ and KOH/NaY catalysts for biodiesel production via transesterification from palm oil. Renew. Energy 2009, 34, 1145–1150. [CrossRef]
10. Shohaimi, N.A.M.; Wan Abu Bakar, W.A.; Jaafar, J. Catalytic neutralization method for naphthenic acid removal in crude oil by alumina supported Ca and Ba catalysts. *Pet. Sci. Technol.* **2014**, *32*, 2365–2375. [CrossRef]

11. Du, L.; Li, Z.; Ding, S.; Chen, C.; Qu, S.; Yi, W.; Lu, J.; Ding, J. Synthesis and characterization of carbon-based MgO catalysts for biodiesel production from castor oil. *Fuel* **2019**, *258*, 116122. [CrossRef]

12. Ahmad Farid, M.A.; Hassan, M.A.; Taufiq-Yap, Y.H.; Ibrahim, M.L.; Hasan, M.Y.; Ali, A.A.M.; Othman, M.R.; Shirai, Y. Kinetic and thermodynamic of heterogeneously K$_3$PO$_4$/AC-catalysed transesterification via pseudo-first order mechanism and Eyring-Polanyi equation. *Fuel* **2018**, *232*, 653–658. [CrossRef]

13. Hazmi, B.; Rashid, U.; Taufiq-yap, Y.H.; Ibrahim, M.L. Supermagnetic nano-bifunctional catalyst from rice husk: Synthesis, characterization and application for conversion of used cooking oil to biodiesel. *Catalysts* **2020**, *10*, 225. [CrossRef]

14. Nayebzadeh, H.; Saghatolleslami, N.; Tabasizadeh, M. Optimization of the activity of KOH/calcium aluminate nanocatalyst for biodiesel production using response surface methodology. *J. Taiwan Inst. Chem. Eng.* **2016**, *68*, 379–386. [CrossRef]

15. Lam, M.K.; Lee, K.T.; Mohamed, A.R. Homogeneous, heterogeneous and enzymatic catalysis for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review. *Biotechnol. Adv.* **2010**, *28*, 500–518. [CrossRef] [PubMed]

16. Tangy, A.; Pulidindi, I.N.; Perkas, N.; Gedanken, A. Continuous flow through a microwave oven for the large-scale production of biodiesel from waste cooking oil. *Bioresour. Technol.* **2017**, *224*, 333–341. [CrossRef]

17. Nomanbhay, S.; Ong, M.Y. A review of microwave-assisted reactions for biodiesel production. *Bioengineering* **2017**, *4*, 57. [CrossRef]

18. Silveira Junior, E.G.; Perez, V.H.; Reyero, I.; Serrano-Lotina, A.; Justo, O.R. Biodiesel production from heterogeneous catalysts based K$_2$CO$_3$ supported on extruded γ-Al$_2$O$_3$. *Fuel* **2019**, *241*, 311–318. [CrossRef]

19. Da Costa Evangelista, J.P.; Gondim, A.D.; Souza, L.D.; Araujo, A.S. Alumina-supported potassium compounds as heterogeneous catalysts for biodiesel production: A review. *Renew. Sustain. Energy Rev.* **2016**, *59*, 887–894. [CrossRef]

20. Zhu, M.; Li, B.; Jehng, J.M.; Sharma, L.; Taborda, J.; Zhang, L.; Stach, E.; Wachs, I.E.; Wu, Z.; Baltrusaitis, J. Molecular structure and sour gas surface chemistry of supported K$_2$O/WO$_3$/Al$_2$O$_3$ catalysts. *Appl. Catal. B Environ.* **2018**, *232*, 146–154. [CrossRef]

21. Ilgen, O.; Akin, A.N. Development of alumina supported alkaline catalysts used for biodiesel production. *Turkish J. Chem.* **2009**, *33*, 281–287. [CrossRef]

22. Ma, G.; Hu, W.; Pei, H.; Jiang, L.; Ji, Y.; Mu, R. Study of KOH/Al$_2$O$_3$ as heterogeneous catalyst for biodiesel production via in situ transesterification from microalgae. *Environ. Technol.* **2015**, *36*, 622–627. [CrossRef] [PubMed]

23. Lee, K.B.; Verdooren, A.; Caram, H.S.; Sirca, S. Chemisorption of carbon dioxide on potassium-carbonate-promoted hydrotalcite. *J. Colloid Interface Sci.* **2007**, *308*, 30–39. [CrossRef] [PubMed]

24. Schaefer, S.; Fierro, V.; Szczurek, A.; Izquierdo, M.T.; Celzard, A. Physisorption, chemisorption and spill-over contributions to hydrogen storage. *Int. J. Hydrogen Energy* **2016**, *41*, 17442–17452. [CrossRef]

25. Abdullah, A.; Rahmawati Sianipar, R.N.; Ariyani, D.; Nata, I.F. Conversion of palm oil sludge to biodiesel using alum and KOH as catalysts. *Sustain. Environ. Res.* **2017**, *27*, 291–295. [CrossRef]

26. Boonprasop, S.; Chalermsinsuwan, B.; Piumsomboon, P. Effect of operating parameters of potassium carbonate supported on gamma alumina (K$_2$O/γ-Al$_2$O$_3$) on CO$_2$ capture capacity using depressurized regeneration. *J. Taiwan Inst. Chem. Eng.* **2019**, *116*, 11503. [CrossRef]

27. Silveira, E.G.; Barcelos, L.F.T.; Perez, V.H.; Justo, O.R.; Ramirez, L.C.; Ribeiro, I.; Serrano-Lotina, A.; Justo, O.R. Biodiesel production from castor oil. *Appl. Catal. B Environ.* **2018**, *36*, 281–287. [CrossRef]

28. Veselovskaya, J.V.; Derevschikov, V.S.; Kardash, T.Y.; Stonkus, O.A.; Trubitsina, T.A.; Okunev, A.G. Direct CO$_2$ capture from ambient air using K$_2$O/Al$_2$O$_3$ composite sorbent. *Int. J. Greenh. Gas. Control.* **2013**, *17*, 332–340. [CrossRef]

29. Silveira, E.G.; Barcelos, L.F.T.; Perez, V.H.; Ramirez, L.C.; Ribeiro, I.; de Castro, M.P.P. Biodiesel production from non-edible forage turnip oil by extrudated catalysis. *Ind. Crops Prod.* **2019**, *139*, 111503. [CrossRef]

30. Sharikh, A.M.; Sulaiman, S.; Azmi, A.S.; Sulaiman, S.Z. Potassium carbonate from pineapple and orange peels as catalyst for biodiesel production. *AIP Conf. Proc.* **2018**, *2030*, 020290. [CrossRef]

31. Malins, K. The potential of K$_2$PO$_4$, K$_2$CO$_3$, Na$_2$PO$_4$ and Na$_2$CO$_3$ as reusable alkaline catalysts for practical application in biodiesel production. *Fuel Process. Technol.* **2018**, *179*, 302–312. [CrossRef]

32. Ruhul, A.M.; Kalam, M.A.; Masjuki, H.H.; Fatthah, I.M.R.; Reham, S.S.; Rashed, M.M. State of the art of biodiesel production processes: A review of the heterogeneous catalyst. *RSC Adv.* **2015**, *5*, 101023–101044. [CrossRef]

33. Mohamed, M.A.; Wan Salleh, W.N.; Jaafar, J.; Rosmi, M.S.; Zul, Z.A.; Abd Mutalib, M.; Ismail, A.F.; Tanemura, M. Carbon as amorphous shell and interstitial dopant in mesoporous rutile TiO$_2$: Bio-Template assisted sol-gel synthesis and photocatalytic activity. *Appl. Surf. Sci.* **2017**, *383*, 46–59. [CrossRef]

34. Islam, A.; Taufiq-Yap, Y.H.; Ravindra, P.; Teo, S.H.; Sivasangar, S.; Chan, E.S. Biodiesel synthesis over millimetric γ-Al$_2$O$_3$/KI catalyst. *Energy* **2015**, *89*, 965–973. [CrossRef]

35. Raj, K.J.A.; Ramaswamy, A.V.; Viswanathan, B. Surface area, pore size, and particle size engineering of titania with seeding technique and phosphate modification. *J. Phys. Chem. C* **2009**, *113*, 13750–13757. [CrossRef]

36. Mohd Hir, Z.A.; Abdullah, A.H.; Zainal, Z.; Lim, H.N. Visible light-active hybrid film photocatalyst of polyelectrolyte–reduced TiO$_2$: Photocatalytic response and radical trapping investigation. *J. Mater. Sci.* **2018**, *53*, 13264–13279. [CrossRef]

37. Shan, R.; Shi, J.; Yan, B.; Chen, G.; Yao, J.; Liu, C. Transesterification of palm oil to fatty acids methyl ester using K2CO3/polygorskite catalyst. *Energy Convers. Manag.* **2016**, *114*, 142–149. [CrossRef]
38. Ibrahim, M.L.; Nik Abdul Khalil, N.N.A.; Islam, A.; Rashid, U.; Ibrahim, S.F.; Sinar Mashuri, S.I.; Taufiq-Yap, Y.H. Preparation of Na2O supported CNTs nanocatalyst for efficient biodiesel production from waste-oil. *Energy Convers. Manag.* 2020, 205, 112445. [CrossRef]

39. Smyrnioti, M.; Tampaxis, C.; Steriotis, T.; Ioannides, T. Study of CO2 adsorption on a commercial CuO/ZnO/Al2O3 catalyst. *Catal. Today* 2020, 357, 495–502. [CrossRef]

40. Rahmani Vahid, B.; Haghighi, M.; Alaei, S.; Toghiyani, J. Reusability enhancement of combustion synthesized MgO/MgAl2O4 nanocatalyst in biodiesel production by glow discharge plasma treatment. *Energy Convers. Manag.* 2017, 143, 23–32. [CrossRef]

41. Ahmad Farid, M.A.; Hassan, M.A.; Taufiq-Yap, Y.H.; Ibrahim, M.L.; Othman, M.R.; Ali, A.A.M.; Shirai, Y. Production of methyl esters from waste cooking oil using a heterogeneous biomass-based catalyst. *Renew. Energy* 2017, 114, 638–643. [CrossRef]

42. Lokman NolHakim, M.A.H.; Mohd Shohaimi, N.A.; Ibrahim, M.L.; Wan Mokhtar, W.N.A.; Abdul Halim, A.Z. Transesterification of waste cooking oil utilizing heterogeneous K2CO3/Al2O3 and KOH/Al2O3 catalysts. *Malays. Inst. Chem. Sci.* 2021, 23, 74–83.

43. Hong, Y.; Wu, G. Heterogeneous and efficient transesterification of *Jatropha curcas* L. seed oil to produce biodiesel catalysed by nano-sized SO4−/TiO2. *R. Soc. Open Sci.* 2018, 5, 181331.

44. Alonso, D.M.; Mariscal, R.; Moreno-Tost, R.; Poves, M.D.Z.; Moreno-Tost, R.; Poves, M.D.Z.; Granados, M.L. Potassium leaching during triglyceride transesterification using K/γ-Al2O3 catalysts. *Catal. Commun.* 2007, 8, 2074–2080. [CrossRef]

45. Astutt, W.; Prilitasari, N.M.; Iskandar, Y.; Bratakusuma, D.; Petrus, H.T.B.M. Leaching behavior of lanthanum, nickel and iron from spent catalyst using inorganic acids. *IOP Conf. Ser. Mater. Sci. Eng.* 2018, 285, 012007. [CrossRef]

46. Saba, T.; Estephane, J.; El Khoury, B.; El Khoury, M.; Khazma, M.; El Zakhem, H.; Aouad, S. Biodiesel production from refined sunflower vegetable oil over KOH/ZSM5 catalysts. *Renew. Energy* 2016, 90, 301–306. [CrossRef]

47. Kalderis, D.; Kotti, M.S.; Malashova, E.; Doutsos, C.; Kritikos, I. Kinetic study and techno-economic indicators for base catalyzed transesterification of Jatropha oil. *Egypt. J. Pet.* 2017, 21, 347–353. [CrossRef]

48. Ning, X.; Zhan, L.; Wang, H.; Yu, H.; Peng, F. Deactivation and regeneration of: In situ formed bismuth-promoted platinum catalyst for the selective oxidation of glycerol to dihydroxyacetone. *New J. Chem.* 2018, 42, 18837–18843. [CrossRef]

49. Yori, J.C.; D’Ippolito, S.A.; Pieck, C.L.; Vera, C.R. Deglycerolization of biodiesel streams by adsorption over silica beds. *Energy Fuels* 2007, 21, 347–353. [CrossRef]

50. Pasupulety, N.; Gunda, K.; Liu, Y.; Rempel, G.L.; Ng, F.T.T. Production of biodiesel from soybean oil on CaO/Al2O3 catalyst. *Energy Convers. Manag.* 2013, 71, 236–242. [CrossRef]

51. Kang, S.; Li, X.; Fan, J.; Chang, J. Characterization of hydrochars produced by hydrothermal carbonization of lignin, cellulose, d-xylene, and wood meal. *Ind. Eng. Chem. Res.* 2012, 51, 9023–9031. [CrossRef]

52. Fadzilah, R.; Rashid, U.; Lokman, M.; Hazmi, B.; Alfarithi, A.; Arbi, I. Bifunctional nano-catalyst produced from palm kernel shell via hydrothermal-assisted carbonization for biodiesel production from waste cooking oil. *Renew. Sustain. Energy Rev.* 2021, 137, 110639. [CrossRef]

53. Kalderis, D.; Kotti, M.S.; Méndez, A.; Gascó, G. Characterization of hydrochars produced by hydrothermal carbonization of rice husk. *Solid Earth* 2014, 5, 477–483. [CrossRef]

54. Mohd Hir, Z.A.; Abdullah, A.H.; Zainal, Z.; Lim, H.N. Photoactive hybrid photocatalyst of polyethersulфоне for the degredation of methyl orange dye: Kinetic study and operational parameters. *Catalyst* 2017, 17, 313. [CrossRef]

55. Rajkhowa, T.; Marin, G.B.; Thybaut, J.W. Quantifying the dominant factors in Cu catalyst deactivation during glycerol hydrogenolysis. *J. Ind. Eng. Chem.* 2017, 54, 270–277. [CrossRef]

56. Gómez del Río, J.; Neves, M.C.; Tarelho, L.A.C.; Nunes, M.I. Solid catalysts obtained from wastes for FAME production using mixtures of refined palm oil and waste cooking oils. *Renew. Energy* 2019, 136, 873–883. [CrossRef]

57. Labib, T.M.; Hawash, S.I.; El-Khatib, K.M.; Sharaky, A.M.; El Diwani, G.I.; Abdel Kader, E. Kinetic study and techno-economic indicators for base catalyzed transesterification of Jatropha oil. *Egypt. J. Pet.* 2013, 22, 9–16. [CrossRef]