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A Heterogeneous Bifunctional Carbon Nanocatalyst from Plastic Waste to Efficiently Catalyze Waste Cooking Oil into Biodiesel

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Abstract: In this study, black carbon derived from polyethylene terephthalate (PET) wastes was utilized as the precursor for heterogeneous bifunctional nanocatalyst, which successively catalyzed waste cooking oil into biodiesel. The nano-sized catalysts were prepared by impregnation method with different heat treatment techniques, such as reflux, hydrothermal, and microwave solvothermal, to provide good distribution of K₂O and NiO particles on PET activated carbon mesoporous surface. The sample treated with microwave solvothermal technique (MAC-K₂O-NiO) exhibited a high surface area of 120 m²/g with good dispersion of nanoparticles, as shown by FESEM image, large crystallite size of 62.2 nm, and consisted of a highest density of basicity (2.58 mmol/g) and acidity (1.79 mmol/g) for improving transesterification to a maximum yield. The catalytic transesterification of MAC-K₂O-NiO was optimized with 3 wt.% of catalyst loading, 18: 1 methanol-oil molar ratio, 65 °C for 3 h of reaction, with a maximum yield of 97.2%. The catalyst reusability was performed, and it was found to maintain the catalytic activity up to six reaction cycles, with a yield of 72.9%. The physiochemical quality of the optimized biodiesel was examined in accordance with the American Society for Testing and Materials, ASTM D6751 testing method.

Keywords: heterogeneous catalyst; physiochemical characterization; transesterification; optimization; reusability; fuel properties

1. Introduction

Energy is the cogwheel of economy, and human beings are dependent on it, which drives thinking of humans to correlate supply with demand by innovating the pool of energy for smart sustenance [1]. Fuels play a prominent role in our lives, as they contribute to the development of a nation and drive connectivity among nations. The current scenario of circular economy involves the use of various sources of energy to meet our energy needs. Fossil fuel depletion and global politics has forced researchers to look for sustainable development goals by thinking of alternative fuels [2]. For instance, biodiesel that can be

produced from renewable resources with the oil qualities that are similar to diesel fuel, so that direct utilization of these is possible without engine modification [3]. However, huge production of biodiesel has posed a challenge of dealing with the by-product glycerol, which can be used for the production of acrolein [4]. The use of various metal salts for the dehydration of glycerol and production of acrolein from it seems to offer a solution to a waste by-product and has not been focused on to a greater extent [5].

Biodiesel is the result of catalyzed free fatty acid (FFA) or triglycerides with short-chained alcohol [6]. The journey of biodiesel production was started in 1893 by Rudolf Diesel, who utilized peanut oil as fuel in a diesel engine, which became the benchmark for replacing diesel fuel with vegetable-oil-based diesel [7]. However, the major drawback of utilizing edible oil is the food security problem, which would cause the production cost to be less economical. Thus, the alternatives are by shifting the feedstock with nonedible oils, such as waste cooking oil, jatropha oil, neem oil, chicken fat, etc. [8,9]. Waste cooking oil (WCO), which is normally dumped into the environment, finds its use in the production of biodiesel, as it might lead to cancer if used repeatedly. The disposal of WCO into ecosystems leads to complex problems associated with flora and fauna [10]. These problems need to be addressed by converting it into biodiesel.

The production of biodiesel is still a challenge in terms of its production cost, especially when utilizing homogeneous catalyst, such as NaOH, KOH, H_2SO_4 , ClSO_3H , H_3PO_4 , etc., due to the complicated washing procedure for catalyst removal upon completing the esterification/transesterification reaction [11]. In addition, the washing water after biodiesel purification process must undergo water treatment in a special pond before releasing it into the river. In addition, the stated catalysts are corrosive towards reactor equipment; thus, it requires regular maintenance and the installation of protective gears to reduce the instant corrosion [12]. The homogeneity of the catalyst with reactants allows the reaction to accelerate at a lower temperature and shorter time. For example, transesterification of *Citrus reticulata* was achieved within 1 h at a low methanol molar ratio of 6:1 and low reaction temperature of 60 °C. Meanwhile, for WCO, the catalytic activity would be less effective due to the FFA content that is slightly higher than virgin oil, which led to emulsification reaction [13]. Thus, catalyst is modified by creating heterogeneous catalyst to overcome the stated challenges.

Heterogeneous catalyst offers the ease of separation through filtration or magnetic field, exclusion of post-transesterification purification treatment, and it is eco-friendly [14]. Heterogeneous catalyst can be functionalized with acid, basic, or acid–basic groups according to the nature of feedstocks [15]. Dahai et al. produced mesoporous basic metal oxide catalyst consisting of Mg–Al impregnated on K (K/OMMA) for transesterification of soybean-based biodiesel (99.8%) [16]. An introduction of basic metal, such as Mg on the magnetic nanocatalyst core, Mg/ Fe_2O_3 – SiO_2 , was effective for catalyzing *Camelina sativa* seed oil into biodiesel at 99% of yield within 4 h and maintaining the reactivity up to six reaction cycles [17]. A solid acid catalyst, SO_3H -aryl- SiO_2 NPs, was synthesized via co-condensation method and successfully esterified FFA for five reaction cycles without leaching for every 2 h, with a yield above 82.3% [18]. Nevertheless, the catalyst 100% made up of metal NPs might be expensive for the production cost, which can be overcome by waste materials for its production. There is a surge in interest in using MOFs for the production of biodiesel, particularly because of their advantages, such as surface area, ultrahigh porosity, and controllable structures, for example, 12-Tungstophosphoric acid-encapsulated metal–organic framework UiO-66 that is applied for the esterification of acetic acid and n-butanol [19].

A huge effort has been put into practice to produce solid catalyst from waste materials [20]. For instance, calcined cocoa pod husk-plantain peel ash catalyst (CPPA) was involved in catalytic activity for producing honne methyl ester. The CPPA catalyst is composed of high basicity due to the presence of 50.96% K, 2.49% Ca, and 2.30% Mg, which contribute to 98.98% yield within 2.5 h of reaction [21]. A 4 wt.% CaO @ carbon-modified catalyst was produced through the impregnation on date pit biomass, the structural con-

firmation of which was characterized by XPS, confirming the presence of Ca-O bonding, which contributed to 98.2% date-pit oil biodiesel-based product [22]. Surface area and pore diameter also have an effect towards biodiesel production by providing the active site for the triglycerides/FFAs and methanol to diffuse and transform into methyl ester, for example, sulfonated rice husk mesoporous carbon that possessed 1233 m²/g surface area with acidity more than zeolite [23].

Many people have used biomass for the production of catalyst but, in the recent times, there has been use of waste PET bottles for the production of catalyst to produce biodiesel [24]. Recently, PET waste activated carbon functionalized with sulfonate group (PWC-SO₃H) was synthesized for the PFAD biodiesel [25]. All these materials tend to use activated carbon as a support for the production of catalyst that has versatile properties, such as high porosity, tendency to incorporate functional groups into its surface, and high stability to sustain in acidic and basic environments so that it can be reused for effective environmental remediation [26]. The advantage of activated carbon lies in its versatility in being easily customizable to fit our needs of impregnating with various metals for various purposes [27]. Various physical and chemical methods have been utilized for the activation of activated carbon, which serve the purpose to customize it for various purposes. Treatment with acids aids in removing minerals from surface and increase acidity. The usage of base for this purpose helps to produce surface which, in a way, aids in the clinging of negatively charged groups to surface [28].

The effective use of a nano bifunctional catalyst developed from activated carbon (AC) from waste PET, which has created havoc on our planet as it is mostly dumped into landfills or oceans, was achieved. In this research a new approach has been developed to convert PET into AC, which is less toxic and can be further utilized in power plants for production of energy. The effectiveness of the material in performing the transesterification speaks about its utility and, thus, lessens the burden of PET piling up, as all of it is not utilized. This material has opened a new branch of using waste polymer materials as compared to biomaterials that were in vogue. In addition, to produce activated carbon, there has been a paradigm shift towards usage of microwave ovens rather than traditional ovens, which shortens the time span for activation and reduces the amount of energy required. The microwave method causes the material to heat from inside and, thus, there is effective dissipation of energy, which is quite apt for wastes from agricultural wastes, as they have high absorbance capacity [29]. Thus, in this study, the bifunctional catalysts supported by PET activated carbon were synthesized by impregnating K₂O and NiO nanoparticles and thermally treating with various heating treatment techniques, such as reflux, hydrothermal, and solvothermal microwave, before carbonizing at 800 °C. Those catalysts treated with reflux were known as RAC-K₂O-NiO, while hydrothermal and microwave heating treatment were identified as HAC-K₂O-NiO and MAC-K₂O-NiO, respectively. The comparison of prepared catalysts was examined by a series of physical and chemical characterization techniques. The effect of catalytic activities for optimization, such as catalyst loading, methanol: WCO molar ratio, reaction temperature, and time, were studied to produce maximum biodiesel yield. In addition, the catalyst reusability and deactivation were investigated. Moreover, the prepared biodiesel with high yield was subjected to ASTM D6751 physiochemical test.

2. Results and Discussion

2.1. Thermal Degradation Analysis

The thermalgravimetric analysis technique was utilized to study the relationship between temperature and the mass loss of nano-sized catalyst, as well as to evaluate the catalyst stability. Three main degradation phases were observed, as depicted in Figure 1. The first degradation region from 25 °C to 200 °C was denoted as removal of physisorbed moisture and volatile materials existing on the catalyst surface by mass loss of 7.5% to 8.0% [30]. The second degradation phase at the temperature range from 200 °C to 800 °C showed the conversion of Ni(NO₃)₂·6H₂O to NiO and water vapor, as specified in Equa-

tions (1)–(4). On average, the mass loss due to NiO formation was recorded at 16%. The mass loss at temperature 800 °C to 950 °C showed the breakdown of K_2CO_3 to K_2O , and further degradation was determined as solid residue with 12% to 17% of mass loss. Hence, the TGA-DTG curves showed that the synthesized catalysts exhibited good thermal stability.

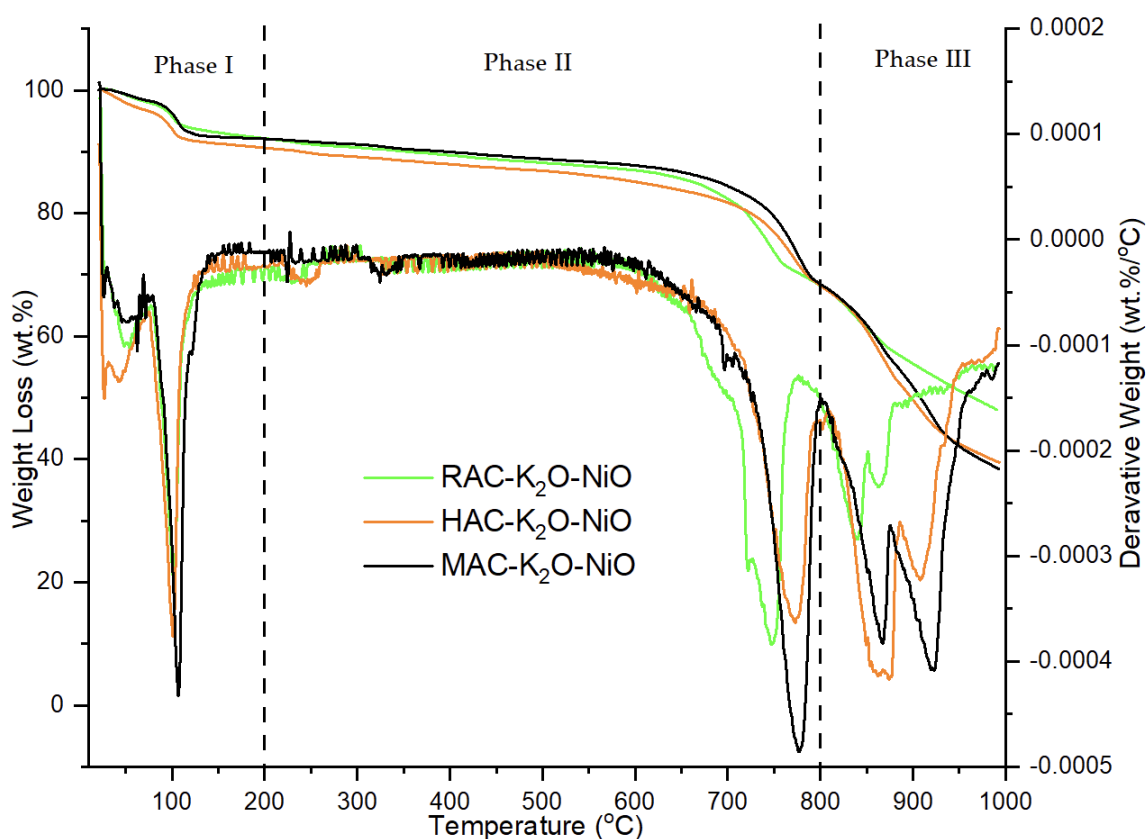
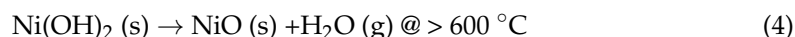
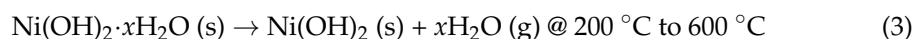
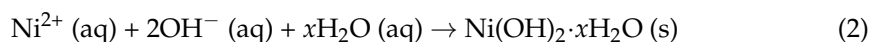


Figure 1. Thermal degradation curves of RAC- K_2O -NiO, HAC- K_2O -NiO, and MAC- K_2O -NiO nanocatalysts.

2.2. Surface Area and Pore Size

The surface area analysis was performed on RAC- K_2O -NiO, HAC- K_2O -NiO, and MAC- K_2O -NiO catalyst samples by BET method, as shown in Figure 2. The nanocatalyst sample possessed type-IV isotherm with H3-type hysteresis loop of slit multilayer mesoporous structure due to crystal agglomeration [31]. The pore size distribution was estimated by BJH desorption method. The nano-sized catalysts revealed mesoporous structure, the sharp and broad curves of which were set in the range of 2 nm to 4.5 nm and 5 nm to 10 nm, respectively. Literally, the surface area of MAC- K_2O -NiO was 120 m^2/g , which is slightly larger than RAC- K_2O -NiO and HAC- K_2O -NiO due to uniform dispersion of K_2O and NiO nanoparticles channeling the porous surfaces during microwave thermal treatment [32]. Meanwhile, the random agglomeration of K_2O and NiO clustering on the precursor causes the reduction in surface area among RAC- K_2O -NiO and HAC- K_2O -NiO samples, as was discussed by Witton et al. [33]. The results were consistent with microscopic scanning im-

ages that microwave-assisted thermal treatment possessed better nano-particle distribution than others.

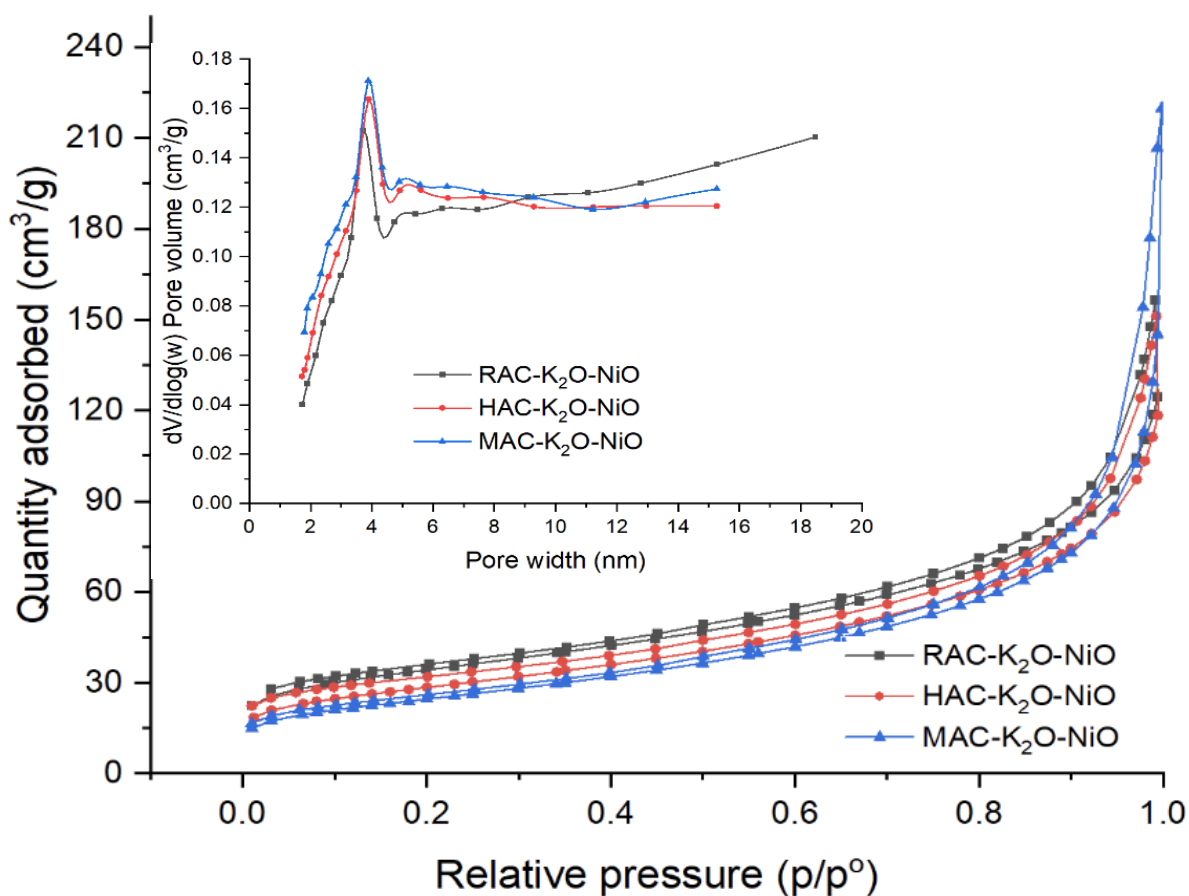


Figure 2. Nitrogen adsorption–desorption curves and pore volume plots of synthesized nanocatalysts.

2.3. Crystallinity Analysis

Figure 3 demonstrates X-ray diffracted signals for RAC-K₂O-NiO, HAC-K₂O-NiO, and MAC-K₂O-NiO samples and the phases were identified using standard library, ICSD file.

The slight characteristic peaks of K monometallic were diffracted at $2\theta = 28.3^\circ$ and 30.1° (ICSD File No. 9011976) due to the trace effect of decomposing K₂CO₃ to K₂O [27]. K₂O diffraction peaks were located at $2\theta = 31.8^\circ$, 35.4° , and 56.6° (ICSD File No. 1537125), respectively. X-ray signals that associated with NiO species were detected at $2\theta = 36.2^\circ$ and 62.3° (ICSD File No. 1010095). Low intensity of diffraction peaks were also identified as the signal of NiSiO₄ (ICSD File No. 1523551) and K₂Si₂O₅ (ICSD File No. 20033026), which indicated the interaction between amorphous silica group with K₂O and NiO component, in agreement with previous findings by Wei et al. [34]. The estimated Debye Scherrer crystallite size of NiO pattern at 36.2° was calculated and is listed in Table 1. The result showed that microwave heat-treated sample MAC-K₂O-NiO nanocatalyst possessed the highest crystallinity due to fast nucleation for crystallization that was facilitated by the microwave beam during the impregnation process [35].

Table 1. Physical and chemical properties of the synthesized K₂O–NiO activated carbon nanocatalyst.

Catalyst	Surface Area (m ² /g)	Average Pore Size (nm)	Pore Volume (cm ³ /g)	Total Desorption (mmol/g)		Crystallite Size (nm)
				CO ₂	NH ₃	
RAC-K ₂ O-NiO	88	5.44	0.13	2.01	1.43	54.99
HAC-K ₂ O-NiO	101	4.70	0.13	2.17	1.51	56.40
MAC-K ₂ O-NiO	120	4.77	0.14	2.58	1.79	62.20

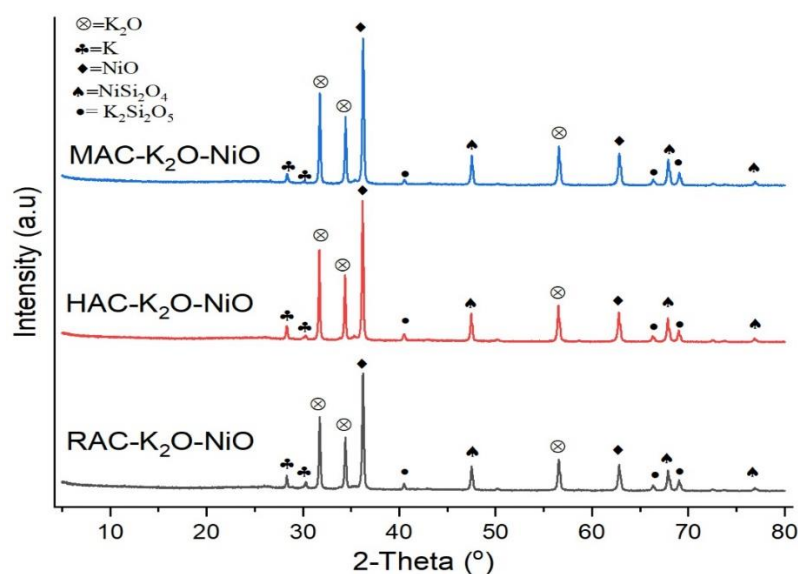


Figure 3. Crystallographic patterns of synthesized nanocatalysts.

2.4. Structural Morphologies

The structural morphologies of prepared catalysts were performed by FESEM at 10 K magnification power in conjunction with N₂ adsorption–desorption analysis. Figure 4a,b revealed the random agglomeration of active compounds (K₂O and NiO) on the external and internal porous surface of the plastic activated carbon. Meanwhile, uniform dispersion of the same compounds in the mesoporous carbon framework could be observed in Figure 4c. The enclosed micrograph of Figure 4c by 20 K magnification demonstrated the thread-like fibrous structure of K₂O and NiO embedded on the surface after being irradiated by microwave. In addition, the EDX mapping in Figure 5 showed the uniform and consistent dispersion of Ni, K, and O on the PET carbon support, which demonstrated that microwave heating contributes to homogeneity impregnation for MAC-K₂O-NiO sample in comparison to the rest of the heating treatments.

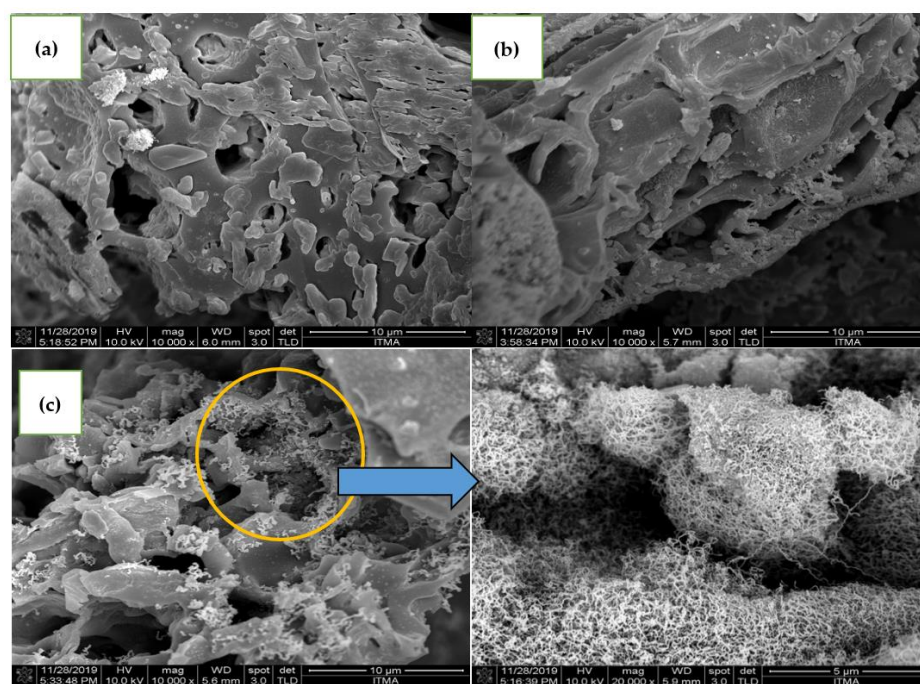


Figure 4. Surface morphologies of synthesized nanocatalyst magnified at 10 K: (a) RAC-K₂O-NiO, (b) HAC-K₂O-NiO, (c) MAC-K₂O-NiO.

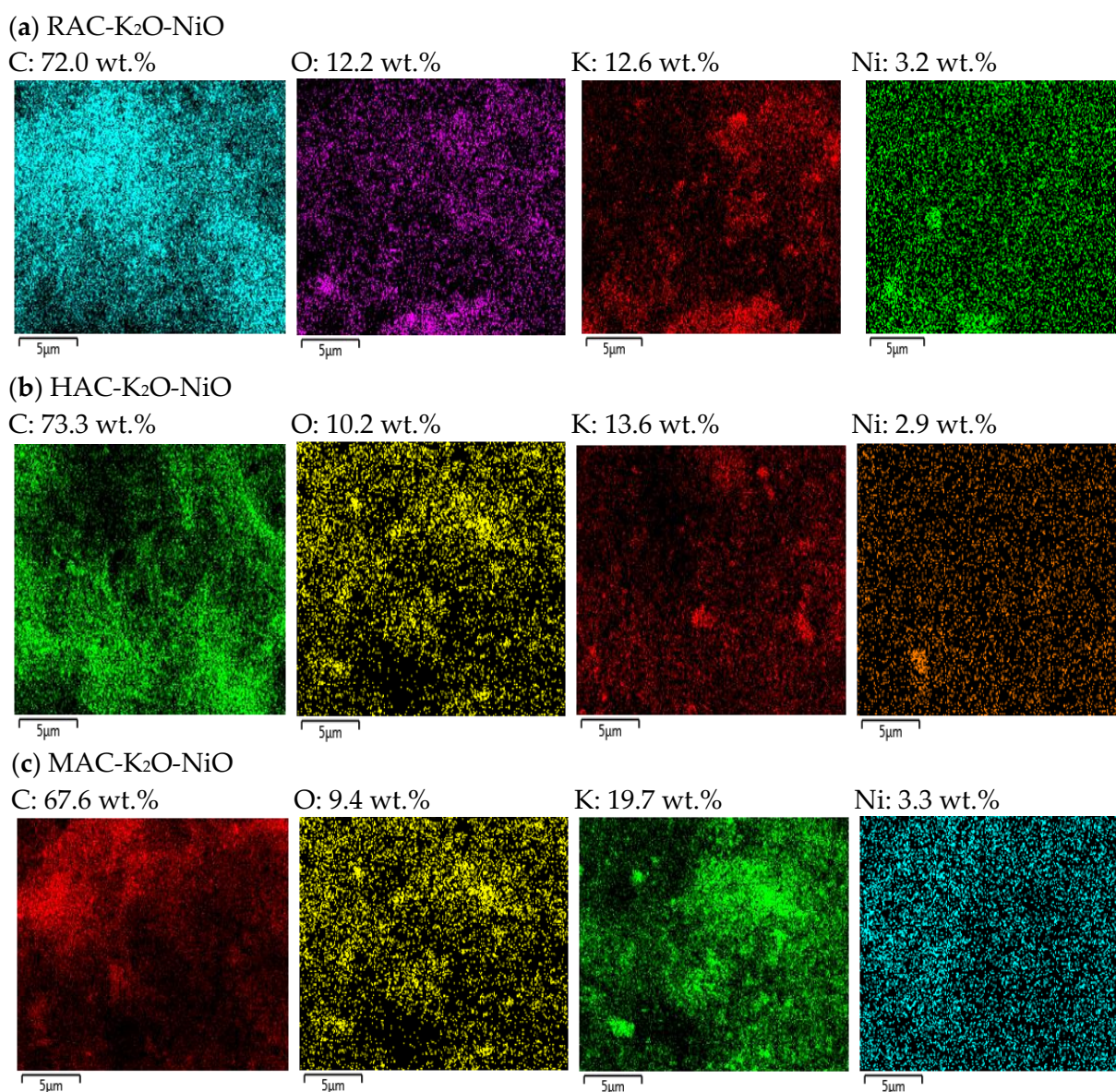


Figure 5. EDX mapping of (a) RAC-K₂O-NiO, (b) HAC-K₂O-NiO, and (c) MAC-K₂O-NiO nanocatalyst.

2.5. Functional Group Analysis

The infrared absorption spectra of nanocatalysts were measured from 4000 to 400 cm^{−1}, as shown in Figure 6. A typical broad absorption at 3102 cm^{−1} was identified as −OH group [36] of moisture physisorption on the catalyst's surface and an asymmetrical C–H stretching absorption peak was located at 2298 cm^{−1} [37]. The sharp and intense peaks at 1642 cm^{−1}, 1436 cm^{−1}, 1369 cm^{−1}, 977 cm^{−1}, and small spectrum at 694 cm^{−1} were associated to O–C–O vibration stretching, C = O asymmetry stretching of CO₃^{2−}, C–O broadening of carbonate bending vibration, and free CO₃^{2−}, respectively, that indicated the impregnation of K₂O (originated from K₂CO₃) on the carbon support [38,39]. C–H wagging absorption spectrum was located at 839 cm^{−1}. Two significant absorption bands of Ni–O were displayed in the region of 618 cm^{−1} and 425 cm^{−1} of stretching vibration mode [40]. The intense and broad Ni–O absorption bands were due to the formation of NiO nanocrystal [41,42]. The presence of K₂O and NiO spectra indicated the successful bifunctional active site impregnation; basic and acid sites, respectively, for promoting catalytic transesterification of triglycerides and free fatty acid of WCO. Thus, the finding was correlative with other characterization techniques.

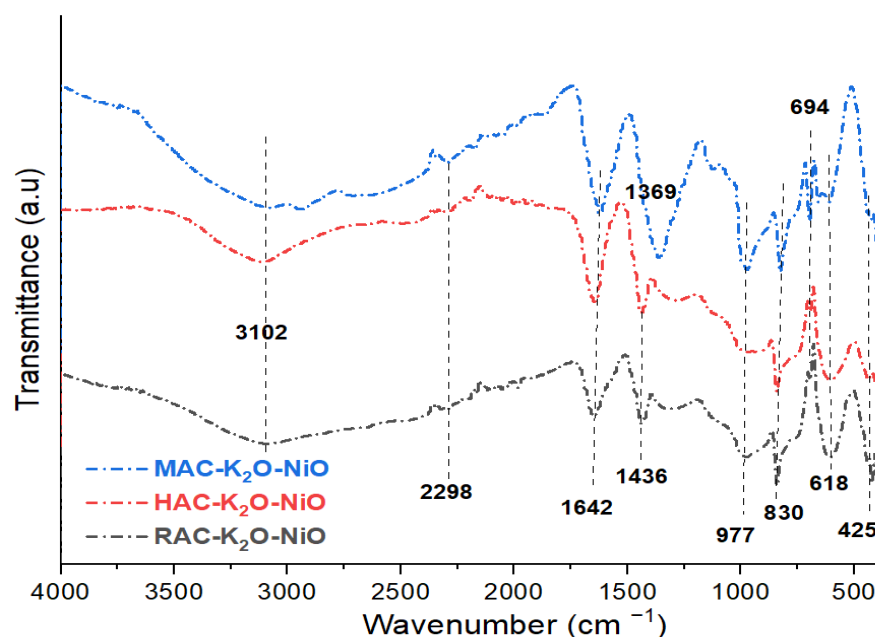


Figure 6. Infrared absorption spectra synthesized nanocatalysts.

2.6. Basicity and Acidity Strength

The catalyst's basicity and acidity strength were measured by TPD per gram of synthesized carbon-supported K_2O - NiO samples, of which the total desorption of CO_2/NH_3 was essentially equivalent to the number of active sites involved during gas adsorption on the catalyst surfaces. Generally, the adsorption–desorption of CO_2/NH_3 species were proportional to temperature, where the synthesized samples chemisorbed at strong temperature regions of 650 °C to 800 °C [4,43], as per the results recorded in Table 1. The MAC- K_2O -Ni catalyst possessed 2.58 mmol/g and 1.79 mmol/g of basicity and acidity, respectively, which contributed to 81.4% of biodiesel yield. Meanwhile, RAC- K_2O -Ni and HAC- K_2O -Ni samples exhibited basic and acid strength at 2.01 mmol/g and 1.43 mmol/g, and 2.17 mmol/g and 1.51 mmol/g, respectively. The slightly lower total basic and acid strength led to slightly lower biodiesel yield of 60.1% and 72.3% for reflux- and hydrothermal-treated catalysts. In this study, the catalyst preparation methods might affect the distribution of basic and acid sites, with the microwave thermal-treated samples possessing slightly higher total desorption in comparison to the reflux and hydrothermal treatment. The microwave radiation could enhance fast nucleation for crystal formation [44,45], which assists for well-developed K_2O and NiO active sites with even distribution on the mesopores, thus providing the highest chemisorption measurement. The catalytic evaluation among three synthesized catalysts were carried out and MAC- K_2O -NiO catalyst showed the highest biodiesel yield of 81.4%.

2.7. Catalytic Performance

2.7.1. Catalyst Screening Evaluation

The catalyst screening evaluation was carried out to study the influence of catalysts' basicity–acidity properties towards biodiesel production yield, given the different quality of reaction rates. The catalytic activities of RAC- K_2O -NiO, HAC- K_2O -NiO, and MAC- K_2O -NiO promoted the transesterification by yielding biodiesel at 60.1%, 72.3%, and 81.4%, respectively, at reaction parameters of 15:1 methanol-oil molar ratio, 2 wt.% of catalyst loading, 65 °C for 2 h reaction time (Figure 7a). Literally, MAC- K_2O -NiO nanocatalyst has strong basicity–acidity active sites (2.58 mmol/g and 1.79 mmol/g), thus providing the highest reaction rate that effectively reduces interfacial tension of waste cooking oil and methanol for biodiesel production [46]. Thus, the MAC- K_2O -NiO was selected for extended optimization studies.

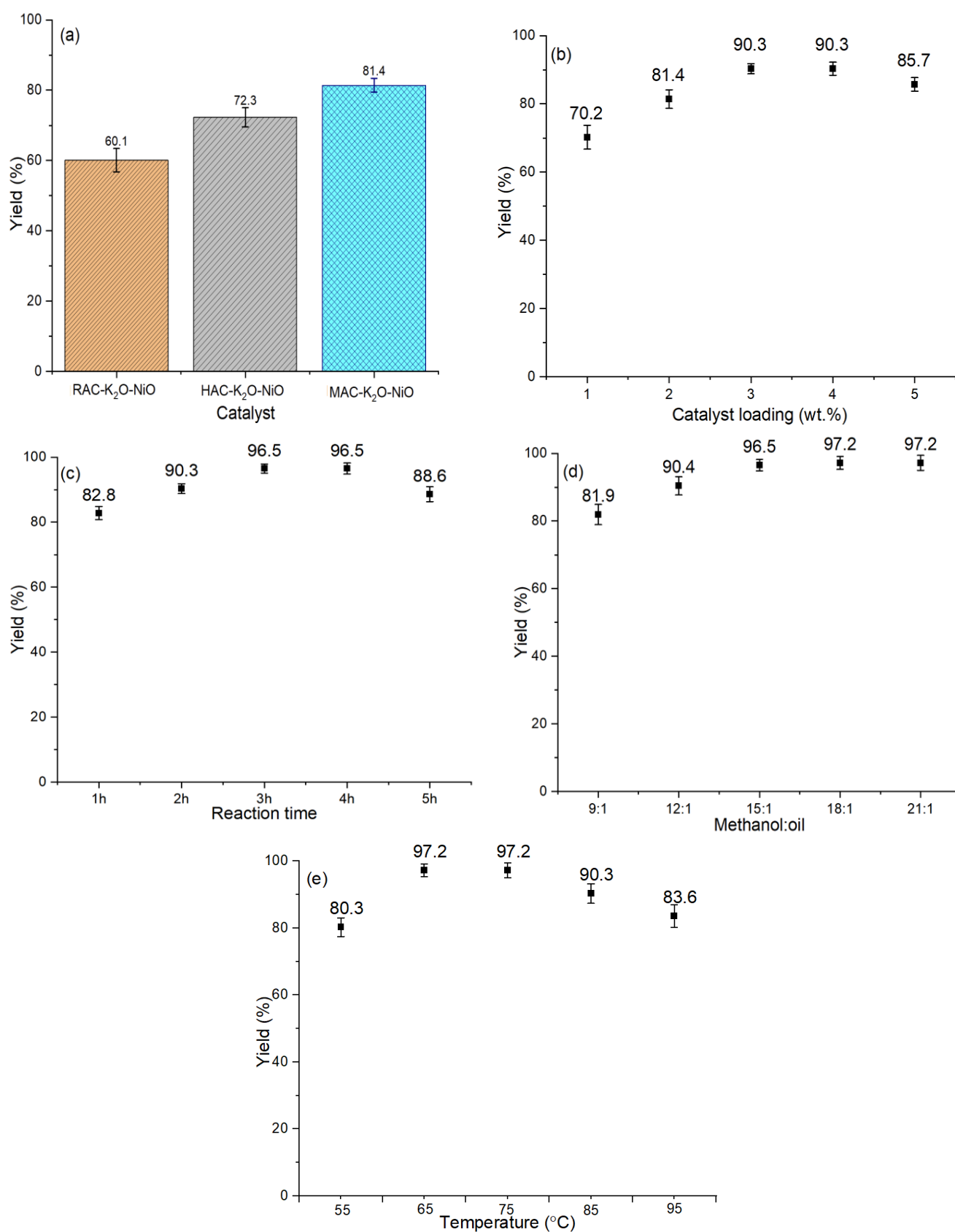


Figure 7. MAC-K₂O-Ni catalyst optimization studies of reaction parameters: (a) catalyst screening, (b) catalyst loading, (c) reaction time, (d) methanol: oil molar ratio, and (e) reaction temperature for biodiesel yield.

2.7.2. Catalyst Loading

The transesterification reaction rate was significantly influenced by the amount of catalyst loading that provided the sufficient active sites for the triglycerides and methanol to convert into biodiesel. Figure 7b demonstrates that the biodiesel yield increased from 70.2% to 81.4% and 90.3% with catalyst loading of 1 wt.%, 2 wt.%, and 3 wt.%, respectively. This was due to the presence of more active sites with increase in catalyst load, which allowed a high rate of diffusion for the reactants [47]. The yield remained constant with a catalyst load of 4 wt.% and subsequently decreased with 5 wt.% of catalyst to 85.7%. The catalyst loading beyond the optimized amount would cause poor diffusion rate among methanol-oil-catalyst phases, thus lowering the mixing capabilities for biodiesel production [48].

2.7.3. Reaction Time

The transesterification duration for catalytic performance was studied from 1 h to 5 h at constant 3 wt.% catalyst loading, 15:1 methanol-oil molar ratio, and 65 °C reaction temperature. The result in Figure 7c revealed that biodiesel yield gradually increased from the first reaction hour (82.8%) to the third hour (96.5%). In the third reaction hour, the reactants were given sufficient time to diffuse in and out of active sites and, thus, produced biodiesel at the highest yield [49]. The yield was slightly decreased to 88.6% at an extended time of 5 h due to reversible reaction that shifted the methyl esters to fatty acids, which then promoted soap formation [50]. Hence, 3 h of transesterification time was selected as an optimal parameter for subsequent catalytic performance tests.

2.7.4. Methanol: Oil Molar Ratio

The effect of methanol-oil molar ratio was studied and performed at optimum catalyst loading of 3 wt.%, reaction time of 3 h at 65 °C, and the results are simplified in Figure 7d. At a low molar ratio of 9:1, the yield obtained was 81.9% due to the lower amount of methanol species to interact with waste cooking oil for higher production of biodiesel. The yields were increased proportionally with the methanol molar ratio up to 18:1, with a yield of 97.2%, due to the presence of more methoxy species for the contact between oil and solid catalyst phases, thus shifting the reaction towards biodiesel production [51]. Therefore, 18:1 molar ratio was chosen for another optimization study.

2.7.5. Reaction Temperature

The effect of reaction temperature towards biodiesel production was carried out at a temperature range of 55 °C to 95 °C within constant parameters of 3 wt.% catalyst loading and 18:1 methanol: oil molar ratio within 3 h reaction. Figure 7e presents the yield for a temperature of 55 °C as 80.3% and optimized at 65 °C with 97.2%, which also remained unchanged up to 75 °C. The heat release was utilized by the reactants for converting into kinetic energy in the form of effective collision that enhanced the miscibility until achieving optimum yield [52]. However, the yield decreased to 90.3% and 83.6% as temperature increased to 85 °C and 95 °C, respectively, due to methanol vaporization that reduced the amount of methanol, thus lowering the contact between oil-methanol-catalyst phases for biodiesel production [53].

2.8. Reusability Study

The MAC-K₂ONiO nanocatalyst was recovered from the reaction mixture and reused for 7-cycle catalytic performance, which was tested at optimal reaction parameters (3 wt.% catalyst loading, 65 °C, 3 h reaction time, and 18:1 methanol: oil molar ratio). As shown in Figure 8a, the catalytic performance trends of MAC-K₂O-NiO slightly slowed down until the fourth cycle with 90.8% of biodiesel yield. However, a significant reduction in yield was clearly observed in the fifth (82.4%), sixth (72.9%), and seventh (64.3%) cycle due to agglomeration impurities on the catalyst's active sites, such as uncreated triglycerides, glycerol, methanol, etc., which reduces catalytic performances for transesterification. This

occurrence has been proved by FESEM image, BET surface area analysis, and CO₂/NH₃-TPD (Figure 8b and Table 2).

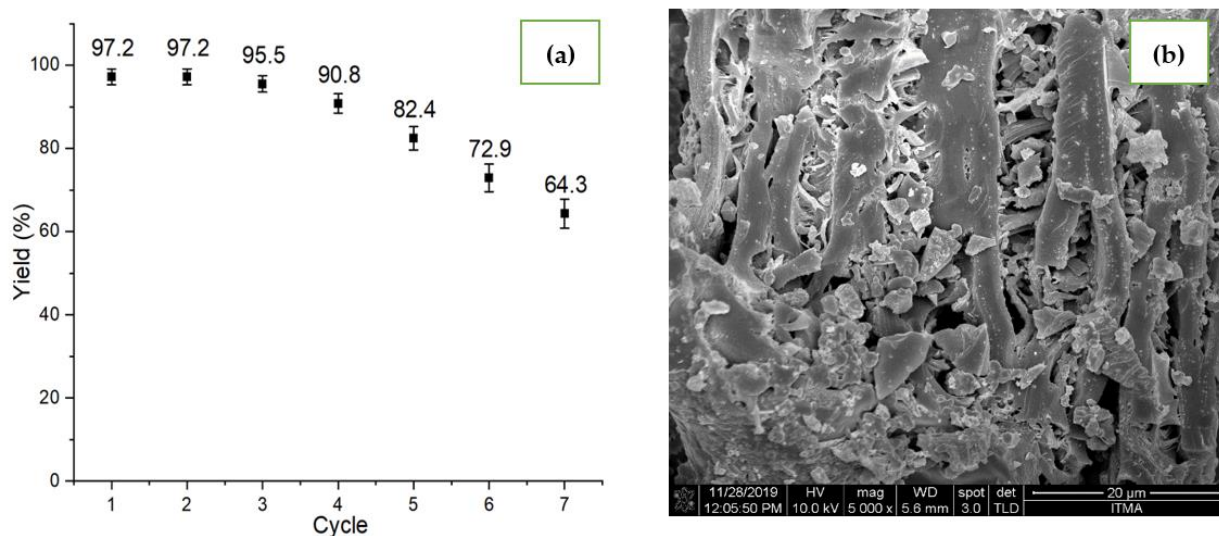


Figure 8. (a) Number of transesterification cycle's plot; (b) FESEM image of spent MAC-K₂O-NiO after 7th reusability cycle.

Table 2. Properties of the MAC-K₂O-NiO before transesterification and after 7th reusability cycle.

Catalyst	Surface Area (m ² /g)	Average Pore Size (nm)	Pore Volume (cm ³ /g)	TPD (mmol/g)	
				CO ₂	NH ₃
MAC-K ₂ O-NiO	120	4.77	0.14	2.58	1.79
Spent MAC-K ₂ O-NiO	50	4.05	0.02	1.03	0.56

2.9. Comparison of Produced Plastic Char Support Catalyst with the Commercial Activated Carbon Support-Based Catalysts

The synthesized catalyst supported on PET activated carbon (MAC-K₂O-NiO) was compared with other catalysts supported on commercialized activated carbon, as shown in Table 3, where the assessment covered textural properties, acidity–basicity strength, type of biodiesel feedstock, transesterification optimization parameters, yield, and reusability cycles. The results showed that the MAC-K₂O-NiO nanocatalyst possessed a large surface area with a sufficient amount of acidity and basicity active sites that facilitated and enhanced the transesterification of WCO at the highest yield of 97.2% at moderate optimized reaction parameters at the shortest time of 3 h compared to others. In addition, this catalyst sample was able to maintain its catalytic performances up to seven reaction cycles, which revealed its reusability and stability. This catalyst can be studied in depth as a suitable catalyst choice for large biodiesel production in future.

Table 3. Commercial activated supported carbon catalysts and MAC-K₂O-NiO nanocatalyst for comparison analysis.

Catalyst	Surface Area (m ² /g)	Acidity/Basicity (mmol/g)	Biodiesel Feedstock	Reaction Parameters	Biodiesel Yield (%)	Reusability Cycle	Ref.
ACPhSO ₃ H	114	0.98	Rapeseed oil	10 wt.%, 7 h, 65 °C, 1:20	95.0	7	[54]
Ca_AC_3_800 °C	97	-	Soybean oil	-	91.0	4	[55]
35%H ₆ PV ₃ MoW ₈ O ₄ /AC-Ag	310	0.11	Soybean oil	8 wt.%, 10 h, 140 °C, 1:30	91.3	5	[56]
MAC-K ₂ O-NiO	120	1.79, 2.58	WCO	3 wt.%, 3 h, 65 °C, 10:1	97.2	7	This study

2.10. Biodiesel Physiochemical Properties

The optimized biodiesel yield (97.2%) was evaluated for physiochemical properties according to international standard method, ASTM D6751, as recorded in Table 4, where the biodiesel quality was within the permissible limit that is safe to handle and utilize as biofuel for a diesel engine. The viscosity of synthesized biodiesel was measured at a middle range value of 3.95 mm²/g, which provided smoothness for fuel injection and atomization to achieve efficient and complete combustion upon consistent tiny droplets from spray and direct penetration in a diesel engine [57]. The moisture content was recorded at 0.01%, considering that the biodiesel was “moisture free”, which could inhibit the corrosion from happening inside the engine compartment and enhancing the calorific value at the optimum point [58]. Flash point can be defined as the lowest temperature of fuel to spark when exposed to ignitable resources and air. In this study, the flash point was 160 °C, which is higher than the permissible limit that can guarantee the safety for handling, storage, and transportation [59]. Cloud point and pour point are the indicators of the lowest temperature for the biodiesel to start forming cloudy wax crystal and stop flowing upon fuel solidification [60], which was recorded at 5 °C and 3 °C, respectively. These two temperature parameters are significantly important for the usage in cold climate regions because fuel solidification can cause its deposition on the fuel filter, thus leading to engine fault. Biodiesel ignition test was measured at 60, given that the cetane number was within the ASTM D6571 limit, and signified that all of triglycerides and fatty acids have been converted into biodiesel, thus lowering its saturation and causing it to ignite at a faster rate [61]. Hence, the physiochemical properties revealed that MAC-K₂O-NiO nanocatalyst catalyzed WCO and methanol at the optimum rate to produce high-quality biodiesel that matches with the ASTM D6571 requirement.

Table 4. Physiochemical properties of biodiesel.

Properties	ASTM D6751	Biodiesel
Viscosity (mm ² /g)	1.9–6.0	3.95
Moisture content (wt.%)	<0.05	0.01
Flash point (°C)	>120	160
Cloud point (°C)	−3–15	5
Pour point (°C)	−5–10	3
Cetane number	47–65	60
Density (g/cm ^{−3})	0.82–0.90	0.82

3. Materials and Methods

3.1. Materials and Chemicals

Waste cooking oil (WCO) was obtained from restaurants in Serdang, Selangor. The chemicals used in this research were analytical reagent grade without the requirement of further purification. Potassium carbonate (K₂CO₃, 99.5%), potassium hydroxide (KOH, 86.0%), nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 98.0%), methanol (CH₃OH, 99.5%), and ethanol (CH₃CH₂OH, 99.8%) were purchased from Merck Sdn Bhd, Petaling Jaya, Malaysia.

3.2. Preparation of Activated Carbon Supported Bifunctional Catalyst

Activated carbon (AC) derived from plastic waste was prepared by cutting soft polyethylene terephthalate (PET) egg box waste into smaller pieces of ~2 cm and was converted into fine powder by using a mechanical grinder. Then, the PET powder was thoroughly mixed with zinc chloride (ZnCl₂) and carbonized at 600 °C at a heating rate of 5 °C/min for 4 h in the absence of oxygen. The activated carbon sample (AC) was alternately washed with 20 mL of 1 M hydrochloric acid and 1 L of distilled water until achieving the neutralization. The neutralized char was dried in the oven overnight at 105 °C.

K₂O-NiO nanocatalysts impregnated on plastic char were prepared by providing thermal treatment of reflux, solvothermal, and microwave solvothermal methods during

the mixing process. Briefly, solutions of K_2CO_3 (20 wt.%) and $Ni(NO_3)_2 \cdot 6H_2O$ (5 wt.%) were drop-wise added and mixed thoroughly with plastic activated carbon powder (AC, 10 g). The mixed solution was transferred into a reflux flask for heating process under controlled temperature (100 °C) and continuous stirring (600 rpm) for 10 h. After thermal mixing, the sample was oven-dried for overnight. The dried black powder was carbonized at 800 °C for 2.5 h for catalyst activation. Similar procedures were repeated by replacing the reflux heating method with solvothermal and microwave solvothermal. The synthesized catalysts were named as RAC- K_2O -NiO, HAC- K_2O -NiO, and MAC- K_2O -NiO due to impregnation heating treatment of reflux, solvothermalization, and microwave, respectively.

3.3. Catalyst Characterization

Decomposition temperature of the prepared catalysts, RAC- K_2O -NiO, HAC- K_2O -NiO, and MAC- K_2O -NiO were characterized by thermogravimetric analyzer (TGA/DSC, Mettler Toledo, TGA-DSC HT 3 Shah Alam, Malaysia) over the temperature range 20–1000 °C. Catalyst surface areas and pore sizes were measured using BET, nitrogen adsorption-desorption method (ASAP-2020). The crystallinity of catalyst samples was evaluated using RIGAKU Smartlab X-ray diffractometer (Tokyo, Japan) with Cu- $K\alpha$ radiation (Hypix-400, $\lambda = 0.154$ nm) generated at 40 kV and 30 mA. Surface microscopic morphologies and elemental composition were characterized by field emission scanning electron microscope coupled with energy dispersive X-ray (FESEM-EDX, FEI; NOVA NANOSEM-230, Brno-Černovice, Czech Republic), respectively. The functional groups were determined with Fourier-transformed infrared spectroscopy analysis (FTIR, Thermo Fisher-Nicolet iS5, Waltham, MA, USA) with a scanning range of 400–4000 cm^{-1} . Basicity and acidity of catalyst sample were determined by Carbon dioxide/Ammonia-Temperature Programmed analysis (Micromeritics Chemisorb 2750 Pulse Chemisorption System, Waltham, MA, USA).

3.4. Transesterification Reaction

Biodiesel derived from WCO was synthesized in a batch reactor of a two-neck round-bottom flask, Liebig condenser, thermocouple, and hot plate with continuous stirring of a magnetic stirrer. The reaction mixture of WCO (10 g), methanol, and RAC- K_2O -NiO/HAC- K_2O -NiO/MAC- K_2O -NiO catalyst was carried out at 65 °C for 2 h. Reactions were conducted using different parameters: catalyst loading of 1–5 wt.%, reaction times of 1–5 h, methanol: WCO molar ratio of 9:1–21:1, and temperatures of 55–95 °C. The biodiesel layer was separated from the catalyst and glycerol by external magnetic force and centrifugation, respectively. Then, hot distilled water was used for the biodiesel purification step for the elimination of unreacted fatty acids. Water residue was removed using ammonium sulfate followed by filtration. The yield was determined by gas chromatography (GC).

3.5. Biodiesel Analysis

European standard method EN14103 was utilized to measure the yield of synthesized biodiesel by using gas chromatography coupled with flamed ionization detector (GC-FID, Agilent 7890A, Petaling Jaya, Malaysia). The GC-FID was equipped with a high polar capillary column (BPX-70; 60 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness) with an oven temperature program of 100–250 °C at a ramp rate of 10 °C min^{-1} , with hydrogen as the carrier gas. Initially, the biodiesel sample was diluted by a dilution factor of 75 with internal standard, 500 ppm methyl heptadecanoate. Then, diluted sample of 1 μL was injected into the GC for qualification and quantification of FAME yield through the calculation of the following formula, as a modified EN 14103 method [62]:

$$Yield (\%) = \frac{\text{Sum of ester peaks area} - \text{area of IS}}{\text{Area of IS}} \times \frac{\text{Concentration of IS} \times \text{Volume of IS}}{\text{Total weight of biodiesel}} \times 100 \quad (5)$$

where IS = internal standard.

In addition, six methyl ester components including internal standard (methyl heptadecanoate) were identified by EN 14103 method of GC-FID, as shown in Table 5, which was used for calculating the biodiesel yield.

Table 5. Methyl ester components of WCO biodiesel.

Fatty Acid Methyl Ester (FAME)	Chemical Formula	Molecular Weight
Methyl myristate	C _{14:0}	242.39
Methyl palmitate	C _{16:0}	270.45
Methyl heptadecanoate (IS)	C _{17:0}	284.48
Methyl stearate	C _{18:0}	298.51
Methyl oleate	C _{18:1} n9c	296.49
Methyl linoleate	C _{18:2} n6c	294.84

3.6. Catalytic Reusability Analysis

The catalyst reusability test and deactivation analysis were performed under optimized transesterification parameters (3 wt.% catalyst loading, 15:1 methanol oil molar ratio, and 65 °C for 3 h of reaction) without catalyst reactivation at 800 °C. The recovered spent catalyst was washed with n-hexane, followed by methanol–acetone mixture, respectively, to ensure no unreacted triglycerides, glycerol, and methyl esters adsorbed on the catalyst's surface. The spent catalyst was oven-dried for overnight for the next transesterification cycle. The reusability test was stopped when the biodiesel yields significantly dropped to 15–20% from the previous cycle's yield. After the 7th reaction cycle, the spent catalyst sample was collected and characterized for catalyst deactivation study.

4. Conclusions

In conclusion, plastic waste activated carbon was utilized as catalyst precursor for the synthesizing bifunctional catalyst loaded with K₂O and NiO nanoparticles. The preparation of catalyst by impregnation method was achieved with different heat treatment approaches, such as reflux, hydrothermal, and microwave solvothermal technique, and subsequently carbonized at 800 °C for activation. The physical and chemical properties of the synthesized catalyst samples were characterized, and the result demonstrated that microwave-prepared sample (MAC-K₂O-NiO) exhibited the highest basicity–acidity strength of 2.58 mmol/g and 1.79 mmol/g, which greatly influenced the transesterification. The deposition of K₂O and NiO on the carbon surface was evaluated by FTIR, at which the spectra appeared at 694 cm^{−1} and 618 cm^{−1}, respectively. The detail structure and phases of sample was determined using XRD, and crystal growth was estimated using Debye Scherrer method. The catalyst screening tests were carried out to select the effective catalyst for transesterification of waste cooking oil and methanol. The MAC-K₂O-NiO was selected for biodiesel optimization, which generated highest yield of 97.2% under reaction parameters of 3 wt.% catalyst loading, 18:1 methanol–oil molar ratio, 3 h reaction time, and 65 °C. Moreover, the reusability of MAC-K₂O-NiO nanocatalyst has been evaluated up to seven cycles, with 64.3% yield. Thus, the effective catalyst was synthesized for the esterification of waste cooking oil that can meet the international properties standard.

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