RESEARCH ARTICLE

Hewei YU, Jinke WU, Wei WEI, Xingyu ZHANG, Changzai REN, Yaoqi DONG, Shen CHENG Synthesis of magnetic carbonaceous acid derived from waste garlic peel for biodiesel production via esterification

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Abstract Waste biomass-supported magnetic solid acids have particular advantages in catalyst separation. First, a novel magnetic carbonaceous catalyst was synthesized from waste garlic peel (GP) via in situ impregnation before conducting carbonization at 450-600°C and sulfonation at 105°C. The physical and chemical properties of the synthesized catalysts were characterized. It was found that the magnetism of the catalyst increased with the carbonization temperature. The optimized catalyst, carbonized at 600°C (C600-S), possessed an excellent magnetization value of 12.5 emu/g, with a specific surface area of 175.1 m²/g, a pore volume of 0.16 cm³/g, and an acidic property of 0.74 mmol/g -SO₃H density. By optimizing the esterification conditions to produce biodiesel, an oleic acid conversion of 94.5% was achieved at w(catalyst dosage) = 10% (w is mass fraction), a molar ratio of n(methanol): n(oleic acid) = 10: 1 (n is the amount of substance), and a reaction for 4 h at 90°C. Further, for catalyst regeneration. it was found that sulfuric acid treatment was more effective for improving the esterification activity than solvent washing, with which a conversion of more than 76% was achieved after the third run.

Keywords garlic peel (GP), magnetic carbonaceous acid, esterification, biodiesel

1 Introduction

It is critical to search for alternative energy due to the gradual depletion of fossil fuels and the aggravation of environmental issues [1]. Renewable bio-based oils exhibit enormous potential for energy use in the near

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future due to their sustainability and environmental friendliness. Biodiesel is a source of reliable green energy, possessing outstanding advantages of being sulfur-free, nontoxicity, renewability, and biodegradability. It has similar characteristics to the conventional petrodiesel fuel and can be used directly without engine modification. Chemically, biodiesel is a series of longacid methyl esters chain fatty derived from transesterification of triglycerides and esterification of free fatty acids (FFAs) with alkaline or acidic catalysts [2]. It can be produced from a wide range of feedstocks, such as peanut oil, rapeseed oil, animal fats, even waste cooking oil (WCO). However, the biodiesel derived from edible oils is expensive due to the imbalance of food supply to meet the market demand [3]. In this regard, using WCO to replace edible oil (as biodiesel feedstocks oil) can effectively reduce production costs while improving food security and environmental protection. Nevertheless, the high content of FFAs and water in WCO depress the efficiency of the basic catalyst due to saponification during transesterification because basiccatalyzed transesterification requires that the acid value of feedstocks oil must be less than 1.5 mg KOH/g. Hence, an acid-catalyzed pre-esterification is generally performed before transesterification to minimize FFAs content in WCO.

Due to the requirements of the green chemical industry, more attention has been paid to the catalyst for biodiesel production. Although the esterification of FFAs with methanol catalyzed by sulfuric acid is highly efficient, its disadvantages include corrosion, tedious catalyst recycling, and large amount of waste acid water generated [4]. Thus, employing solid acid catalyst to replace liquid acid (such as sulfuric acid) is pertinent to realizing green and safe catalysis. Zeolites, sulfonated carbon materials, ion exchange resins, heteropoly acids, metal oxides, and solid superacids [5–7], are the solid acids widely studied, of which, sulfonated carbonaceous solid acid catalysts, with high acidity, easy separation, pollution-free, and simple preparation, have attracted

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more research attention. Through sulfonation reaction, such catalysts can be derived from biochar-based materials, supported by acid groups on the surface. To date, there are an enormous amount of research reports on sulfonated biomass solid acids derived from açaí berry seeds [8], sugarcane bagasse [4], de-oiled microalgae [9], undaria pinnatifida [10], and rice-straw [11].

During heterogeneous catalytic esterification/transesterification, solid catalysts are usually separated via centrifugation, filtration, and other mechanical methods from the liquid product. The process may be accompanied by high energy consumption, resulting in catalyst loss. Magnetic solid acid catalyst is an excellent composite material that significantly simplifies the catalyst separation steps and reduces the production cost because of its magnetic separation capabilities. Recently, a magnetic mesoporous solid acid catalyst (FCHC-SO₃H) was successfully prepared from renewable chitosan, achieving a biodiesel yield of 96.7% [12]. Elsewhere, Quah et al. [13] utilized palm kernel shell to synthesize a magnetic catalyst (PMB-SO₃H) which possessed comparable magnetization saturation of 8.458 emu/g and achieved an optimum biodiesel yield of 90.2%. Li et al. [14] established a magnetic catalyst through immobilizing an ionic liquid precursor onto a magnetic core that achieved a total yield of 98.9% (by mass) from WCO under moderate conditions (70°C for 9 h).

Garlic is a traditional food plant of tremendous interest due to its unique medicinal potentials. The global garlic planting area and output are increasing annually. In 2020, the planting area was 1.68 million hectares and the output was 32 million tons. Dehydrated garlic chips are one of the important international trade garlic products, with large quantities of garlic peel (GP), garlic stem, and other by-products produced. Such by-products are often discarded or burned, resulting in unnecessary wastes and environmental pollution. Considering the resource utilization of GP, some studies have reported the modification of GP dietary fiber [15], and extraction of antioxidant and cellulose microfibers [16]. Besides, GP could serve as an alternative carbonaceous precursor in innovative methods. Veerakumar et al. [17] utilized GPderived activated carbon to immobilize palladium nanoparticles to reduce toxic Cr^{6+} . Zhang et al. [18] synthesized a GP-derived porous carbon with a high specific surface area of 2818 m²/g, exhibiting an outstanding electrochemical performance and a cycling stability in supercapacitors. In the early stage, Wei et al. [19] used GP to prepare a carbon-based solid acid by the incomplete carbonization-sulfonation utilizing method, which showed a good performance in catalytic esterification. To the best of the authors' knowledge, there is barely any report on adopting GP as a precursor to synthesize magnetically sulfonated catalysts for biodiesel production.

The novelty of this study lies in the synthesis of a

magnetically sulfonated biochar catalyst derived from waste GP biomass and its application in esterification. The synthesized catalyst was characterized using X-ray diffraction spectroscopy (XRD), N₂ adsorption-desorption, Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric analysis (TGA), vibrating sampling magnetometer (VSM), and X-ray photoelectron spectroscopy (XPS). Furthermore, the catalytic performance of the synthesized catalyst was evaluated by the esterification of oleic acid with methanol.

2 Materials and methods

2.1 Materials

The GP waste biomass was collected from a garlic processing factory in Jining, Shandong Province, China. The results of proximate and ultimate analyses of the GP are listed in Table 1. Chemical reagents as supplied by (a) Sinopharm (China): w(iron chloride hexahydrate (FeCl₃·6H₂O)) \geq 99.0%, w(methanol) \geq 99.5%, and w(ethanol) \geq 99.7%; (b) Kermel (China): w(sodium chloride) \geq 99.5%, w(sodium hydroxide) \geq 96.0% and w(potassium hydroxide (KOH)) \geq 85.0%; (c) Far Eastern (China): w(concentrated sulfuric acid) = 95%–98%. All reagents used were of pure analytical grade.

2.2 Catalyst synthesis

The GP was washed with tap water to remove the impurities that cling to the surface. Then, it was dried at 105° C for 12 h, and pulverized with a crusher. The sample was sifted between 100 and 200 mesh sizes. The Fe-loaded carbonaceous precursor was synthesized using the impregnation method. In brief, 10 g of the GP powder was mixed with 150 mL of FeCl₃ aqueous solution (0.6 mol/L) in a beaker and stirred at room temperature for 2 h. Then, the mixture was dried overnight in an oven at 105°C. Subsequently, the aliquots of the Fe-loaded

Table 1 Values of proximate and ultimate analyses of GP

Analysis methed	Composition	Mass fraction/%	
Proximate analysis	Moisture (air dry basis)	8.65	
	Volatile matter (air dry basis)	71.12	
	Ash content (air dry basis)	6.06	
	Fixed carbon (air dry basis)	14.17	
Ultimate analysis	Carbon (dry basis)	38.75	
	Hydrogen (dry basis)	5.66	
	Oxygen (dry basis)	48.01	
	Nitrogen (dry basis)	0.55	
	Sulfur (dry basis)	0.40	

carbonaceous precursor were carbonized (heating rate of 5°C/min) in a tubular furnace for 1 h at 450, 500, 550, and 600°C, respectively. The magnetically solid acid catalyst was prepared by liquid-phase sulfonation, in which 5 g of the carbonized sample and 30 mL of concentrated sulfuric acid were stirred for 4 h at 105°C. After that, the mixture was repeatedly filtered and cleaned with deionized water and tested (with pH strips) until a pH of 7 was reached. Finally, the sample was placed in the oven for 12 h to dry at 105°C. The carbonaceous samples obtained were designated C(T_1)-S, where C and S represent carbonization and sulfonation, respectively, and T_1 was the carbonization temperature.

2.3 Catalyst characterization

Ultimate analysis was carried out using a Vario EL cube elemental analyzer (Germany) with precision of CHNS \leq 0.1% and $O \leq 0.2\%$. Proximate analysis was performed using a SDTGA5000 industrial analyzer (China). To evaluate the microstructure of magnetic catalysts, nitrogen adsorption-desorption analysis was performed using a fully automated ASAP 2460 Micromeritics equipment (USA). The sample was first degassed for 3 h at 150°C before nitrogen adsorption at -196°C. Further, a Rigaku D-MAX 2500 of Powder X-ray diffractometer (Japan) studied catalyst crystallinity, with a step size of 0.02° and a scanning speed of 8°/min from 10° to 80°. The surface morphology of magnetic catalysts was examined using a Tescan MIRA3 field-emission SEM (Czech Republic) with an acceleration voltage of 15 kV, an emission current of 10 μ A, and a magnification of 6000-25000X. In addition, the TEM images of the magnetic catalysts were observed using a JEM-2100F (Japan) with an accelerating voltage of 200 kV. The thermal stability was studied on a METTLER TGA2 thermogravimetric analyzer (Switzerland), at a temperature range from 25 to 800°C nitrogen atmosphere. Moreover, the saturation magnetization of the magnetic catalysts was studied using a JDAW-2000B vibrating sample magnetometer (China). A Thermo Fisher Scientific THERMO iS50/6700 spectrometer (USA) was used to examine the chemical bonds in magnetic catalysts within the spectrum range of 4000-400 cm⁻¹. Furthermore, the surface elemental information was studied by a Thermo Fisher Scientific Escalab 250Xi (USA), equipped with a monochromatized Al Ka radiation source. Finally, the total acid site density and -SO₃H density of the magnetic catalysts were measured via acid-base titration described elsewhere [20,21].

2.4 Esterification and product analysis

The esterification of oleic acid and methanol was conducted in a 50 mL miniature high-pressure reactor to determine the catalytic activity of magnetic catalysts. In each procedure, 10 g of the oleic acid with different amounts of methanol (*n*(methanol): n(oleic acid) = 4–12: and various catalyst percentages (w(catalyst 1) percentages) = 2%-12%) were mixed in the inner tank of the reactor. Then, the reaction temperature range was set at 50-100°C, and lapsed from 1 to 6 h. The esterification was vigorously agitated and homogenized by a magnetic stirring at 500 r/min. As the esterification was completed, the catalyst was recovered by an external magnet, and the excess methanol was recovered by rotary evaporation. The conversion of oleic acid was determined by KOH titration (Eq. (1)), where the acid values of the initial oleic acid and esterified sample were evaluated based on the GB (National Standard in Chinese) 5009.229-2016 standard method [22].

$$Conversion\% = \frac{\text{Initial acid value} - \text{final acid value}}{\text{Initial acid value}} \times 100.$$
(1)

In addition, all experimental data were performed in triplicates to certify the reproducibility and reliability.

3 Results and discussion

3.1 Synthesis and characterization of the carbonaceous catalysts

The wide-angle XRD patterns of the magnetic catalysts obtained at different carbonization temperatures are displayed in Fig. 1. Judging by the standard Fe₃O₄ peaks (Joint Committee on Powder Diffraction Standards (JCPDS) database file, 19-0629), six diffraction peaks at $2\theta = 30.04^{\circ}, 35.46^{\circ}, 43.42^{\circ}, 53.36^{\circ}, 56.98^{\circ}, and 62.48^{\circ}$ can be ascribed to the (220), (311), (400), (422), (511), and (440) crystallographic planes of Fe₃O₄ particles, respectively [12]. Besides, the wide peak at $2\theta = 20^{\circ}-30^{\circ}$ is typically attributed to the aromatic carbon sheets oriented randomly. Hence, the XRD diffraction peaks indicated that Fe₃O₄ particles were successfully formed and embedded into the carbonaceous GP [21], thus, confirming the magnetic property of the catalysts. Although the XRD patterns of the catalysts prepared at different carbonization temperatures were similar, the peak intensity of Fe₃O₄ particles increased gradually with temperature, while those of amorphous carbon declined gradually.

Further, VSM analysis studied the saturation magnetization of the catalysts obtained at various carbonization temperatures (Fig. 2). Here, C450-S and C500-S catalysts were weakly ferromagnetic, but the magnetization increased with the carbonization temperature. The C550-S and C600-S catalysts showed saturation magnetization values of 3.47 and 12.5 emu/g, respectively. Similar saturation magnetization (13.3 emu/g) was reported for magnetic fruit bunch-based solid acid [23]. In addition,



Fig. 1 XRD patterns of the magnetic catalysts obtained at different carbonization temperatures.



Fig. 2 Hysteresis curves of the catalysts obtained at different carbonization temperatures.

the C600-S catalyst showed the remanence magnetization and coercivity values of 1.45 emu/g and 125.94 Oe, respectively, demonstrating superparamagnetism. This result was consistent with the previous research [13], whereby magnetic palm kernel shell-based catalyst exhibited remanence magnetization and coercivity values of 1.733 emu/g and 125.47 Oe, respectively. Hence, the catalyst barely shows any magnetism without any external magnetic field. It does not cause agglomeration of the particles due to magnetic mutual attraction. Moreover, Gardy et al. [24] reported that the remanence magnetization of the magnetic catalyst was 0.65 emu/g which was sufficient to separate the catalyst from reaction media effectively. Thus, the strong magnetism of C600-S catalyst guarantees easy recovery from esterification products via external magnetic fields instead of recycling by filtration or centrifugation. Besides, the catalytic performance of the C450-S, C500-S, C550-S, and C600-S was determined to be 96.9%, 95.6%, 94.8%, and 94.5%, under the conditions of n(methanol): n(oleic acid) = 10: 1 and w(catalyst dosage) = 10% at 90°C. After comprehensive consideration of magnetism and catalytic activity, C600-S was selected as the catalyst for this study.

The microstructural parameters and acid density of the carbonaceous materials are summarized in Table 2. The raw material GP and C600 had low surface areas of 4.32 and 9.83 m²/g, with small pore volumes of 0.02 and 0.05 cm³/g, respectively. Such values could be ascribed to the release of volatile substances (such as HCl, H₂O, CO_2 , and CO_2) from the dehydration and decomposition of the carbon matrix and FeCl₃, which increased the surface area and pore volume of C600. However, the surface area and pore volume of C600-S significantly increased to 175.1 m^2/g and 0.16 cm³/g, respectively. The specific surface area of the magnetic carbonaceous carrier increased significantly after sulfonation, possibly due to the corrosion of embedded Fe₃O₄ and carbon surface by concentrated sulfuric acid. Zhang et al. [27] reported a similar result with the synthesized Jatropha hulls-based magnetic acid catalyst. Moreover, Fig. 3 showed the N_2 adsorption-desorption isotherms and pore size distribution of the C600-S catalyst. As Fig. 3(a) illustrates, the C600-S catalyst exhibited a Type-IV isotherm profile, with a notable H₄ type hysteresis loop, characteristic of mesoporous materials. Furthermore, Fig. 3(b) illustrates that the pore size distribution of C600-S was centered at 3.87 nm. Based on the relatively large surface area and mesoporosity, reactants could also access the active sites on the internal pore walls [28], significantly reducing diffusion difficulty and ensuring improved catalysis. In addition, Table 2 indicates that the total acid (including -OH, -COOH and -SO₃H groups) and -SO₃H densities of C600-S were 3.38 and 0.74 mmol/g, respectively. The

 Table 2
 Microstructural parameters and acid density of the carbonaceous materials

Sample	Surface area /(m ² ·g ⁻¹)	Pore volume /(cm ³ ·g ⁻¹)	Total acid density /(mmol·g ⁻¹)	-SO ₃ H density /(mmol·g ⁻¹)	Ref.
GP	4.32	0.02	_	_	This study
C600	9.83	0.05	-	-	This study
C600-S	175.1	0.16	3.38	0.74	This study
FCHC-SO ₃ H	41.4	0.085	1.20	-	[12]
C-SO ₃ H	1.38	0.004	3.12	0.81	[25]
MCC-SO ₃ H	35.34	0.124	3.55	1.28	[21]
MBC02-SO ₃ H	38.51	0.03	0.28	-	[26]
Pyr-S	77.76	0.1803	1.92	0.191	[10]



Fig. 3 N₂ adsorption characterization.(a) N₂ adsorption-desorption isotherms; (b) pore size distribution.

acidic property of C600-S was similar to those of other sulfonated biomass-based catalysts but with a superior surface area (Table 2).

The microstructure and morphology for the raw GP and magnetic catalyst were examined by SEM. Figure 4(a)

demonstrates that the GP surface showed irregular fibrous strips. When the fiber strip was enlarged, as shown in Fig. 4(b), it was found that the surface was very dense with almost no pore structure. After carbonization at 600°C for 1 h and sulfonation with sulfuric acid for



 EM HV: 15.0 HV
 WO: 12.88 mm
 10 μm
 MRA3 TEBCAR

 View Heids: 46.1 µm
 Date(midity): 11/21/21
 10 μm
 MRA3 TEBCAR

 (c)
 (d)

Fig. 4 SEM images.

(a) GP at a 6.00 kX magnification; (b) GP at a 25.00 kX magnification; (c) C600-S at a 6.00 kX magnification; (d) C600-S at a 25.00 kX magnification.

4 h, the surface morphology of GP changed significantly. As shown in Figs. 4(c) and 4(d), the fiber strip of the GP sample was broken. Thus, the catalyst evinced a rough and irregular shape with fine surface pores, consistent with the results of N₂-adsorption. On the other hand, the TEM images of the magnetic catalyst (Fig. 5) showed numerous irregular blocks and strips.

Figure 6 displays the TGA and derivative thermogravimetric (DTG) results of the fresh C600-S catalyst. The catalyst exhibited the weight loss within the predicted range. One peak at 25–200°C (with 1.53% weight loss) is associated with the removal of the physisorbed water and gases [29]. Another peak at 200–550°C (with 9.67% weight loss) probably arose from the desorption of polycyclic aromatic hydrocarbons bonded to sulfuric groups [30]. Then, the catalyst was further exhibited weightless at elevated temperatures, ascribed to the decomposition of the carbon matrix. However, the C600-S catalyst possessed excellent thermal stability below 200°C region (esterification synthesis temperature).

The chemical composition results of C600-S using XPS characterization are shown in Fig. 7. The survey in Fig. 7(a) demonstrated that the catalyst consisted of C, O, N. S. Cl. and Fe with a respective relative atomic of y(C) = 85.03%, y(O) = 10.07%, y(N) = 1.60%, y(S) =0.69%, y(Cl) = 0.89% and y(Fe) = 1.71% (y is atom precentage). The high-resolution XPS spectra of Fe 2p and S 2p were deconvoluted as depicted in Figs. 7(b) and 7(c), respectively. Fe 2p exhibited three deconvoluted peaks, of which two distinct peaks situated at 724.2 and 711.3 eV originated from Fe $2p_{1/2}$ and Fe $2p_{3/2}$ of Fe₃O₄ [21]. Besides, the satellite peak situated at 717.7 eV is attributed to Fe^{3+} in Fe $2p_{3/2}$ [31]. As for the deconvoluted S 2p spectrum, a distinct peak (at 168.8 eV) and a weak peak (at 164.2 eV) were identified, respectively typical of -SO₃H and -SH [14].

Further, the FTIR analysis detected the functional groups attached to the carbonaceous materials (Fig. 8). For C600, the obvious bands at around 3415 and

1595 cm⁻¹ are assigned to O-H group and the aromatic ring mode, respectively. In addition, the characteristic band situated at 595 cm⁻¹ is attributed to the Fe-O stretching vibration [32]. For the C600-S catalyst, the bands located at 3384 and 1584 cm⁻¹ show the presence of the O-H group and the aromatic ring mode, respectively. Moreover, the band at 608 cm⁻¹ confirmed that Fe₃O₄ was successfully incorporated onto the C600. In particular, the stretching vibration bands of S = O and -SO₃⁻, respectively situated at 1172 and 1040 cm⁻¹, are principally ascribed to the -SO₃H groups [33].

3.2 Catalytic activity

The C600-S catalyst was tested at 90°C for 4 h using a molar ratio of n(alcohol): n(oleic acid) = 10: 1 and w(catalyst dosage) = 8% to study the effect of alcohol type on the esterification. The conversion of oleic acid decreased with the increase in the molecular weight of alcohol (Fig. 9). For methanol, ethanol, *n*-propanol, and *n*-butanol, the final conversions of oleic acid catalyzed by C600-S catalyst were 93.6%, 89.1%, 82.4%, and 77.7%, respectively. These results suggest that the steric hindrance increases with the number of carbon atoms in alcohols, thus deteriorating the nucleophilicity of alcohols, which hinders the interaction between oleic acid carbocation and the catalyst, leading to a reduced efficiency [34]. Thus, the reasonable price, short carbon chain, and strong polarity of the methanol make it suitable for such esterification.

The reaction was performed between 50 and 100°C to study the influence of temperature on oleic acid conversion using C600-S catalyst with the other esterification conditions of n(methanol): n(oleic acid) = 10: 1 and w(catalyst dosage) = 8% for 4 h. As shown in Fig. 10(a), the conversion promptly increased from 78.9% to 85.0% when the reaction temperature increased from 50 to 60°C, reaching 93.6% at 90°C. The esterification, is generally endothermic. Therefore, the molecular conversion could



Fig. 5 TEM images of C600-S catalyst.(a) C600-S catalyst at a 9.90 kX magnification; (b) C600-S at a 5.00 kX magnification.



Fig. 6 TGA and DTG curves of C600-S catalyst.

be accelerated with the increased temperature [35]. However, raising the reaction temperature to 100°C made no obvious improvement in conversion. Consequently, it is inferred in this study that 90°C was the optimum reaction temperature for the C600-S catalyst.

Additionally, the influence of the molar ratio n(methanol): n(oleic acid) on the esterification was studied. The ratio was varied from 4 to 12, using C600-S catalyst under the other esterification conditions of w(catalyst dosage) = 8% at 90°C for 4 h. Esterification is

a reversible reaction that requires excess methanol to promote the reaction to increase methyl oleate yield, although the stoichiometric molar ratio of n(methanol): n(oleic acid) is 1: 1 [36]. As evident in Fig. 10(b), the substrate molar ratio exhibited a prominent influence on esterification. The achievable level of the oleic acid conversion increased from 74.6% to 93.6% as the molar ratio increased from 4 to 10. With the further increase of the ratio to 12, the oleic acid conversion slightly decreased. Therefore, an optimized molar ratio of n(methanol): n(oleic acid) = 10: 1 was recommended to save methanol consumption.

Moreover, the impact of catalyst dosage, relative to the weight of oleic acid was investigated. The ratio was varied at w(C600-S catalyst) = 2%, w(C600-S catalyst) = 4%, w(C600-S catalyst) = 6%, w(C600-S catalyst) = 8%, w(C600-S catalyst) = 10%, and w(C600-S catalyst) = 12% under the other esterification conditions of molar ratio of n(methanol): n(oleic acid) = 10: 1 at 90°C for 4 h. The catalyst can reduce the energy required for the reaction, enabling more reacting molecules to be activated. This process increases the percentage of active molecules per unit volume of the reactant, thus increasing the esterification rate [37]. Figure 10(c) demonstrated that w(catalyst dosage) = 2% catalyst dosage exhibited a



Fig. 7 XPS survey spectra of the C600-S catalyst.(a) XPS scan; (b) deconvoluted spectrum of Fe 2p; (c) deconvoluted spectrum of S 2p.



Fig. 8 FTIR spectra of C600 and C600-S catalyst.

comparatively low conversion of 81.6%, suggesting that the available catalytic sites for esterification were insufficient. However, at w(catalyst dosage) = 10%, the oleic acid conversion increased to 94.5%. Although, a further increase to w(catalyst dosage) = 12% did not influence the conversion noticeably. Therefore, w(catalyst dosage) = 10% was the optimized catalyst dosage for esterification.



Fig. 9 Effect of alcohol type on the esterification (reaction conditions: 90°C; 4 h; n(alcohol): n(oleic acid) = 10: 1; w(catalyst dosage) = 8%).

Finally, the esterification duration was varied at 1, 2, 3, 4, 5, and 6 h to study its influence on oleic acid conversion using C600-S catalyst under the other conditions of molar ratio of n(methanol): n(oleic acid) = 10: 1 and w(catalyst dosage) = 10% at 90°C. The heterogeneously catalyzed esterification involves blending oleic acid,



Fig. 10 Optimization of esterification conditions.

(a) Reaction temperature; (b) molar ratio of *n*(methanol): *n*(oleic acid); (c) catalyst dosage; (d) reaction duration.

methanol, and C600-S catalyst. Therefore, sufficient duration was required for the reactants to contact the catalyst to achieve excellent conversion. As depicted in Fig. 10(d), the oleic acid conversion gradually increased with contact time. It showed that the conversion increased from 81.6% at 1 h to 94.5% at 4 h, which was the equilibrium (optimum) time. Further prolonging the reaction duration showed a plateaued conversion, probably due to the chemical equilibrium on the C600-S catalyst.

3.3 Reusability and deactivation of the catalyst

The deactivation and recyclability of the C600-S catalyst were studied using the catalyst repeatedly in esterification. The catalyst was recovered by washing with ethanol to remove adsorbed organic matter, by washing with *n*-hexane to remove adsorbed organic matter, and by washing with ethanol followed, by regeneration with $w(H_2SO_4) = 5\%$ for 3 h, before washing with deionized water until pH = 7. Subsequently, the spent catalyst was dried at 105°C for 5 h for the next reaction cycle. As shown in Fig. 11(a), the conversion achieved with C600-

S catalyst dropped substantially (from 94.5%) to 70.4% and 43.6% in the second and third cycles, respectively. Similarly, the C600-S catalyst activity recovered by nhexane washing decreased significantly after repeated use for three cycles. As described in the reported literature, leaching of polycyclic aromatic hydrocarbons containing -SO₃H groups or formation of methyl sulfonate groups caused by methanol phase could deactivate sulfonated carbon catalysts [38,39]. Deactivation of sulfonated carbonaceous solid acids has been widely reported. Dechakhumwat et al. [40] prepared an acid catalyst derived from corncob and found the biodiesel yield obtained with this catalyst dropped substantially from 77.51% to 44.91% and 28.76% in the second and third cycles, respectively. Similarly, sulfonated carbonaceous catalyst derived from bio-oil prepared by Ballotin et al. [41] exhibited depreciated activity from 95% to 54% and 20% after the first and fourth cycles, respectively.

In recent years, regenerating carbonaceous catalysts by acid treatment has become a hot research topic for maintaining the ideal ratio of -SO₃H groups attached to the carbon matrix. Hence, the catalyst was treated during each cycle by ethanol washing, followed by regeneration



Fig. 11 Reusability test of C600-S catalyst using different regeneration methods.

(a) Ethanol washing; (b) *n*-hexane washing; (c) regeneration treatment with $w(H_2SO_4) = 5\%$ (Reactions for 4 h at 90°C and a molar ratio of *n*(methanol): *n*(oleic acid) = 10: 1 and *w*(catalyst dosage) = 10%).

with $w(H_2SO_4) = 5\%$ (1g catalyst dissolved in 50 mL acid solution), before copious washing with distilled water to pH 7, and finally desiccated in an oven. As depicted in Fig. 11(c), sulfuric acid treatment was more effective than solvent washing as more than 76% of the conversion was achieved by the former after the third run (compared to 43.6% achieved by the latter). Ibrahim et al. [42] obtained similar results for sulfonated functionalization of corncob-based catalyst. Besides, the reused C600-S catalysts were characterized by XPS to determine the impact of catalytic activity on catalyst properties, and the results are shown in Fig. 2. After the 1st use, the C600-S catalyst treated with ethanol washing showed a decrease in the S and Fe contents. The respective relative atomic of S and Fe was decreased from v(S) = 0.69% to v(S) =0.47% and from y(Fe) = 1.71% to y(Fe) = 0.9%, which could be the possible reason for the catalytic activity of the C600-S catalyst decreased during repeated use. Moreover, the respective relative atomic of S and Fe was decreased from v(S) = 0.69% to v(S) = 0.52% and from y(Fe) = 1.71% to y(Fe) = 0.89% for the 1st reused C600-S catalyst treated with $w(H_2SO_4) = 5\%$, the more -SO₃H groups could guarantee the catalytic activity of C600-S during repeated use. However, future studies could focus on improving the reusability of C600-S for industrial application.

4 Conclusions

The relationship between the physical-chemical characteristic and the catalytic activity of the magnetic carbonaceous acid derived from waste GP were studied. The catalyst was synthesized via a cost-effective and straightforward impregnation-carbonization-sulfonation process. The optimized C600-S catalyst possessed sufficient magnetism (12.5 emu/g) for separation and enhanced porosity (surface area of 175.1 m²/g) and acidity (0.74 mmol/g of -SO₃H density), which exhibited a satisfactory catalytic performance in the esterification



Fig. 12 XPS survey spectrum of reused C600-S catalyst.

of oleic acid and methanol for biodiesel production. A conversion of 95.4% was achieved under the optimized esterification conditions of 90°C, 4 h, molar ratio of n(methanol): n(oleic acid) = 10: 1 and w(catalyst dosage) = 10%. Although the C600-S catalyst decreased in activity upon reuse, sulfuric acid treatment can effectively regenerate the catalyst to achieve a conversion of more than 76% after three consecutive cycles. Consequently, this study provides a simple strategy for synthesizing an effective, easily separated, and environmentally friendly magnetic biomass-based carbonaceous catalysts for biodiesel production.

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