



Co-transesterification of waste cooking oil, algal oil and dimethyl carbonate over sustainable nanoparticle catalysts

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ABSTRACT

Key challenges for the application of biodiesel include their high acid value, high viscosity, and low ester content. It is essential to develop later-generation biodiesel from unexploited non-food resources for a more sustainable future. Reuse of biowaste is critically important to address these issues of food safety and sustainability. Thus, the co-transesterification of waste cooking oil (WCO), algal oil (AO) and dimethyl carbonate (DMC) for the synthesis of fatty acid methyl esters (FAMES) was investigated over a series of nanoparticle catalysts containing calcium, magnesium, potassium or nickel under mild reaction conditions. Nanoparticle catalyst samples were prepared from biowaste sources of chicken manure (CM), water hyacinth (WH) and algal bloom (AB), and characterized using XRD, Raman and FESEM techniques for the heterogeneous production of biodiesel. The catalyst was initially prepared by calcination at 850 °C for 4 h in a major presence of $\text{Ca}_x\text{Mg}_y\text{CO}_3$, KCl and K_2CO_3 . The WCO and AO co-conversion of 98% and FAMES co-selectivity of 95% were obtained over CM nanoparticle catalyst under the reaction conditions of 80 °C, 20 mins and DMC to oil molar ratio of 6:1 with 3% catalyst loading and 3% methanol addition. Under the optimum condition, the density, viscosity, and cetane number of the biodiesel were in the range of diesel standards. Nanoparticle catalysts have been proven as a promising sustainable material in the catalytic transesterification of WCO and AO with the major presence of calcium, magnesium and potassium. This study highlights a sustainable approach via biowaste utilization for the enhancement of biodiesel quality with high ester content, low acid value, high cetane number, and low viscosity.

1. Introduction

Food safety is a general issue with first-generation biodiesel and COVID-19 puts further stress on our local food supply chain and thus the development of later-generation biodiesel becomes increasingly important to mitigate climate change and achieve sustainability [1,2]. The main challenges for the later-generation biodiesel production include environmental sustainability, economical feasibility and social acceptability [3]. These goals need to be achieved to substitute the unsustainable production of energy and transportation fuels in particular. Both waste cooking oil (WCO) and algal oil (AO) are non-food feedstock and have attracted attention as promising sources for next-generation biodiesel production to conquer these challenges, especially in this special period of COVID 19 outbreak [4,5].

Researchers have investigated the utilization of WCO and AO via process optimization and catalyst engagement for a sustainable

biodiesel production. Maneerung et al. [6] investigated the catalytic transesterification of WCO for biodiesel production using chicken manure as a sustainable and economical source of Ca catalyst. They found that the ash-derived Ca catalyst is of high interest in the biodiesel production and more than 90% fatty acid methyl esters (FAMES) was produced under the optimum conditions of catalyst ratio of 7.5%, 65 °C and methanol ratio of 15:1. Jung et al. [7] also reported the transesterification of WCO using chicken manure. They illustrated that organic waste like chicken manure is a promising source of CaCO_3 in catalytic transesterification of WCO and the highest FAMES yield of 95% was achieved under the conditions of catalyst ratio of 5%, 350 °C and methanol ratio of 20:1. Khounani et al. [8] investigated the biodiesel production using walnut husk methanolic extract as an efficient catalyst in the process of WCO transesterification. Malpani et al. [9] investigated biodiesel production from AO using Ca-based catalysts at a calcination temperature of 700 °C. They pointed out the optimum conditions were

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methanol to oil molar ratio of 15.68, catalyst loading of 5.12%, reaction time of 8.5 h and reaction temperature of 50 °C. The biodiesel yield reached 86.4% and its carbon numbers varied between C₁₄ and C₂₉ under the optimum parameters while satisfying biodiesel standards.

The development of economical catalysts is essential for the production of sustainable biodiesel. Thus, there is a need to develop low-cost catalysts derived from biowaste. In recent years, the biomass waste like chicken manure (CM), water hyacinth (WH) and algal bloom (AB) caused serious environmental problems. It is necessary to convert these considerable amounts of unexploited bioresources into valuable products for environmental and economic benefits. Common effective catalysts for transesterification reaction contain basic metals like Ca, Mg, K, Al and Na [9] or Al-Mg-hydrotalcites doped with other ions [4–6]. Poultry manure like CM is a promising catalyst candidate due to the high content of Ca, Mg and Zn. Besides, WH and AB have strong phytoremediation potential because they absorb and accumulate many types of pollutants from the wastewater, such as Ca, Mg, Zn, Ni, K, P and Fe. Solid residues produced from thermal process (e.g. bottom ash or fly ash) have been addressed as the heterogeneous catalyst for biodiesel synthesis [6]. It is evident that ash derived from CM, WH and AB have high feasibility as transesterification catalysts due to the potential abundant presence of Ca, Mg, Zn, Na or K [3,6]. Hence, in this study, three different sources of ash were investigated for the high-quality biodiesel production with high stability and compatibility including low acid content, low viscosity and high cetane number.

Dimethyl carbonate (DMC) has attracted attention as an economical and successful acyl acceptor in the transesterification process. Moreover, DMC can be produced in a sustainable manner through the reaction of renewable methanol with CO₂. Lee et al. [10] reported biodiesel production via catalytic transesterification of olive oil using solid waste derived from maize residue in the presence of DMC. It was found that the biodiesel yield reached 95.4% under the conditions of 380 °C and DMC ratio of 36. Additionally, the study highlighted the use of DMC as a reagent to delay the thermal cracking of FAMES. Borton et al. [11] investigated catalytic conversion of canola oil into biofuel in the presence of DMC and triazabicyclodecene catalyst and the highest conversion reached 80% at a moderate temperature of 60 °C. The results suggested that DMC and triazabicyclodecene are effective in the transformation of unrefined waste oils.

To further enhance the FAMES yield at a lower reaction temperature, production of biodiesel via nano-catalysis transesterification is a potential strategy to overcome the bottlenecks encountered in the use of conventional catalysts [12,13]. A recent study suggested that a Ni nanoparticle catalyst is of interest in the deoxygenation of stearic acid for a high-quality biodiesel with lower acidity and viscosity [14]. Importantly, there is a need to improve the transesterification process, reflected in improved properties like lower reaction temperature and shorter reaction time, increased biodegradability and FAMES yield and reduced density, viscosity and acidity for the most convenient handling, transport and storage. Hence, in this study, nanoparticle ash was investigated for a feasible biodiesel generation under a mild reaction condition.

Herein, catalytic transesterification reactions were carried out in a round bottom flask containing a mixture of DMC, WCO and AO or a mixture of WCO and AO (WAO) for the production of FAMES under mild reaction conditions. The successive parameters were studied for the improvement of the FAMES content and physiochemical properties of the biodiesel including: (1) three nanoparticle catalysts derived from CM, WH and AB, (2) a series of nano-catalyst loadings (0–5%), (3) methanol addition (0–7%), (4) catalyst pre-treatment and regeneration. The newly introduced biodiesel production approach in this study is more time- and energy-saving and greener than conventional transesterification processes. To our knowledge, there is no open literature investigating the co-transesterification of WCO and AO, and the use of sustainable nanoparticle catalysts derived from CM, WH and AB in the biodiesel production. Besides, the study on catalyst pre-treatment and

recrystallization with methanol addition is first proposed in this work. This study provides a sustainable approach of producing transportation fuels with economic feasibility, high quality and stability.

2. Materials and methods

2.1. Materials

Waste cooking oil (WCO) from palm oil was collected from the Utown Flavours refectory at the National University of Singapore. Algal oil (AO) was produced from the pyrolysis of algal bloom at 500 °C in N₂. The characteristics of the oil samples were discussed in section 3.1. Chicken manure (CM) was collected from an egg farm in Singapore. Water hyacinth (WH) and algal bloom (AB) were harvested from Lim Chu Kang Pier in Singapore.

2.2. Catalyst preparation

Catalysts derived from CM, WH and AB were initially prepared similar to a previous study [6]. The resulting solids derived from CM, WH and AB were formulated via calcination at 850 °C in air for 4 h. CM, WH and AB nanoparticles were subsequently produced as catalyst in this study and the process is described below.

The nanoparticle catalyst was prepared by sequential steps of milling, sieving, centrifugation and filtration [15]. Initially, the powder samples were ground using a miller for 15 mins. Then, the ultrafine particles were obtained by sieving via a 74 µm sieve. The undersized particles were dissolved in the distilled water and separated using a centrifuge at 5000 rpm for 3 mins. Finally, the nanoparticle catalyst in the supernatant was separated by ultrafiltration with syringe filters in size between 100 and 800 nm [16]. After drying in an oven at 105 °C overnight, the resulting nanoparticles were stored in a desiccator for use in transesterification reactions. The performance of nanoparticle catalyst on oil transesterification process was tabulated in [Supplementary Materials](#).

The methanolic process was referred to a previous study [17]. The methanol catalyst solution was transferred to a distilling flask to evaporate the solvent by a rotary vacuum evaporator at 50 °C for 30 mins. A catalyst slurry was prepared including recrystallized nanoparticles suspended in a methanol solution.

2.3. Characterization methods

For powder X-ray diffraction (XRD) experiments, the catalyst samples were placed on an XRD holder, and measurements were performed with a Bruker D8 Advance X-ray diffractometer between 5 and 80°. Raman spectra were collected using a Horiba Jobin Yvon Modular Raman spectrometer. A 660 nm laser with a 1200 mm⁻¹ grating, 1% filter and a 50x objective was used and spectra of multiple particles were measured at ambient temperature. A silicon wafer was used to calibrate the Raman shifts. Field emission scanning electron microscopy (FESEM) was performed on a JEM-6700F (JEOL) microscopy with an acceleration voltage of 5 kV in the secondary electron image mode. The elemental composition in the catalyst samples was measured using ICP-OES analysis.

Both the quantitative and qualitative analysis (MassHunter Workstation Software) of the oil samples were performed using a 5975C GC/MS (Agilent Technologies Inc) with a Triple Axis Detector and an HP-5 capillary column. Dilute oil samples were filtered through a 0.05 µm PCTE membrane filter. Sample injection volumes were 5 µL and the temperature program was set as follows: 50 °C to 300 °C (3 °C min⁻¹). FAMES and TG concentration were identified by the internal standard method and the NIST 98 mass spectrometry database. The acid value, HHVs and viscosity were determined via titration, bomb calorimetry and viscometry, respectively.

2.4. Transesterification procedure

Transesterification reactions were conducted in a 100 mL flask equipped with stirrer and thermometer placed in a water bath. The transesterification procedure was conducted in accordance with a previous study [6]. Nanoparticle catalysts were mixed together with DMC prior to transesterification. Approximately 5 g of oil sample (WCO, AO or 1:1WAO) was mixed with the acyl acceptor under the condition of DMC to oil molar ratio of 6:1, catalyst concentration of 3% and reaction temperature of 80 °C. After 20 mins, the solid product was initially separated by centrifugation and syringe filter and the excess DMC was evaporated from the biodiesel product. The by-product of glycerol could be easily removed and recovered from the biodiesel product by settling and funnelling method. The effect of various catalysts loading (0, 1, 3 and 5%) and a series of methanol addition (1, 3, 5 and 7%) were investigated on the TG conversion and FAMES content. All the experiments were carried out in triplicates. A summary on different reaction conditions in oil transesterification process was tabulated in [Supplementary Materials](#).

2.5. Statistical analysis

Statistical analysis of the experimental data was conducted to guarantee the accuracy, reproducibility and comparability via OriginPro 9.1 software ($P \leq 0.05$). The Variance (ANOVA) of the parameters included FAMES yield, TG conversion, characteristics of feedstock, catalysts and biodiesel among different samples and transesterification conditions.

3. Results and discussion

3.1. Feedstock and catalyst characterization

The feedstock properties were characterized and tabulated in [Tables 1 and 2](#), respectively. It is evident that the saponification value, acid value, density, free fatty acid and HHVs were similar for both WCO and AO. However, WCO had a higher value of viscosity and cetane number than AO. The values of viscosity were 29.92 mm²/s and 5.12 mm²/s for WCO and AO, respectively. The cetane numbers were 52 for WCO and 10 for AO. Cetane number can be affected by the length of the carbon chain and the concentration of the unsaturated compounds [18]. The presence of a higher carbon chains and a lower fraction of unsaturated bonds contributes to the increase of the cetane numbers [18]. The cetane number has an optimum range of 49–55 for engines to perform the best [2].

It was found that WCO possesses a slightly higher acid value, higher viscosity and higher density compared with the conventional diesel [2]. Issues facing the utilization of AO included a marginally higher acid value, lower cetane number and lower HHVs compared with diesel oil. The fatty acid composition of WCO was different from that of AO. The total amount of saturated fatty acids were 18.98% and 45.48% for WCO and AO, respectively, while the unsaturated fatty acid content amounted to 81.02% and 54.52% for WCO and AO. WCO had a high proportion of oleic acid (C18:1) of 70.15%, while the percentage for AO was 42.15%. In contrast, AO had a high palmitic acid (C16:0) content of 42.10%,

Table 1
Feedstock properties and specifications.

Properties	Waste cooking oil	Algal oil
Saponification value (mg of KOH/g of oil)	188 ± 0.62	194 ± 0.55
Acid value (mg of KOH/g of oil)	1.88 ± 0.45	1.92 ± 0.50
Free fatty acid (FFA %)	1.10 ± 0.056	1.14 ± 0.042
Water content (%)	0.58 ± 0.050	0.80 ± 0.032
Density at 15 °C (kg/m ³)	900 ± 2.21	865 ± 1.08
Viscosity at 40 °C (mm ² /s)	29.92 ± 0.62	5.12 ± 0.24
Cetane number	52 ± 1.40	10 ± 1.55
HHVs (MJ/kg)	39.62 ± 1.06	28.45 ± 0.88

Table 2
Feedstock fatty acid composition.

Fatty acid composition (% mass)	Waste cooking oil	Algal oil
Palmitic acid (C16:0)	12.88 ± 0.33	42.10 ± 0.54
Palmitoleic acid (C16:1)	0.15 ± 0.022	0.25 ± 0.012
Stearic acid (C18:0)	6.10 ± 0.13	3.38 ± 0.20
Oleic acid (C18:1)	70.15 ± 0.58	42.15 ± 0.42
Linoleic acid (C18:2)	10.72 ± 0.45	12.12 ± 0.36
Saturated fatty acids	18.98 ± 0.44	45.48 ± 0.54
Unsaturated fatty acids	81.02 ± 0.34	54.52 ± 0.56

whereas for WCO, the percentage was relatively low (12.88%). The distinct composition of oil is suitable for studying how generally applicable the three kinds of materials are for biodiesel production. Overall, the characteristics of WCO and AO are partially complementary, and there is a need for the co-transesterification of them for the implementation of feasible biodiesel.

Different from other types of bio-waste, solid residue from thermochemical conversion of CM, WH and AB is a major concern for direct use in agriculture or environmental remediation due to the high concentration of heavy metals. However, they are suitable sources for catalyst formulation for the biodiesel production process. The elemental composition and physiochemical properties of the ash-derived catalysts from CM, WH and AB are presented in [Table 3](#) and [Table 4](#), respectively.

Both CM nano-catalyst and AB nano-catalyst presented the highest Ca content of 44.03% and 30.64% based on individual elemental composition, respectively while WH nano-catalyst had a relative low Ca content of 10.91% but the highest K content of 39.62% among the three catalysts. It is evident that ashes derived from CM, WH and AB have high potential in biodiesel production due to the high content of Ca, K and Mg [6]. The physiochemical characteristics of density, diameter range and porosity were similar for the three ash-derived products. However, CM nano-catalyst showed a lower pH and a higher surface area, pore volume and pore size than WH and AB. These differences may partly affect the activity performance of the nano-catalyst.

Based on the feedstock characterization, the performance evaluation of co-transesterification were investigated from three aspects: (1) the physiochemical characteristics of WCO shows a lack of saturated acids and AO can amend this limitation, (2) the presence of AO can contribute to reducing heterogeneous reactions and benefiting the process and conversion optimization, (3) the presence of AO can contribute to lowering viscosity and increasing cetane numbers.

The prepared nanoparticle catalysts were further characterized via XRD, Raman, particle size distribution and FESEM images and the results were demonstrated in [Fig. 1\(a\)–\(d\)](#), respectively. The XRD spectra were consistent with the presence of various metal oxides and carbonates in different compositions and oxidation states. It appeared that the main mineral composition in CM and AB was Ca_xMg_yCO₃. Besides, small amounts of KCl appeared to be present in AB. However, compared to CM and AB, there were large peaks at 28.25 and 40.50 (2θ) in the XRD spectrum for the WH sample due to the presence of KCl. Besides, there was a small amount of K₂CO₃ examined from the Raman spectra at 1082

Table 3
Elemental composition of nano-catalysts derived from CM, WH and AB.

Elemental analysis ^a /wt% (dry basis)	CM nano-catalyst	WH nano-catalyst	AB nano-catalyst
Ca	44.03 ± 0.17	10.91 ± 0.07	30.64 ± 0.01
K	3.13 ± 0.18	39.62 ± 0.17	8.45 ± 0.19
Mg	7.46 ± 0.12	1.31 ± 0.05	10.43 ± 0.16
Na	1.65 ± 0.06	1.32 ± 0.11	1.50 ± 0.20
P	3.52 ± 0.18	0.75 ± 0.23	1.25 ± 0.21
Cl	–	5.54 ± 0.20	3.54 ± 0.22
Fe	0.42 ± 0.02	2.09 ± 0.22	2.46 ± 0.14
Al	0.26 ± 0.14	1.08 ± 0.15	0.38 ± 0.19

Note: ^aLess than 0.20% not available or detected; –, not available or detected.

Table 4
Physiochemical properties of nano-catalysts derived from CM, WH and AB.

Properties	CM nano-catalyst	WH nano-catalyst	AB nano-catalyst
pH	7.94 ± 0.09	9.77 ± 0.08	9.75 ± 0.07
Diameter range (nm)	100–800	100–800	100–800
Surface area (m ² /g)	28.44 ± 0.11	22.30 ± 0.13	19.12 ± 0.17
Pore volume (cm ³ /g)	0.14 ± 0.014	0.068 ± 0.018	0.077 ± 0.017
Pore size (Å)	21.225 ± 0.16	17.132 ± 0.14	20.756 ± 0.15
Density (g/cm ³)	1.35 ± 0.08	1.46 ± 0.05	1.37 ± 0.06

cm⁻¹ for WH-derived catalyst. The XRD spectra for the CM and AB catalysts were similar to the catalyst derived from waste Date pits biomass [19].

These data indicated the existence and participation of Ca, Mg, K and the corresponding oxides and carbonates in catalytic transesterification process with nano-catalysts derived from CM, WH and AB. It can be seen that the particle distribution for the three catalysts varied between 100 and 800 nm from Fig. 1 (b). There was no significant difference as for the global curve fluctuation. In general, the three products illustrated a similar tendency in particle distribution while the particle distribution for WH was in difference at 300 nm with a higher percentage of 12% and at 200 nm with a lower percentage of 1%. All the catalysts showed the highest particle percentage at 700 nm with the numbers of 23%, 25% and 25% for CM, WH and AB, respectively.

The nanostructure analysis of catalysts derived from CM, WH and AB shows that the nano-catalysts derived from CM and AB were abundant in Ca_xMg_yCO₃, which contributed to catalyze the transesterification reaction. The calcite was mainly distributed on the surface of the CM catalyst while a bit inside of the AB catalyst. The shapes of the nanoparticles resembled snowflakes, polyhedra and balls for CM, WH and AB, respectively. The different shapes were partially related to the surface area in the order of CM > WH > AB as presented in Table 4.

Overall, the results suggested that nanoparticles derived from CM, WH and AB have high potential in catalytic transesterification process due to the abundant presence of Ca_xMg_yCO₃, KCl, as well as certain

amounts of K₂CO₃, Na, Fe, Al and other metal components, and the feasible physiochemical properties [20].

3.2. Effect of catalysts on transesterification process

Ash has been proved as a promising sustainable material for the heterogeneous production of biodiesel and other high-value chemicals [6]. Hence, in this section, three different sources of ash were investigated for the high-output and high-quality biodiesel production. The ash-derived nanoparticles are particularly rich in Ca_xMg_yCO₃, KCl or K₂CO₃ as prepared from different renewable biowastes of CM, WH and AB.

The effect of CM, WH and AB nano-catalysts on the transesterification process for WCO, AO and WAO (1:1v WCO and AO) are presented in Fig. 2. Overall, the mixture oil of WAO presented an advantage in both TG conversion and FAMES yield with the involvement of all the three catalysts. Among the catalysts, CM nano-catalyst demonstrated the highest performance for the TG conversion and FAMES production. The highest values of TG conversion and FAMES production reached 98% and 94%, respectively, as for the co-transesterification process of WAO. This represents an enhancement of TG conversion of 4 and 6% for WAO compared to WCO and AO while the increase in FAMES content was around 3% compared to both individual WCO and AO.

As for the co-transesterification process of WAO using AB nano-catalyst, the growth in FAMES content was 6% higher compared to WCO. The catalytic performance could be related to the presence of high concentration of Ca_xMg_yCO₃. As for the co-transesterification process of WAO using WH nano-catalyst, the growth in FAMES content was 10% higher compared to WCO. The WH-derived material, containing mostly KCl based on Fig. 1 (a), was also active in TG conversion and FAMES production but not as good as the other two catalysts. Moreover, the higher activity of CM nano-catalyst may have a positive relation with higher Ca concentration and larger surface area compared with WH and AB nano-catalyst based on Tables 3 and 4.

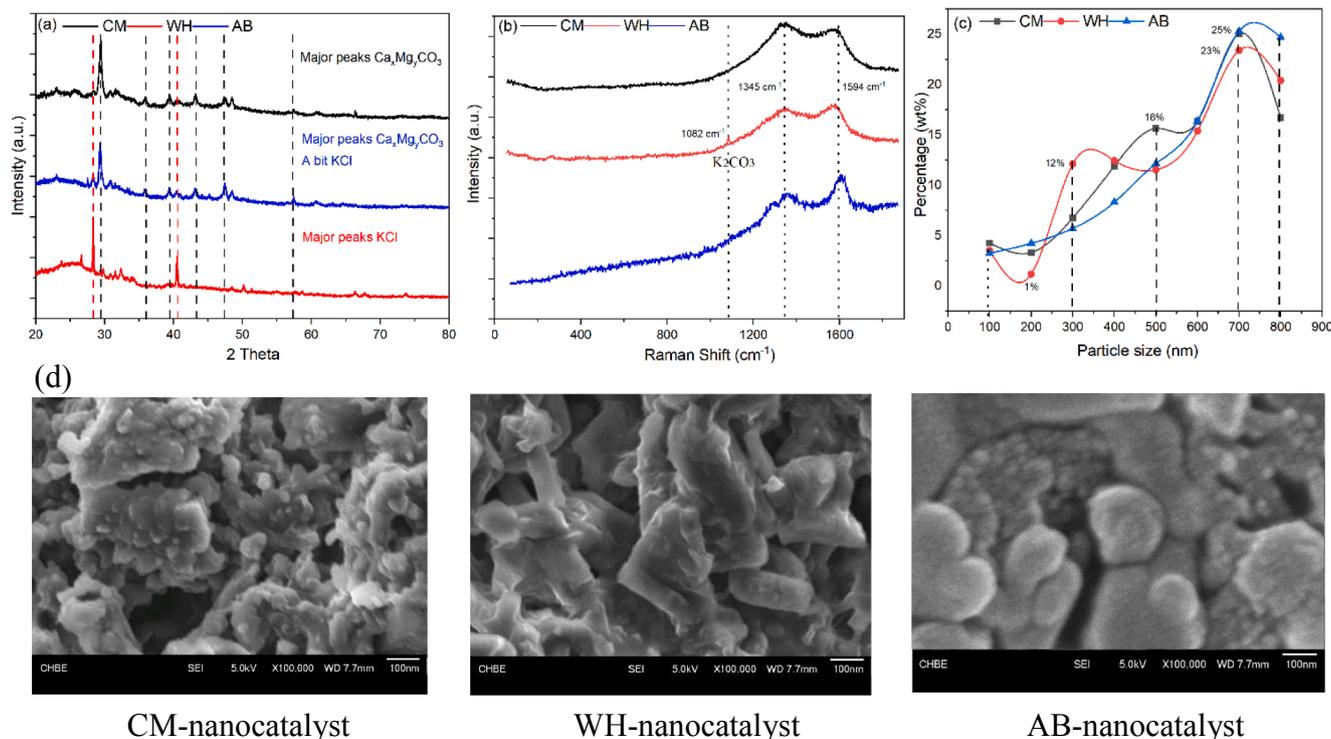


Fig. 1. Characterization of nano-catalysts derived from chicken manure (CM), water hyacinth (WH) and algal bloom (AB). (a) XRD spectra, (b) Raman spectra, (c) Particle size distribution (Particle size with occurrences < 1% not available or plotted) and (d) FESEM images.

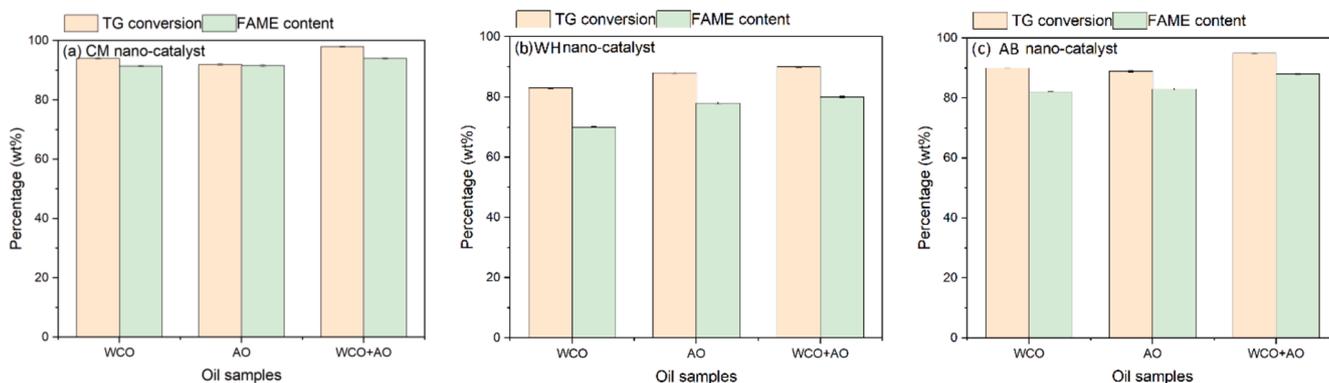


Fig. 2. Effect of nanoparticle catalysts on the transesterification process of WCO, AO and WCO + AO (a) CM, (b) WH and (c) AB with 3% catalyst loading at 80 °C for 20 mins.

Besides, it has been reported that the reaction mechanisms of Ca were related to the distribution of Lewis base on the surface of the catalysts which could react with acyl acceptor to produce calcium alkoxide subsequently producing glycerol and FAMES in the presence of TG [21]. Moreover, the reaction rate was affected by the concentration of TGs in the bio-oil transesterification process which followed a zero or first order kinetic model. The higher performance for co-transesterification may be due to the change in internal pressure, molecular interaction, bond affinity, and surface collision [22,23]. The higher TG conversion and FAMES content can be attributed to certain synergistic effects during the co-transesterification of WCO and AO.

Moreover, according to the elemental composition of the catalyst in this study, the concentration of Ca in CM was three times higher than the value for WH. However, the catalytic activity of the WH nano-catalyst was not proportional to the Ca concentration, indicating the amount of Ca was not the only participator for catalytic activity in this study.

To summarize, co-processing of WCO and AO demonstrates an advantage in biodiesel production and the CM nano-catalyst illustrates the best performance for the transesterification process. The TG conversion and FAME content using CM nano-catalyst were summarized in [Supplementary Materials](#) for the co-transesterification of WAO. This study provides a feasible approach for sustainable biodiesel production in

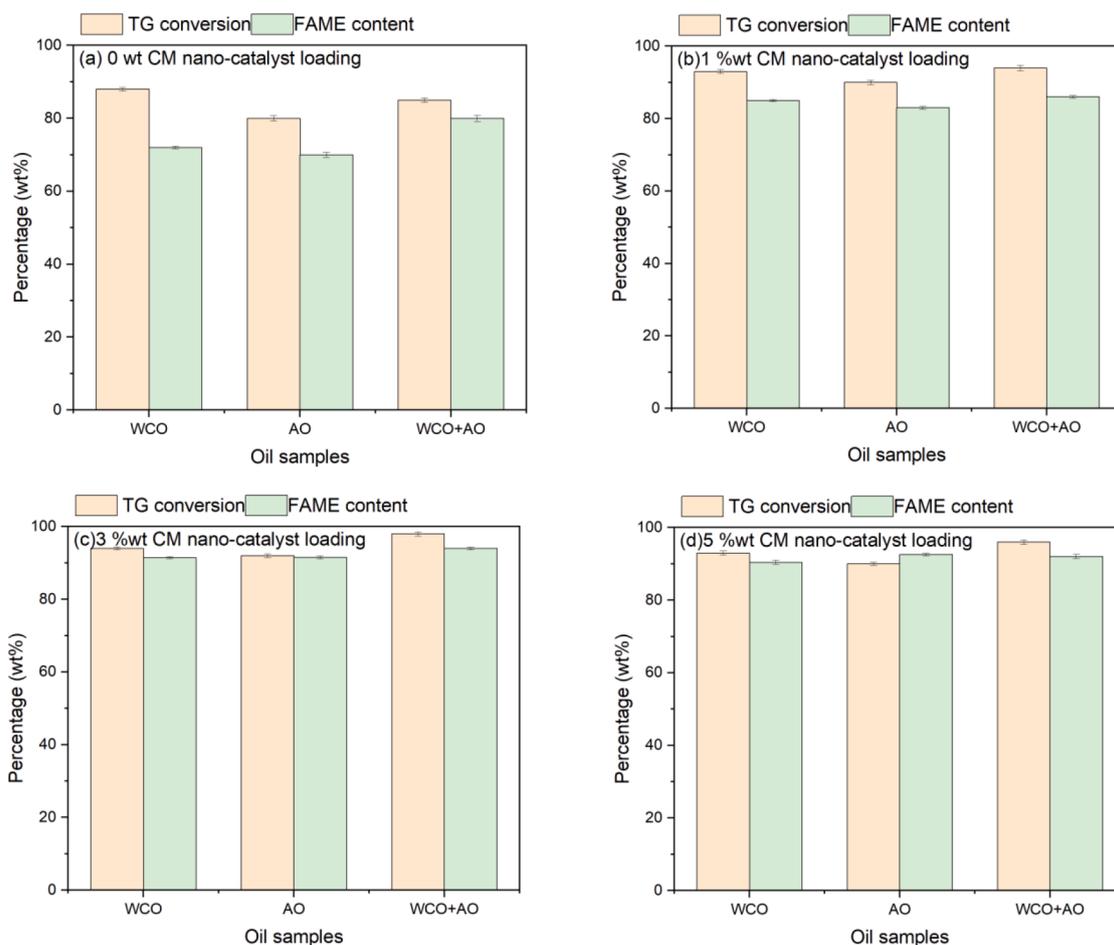


Fig. 3. Effect of CM nano-catalyst loadings on transesterification process of WCO, AO and WCO + AO (a) non-catalysis, (b) 1%, (c) 3% and (d) 5% loading at 80 °C for 20 mins.

coordination with biowaste management and development.

3.3. Effect of CM nano-catalyst loadings on transesterification process

The effects of CM nano-catalyst loadings on the transesterification process for WCO, AO and WAO are presented in Fig. 3. The results show that a 3% catalyst loading presented the best performance for co-transesterification of WCO and AO. The values were 98% and 94% for TG conversion and FAMES content, respectively. There was no significant variation with a higher catalyst loading. There were 13% improvement and 18% growth with the increase of the catalyst loading from 0% to 3% for the co-transesterification process. There was also obvious enhancement for individual AO corresponding to 12% and 22% for TG conversion and FAMES content. The TG conversion and FAMES content increased to 94% and 91% from 88% and 72%, respectively, with the increase of the catalyst amount from 0 to 3% as for the WCO. This suggests that the concentration of the active sites on the catalyst surface with 3% loading should be sufficient to maintain a maximum biodiesel production for all three oil samples. However, the FAMES content decreased with excess catalyst loading and the reasons may be due to mass transfer issues, product desorption limitations and interfering interactions between active sites and reactant [24]. Besides, there may be a chance that the base catalyst further converts the FAME product into other side products when the catalyst loading is too high. Thus, an optimum CM-catalyst loading plays an important role in the maximum biodiesel production.

In this section, the optimum biodiesel yield was achieved at the 3% catalyst loading, reaction temperature of 80 °C for 20 mins. It was found

that a lower catalyst loading of 3% could lead to a higher biodiesel yield compared to previous similar studies on the effect of catalyst loading on the biodiesel yield [19,25]. Besides, the reaction temperature and time were both relatively low in comparison to previous research on transesterification of waste oil for clean fuel production [24]. These results suggested that the catalyst in this study is more economically feasible and the transesterification process is energy- and resource-saving.

3.4. Effect of methanol on the transesterification process

Methanol is generally used as a traditional reactant for biodiesel production. The effects of slight methanol addition on transesterification process for WCO, AO or WAO are investigated in this section and the results are presented in Fig. 4. The results show that 3% methanol loading performed the best with 2% and 1% higher of FAMES yield compared to non-methanol loading for WCO and WAO, respectively. The highest TG conversion and FAMES content were 98% and 95%, respectively with 3% methanol loading. A high concentration of methanol loading had no positive effect on the TG conversion and FAMES yield, which may be due to the over dilution of the reaction system [17]. The results suggest that methanol addition contributed to a higher FAMES content, but the methanol addition had no significant effect on the TG conversion. As for the AO, there was a 2% increase of TG conversion and 1% increase of FAMES content with 1% methanol loading, however, there was no significant influence on the TG conversion and FAMES content with the methanol loadings of 3, 5 and 7%.

The formation of FAMES can be driven by the existence of methoxide ions from intermediate products like fatty acid glycerol carbonate [17].

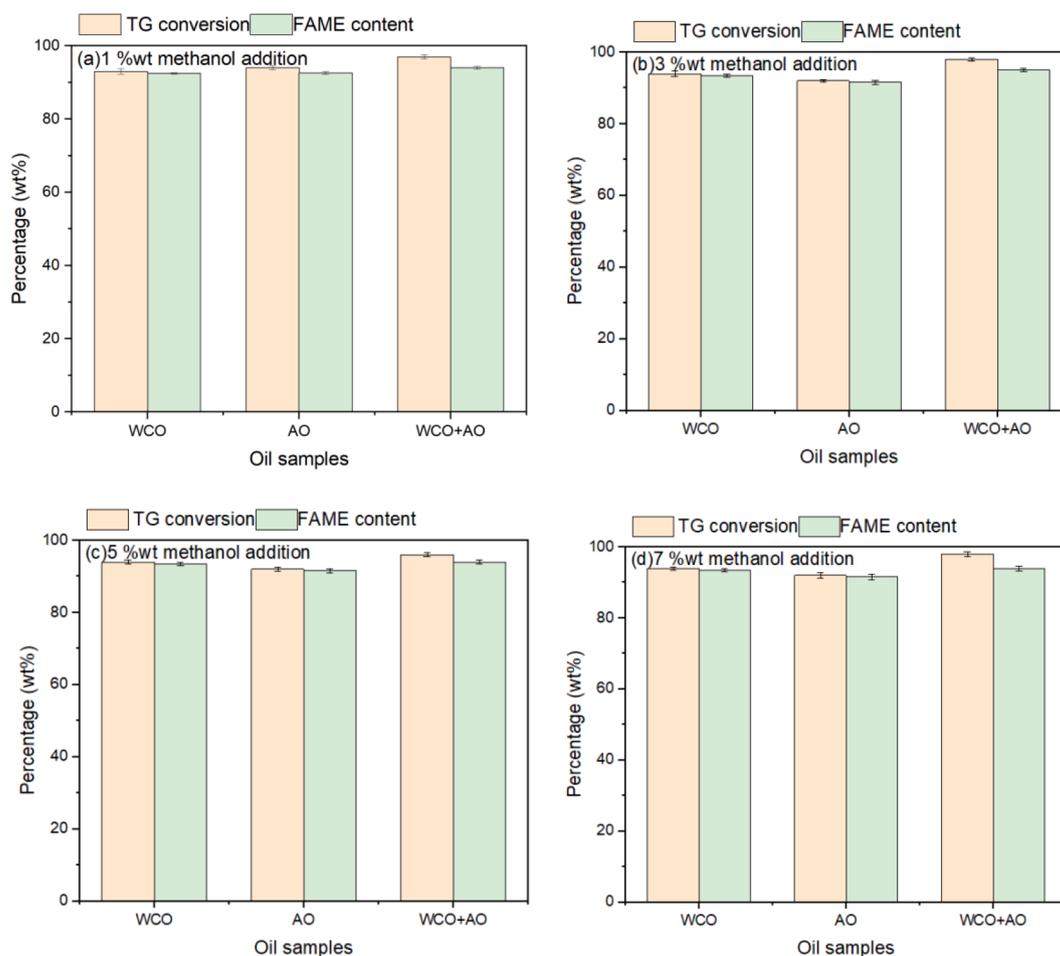


Fig. 4. Effect of methanol on transesterification of WCO, AO and WCO + AO. (a) 1%, (b) 3%, (c) 5% and (d) 7% addition at the temperature of 80 °C for 20 mins with 3% CM nano-catalyst loading.

However, a high affinity between oil samples and DMC may not be easily affected by the loading of the methanol. The results suggest that DMC can be more attractive than methanol in the oil transesterification process. Besides, DMC is more preferred in biodiesel synthesis for being non-toxic, abundant, and environmentally friendly for a cleaner production. In general, methanol loading caused a slightly higher FAMES content but had no significant effect on the TG conversion for all the oil samples.

Overall, in this section under the optimal reaction conditions of 80 °C, 20 mins and DMC to oil molar ratio of 6:1 with 3% CM nanoparticle catalyst and 3% addition of methanol, the TG conversion reached 98%, 94% and 92% for WAO, WCO and AO, respectively. Besides, the FAMES content of 95%, 93% and 92% were obtained for WAO, WCO and AO, respectively.

3.5. Effect of catalyst preparation with methanol pre-treatment

The effects of catalyst preparation with methanol pre-treatment on transesterification process for WCO, AO and WAO are presented in Fig. 5. It is evident that the FAMES yield increased with 2%, 1% and 1% for WCO, AO and WAO, respectively, compared with Fig. 3 (c) without methanol pre-treatment. However, the newly introduced method had no significant effect on TG conversion. In general, methanol pre-treatment had a positive effect on the transesterification performance. Thus, the nano-catalyst could be recycled and reused via methanol reprocessing (Fig. 6).

3.6. Investigation on catalyst deactivation and regeneration

The reusability of spent catalyst was investigated to identify the deactivation problem. The spent CM-derived catalyst was retreated with methanol and reused for the next cycle as presented in Fig. 6. The results show that the catalyst remained highly active after three cycles. The activity performance reduced in the fourth recycle, the TG conversion and FAMES yield decreased to 88% and 82% for the co-transesterification process from 98% and 94%. It was found that the basicity of nanoparticle catalysts was obviously changed after the fourth cycle and the catalytic performances were highly dependent on the content and strength of basic sites on the catalyst surface. The reduction of catalytic activity in the subsequent transesterification cycles may be

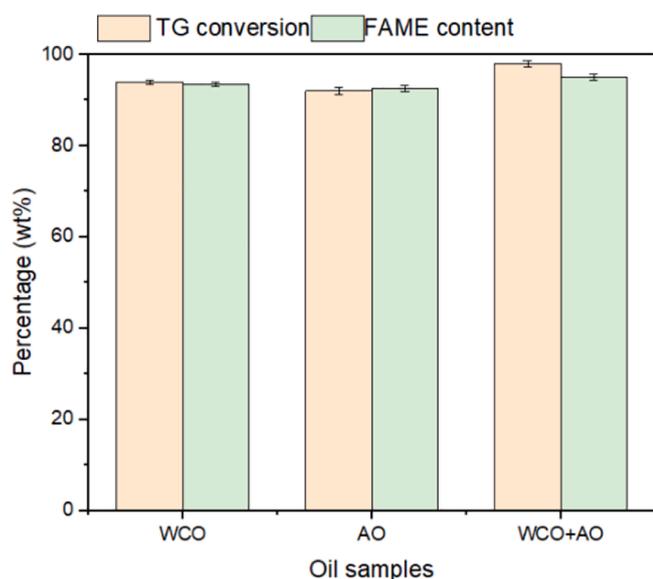


Fig. 5. Effect of catalyst preparation with methanol pre-treatment on transesterification of WCO, AO and WCO + AO at the temperature of 80 °C for 20 mins with 3% CM nano-catalyst loading.

because of the saponification reactions with fatty acids and partial transformation of the CaO to CaCO₃ or hydrated state like Ca(OH)₂, which resulted in a reduced reactivity of the spent catalysts [6]. In short, the nano-catalyst has a potential to be reused for at least three times with methanol pre-treatment.

Large-scale development of nanoparticle catalysts is increasing considerably in contemporary [26]. The utilization of nano-catalyst derived from CM can both reduce environmental impacts and recycling costs. It was found that the recovery of biodegradable catalyst is more advantageous than the reuse of traditional catalysts [17]. This strategy requires the risk assessment of contaminants and the deployment of purification and separation processes for recovered Ca catalyst. It is important for the recycling industry to exploit adaptable recycling infrastructure in line with green catalytic technology [27].

3.7. Fuel properties via catalytic transesterification process

The biodiesel derived from various feedstocks under optimum conditions was characterized by physiochemical properties including density, viscosity, acid value and cetane number et al. in this section (Table 5).

It is evident that the acid value for the three kinds of biodiesel was similar and highly decreased compared to the feedstock. The density, viscosity and cetane number of the biodiesel produced from WAO and AO were in the range of diesel standards. Besides, the HHVs of the co-transesterification biodiesel was similar with diesel. Furthermore, the co-transesterification process led to a higher ester content of 94.52% compared with previous studies on biodiesel production from WCO and AO [6,9]. The biodiesel produced from WCO showed a slightly higher level of density, viscosity and cetane number compared to the diesel level. However, the WCO biodiesel showed the highest HHVs of 41.08 MJ/kg among the investigated oils in this study.

The acid value in the raw feedstocks was highly reduced through the nanoparticle catalytic transesterification process. However, the acid value was slightly higher than the diesel fuel. In this study, the biodiesel produced from WH nano-catalyst showed a lower acid value compared to the number from CM nano-catalyst due to the presence of K₂CO₃, indicating a multi-catalyst system is favourable for high-quality biodiesel production with low acid value and high ester content. Furthermore, AO is beneficial for enhancing the properties of biodiesel and comparable with those of edible oils and WCO [30]. Moreover, AO is a renewable non-food source for cleaner-burning fuels and carbon sequestration. The presence of AO reduced the immiscibility and reaction reversibility, and guaranteed the production of high purity biodiesel. The presence of WCO contributed the highest biodiesel yield and HHVs. Overall, there is a considerable benefit using AO blended with WCO as fuel for diesel engines based on the improvement in cetane number, density and viscosity.

4. Conclusions

This study highlighted biodiesel production over nanoparticle catalysts prepared from biowaste of CM, WH and AB. Co-transesterification of WCO and AO was investigated to achieve the sustainable waste management in green chemistry. AO is a promising sustainable source from AB pyrolysis to supply sufficient saturated acids and homogeneous reactions in co-transesterification with WCO. The improvement in TG conversion, FAMES content and physiochemical properties reflected that the transesterification efficiency was enhanced during the co-processing of WCO and AO. The following parameters were investigated and optimized under the conditions of DMC to oil molar ratio of 6:1, 80 °C and 20 mins: (1) nanoparticle catalysts derived from CM, WH and AB, (2) catalyst loadings, (3) methanol addition and (4) catalyst pre-treatment and reusability. It was found that the highest TG conversion of 98% and FAMES content of 95% achieved over CM nanoparticle catalyst with 3% catalyst loading and 3% methanol addition. The amount of catalyst

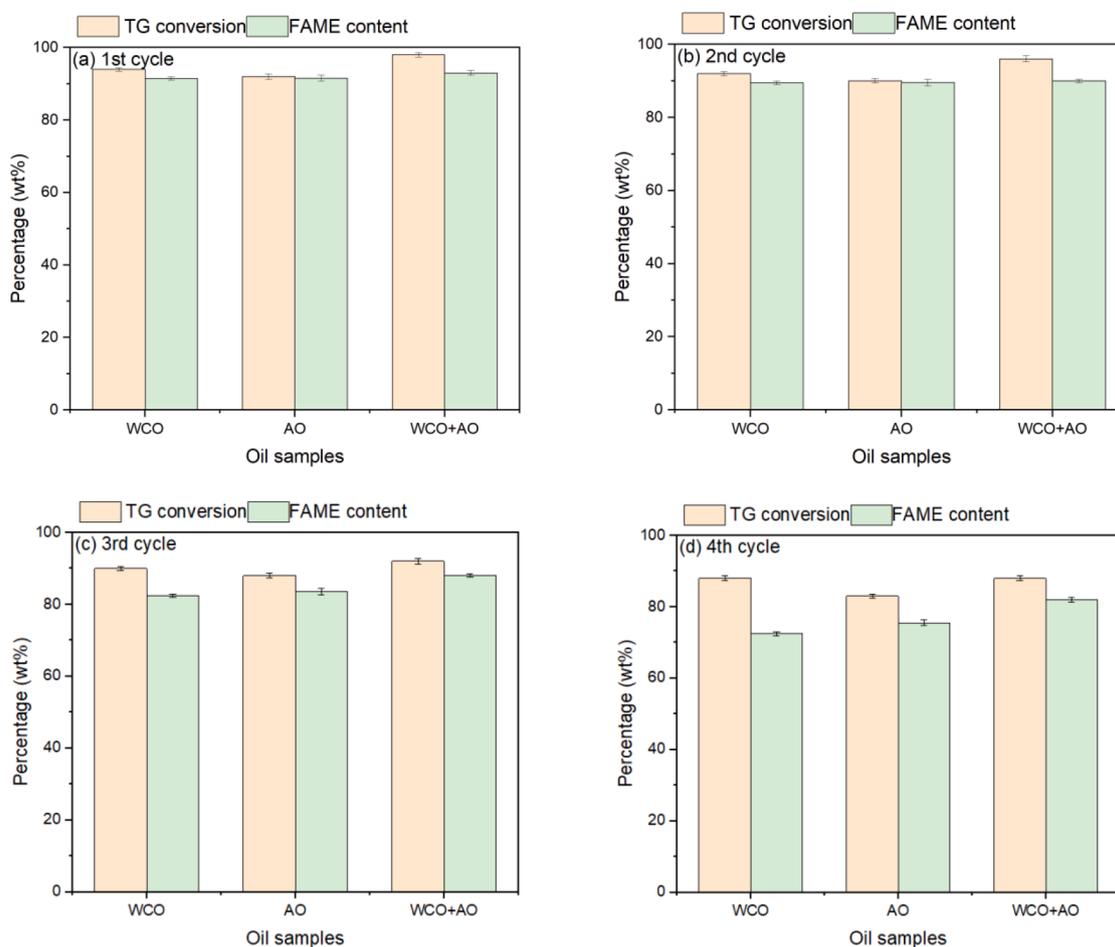


Fig. 6. Reusability of catalyst at DMC-to-oil molar ratio of 6:1, CM catalyst loading of 3% and reaction temperature of 80 °C for 20 mins.

Table 5

Biodiesel properties and specifications under optimum conditions.

Properties	Biodiesel_WCO	Biodiesel_AO	Biodiesel_WCO + AO	Diesel [28,29]
Acid value (mg of KOH/g of oil)	0.56 ± 0.02	0.50 ± 0.03	0.52 ± 0.02	0.2–0.3
Density at 15 °C (kg/m ³)	885 ± 1.45	843 ± 2.22	852 ± 1.38	820–860
Viscosity at 40 °C (mm ² /s)	4.32 ± 0.11	3.01 ± 0.52	3.45 ± 0.22	2.5–3.5
Cetane number	56.66 ± 1.12	53.16 ± 1.41	50.15 ± 1.32	49–55
HHVs (MJ/kg)	41.08 ± 0.33	39.66 ± 0.52	40.45 ± 0.48	42.7
Ester content (wt%)	92.46 ± 0.41	91.02 ± 0.34	94.52 ± 0.46	–

loading, reaction temperature and reaction time in this study were relatively low in the presence of the nanoparticle catalyst compared to conventional methods. Besides, the nano-catalyst could be reused for three times with an optimal 3% catalyst loading. In conclusion, the catalytic co-transesterification of WCO, AO and DMC is a promising strategy to achieve sustainable waste management and moderate nature climate change. This study provides an environmentally friendly and cost-effective approach for cleaner biodiesel production via biowaste conversion and utilization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2020.127036>.

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