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Supermagnetic Nano-Bifunctional Catalyst from Rice Husk: Synthesis, Characterization and Application for Conversion of Used Cooking Oil to Biodiesel

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Abstract: The present work investigated the biodiesel production from used cooking oil catalyzed by nano-bifunctional supermagnetic heterogeneous catalysts (RHC/K₂O/Fe) derived from rice husk doped with K₂O and Fe synthesized by the wet impregnation method. The synthesized catalysts (RHC/K₂O/Fe) were characterized for crystallinity by X-ray diffraction spectroscopy (XRD), total acidity and basicity using CO₂/NH₃-TPD, textural properties through Brunauer-Emmett-Teller (BET), thermal stability via thermogravimetric analyzer (TGA), functional group determination by Fourier-transform infrared spectroscopy (FTIR), surface morphology through field emission scanning electron microscopy (FESEM), and magnetic properties by vibrating sample magnetometer (VSM). The VSM result demonstrated that the super-paramagnetic catalyst (RHC/K₂O-20%/Fe-5%) could be simply separated and regained after the reaction using an external magnetic field. The operating conditions such as catalyst loading, methanol/oil molar ratio, temperature, and reaction duration were studied. The screened RHC/K₂O-20%/Fe-5% catalyst was selected for further optimization and the optimum reaction parameters found were 4 wt % of catalyst, a molar ratio of methanol/oil of 12:1, 4 h reaction duration, and 75 °C reaction temperature with a maximal yield of 98.6%. The reusability study and reactivation results revealed that the nano-bifunctional magnetic catalyst (RHC/K₂O-20%/Fe-5%) could be preserved by high catalytic activity even after being reused five times.

Keywords: rice husk; nano-magnetic catalyst; heterogeneous catalyst; used cooking oil; biodiesel

1. Introduction

An increasing supply of petrochemical resources to fulfill the high energy demands for industrialization and metropolitan growth over the last decades has caused the depletion of non-renewable conventional fuels [1,2]. The emission of toxic gases from the burning of fossil



fuels can cause serious health effects and environmental problems [3]. In addition, the fluctuation of global petroleum prices and the emission of greenhouse gases (GHG) have initiated the search for alternative fuels from renewable resources [4]. Thus, biodiesel is a suitable source of energy which is sustainable, ecologically safe, and non-toxic as an alternative to replace fossil-based fuels [5].

The triglycerides of used cooking oil can chemically convert into biodiesel through transesterification with alcohols (methanol and ethanol) in the presence of homogeneous or heterogeneous catalysts Recently, used cooking oil (UCO) has recognized as an option towards cheap and discarded feedstock for the production of biodiesel to replace the high-priced vegetable and food oils raw materials, such as soybean oil, palm oil, canola oil, and sunflower oil [6]. It is estimated that the price of used cooking oil is approximated to be around half or less than half of the price of virgin cooking oil. In addition, utilization of used cooking oil or discarded oil can decrease the dependency on food oils for the production of biodiesel, and it can help to resolve the food versus fuel competition [7]. The used cooking oil (UCO) is considered as one of the waste oils, and its vast quantity is available all over the world, which is generated locally from restaurants and food manufactures. The improper ways of handling UCO can create a major disposal issue which is the source of pollution of land and water resources; that is why using UCO as a source for biodiesel synthesis could not only helps in the disposal or reduction of pollution but also can reduce the biodiesel production cost which could be a valuable addition of energy in the existing energy grid [1].

The use of conventional homogeneous catalysts has a complication in separation after the reaction, which tends to emulsification of UCO, requires a large amount of water for biodiesel purification, and recovery of catalyst is not possible [8]. The application of a homogeneous base catalyst for the transesterification process with low-cost and discarded feedstock which contains high free fatty acid content, i.e., UCO is unfavorable because the chemical reaction has a tendency for soap formation and slowly reverts the reaction backward, subsequently reducing the biodiesel yield [9]. Recently, the major drawbacks of homogeneous catalyst have been overcome by the development of heterogeneous catalyst which can be easily recovered from the reaction mixture by filtration, is recyclable, eco-friendly, and cuts off the need for neutralization which can reduce the cost of production [10]. Heterogeneous catalysts can be categorized into solid acid catalyst such as AC-Fe₍₅₎-SO₃Cl [3], SO₃H–ZnAl₂O $_4$ [11], Go-Fe₂O₃-SO₃H [12] and basic solid catalyst, for example, Sr/MgO [13], MgO/MgAl₂O₄ [14] and K₂O-KCl alkaline catalyst [15]. Although heterogeneous catalysts have many advantages, the application of solid catalysts for transesterification reaction is still limited, owing to the low availability of active sites for the catalytic activity to occur [16]. In addition, it needs a high reaction temperature and pressure to perform, unlike the commonly used homogeneous catalysts [17]. Besides that, catalyst deactivation through coking, sintering, poisoning, and leaching of active catalytic sites in the reaction medium are the common difficulty facing by heterogeneous catalysts, which will affect the catalytic performance for the next reaction cycle [18].

In the past few years, the application of nanoparticles as catalyst has gained considerable attention because of their nano-dimension and morphological structure with large surface area that consists of higher number of active sites [19] and pore size with high surface-volume ratio that enhance the selectivity and produce higher catalytic activity compared to the normal heterogeneous catalyst [20]. The incorporation of nano-magnetic particles such as ferrite ion through impregnation, precipitation, co-precipitation, and sol-gel method as a supporting agent to the solid catalyst aids in the easy separation between the catalyst and reaction media after the transesterification process [21]. The biodiesel conversion of canola oil through transesterification by using 9.03 wt % of magnetic mesoporous KOH/ZMS-5-Fe₃O₄ at 65 °C reaction temperature, 12.3 molar ratio of alcohol to oil for 3.26 h resulted in 93.65% of biodiesel [22]. The nano-magnetic ZnO/BiFeO₃ catalyst showed highly catalytic performance in transesterification in which the FAME/biodiesel yield was more than 92.08% even after the use of five times under optimum reaction conditions (molar ratio of methanol/canola oil of 15:1, temperature of 65 °C, and a catalyst amount of 4 wt %) [23].

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The world rice production is estimated at 700 million tons every year [24], with approximately 20% of the paddy production is paddy residue such as rice husk (RH) and rice straw (RS) [25]. According to the statistic compiled by the Malaysian Ministry of Agricultural, the estimated amount of rice husk produced in Malaysia is 0.48 tons generated during the harvesting and milling processes [26]. In Malaysia, RH is mostly used as a fuel boiler for generating power for sugar industries and drying wet paddy. Unfortunately, the disposal problem of RH has risen due to the closure of power generation operations of sugar industries in northern Malaysia since 2012 [27]. Thus, a bulk quantity of unused RH is left or generally charred in the open fields. The burning practice of RH waste will lead to air pollution, and the airborne particles have been linked to respiratory diseases in humans [28] Activating the rice husk in the inert condition under nitrogen flow produces a highly porous carbon with a very high surface area that is good for catalytic applications. RH consists of 15 wt % silica [29], 30 wt % lignin, 65 wt % holo-cellulose and 5 wt % extracts [30]. Chen et al. reported that the RH and its ash have concerned immense attention for the extraction of silica (SiO₂) component, which could act as cheap sources for catalyst's precursor [31], to form stable and much effective metal/Si and composite for the transesterification reaction [29] such as Li₂CO₃/RHA [32] and rice husk-derived sodium silicate [33]. Indeed, the use of RH-derived biochar could be an efficient catalyst support for biodiesel production, but it can also resolve the issue of utilization of generated waste RH to a valuable product.

Over the past decade, the use of activated carbon (AC) as a catalyst or catalyst precursor for the production of biodiesel has become popular due to its significant surface area accessible for physisorption or chemisorption [34]. Moreover, carbon as a catalyst precursor has numerous advantages, i.e., high stability in both acidic and basic media, ease in the recovery of metals doped on it, and flexible to tailor its textural and surface chemical properties [35]. Biochar is organic solid char that is rich with carbon content with porous nature, which is formed through the pyrolysis or thermal decomposition of the biomass under the flow of nitrogen gas. Biochar surface consists of functional groups which could be modified with several other functional groups via functionalization step [36].

Previously, magnetic carbonaceous basic catalyst derived from Jatropha hull (Na₂SiO₃@Ni/JRC) was used as catalyst for biodiesel production from Jatropha oil with a high biodiesel yield of 96.7% under optimum conditions (7 wt % catalyst, 9:1 methanol/oil ratio for 2 h reaction duration at 65 °C) [37]. Sano et al. [38] reported that the $Ca_2Fe_2O_5$ -CHN//CO₂ catalyst was able to produce FAME yield up to 100% for three times of catalyst reusability before the conversion dropped to 86.6% after the fifth cycle due to formation of calcium glyceroxide that led to catalyst deactivation. The purpose of this study was to synthesize nano-magnetic bifunctional heterogeneous catalysts derived from rice husk char (RHC) for conversion of biodiesel from used cooking oil. The physical and chemical properties of the resulting catalysts were characterized by using X-ray diffraction spectroscopy (XRD), Brunauer-Emmett-Teller (BET), temperature programmed desorption-carbon dioxide (TPD- CO_2), temperature programmed desorption-ammonia (TPD-NH₃), thermogravimetric analysis-differential thermal analysis (TGA-DTA), Fourier-transform infrared spectroscopy (FTIR), field emission scanning electron microscopy with energy dispersive X-Ray spectroscopy (FESEM-EDX), and vibrating sample magnetometer (VSM). The influence of catalyst preparation conditions on the RHC and the effects of the operating parameters on the transesterification reaction of UCO in terms of obtained biodiesel yield and reuse of the catalyst, were evaluated. Furthermore, a detailed of spent supermagnetic nano-bifunctional catalyst was also performed. The biodiesel confirmation was tested using ¹H-NMR, FTIR, and discussed.

2. Results and Discussion

2.1. Characterization of Supermagnetic Nano-Bifunctional Catalysts

2.1.1. Crystallinity Investigation

The X-ray diffraction (XRD) pattern of rice husk char (RHC) and supermagnetic nano-bifunctional catalysts are depicted in Figure 1 and the diffraction peaks were identified using the standard ICSD file. A broad diffraction peak within 5.0° to 35.0° of RHC was attributed to amorphous carbon

with randomly oriented carbon sheets [39]. The two additional peaks of 44.2° and 64.6° on RHC corresponded to the characteristic peaks of SiO₂ with the monoclinic phase (ICSD File No. 01-083-1413) that consisted of more ordered graphite-like carbon lattice structure [40]. After loading of K_2CO_3 and FeCl₃ with different concentrations, intensities of the main peaks of RHC decreased gradually and more new peaks exhibited in the XRD pattern. K₂O peaks appeared at 20: 13.3° (ICSD File No. 00-039-1380), 28.8° (ICSD File No. 01-018-0994) and 50.6° (ICSD File No. 00-019-0927). The peak of K₂CO₃ appeared at 2θ: 33.2° (ICSD File No. 00-049-1093) [41]. Meanwhile, peaks related to Fe groups were located at 2 θ : 31.8° of α -Fe₂O₃ (ICSD File No. 01-088-2359), 41.0°, and 45.2° of Fe₂O₃ (ICSD File No.01-075-0449). Both crystal systems of α -Fe₂O₃ and Fe₂O₃ were rhombohedral. The intensities of potassium and iron were increased gradually as the dopants' concentrations varied from 20% to 30% and 5% to 10%, respectively [29]. The XRD pattern of RHC/K₂O-20/Fe-10% clearly showed that the small diffraction peak of K_2CO_3 compared to other catalysts due to the surface of K_2CO_3 particles were dispersed and hindered by Fe particles due to which the X-ray beam unable to diffract on catalysts' surface [42]. Small peaks of Potassium Iron Silicate (K₂Fe₂SiO₂₉(O₄)₅₈) and Potassium Iron Oxide (K₃FeO₂) were observed at 20:66.8° (ICSD File No. 00-043-0264) and 74.6° (ICSD File No. 00-048-0957) with cubic and tetragonal phase respectively. Alternatively, the formation of both of the peaks was due to the interaction of K₂O, Fe₂O₃, and SiO₂ substances on the catalyst during the calcination process [43].



Figure 1. X-ray diffraction (XRD) patterns of rice husk char (RHC) and RHC-derived catalysts.

2.1.2. Temperature Programmed Desorption (TPD)

Both acidic and basic properties of RH, RHC, and RHC derived catalysts were determined using CO_2 and NH_3 –TPD, respectively, as tabulated in Table 1. Based on the results, the derived catalysts from RHC were exhibited as bifunctional properties that consisted of both basic and acid sites. The patterns showed major CO_2 and NH_3 desorption at various degrees of temperature that indicated the level of the basic and acidic strength of the catalyst. The peaks that appeared below 360 °C represented a weak desorption site [44] while peaks of moderate and strong desorption site arose at between 360 °C and 700 °C and above 700 °C, respectively [45].

Catalyst	$S_{BET} (m^2 g^{-1})^{a}$	D_p (nm) ^b	$V_p (cm^3 g^{-1})^{c}$	TPD-CO ₂	TPD-NH ₃	FAME Yield	
				Total Basicity (mmolg ⁻¹)	Total Acidity (mmolg ⁻¹)	(%) ^d	
RH	3.97	5.30	0.0097	2.07	15.57	No reaction	
RHC	203.54	4.09	0.1644	2.71	37.34	No reaction	
RHC/K2O-15%/Fe-5%	76.06	4.52	0.0632	3.34	37.36	67.29	
RHC/K2O-20%/Fe-5%	57.89	4.70	0.0588	4.43	24.59	78.41	
RHC/K2O-20%/Fe-10%	41.17	4.15	0.0486	2.07	30.15	No reaction	
RHC/K2O-25%/Fe-5%	36.17	4.98	0.0474	2.69	17.22	75.27	
RHC/K2O-30%/Fe-5%	27.62	4.77	0.0343	2.54	11.87	77.59	

Table 1. Textural properties and total desorption of CO₂ and NH₃ for RH, RHC, and RHC/K₂O/Fe.

^a Specific surface area; ^b Average pore diameter; ^c Total pore volume at p/po = 0.99; ^d Reaction condition (non-optimized): 10:1 methanol molar ratio, 3 wt.% catalyst, 65 °C reaction temperature, 4 h reaction time.

Generally, RH and RHC exhibited weak and moderate strengths of base and acid properties with total desorption, with basic density of 2.07 mmol g^{-1} , 2.72 mmol g^{-1} and acidic density 15.57 mmol g^{-1} , 15.01 mmol g^{-1} , respectively. As the rice husk char was doped with K₂CO₃ (from 15% to 30%) and FeCl₃.6H₂O (from 5% to 10%), the strength and total basicity and acidity increased significantly. TPD-CO₂ analysis showed the desorption of CO₂ gas at a temperature range of 550 °C to 850 °C, which was maximized at around 707 °C to 788 °C, could be considered as the strong strength of basic sites from K₂O. The basicity value of the synthesized catalyst loaded with 20% of potassium was significantly higher than lower K₂O loading. Meanwhile, the further increment of K₂O loading caused the total absorption-desorption of CO_2 to reduce due to less interaction between the probe gas and fully covered active sites [44,46]. The same goes for the acidity properties of the catalysts; as the loading percentage of K₂O increased, the total desorption of NH₃ reduced. In addition, the basicity of RHC/K₂O-20%/Fe-10% reduced after being doped with 10% of Fe due its acidity strength that suppressed the basic site that might neutralize the catalyst and cause no conversion of biodiesel to happen. Besides that, random distributions of excess agglomerated Fe (10% of Fe) on the catalyst might cover the active K-active site on porous RHC support which imbalanced the basicity characteristic, also reduced the catalyst pore size that will prevent the penetration of methanol and triglyceride; hence, it discourage the transesterification to occur [47]. The excess phase of K_2O and Fe_2O_3 on the surface of RHC support led to reduction of its porosity, hence decreasing the BET surface area [48]. The biodiesel yield depended on to the basicity of the catalyst where the higher the basicity, the greater the FAME formation, as stated in Table 1, in which RHC/K₂O-20%/Fe-5% showed better biodiesel yield among others. The further increment of dopant compounds will slightly reduce of catalytic activity of converting triglycerides into fatty acid methyl ester (FAME) which related to the mass transfer and poor mixing between reactants and catalyst performance [49–51]. Thus, magnetic RHC/K₂O-20%/Fe-5% was chosen for further characterization analysis and catalyst optimization in biodiesel production.

2.1.3. Surface Area and Porosity Measurement

Textural properties of rice husk (RH), rice husk char (RHC) and magnetic RHC/K₂O/Fe catalysts were evaluated by adsorption and desorption of N₂ at 77 K. Table 1 shows that the specific surface area for RH was $3.97 \text{ m}^2 \text{ g}^{-1}$ whereas the surface is for RHC 203.54 m² g⁻¹ after being calcined was at 450 °C. Carbonisation of biomass at high temperature can increase the carbon content and produce high porosity material [52]. A study conducted by Zhao [29] stated the use of potassium hydroxide in pre-treatment as a chemical activation agent to improve the surface area and pore diameter of RHC. A significant reduction of surface area from 203.54 m² g⁻¹ to 57.89 m² g⁻¹ may be due to the surface of catalyst precursor which was covered by potassium and ferric doping, and the decrement of pore volume from 0.1644 cm³ g⁻¹ to 0.0588 cm³ g⁻¹ was due to the blockage of catalyst pores which confirmed the impregnation of K and Fe on the catalyst's surface. As shown in Figure S1a, RH, RHC and RHC nano-magnetic catalysts exhibited a Type-IV adsorption isotherms at a lower p/p⁰ values with narrow hysteresis loop of desorption, according to the International Union of Pure and Applied

Chemistry (IUPAC) classification which proved the presence of mesoporous structure and may be characterized by the formation of slit-shaped pores [53].

The perfect transesterification reaction depends on the pore structure of the heterogeneous catalyst. The size of the distribution of the catalyst is shown in Figure S1b RHC, and RHC nano-magnetic catalysts demonstrated comparable pore size distributions in the mesoporous pore diameter distribution range of 2 nm to 50 nm [50]. Boz et al. [20] reported that the diameter of triglycerides and glycerol molecules was 2.5 nm, which was small enough to pass through into the porous catalysts and would be employed throughout the transesterification reaction.

2.1.4. Thermal Gravimetric Analysis

The thermal stability of RH and RHC/K₂O-20%/Fe-5% catalyst was ascertained by using thermogravimetric analysis (TGA)/differential thermal analysis (DTA) as presented in Figure 2. Three main stages of thermal decomposition consisted of removal of the adsorbed water molecule at a temperature below 100 °C, followed by the secondary stage of primary pyrolysis temperature range between 200 °C to 650 °C and the third phase of decomposition at high temperature over 700 °C [20], as shown in Figure 3.

The first stage of thermal decomposition of RH at the range of 26 °C to136 °C with a weight loss of 6.59% was associated with the elimination of adsorbed water molecule on the RH surface. The second phase with a temperature range of 152 °C to 303 °C corresponded to the decomposition of hemicellulose and cellulose with a weight loss of 15.18%. The degradation of lignin occurred at a higher temperature range from 303 °C to 633 °C with a major weight loss of 44.40%. The leftover after 632 °C to 991 °C was annotated as solid residue [54–56]. The TGA-DTA curves of RHC did not exhibit apparent mass loss event, which demonstrated that the synthesized RHC has good thermal stability. For the supermagnetic nano-bifunctional RHC/K₂O-20%/Fe-5% catalyst, the first weight loss of 17.11% at about 26 °C to 176 °C may be due to the elimination of adsorbed or chemisorbed H₂O molecule [57]. Another weight loss of 3.65% between 523 °C to 648 °C was attributed to the dehydroxylation of OH ions of supermagnetic RHC nano-bifunctional catalysts as well as disintegrate of FeCl₃ into its oxide (Fe₂O₃). The decomposition of K₂CO₃ to K₂O exhibited a major weight loss of 18.43% at a temperature range between 705 °C to 1000 °C.



Figure 2. Thermogravimetric analysis- Differential thermal analysis (TGA-DTA) curves of the rice husk (RH), rice husk char (RHC) and nano-magnetic RHC/K₂O-20%/Fe-5% catalysts.





Figure 3. Fourier transform infrared (FTIR) spectra of RH, RHC and RHC/K₂O-20%/Fe-5%.

2.1.5. Functional Group Analysis

The Fourier Transform Infrared (FTIR) spectra of rice husk (RH), rice husk char (RHC), and supermagnetic RHC nano-bifunctional catalyst are illustrated in Figure 3. Broad absorption bands at range 3488.67 cm⁻¹ to 3359.29 cm⁻¹ and 1672.20 cm⁻¹ to 1637.26 cm⁻¹ corresponded to the hydroxyl group –OH and silanol, Si–OH stretching and bending, respectively that indicated physisorption of a water molecule on the surface of RH, RHC and magnetic RHC/K₂O-20%/Fe-5% catalyst [58]. The band around 2917.66 cm⁻¹ was assigned to the asymmetric and symmetric methylene stretching vibration of the saturated aliphatic compound present in the cellulose and hemicellulose of RH [59]. A spectra band around 1732.30 cm⁻¹ was associated with the acetyl and ester group of the C=O bond in hemicellulose while lignin infrared spectra appeared at 1509.22 cm^{-1} , which represented C=C aromatic vibration. The lignin absorption spectra characteristic was found at 1463.53 $\rm cm^{-1}$, and cellulose plane bending vibrations, CH_2 of RH were clearly visible at 1420.90 cm⁻¹. The spectra of 1312.94 cm⁻¹ showed the C-H deformation in RH's cellulose and hemicellulose. The high-intensity band spectrum around 1031.81 cm⁻¹ was detected due to the asymmetric and symmetric band stretching of the Si–O–C and Si–O–Si bonds corresponding to the silica and the cellulose of RH. The peaks related to lignin and cellulose disappeared in the RHC spectrum band after the RH calcination due to biomass degradation at high temperatures. New spectra band which corresponded to the asymmetrical stretching vibration of the siloxane, Si–O–Si bond was formed and slightly shifted to 1057.80 cm⁻¹ of RHC after calcination of RH. A sharp peak of symmetric stretching vibration of Si-O and vibration-bending modes of the Si-O-Si bond appeared at 800.29 cm⁻¹ and 466.67 cm⁻¹ in both RH and RHC spectra respectively. The silica functional group spectra remained before and after the calcination process and provided a mesoporous structure for RHC as support [60]. A sharp and intense spectrum peak at 1418.36 cm⁻¹ of RHC/K₂O-20%/Fe-5% was attributed to the carbonate species from K₂CO₃ doped on the RHC support [40]. The peaks at 1331.76 cm⁻¹ and 837.37 cm⁻¹ were assigned to the stretching vibration C-O and the deformation vibration of C-O-C, respectively [61]. The weak vibration of M+-O stretching adsorption bands at 544.80 cm⁻¹, and 463.04 cm⁻¹ belonged to Fe–O and K–O bonding, respectively [62]. The deformation bands of M⁺–OH converted to Si–O–M⁺ located at 964.71 cm⁻¹ and 912.26 cm⁻¹ were assigned to Fe and K, respectively [63]. Upon the formation of Si–O–M⁺, the intensity of the siloxane absorption band was reduced and shifted to lower frequency due to the reduction of electron density [64].

The surface morphologies of RH, RHC, and supermagnetic RHC/K₂O-20%/Fe-5% nanobifunctional catalysts were studied using FESEM, as shown in Figure 4. Figure 4a shows that the RH sample consists of an external surface with a well-organized corrugated structure [54]. The asymmetrical porous layer of RH can be observed through the cross-section view with a magnification of 10,000×, as shown in Figure 4b. Highly porous structure with a large surface area of RHC, as shown in Figure 4c, was formed after carbonization due to thermal decomposition of organic material from RH. Figure 4d shows that nano-magnetic RHC/K₂O-20%/Fe-5% catalyst was made up of the agglomeration of irregular small and large particles, mainly potassium and iron attached to the porous surface of the RHC precursor. The elemental compositions of RH, RHC, and nano-magnetic RHC/K₂O-20%/Fe-5% were verified by energy-dispersive X-ray spectroscopy analysis (EDX) with a detector mounted on a microscope. The RH was made up of 39.83 wt % C, 53.29 wt % O, 6.56 wt % Si and a trace amount of 0.33 wt % K. Meanwhile, the elemental compositions of RHC were; 61.07 wt % C, 27.50 wt % O, 9.76 wt % Si and 1.67 wt % K after carbonization and pre-treatment process. The nano-magnetic catalyst consisted 41.02 wt % C, 27.25 wt % O, 3.60 wt % Si, 21.34 wt % K, and 2.01 wt % Fe. The interaction between K and Fe of the prepared catalyst resulted in a well-developed porous structure believed to have contributed to its high catalytic activity. It was observed that the presence of K indicated a high basicity of prepared catalyst, which can contribute to the transesterification of used cooking oil. Also, the high oxygen atomic percentage suggested that the metallic and synergetic compound formed consisted of oxygen atom mainly bonded to the KFeSi composite rather than being bonded to individual metal oxides. The experimental weight percentage of potassium in nano-magnetic catalyst exceeded its theoretical weight due to the amount of potassium from the pre-treatment process that was not completely washed off from RHC.



Figure 4. Field emission scanning electron microscopy (FESEM) image; (**a**) External surface RH (200×), (**b**) Cross-section view of RHC (10,000×), (**c**) RHC (10,000×), (**d**) Nano-magnetic RHC/K2O-20%/Fe-5% catalyst (10,000×).

2.1.7. Vibrating Sampling Magnetometer Analysis

The magnetic property of RHC/K₂O-20%/Fe-5% was studied using a vibrating sampling magnetometer (VSM), as shown in Figure 5. The M–H loops of fresh magnetic catalyst showed strong magnetization of 7.88 emug⁻¹, and there was a closed hysteresis loop of the catalysts which can be concluded as a superparamagnetic material at room temperature that can be easily separated from the biodiesel reaction system by introducing an external magnet [61,65].



Figure 5. Vibrating sample magnetometer (VSM) magnetization curve of RHC/K₂O-20%/Fe-5% catalyst and the magnetic separation of the catalyst from biodiesel.

2.2. Influence of Process Parameters on the Transesterification of Used Cooking Oil

2.2.1. Effects of Catalyst Amount for Catalyst Screening and Catalytic Performance

The catalytic activity of transesterification of used cooking oil (UCO) was carried out in the presence of synthesized catalysts at the following reaction conditions; methanol to oil molar ratio of 10:1 at a temperature of 65 °C, for 4 h with various catalyst loadings of 1 to 8 wt % (Figure 6). Among the four catalysts tested, the RHC/K₂O-20%/Fe-5% presented the best reaction activity and produced the highest yield of 91.8%; thus, all the optimizations were carried out with this catalyst material. The presence of optimum strength for both acidic and basic properties on the surface of catalysts could affect the formation of highly reactive methoxide species in transesterification. The catalyst of RHC/K₂O-15%/Fe-5%, RHC/K₂O-25%/Fe-5% and RHC/K₂O-30%/Fe-5% likely showed the same result of biodiesel production. Generally, a higher concentration of K-loading is inessential as the best catalyst because the very high basicity characteristic tends to cause difficulty for fatty acid methyl ester (FAME) molecule to desorb after the reaction and vice versa for lower loading concentration in which the reaction itself will not initiate due to low basicity for adsorption of reactant molecules [66]. According to the attained results, the biodiesel yields increased as the catalyst loading was increased from 1 to 4 wt % respectively. Meanwhile, further increase of catalyst loading up to 8 wt % showed the drop of biodiesel yield due to agglomeration of catalyst particles, causing the reactant mixture to become, viscous which led to poor blending between the catalyst and reactants [23]. The result exhibited that 4 wt % of RHC/K₂O-20%/Fe-5% was the optimal amount of catalyst loading for the reaction.



Figure 6. Screening of supermagnetic nano-bifunctional catalyst based on the catalyst loading for transesterification reaction with methanol: oil; 10:1, at temperature 65 °C for 4 h.

2.2.2. Effects of Methanol to Oil Molar Ratio

Transesterification reaction requires methanol as the basic reactant to react with UCO, and the molar ratio of methanol to oil is one of the significant parameters which influence the conversion of triglycerides to fatty acid methyl ester (FAME). Basically, the transesterification reaction is an equilibrium reaction where the conversion of biodiesel could be raised by applying the excessive methanol to force the equilibrium to the product formation [67,68]. The relationship between methanol to oil molar ratio is shown in Figure 7a. Based on the experimental data, the conversion rate increased from 71.4% to 92.5% as the methanol to oil molar ratio increased from 6:1 to 12:1, and the best result of the molar ratio was 12:1. Meanwhile, biodiesel production decreased to 70.44% with an additional increase of the molar ratio of methanol to oil to 27:1. The excesses amount of oil to methanol ratio enables the contact among reagents and catalyst to fasten the reaction, whereas, the surplus methanol give negative impact on transesterification because it could diminish the catalyst concentration and UCO that hinders the triglyceride molecules to the active sites, which leads to the reduction of biodiesel yield [69]. Also, the transesterification of excess methanol to oil ratio will favor glycerolysis reaction, which interferes with the phase separation of glycerol due to an increase in glycerol solubility in methanol, which drives the equilibrium to the reactants and reduces the ester yield [29,67]. As per the above results, the 12:1 methanol to oil molar ratio was selected as the optimum ratio.



Figure 7. (a) Effect of methanol to oil molar ratio on the biodiesel yield using RHC/K₂O-20%/Fe-5% catalyst (b) Effect of temperature on the biodiesel yield using RHC/K₂O-20%/Fe-5% (c) Effect of reaction time on the biodiesel yield using RHC/K₂O-20%/Fe-5%.

2.2.3. Effects of Reaction Temperature

Transesterification was performed to determine the optimum reaction temperature by changing temperature range from 35 °C to 105 °C through the increment of 10 °C. The reaction rate can be improved exponentially by the increase of reaction temperature. Also, the reactant was more mixable which permits higher reaction rate [70]. Figure 7b displays the effect of reaction temperature on the biodiesel yield. At temperature between 35 °C to 55 °C, the conversion yield of methyl ester was below 60% due to the limitations of mass transfer and reactant solubility while at higher temperature, the reactants gained enough kinetic energy, which speeds up the mass transfer rate among the oil, methanol and catalyst phases, which results in the maximum conversion, 98.6% at 75 °C. However, when the reaction temperature proceeded above 75 °C, a slight loss in activity was observed because of high vaporization of the methanol that remained in the vapor phase. In addition, at a higher temperature reaction, the polarity of methanol decreased and resulted in a low concentration of methoxide species in reaction mixture [29,66,71].

2.2.4. Effects of Reaction Duration

The optimized reaction time can play a vital role in producing economical biodiesel. The result shown in Figure 7c indicated that the conversion of FAME improved significantly as the reaction time was amplified, and a maximum conversion was obtained at an optimum reaction time of 4 h. The low biodiesel yield at lower conversion time intervals was reported due to insufficient conversion of FAME while the transesterification decreased as the reaction extended more than 4 h due to the formation of soap [23,72]. Besides, the decreasing of biodiesel yield beyond the optimized duration can be deduced to the reversible nature of the conversion reaction of oil to biodiesel [73].

2.3. Reusability and Study of Deactivation of Supramagnetic RHC/K₂O-20%/Fe-5% Nano-Bifunctional Catalyst

The recovery and reusability of heterogeneous catalysts are one of the significant factors that influence the economics of biodiesel productions. The regenerated supramagnetic RHC/K₂O-20%/Fe-5% nano-bifunctional catalyst was evaluated at the optimal reaction conditions for reusability study, as presented in Figure 8a. It was noticed that after a second cycle, the biodiesel yield dropped from 98.4% to 91.3%. Whereas, in the third cycle, the biodiesel yield was reduced to 88.7%, and it was observed that the catalytic activity considerably reduced to 44.1% after the sixth cycle. Thus, the produced catalyst can be used for at least five cycles with significant yield. The reduction in the biodiesel yield was probably due to the deposition of remaining organic impurities or product intermediate (such as oil, biodiesel, glycerol, and FFAs) on the active site of the nano-magnetic RHC/K₂O-20%/Fe-5% catalyst which hindered the reagents' access [74]. Contamination by moisture and carbon dioxide in the air during the separation process by the external magnetic field also contributed to the deactivation of the nano-magnetic catalyst [18].

Further studies of catalyst deactivation were conducted using N₂ adsorption-desorption, TPD-CO₂/NH₃, XRD, and VSM characterization for fresh RHC/K₂O-20%/Fe-5% and spent RHC/K₂O-20%/Fe-5% (6th cycle). The specific surface area and pore volume of spent catalyst dropped from 57.89 m² g⁻¹ to 2.78 m² g⁻¹ and 0.0588 cm³ g⁻¹ to 0.0102 cm³ g⁻¹ respectively, probably due to the attachment of large molecules from transesterification products such as FAME, glycerol and unreacted oil which caused less interaction for adsorption-desorption between nitrogen gas and catalyst surface. The basicity and acidity concentration of the catalyst were related to its surface area, where low adsorption of probe gases (CO₂/NH₃) showed lower basicity and acidity strength compared to the fresh catalyst, as stated in Table 2. The XRD pattern (Figure 8b) of the spent nano-magnetic catalyst predicted no noticeable structural variation as compared to the fresh catalyst, whereas the intensity of few diffraction peaks of the spent supermagnetic nano-bifunctional catalyst was lower than the fresh nano-magnetic catalyst after six consecutive cycles. Also, the crystal structure of the reused catalyst was altered. The masking of the impurities on the active site of supermagnetic nano-bifunctional spent catalyst did affect the magnetization strength, which reduced to 2.76 emug⁻¹ as shown in Figure 8c. Instead of deactivation of nano-magnetic catalyst by a poisoning mechanism through the attachment of large molecules [18], the repeating process of catalyst reactivation by calcining at high temperature of 550 °C or known as thermal degradation might cause the mesoporous catalyst active site to collapse and result in the decrease in surface area and pore volume which would thus reduce the catalytic activity [75].

Table 2. Textural properties and total CO_2 , NH₃ desorption of fresh nano-magnetic RHC/K₂O-20%/Fe-5% and spent nano-magnetic RHC/K₂O-20%/Fe-5%.

Catalyst	$S_{BET} (m^2 g^{-1})$	D _p (nm)	$V_p (cm^3 g^{-1})$	Total Basicity (mmolg ⁻¹)	Total Acidity (mmolg ⁻¹)
RHC/K2O-20%/Fe-5%	57.89	4.70	0.0588	4.43	24.59
Spent RHC/K ₂ O-20%/Fe-5%	2.78	14.66	0.0102	0.53	6.47



Figure 8. (a) Reusability of the RHC/K₂O-20%/Fe-5% catalyst in biodiesel production (b) XRD pattern of fresh RHC/K₂O-20%/Fe-5% and spent RHC/K₂O-20%/Fe-5%, (c) Magnetic strength (VSM).

2.4. Comparative Study of Catalytic Activity with Literature Reported on Biochar Supported Catalysts

The comparative study of catalytic activity in the transesterification reaction between nanomagnetic RHC/K₂O-20%/Fe-5% catalyst and other reported biochar supported catalysts is listed in Table 3. The compiled data suggested that the as-synthesized RHC/K₂O-20%/Fe-5% catalyst depicted that catalyst produced in the present study was comparable in terms of catalytic activity to previously reported biochar catalysts in the literature. It was noted that the RHC/K2O-20%/Fe-5% catalyst was an effective and efficient supermagnetic nano-bifunctional catalyst for the transesterification of UCO.

Catalyst	Support	Reaction Condition				FAME	
		Catalyst Loading (wt %)	Duration (h)	Molar Ratio	Temperature (°C)	Yield (%)	Ref.
CTPAC (K, P, CaMg)	Tucumã peels	1	4	15:1	80	97.3	[41]
K/BC-Fe ₂ O ₃	Bamboo charcoal	2.5	1	8:1	60	98.0	[19]
Ca ₂ Fe ₂ O ₅ –CNH	Carbon nanohorn	-	3	-	-	97.0	[38]
25K/AP-600	Pomelo peel	6	2.5	8:1	65	98.0	[40]
RHC/K ₂ O- 20%/Fe-5%	Rice husk char	4	4	12:1	75	98.6	This work

Table 3. Comparison of RHC/K₂O-20%/Fe-5% catalyst activity with biochar-supported catalysts.

2.5. Biodiesel Confirmation Using ¹H-Nuclear Magnetic Resonance (¹H-NMR) and Fourier-Transform Infrared Spectroscopy (FTIR)

The confirmation of biodiesel production was characterized using ¹H-NMR and FTIR spectroscopy and was compared with used cooking oil. The ¹H-NMR spectrum of biodiesel and UCO is presented in Figure S2a,b. The typical peak of deuterated chloroform (CDCl₃) was detected at 7.29 ppm [72]. The spectra of biodiesel had a characteristic peak of singlet methoxy proton at 3.61 ppm, and a triplet of an α -methylene group of esters approximately found at 2.24 ppm [76]. These two peaks were not observed in UCO, therefore validating the conversion of triglyceride into respective fatty acid methyl ester. The other signals of multiplet formed at 5.26 ppm–5.34 ppm were identified as olefinic hydrogen [77]. A multiplet peak signal at 0.83 ppm–0.86 ppm was recognized as terminal methyl protons. A multiplet signal of methylene protons of carbon chain was located at 1.22 ppm–1.34 pm, and the signal of β -carbonyl methylene protons was observed at 1.56 ppm–1.60 ppm [63,78,79].

The functional groups and vibration bands of the synthesized biodiesel and UCO were identified in which both FTIR spectra of biodiesel and UCO samples were nearly alike but significantly different in the methyl ester functional peak observed as shown in Figure S3. The absorption band of =C–H stretching vibration of UCO and biodiesel samples was observed at 3005.47 cm⁻¹. Carbon-carbon single bonds of asymmetric and symmetric, –C–H stretching vibration were located at 2921.14 cm⁻¹ and 2852.35 cm⁻¹. The absorption peaks at 1742.78 cm⁻¹, 1641.15 cm⁻¹ belonged to the stretching vibration of carbonyl–C=O functional group and olefin carbon-carbon double bond –C=C–, respectively. 1460.77 cm⁻¹ peak corresponded to –C–H, alkane bending. Stretching vibrations of the C–O–C ester group were observed at 1158.64 cm⁻¹ and 721.20 cm⁻¹, indicating that C–C–H was out of the plane of stretching vibration. The presence of two extra peaks in the biodiesel sample at 1437.64 cm⁻¹ and 1195.76 cm⁻¹ were determined as the asymmetric stretching vibration of methyl carbon-hydrogen bond and stretching vibration of –O–CH₃ group of mono-, di-, and triglyceride to indicate the formation of biodiesel [62,80,81].

3. Materials and Method

3.1. Materials

The rice husk was obtained from PLS Marketing (M) SHD BHD and used cooking oil (UCO) was procured from a local restaurant in Serdang, Selangor. All the materials, i.e., potassium hydroxide (KOH; J.T Barker, St. Phillipsburg, NJ, USA, 86.0%), potassium carbonate (K₂CO₃; R&M Chemicals,

Subang, SGR, MY, 99.5%), iron (III) chloride hexahydrate (FeCl₃.6H₂O; Friedmann Schmidt, Kajang, SGR, MY, 98.0%) and methanol (CH₃OH; Systerm, Shah Alam, SGR, MY, 99.8%) were analytical grade and used without further purification.

3.2. Synthesis of Rice Husk Char

The rice husk (RH) was washed with distilled water (H₂O) to remove rice residue, clay particles, and sieved it. After multiple washing with distilled water, the RH was filtered and oven-dried (105 °C) until it achieved constant weight. The rice husk char (RHC) was prepared by carbonization at 450 °C for 3 h under nitrogen (N₂) flow. The RHC was treated with 1 M potassium hydroxide to eliminate traces of minerals and enhance the pore size of the char. The treated RHC was washed with hot distilled water until pH 7 and dried in the oven at 105 °C [31,82].

3.3. Preparation of Nano-Magnetic RHC/K₂O/Fe Catalyst

A series of RHC/K₂O/Fe catalysts with varying potassium oxide loadings (K₂O: 15, 20 25 and 30 wt %) with 5% and 10% iron (III) oxide were prepared by wet impregnation method of RHC supported with aqueous solution of potassium carbonate (K₂CO₃) and iron (III) chloride hexahydrate (FeCl₃.6H₂O). Both solutions of K₂CO₃ and FeCl₃.6H₂O were dropped simultaneously into wet RHC and mixed vigorously for 6 h. The mixture was filtered and dried in the oven overnight at 70 °C. The dried solid base catalyst was carbonized in the furnace at 700 °C for 3 h with a heating rate of 3 °C min⁻¹ [83].

3.4. Characterization of RHC/K₂O/Fe Catalysts

The crystallinity behavior of synthesized supermagnetic nano-bifunctional catalysts was characterized by using X-ray diffraction XRD-6000, (Shimadzu, Kyoto, JPN) coupled with Cu-K α radiation (30.0 kV, 30.0 mA) at a scanning rate of 2° min⁻¹ and a scanning range of 2° to 80° [83].

Temperature programmed desorption method of carbon dioxide and ammonia gas (CO_2-TPD/NH_3-TPD) as probe gas were used to analyze the basicity and acidity strength of supermagnetic nano-bifunctional catalysts derived from rice husk using TPD/R/O/1100 series (Thermo Finnigan, Kyoto, JPN) apparatus coupled with thermal conductivity detector (TCD). The RHC/K₂O/Fe catalysts samples were pretreated under N₂ gas flow for 1 h at 150 °C, during the acid site distribution analysis. The absorption of NH₃ was carried out under the flow of NH₃ stream for 1 h, and then the RH, RHC, and RHC/K₂O/Fe catalysts were again flowed with N₂ gas for 45 min to remove excess NH₃ gas prior to analysis. Also, the basicity of RH, RHC, and RHC/K₂O/Fe catalysts sample were subjected to only a single pretreatment under the flow of CO₂ gas. The chemisorption of CO₂ and NH₃ was carried out by CO₂ and NH₃ gas at a flow rate of 20 mL min⁻¹ for 1 h, respectively. The additional CO₂ or NH₃ was then flushed with Helium (He) gas for 30 min at a flow rate of 30 mL min⁻¹. The desorption of CO₂ and NH₃ proceeded with the flow of He gas as carrier gas with a ramp of 10 °C min⁻¹ from 50 °C to 950 °C and held for 30 min. The amounts of desorbed CO₂ and NH₃ were measured and noted [84].

The textural properties such as surface area, pore volume and pore size distribution of RH, RHC, and RHC/K₂O/Fe catalysts samples were performed by using Brunauer–Emmer–Teller (BET) and Barrett–Joyner–Halenda (BJH) techniques from the desorption loop method with a Micromeritics ASAP-2020 (Micromeritics Instrument, Norcross, GA, USA). The catalyst sample was degassed at 120 °C to remove adsorbed contaminants and water vapor on the surface of the catalyst [85].

The active functional group on the surface of raw RH, RHC, and RHC/K₂O-20%/Fe-5% were characterized by Fourier transform infrared (FTIR) spectroscopy in the range 400–4000 cm⁻¹ using Thermo Nicolet-7000.(Thermo Fisher Scientific, Waltham, MA, USA) Potassium bromide (KBr, Merck, Darmstadt, DE, 99.0%) was utilized as the sample matrix for determining FTIR spectra with a spectral resolution of 4 cm⁻¹ [31].

Thermogravimetric analyzer (TGA-DTA) was used to evaluate the thermal decomposition rice husk (RH), rice husk char (RHC) and RHC/ $K_2O-20\%$ /Fe-5% catalyst using TG-50 Mettler instrument

(Mettler Toledo, Shah Alam, SGR, MY) under airflow of 50 mL mol⁻¹ with a heating rate of 10 °C min⁻¹ from room temperature to 1000 °C [19].

The morphologies of RH, RHC, and nano-magnetic RHC catalysts were determined with field-emission scanning electron microscopy (FESEM, Novananosem-230). The sample was sputter-coated with 7 nm gold (Au) to enhance the conductivity for better image resolution [86].

The magnetization of supermagnetic nano-bifunctional RHC/K₂O-20%/Fe-5% was measured using a vibrating sample magnetometer (VSM, Lake Shore 7404 series, Lake Shore Cryotronics, Westerville, OH, USA). The VSM was calibrated with a pure nickel sphere with a standard value of 6.95 emu g⁻¹. A pinch of the pre-weighed magnetic catalyst was sandwiched with clear duck tapes and attached on the surface of the VSM sample tail. The sample tail was inserted into a sample chamber, and the VSM was operated with 1.4 Tesla at room temperature.

3.5. Catalytical Activity Reactions Via Transesterification

Transesterification of biodiesel was carried out in 100 mL of 3-necked round-bottomed flask equipped with a water-cooled condenser and mechanical stirring under atmospheric pressure. Approximately 10 g of used cooking oil (UCO), the desired amount of methanol, and RHC/K₂O/Fe catalyst was weighed and placed in the round-bottomed flask. The reaction sample was heated at 65 °C for 4 h and stirred by using the magnetic stirrer. After transesterification, the magnetic base catalyst was removed by using an external magnetic bar, and two phases of products were formed, which consisted of glycerol and biodiesel at the bottom and top layers, respectively. The excess methanol was removed by using a rotary evaporator. The unreacted oil from the synthesized biodiesel was removed by washing with hot distilled water, and the excess water was dried by adding ammonium sulfate ((NH₄)₂SO₄, Merck, Darmstadt, DE, 99.0%) based on the weight of oil. Next, the purified biodiesel was analyzed by gas chromatography, and methyl heptadecanoate was used as the internal standard with hexane (Merck, Darmstadt, DE, 98.5 %) as a solvent. The diverse parametric conditions for the transesterification of UCO allowed to ensure the achievement of an optimized reaction [87].

3.6. Biodiesel Analysis

The qualitative properties of purified methyl ester were examined using gas chromatography (GC) with flame ionization detector (FID) detector and a polar BPX-70 capillary column (60 m length; 0.25 mm ID; 0.25 μ m capillary diameter) (Trajan Scientific, Ringwood, VIC, AUS). The *n*-hexane was used as GC solvent; whereas, methyl heptadecanoate was applied as an internal standard. The reference standards were prepared as; 500 ppm of each standard methyl palmitate, methyl oleate, methyl myristate, methyl stearate, and methyl linoleate. Briefly, 1 μ m of prepared biodiesel sample was injected into the injection port; the GC oven temperature was fixed to increase from 100 °C–250 °C with 10 °C min⁻¹ of the temperature ramp rate. The FAME yield (%) was measured using the formula stated below [11]:

FAME yield (%) =
$$\frac{\Sigma A - A_{meh}}{A_{meh}} \times \frac{C_{meh} \times V_{meh}}{Wt} \times 100$$
 (1)

where; $\sum A (mm^2)$ = Total area of peaks; $A_{meh} (mm^2)$ = Peak area of methyl heptadecanoate; $C_{meh} (ppm)$ = Concentration of methyl heptadecanoate; $V_{meh} (mL)$ = Volume of methyl heptadecanoate; Wt (g) = Weight of the product.

In addition, the confirmation of biodiesel production was characterized by using ¹H-NMR and FTIR spectroscopy and was compared with used cooking oil. ¹H-NMR spectra were recorded on Bruker AVANCE-500 MHz instrument (Bruker Corporation, Billerica, MA, USA) and the deuterated chloroform (CDCl₃, Merck, Darmstadt, DE, 99.96 %and tetramethylsilane (TMS) were used as a solvent and internal standard, respectively. The FTIR spectra was recorded using Thermo Nicolet-7000 Spectrometer equipped with attenuated total reflectance (ATR) sampling accessory. A Diamond-ATR accessory with a removable ZnSe crystal was mounted on the sample compartment of the spectrometers. The liquid sample of UCO and biodiesel were filled onto the trough plate, respectively, and the cover

was placed over the trough plate. The infrared spectra were scanned from 400–4000 cm^{-1} with a spectral resolution of 4 cm^{-1} .

3.7. Catalyst Regeneration and Spent Catalyst Characterisation

The spent nano-magnetic catalyst from the synthesized biodiesel was collected by using the external magnetic field and washed with acetone and *n*-hexane to remove the impurities trapped on the catalyst surface. Then, the washed catalyst was dried in the oven for 6 h at 80 °C and was reactivated at 550 °C for 2 h in a furnace with nitrogen flow. The recovered nano-magnetic catalyst was reused at optimum conditions to study the reusability of the catalyst and characterization of spent nano-bifunctional supermagnetic catalyst using BET, TPD, XRD, and VSM were performed.

4. Conclusions

The super-magnetic nano-bifunctional RHC/K₂O/Fe catalyst was successfully synthesized for the transesterification of UCO. The optimum super-magnetic nano-bifunctional RHC/K₂O-20%/Fe-5% catalyst, possessed a specific surface area of 57.89 m² g⁻¹ and bifunctional properties for basic and acid densities of 4.43 mmolg⁻¹ and 24.55 mmolg⁻¹, respectively. The supermagnetic nano-bifunctional RHC/K₂O-20%/Fe-5% catalyst, showed excellent catalytic activity and rigidity that can be reused until the fifth cycle. Its recoverability by using an external magnetic field has presented the most effective separation process due to its high magnetic property (7.88 emug⁻¹). The optimized conditions (amount of catalyst, 4 wt; methanol/oil molar ratio, 12:1; reaction time, 4 h; reaction temperature, 75 °C) gave the highest biodiesel yield (98.6%) through the conventional reflux system. A slight deactivation of the catalyst was found mainly due to non-selective poisoning in which the reactants deposited on the surface of active sites. Therefore, the supermagnetic nano-bifunctional RHC/K₂O-20%/Fe-5% catalyst depicts to be an ideal magnetized catalyst as a replacement for conventional homogeneous and heterogeneous catalysts due to its potential for conversion of UCO to biodiesel, its effectiveness, and its practicability.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/10/2/225/s1, Figure S1. (a) Nitrogen adsorption-desorption isotherms of the RH, RHC and RHC nano-magnetic catalysts, (b) Pore volume of the RH, RHC and RHC nano-magnetic catalysts, Figure S2. (a–b) ¹H-NMR spectra of UCO and biodiesel, Figure S3. FTIR spectra of UCO and biodiesel

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