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An innovative approach in the synthesis of solid acid catalyst from sugarcane bagasse for the esterification of oleic acid and methanol

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ABSTRACT

Sugarcane bagasse (SCB) generated in the commercial sector would need to have means to convert the low-cost material into a high-value product(s). One possible high-value product is a solid acid catalyst (SAC) derived from SCB for possible applications in biodiesel production. In this study, a new approach and concept to simultaneously carbonize and sulfonate SCB under less severe conditions, while also recovering available sugars in SCB in the form of sugar-rich hydrolysates were explored. The approach involved a 2-h dilute acid hydrolysis (DAH) step with dilute H_2SO_4 (4 wt%) at 100 °C, as pre-treatment to recover about 73% of the available sugars in the hydrolysate. The post-hydrolysis SCB (PHSCB) left after the DAH along with the residual acids were then subjected to drying at 100–150 °C for 12–36 h, to induce simultaneous partial carbonization and sulfonation. The process was successfully carried out and enables the synthesis of carbonized and functionalized PHSCB. The catalyst was successfully used in the esterification of oleic acid and methanol while achieving a conversion of up to 95%. Other process parameters including the influence of solvent-to-oil ratio, catalyst loading, temperature, as well as reusability of the synthesized catalyst were also investigated.

Declaration of interest

None.

1. Introduction

The interest in the use of an acid catalyst for biodiesel (fatty acid alkyl ester, FAEE) is due to its ability to catalyze both esterification and transesterification reaction, which then allows the utilization of oils or lipids with high free fatty acid (FFA) content. Preferentially, sulfuric acid and sulfonic acids have been adopted for such reactions among the different mineral acids and organic acids, respectively [1,2]. The use of such acids as a catalyst has always been criticized for their lower catalytic activity when compared with base catalysts used to catalyze the transesterification reaction [3]. Further, the use of these homogeneous acids also gives rise to challenges in the later separation of the catalyst and glycerol that is generated [1,2]. As means of addressing these concerns, heterogeneous counterparts have been developed and explored, which could then be used in (trans)esterification processes. In principle, the use of a heterogenous acid catalyst or solid acid catalyst (SAC) allows ease of separation and reuse of the catalyst [2]. The use of SACs may be adopted solely for esterification which would allow subsequent base-catalyzed transesterification to be carried out subsequently without complex separation and neutralization steps.

Solid acid catalyst (SAC) may be derived from various materials which would exhibit properties of an acidic catalyst for (trans)esterification, or by functionalization of suitable materials with existing homogeneous catalyst. Among the many possibilities, Toda et al. [4] in 2005 introduced the use of partially carbonized monomeric or polymeric sugars as a renewable support material, whereby it is later functionalized with a sulfonic group ($–SO_3H$) by treatment with sulfuric acid via sulfonation process. The reaction mainly involves the dehydration of

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sugars to form polycyclic chains and subsequent formation of aromatic carbon rings during partial carbonization, which then serves as the backbone for attaching –SO_3H [5]. This concept has since been extended to various related starting materials, including glucose [4–6], sucrose [4,7], cellulose [7–9], and starch [7,10], and in application to several important industrial reactions like hydrolysis [5,9], esterification [4,6,8], and transesterification [7,10]. These types of catalysts have been found to have better performance than commercially available catalysts functionalized with –SO_3H like Nafion NR50, and Amberlyst-15 or by conventional SACs including niobic acid or H-mordenite [4,7,9].

The concept introduced by Toda et al. [4] was later adopted by Dekhoda et al. [11,12] where the authors have sulfonated different wood-derived biochars and were successfully used to catalyze (trans) esterification reaction of canola oil having different FFA content, but was found to be most effective in catalyzing the esterification of FFA. Considering that wood contains substantial amounts of lignin apart from cellulose, and with its chemical composition primarily that of aromatic substructures, it may well serve as the starting material for deriving SACs instead of carbohydrate-based materials. In 2011, Pua et al. [13] made an early attempt to utilize kraft lignin, as the starting material since lignin is the second most abundant natural polymer after cellulose and could potentially avoid the use of high-cost carbohydrate based materials like glucose and starch. The said authors were able to synthesize SAC from lignin via phosphoric acid-pretreatment and subsequent pyrolysis (carbonization), and sulfonation steps, which resulted in a SAC capable of converting Jatropha oil with high acid value to biodiesel. In a related work by Guo et al. [14], lignin from hulls of *Xanthoceras sorbifolia* Bunge was also further successfully converted into a lignin-derived carbonaceous catalyst (LCC) by simultaneous carbonization and sulfonation by directly exposing lignin to concentrated sulfuric acid (98%). The said LCC was successfully adopted for use in converting soap stock from soybean oil refining into fatty acid methyl ester (FAME).

In view of the discussed developments in the field, it is safe to say that any lignocellulosic material could be tapped as raw material for the synthesis of SAC. In Asia, sugarcane has consistently been tapped as the main source of table sugar, with sugarcane bagasse (SCB) being an inevitable residue generated during sugar milling. For each ton of sugarcane milled about 139 ± 19 kg of dry is generated, which is rich in cellulose (40.89 ± 2.83 wt%), hemicellulose (28.38 ± 1.65 qt.%) [15], and the remainder primarily being lignin. Although SCB has been mostly explored for use as raw material in bioethanol production, many researchers have also tapped it as a starting material for the synthesis of SAC owing to its inherent chemical composition. From 2012 to 2014, SCB-derived SACs have been successfully synthesized and used in the conversion of palm fatty acid distillate [16], palmitic acid [17], and oleic acid [18] to FAME or in the treatment of waste cooking oil for biodiesel production [19]. Generally, SCB is first subjected to partial carbonization followed by a sulfonation step [16–19], with carbonization preferentially carried out at 375–450 °C for 0.5–4 h and sulfonation at 150 °C for 5–15 h. From the reported works, there seems to be a wide range of carbonization and sulfonation time, with shorter carbonization time requiring much longer sulfonation time and vice versa. Although not explicitly discussed and elucidated by the different researchers, one major difference that could be observed from the reported works is the source of their SCB. The SCB utilized for the synthesis of SACs are generally obtained from 2 distinct sources, with the first being those generated from sugar mills (industrial) [18–20], and the second sourced from food stalls or sugarcane juice vendors (domestic or commercial) [16,17,21]. For SCB sourced from food vendors, these may contain higher quantities of sucrose, and would probably require longer carbonization time as it would still need to undergo dehydration to form the required polycyclic chains before the actual partial carbonization. Nevertheless, these results so far reported indicate that SAC could be derived from SCB but would require the best carbonization and sulfonation condition to be determined empirically depending on the quality of the SCB.

In 2015, two independent works have been published exploring two different aspects in the synthesis of SAC from SCB. One interesting work was carried out by Zhang et al. [22], where their group investigated the influence of pretreating the SCB before carbonization and subsequent sulfonation. From the said work, it was observed that hydrothermal treatment of SCB resulted in SACs with better catalytic activities, and hydrothermal treatment (200 °C, 10 h) using dilute sulfuric acid solution (0.05 mol/L) proved to be more active. In relation to the observed improved catalytic activity, the researchers attributed this to the removal of residual sugars (sucrose) and structural sugars (hemicellulose and cellulose) during hydrothermal treatment, leaving behind most of the lignin, which when carbonized results in hydrogen saturated polycyclic aromatic skeleton. However, it was not detailed in the said work regarding the resulting hydrolysate that was generated after the hydrothermal treatment. The other related study was reported by Savaliya and Dholkiya [20], where they investigated the possibility of simultaneously carbonizing and sulfonating SCB. The authors refer to their process as *in-situ* carbonization and sulfonation where SCB was directly mixed with sulfuric acid and was allowed to react at 180 °C for 10 h, where the resulting SAC was successfully used in the conversion of soap stock oil into biodiesel. However, their work did not investigate nor discuss how they have arrived or chosen their catalyst synthesis condition. It was not until 2019 when the same idea was revisited by Flores et al. [21] where it was found that simultaneous carbonization and sulfonation temperatures greater than 150 °C results in catalyst with lower sulfonic acid densities and treatment time less than 8 h to have poorer attachment or retention of the active sites.

Although progress has been made in the different aspects of synthesizing SAC from SCB, one main concern remains to be addressed. The sulfonation step typically employs the use of concentrated sulfuric acid, which would normally require to be diluted during the recovery of the synthesized catalyst and would thus, result in the generation of large quantities of acidic wastewater containing high concentrations of dissolved organic materials. In addition, a large fraction of the raw material, up to 80% is lost during the synthesis process, which may not be an effective means of utilizing SCB as a resource for bioenergy applications. A workaround in hopes to address some of the concerns related to the utilization of SCB and the impact of the synthesis process on the environment would be to explore the possibility of employing dilute acid hydrolysis (DAH) using sulfuric acid as the catalyst as a pre-treatment step and subsequent direct sulfonation. The concept lies in the fact that dilute acid hydrolysis may be adopted to hydrolyze in part or in full the available sugars to generate hydrolysates rich in sugar [23–25], and the wet residues containing having about 70–80 wt% acid solution. Upon subjecting the collected wet residue to drying, it is expected that water will be removed while leaving behind the sulfuric acid and the solid residue, which over time would induce simultaneous carbonization and sulfonation. The successful incorporation of acid sites has been observed drying post-hydrolysis residues of rice bran [24,25] and cellulosic filter cake from the carrageenan industry [23]. Further, considering that SACs are high-value products compared to bioethanol and that it has the possibility of being reused, it would best exploit the use of non-industrially generated SCB to make better use of the residual sucrose and valorize the domestically generated waste, so as not to compete with the use industrially generated SCB for bioethanol production.

Many works have been carried out and have adopted different strategies to synthesize or produce SAC from SCB. However, many of these approaches fail to consider the maximized use of the raw material and potentially generate highly acidic waste streams after the synthesis of the SAC. In view of the existing research and technological gaps, the goal of this research is to maximize the use of domestically or commercially generated SCB as starting material to produce possible raw materials for biofuel production. More specifically, DAH was employed at different solvent-to-solid ratios (SSR), acid concentrations, and time to recover the easily hydrolyzable polysaccharides into reducing sugars and

dissolved in the hydrolysate. The wet residues obtained after DAH or post-hydrolysis SCB (PHSCB), which contains residual sulfuric acid, were subjected to drying at different drying times and temperatures to induce direct sulfonation in hopes of synthesizing an acid catalyst. The products obtained after drying were then determined of their acid density, and their catalytic activity and reusability when used as a catalyst during the esterification of oleic acid and methanol as a model system.

2. Materials and methods

Sugarcane bagasse, free of rind, were collected fresh from a local juice stand in Taipei and were immediately subjected to drying at 50 °C until the moisture content was below 10%. Moisture was monitored and determined gravimetrically with an aid of a freeze dryer. The collected and dried SCB were then milled using a food processor or blender and were then stored in polypropylene bottles and kept at room temperature (25–30 °C) for further analysis and use. Other chemicals were obtained from local distributors or suppliers which are of analytical, or reagent grade and were used directly without further treatment or processing. The chemicals and reagents included the following: Sodium hydroxide 95 %w/w (Fisher chemical, USA), 3,5-Dinitrosalicylic acid 98 %w/w (Acros Organic, Belgium), Xylose 95 %w/w (Acros Organic, Belgium), Sodium sulfite 96 %w/w (May & Baker, UK), Potassium Sodium Tartrate 99 %w/w (Showa, Japan), Hydrochloric acid 37 %v/v (Acros Organics, USA), Sodium chloride 99.5 %w/w (Showa, Japan), Phenol 99 %w/w (Fujifilm Wako Chemical, USA), Oleic acid 88 %w/w (Showa, Japan), Acetic acid glacial 99.8 %w/w (Scharlau, Spain), Ethyl acetate 99 %v/v (Echo Chemical Co., LTD, Taiwan), Sulfuric acid 95 %v/v (Scharlau, Spain), Methanol 99%/v/v (Aencore, Australia), *n*-hexane (Echo Chemical., Ltd, Taiwan), Acetonitrile (Aencore, Australia), Furfural 99 %w/w (Sigma-Aldrich, Germany), 5-hydroxymethylfurfural 99 %w/w (Sigma-Aldrich, Germany), Potassium bromide 95 %w/w (Fisher chemical, USA), Methyl oleate 99%w/w (Sigma-Aldrich, Germany).

2.1. Characterization of sugarcane bagasse

Collected SCB was determined of its particle size, moisture, extractives content, total sugar content, elemental composition as well as proximate composition. The mean particle size was estimated by sieving 10–15 g of samples through a set of standard Tyler sieves (1.000, 0.840, 0.710, 0.590, 0.500, 0.420, 0.350, 0.297, 0.250, 0.210, 0.177, 0.125 mm) while taking note of the mass retained in each sieve by weighing the sieves with the samples with an analytical balance. Determination of moisture was done by drying 5 g of samples, which were placed in pre-dried and pre-weighed glass vials and covered with filters to avoid loss in the material analyzed but allow moisture to pass through. The drying was carried out using a freeze dryer and the difference in weight before and after for 24 h was taken as the amount of moisture present in the sample. The samples and glass vials along with the filters were accurately weighed with an analytical balance with an accuracy of up to 0.1 mg. Extractive contents were determined following LAP TP-510-42,619 [26], where samples were extracted with water for 18 h and ethanol (95 %v/v) for 12 h. As for the sugars, native SCB after milling and extractive-free SCB were subjected to hydrolysis with sulfuric acid following procedures outlined in LAP TP-510-42,618 [27]. The collected hydrolysates were neutralized using calcium carbonate until effervescence has seized then the solution was filtered and diluted to 100 mL for further analysis. Determination of total reducing sugar (TRS) in the collected hydrolysate to estimate the total available sugar was done by adopting the dinitrosalicylic acid-method (DNS-method) outlined by Miller [28] while using 2% NaOH solution to prepare the DNS reagent to neutralize the excess acid in the samples. Samples were also determined of its proximate components (moisture, volatile matter (VM), fixed-carbon (FC), and ash) using a thermogravimetric analyzer (TGA 550, Waters, USA) under nitrogen and oxygen atmospheres.

2.2. Dilute acid hydrolysis of sugarcane bagasse

The collected and milled SCB were subjected to DAH to generate sugar-rich hydrolysate first before the subsequent simultaneous carbonization and sulfonation process. The hydrolysis experiments are divided into two different scales, with the small-scale experiments carried out to monitor the release of sugars and generation of inhibitors during DAH of SCB and to quickly screen the appropriate conditions to be adopted. Once an appropriate condition was found these were then scaled up to generate enough quantities of PHSCB for subsequent simultaneous carbonization and sulfonation experiments.

2.2.1. Small-scale

For the small-scale experiments, 10-mL screw-capped tubes were used as a reaction vessel. About 0.5 g of moisture-free SCB were weighed into the tubes and acid solutions of different concentrations (2, 4, 6 wt% H_2SO_4) and at different SSR (7.5, 10.0, 12.5 mL/g) were added. The DAH reaction was carried out for 12 h with a replicate of the given reaction mixture taken out or sampled at a predetermined time interval within the investigated reaction period. The reaction was stopped by immediately quenching the tubes into an ice bath and the contents separated by filtration. To determine the total amount of reducing sugar extracted and/or released, the vials and the residues were thoroughly washed with deionized water, with the hydrolysates and washings collected into a 100-mL volumetric flask. The hydrolysates were then analyzed of their total reducing sugar (TRS) and inhibitor concentrations (furfural and 5-HMF).

2.2.2. Large-scale

After determining the appropriate acid concentration and hydrolysis time, the DAH was scaled up using 32 g moisture-free SCB at different SSR with the reaction mixture carried out in a 500-mL screw-capped media bottle. The bottles containing the reaction mixture were incubated in a water bath at 100 °C with intermittent shaking at 30-min intervals. After the DAH the bottles were quenched in an ice bath and the mixture was filtered through a Buchner funnel while using Advantec No. 2 filter paper, the biomass left in the bottles was recovered by washing with 20 mL water. The collected hydrolysate was then measured of its volume using a graduated cylinder and 50 mL aliquots were kept for determination of total reducing sugar and furan concentrations. As for the PHSCB, these were collected and transferred into 400-mL beakers for subsequent drying.

2.2.3. Reducing sugar concentration

Total reducing sugar content in collected hydrolysates was estimated adopting the method outlined by Miller [28]. An appropriate amount of a given hydrolysate was transferred into an 8-mL screw-capped vial and equalized to a volume of 3 mL using deionized water. About 2.4 mL of DNS (dinitrosalicylic acid) and 0.6 mL sodium sulfite solution prepared in 2% NaOH solution were pipetted and added into the vials containing the sample. The vials containing the samples were then incubated at 95 °C in a water bath for 5 min. Upon removal of the vials from the water bath, 1 mL of 40% Rochelle salt solution was added to the vials to stabilize the color of the reaction mixture. The vials were then quenched in a water bath (~30 °C) for 10 min, mixed thoroughly for 10 s using a vortex mixer, and analyzed using a UV–Vis spectrophotometer (UV-2600, Shimadzu, Japan) at 540 nm. Results were expressed in terms of glucose equivalents.

2.2.4. Furan concentration

Concentrations of 5-hydroxymethylfurfural (5-HMF) and furfural in the hydrolysate were determined using high-performance liquid chromatography (HPLC) equipped with high-pressure pump (Waters-1525), reversed-phase C_{18}-column (RP18, Nucleoshell, Macherey-Nagel), and UV-detector (Waters-2489). Hydrolysate samples were diluted using deionized water and filtered through PVDF syringe filters before

analysis. The diluent used was a mixture of Acetonitrile: water: acetic acid (11:88:1, v/v/v), introduced isocratically at a flow rate of 1 mL/min with the column maintained at a temperature of 30 °C and the detector set to a wavelength of 276 nm. Actual concentrations were calculated using preestablished external calibration curves using reference materials, 5-hydroxymethylfurfural (purity ≥99%, Sigma-Aldrich) and furfural (purity 99%, Sigma-Aldrich), and accounting for the dilution factor.

2.3. Direct sulfonation of post-hydrolyzed sugarcane bagasse and characterization

After DAH of SCB under different SSR, the collected wet PHSCB were dried in an oven at different temperatures (100, 125, 150 °C) for the different duration (12, 24, and 36 h), with the samples intermittently mixed with a spatula at an interval of 2 h for the first 12 h and left to simultaneously carbonize and sulfonate. The drying and subsequent carbonization and sulfonation were carried out in an oven with a constant air flow of 12 m^3/h facilitated using a vacuum pump (Edwards RV12). To distinguish the different SAC derived from SCB (SAC-SCB) synthesized under different conditions, the synthesized SAC-SCBs were coded and labeled adopting the following mnemonics or code, H#-SSR-HT-Ht/S-ST-St, to represent the acid concentration used during hydrolysis (H#), the hydrolysis temperature (HT), the hydrolysis time (Ht) and simultaneous sulfonation (S) at a sulfonation temperature (ST), and sulfonation time (St). For instance, H4-07.5-100-02/S-100-36 is used to indicate that the hydrolysis was carried out with 4 wt% H_2SO_4, with an SSR of 7.5 mL/g, at 100 °C for 2 h and subsequent simultaneous carbonization and sulfonation were carried out at 100 °C for 36 h. The resulting SAC-SCBs were then collected and stored in polyethylene bottles and sealed for further determination or analysis of their average particle size, functional groups, acid density, and some textural properties.

2.3.1. Fourier transform infrared spectroscopy

To determine and verify the attachment of sulfonic sites onto the treated SCB, SAC-SCB samples were ground using mortar and pestle and mixed with pre-dried and ground KBr. The samples with KBr were then pressed into pellets with a pelletizer at a force of ~6 tons. Shimadzu IRTracer-100 was used in acquiring the FT-IR spectral scans.

2.3.2. Acid density

To have a more quantitative basis, the acid sites were determined via titration. The total acid density (TAD) and strong acid density (SAD) of the synthesized SAC-SCBs were determined following the methods described by Ezebor et al. [29], with some modifications. Briefly, 0.5 g of sample was weighed into a 50-mL vial and added with 30 mL standardized 0.1 M NaOH solution for the determination of the TAD. The mixture was stirred for 24 h before separating the liquid and solid phases. The separation was done via filtration and an aliquot of 10 mL was sampled for titration with a 0.1 M standardized HCl solution until equivalence point. As for SAD, a similar process was done, but this time 2 M NaCl solution was used instead to facilitate ion exchange with the strong acids (–SO_3H and –COOH). The liquid was separated via filtration and an aliquot of 10 mL was sampled for titration with a 0.1 M standardized NaOH solution until equivalence point. The difference between TAD and SAD is taken to be the weak acid density (WAD). All analyses were carried out in duplicates and the acid densities are reported as mmol H^+/g of SAC-SCB.

2.3.3. Brunauer-emmett-teller (BET) analysis

Determination of surface area, pore size, and volume were carried out for selected SAC-SCB. The analysis was done using a surface area and pore size distribution analyzer, BELSORP-max (BEL, Japan). Degassing of samples was first carried out at 125 °C for 16 h using BELprep VAC II (BEL, Japan) before the adsorption and desorption of N_2. Using the N_2 isotherms collected at 77 K and employing the Brunauer Emmett-Teller (BET) equation, the surface area was estimated. As for the pore size and volume, these were deduced from the obtained t-plots and the Barrett–Joyner–Halenda (BJH) equation.

2.4. Catalytic activity and reusability of sulfonated sugarcane bagasse residue

To determine the catalytic activity of the synthesized SAC-SCB, the catalysts synthesized under different conditions were used to catalyze the esterification reaction of oleic acid and methanol. The reactions were generally carried out in a screw-capped conical flask (250 mL) and incubated in an incubator equipped with an orbital shaker. Details of the experiments are elaborated below, with the best catalyst further used in optimizing the esterification of oleic acid with methanol and investigated its stability through subsequent reuse of the spent SAC-SCB following procedures previously established [21], with some modifications.

2.4.1. Esterification

The different catalysts synthesized were first screened by using them to catalyze the esterification of oleic acid and methanol at a solvent-to-oil molar ratio (SOR) of 20:1 with the catalyst loading (CL) at 10 wt% of the available oleic acid for a period of 1 h at 60 °C. After the predetermined reaction time, the reaction mixture was separated via vacuum filtration with Advantec No. 2 filter paper (8 μm pore size) to separate the solid catalyst from the mixture. The catalysts were washed with 30 mL methanol to recover the entrained oleic acid and methyl oleate. Methanol was first removed from the collected mixture using a rotary evaporator, and the concentrated crude product was suspended in 50 mL of hexane. The dissolved product was transferred to a separation funnel for washing, with the mixture washed with 30 mL NaCl solution (5 wt%) at least 3 times, to remove the residual acids that may have leached out from the catalyst. The hexane-rich-phase containing the products was then withdrawn and concentrated for subsequent analysis using via GC.

After screening, the best performing catalyst is then synthesized in multiple batches to accumulate enough material for further test. The chosen catalyst was then further tested in terms of its activity under different SOR (3, 5, 10, 15, 20), CL (5, 10, 15, 20 wt%), reaction temperature (30, 45, 60 °C), and time. In the case of reaction time, the reaction mixture of a given CL, MOR, and reaction temperature, was allowed to proceed for a period of 24 h and 100-μL aliquots were taken at predetermined time intervals (2.5, 5, 10, 15, 30, 45, 60, 90, 120, 180, 240, 360, 480, 720, 1440 min). The obtained aliquots were immediately centrifuged to separate the catalyst, the catalyst was washed with 1 mL of methanol and centrifuged to recover all the reactants and products. The pooled supernatants were then placed in a pre-weighed centrifuge tube and placed in a vacuum oven to remove the methanol. The collected samples were then weighed and dissolved in ethyl acetate for subsequent GC analysis.

2.4.2. Reusability

Based on the determined local optimum conditions, the reusability of the catalyst was assessed. Eight identical reaction mixtures were prepared and allowed to react under the optimum conditions. The crude product and the catalyst in the mixtures were separated and recovered as previously described, with the catalyst pooled together and dried at 50 °C for about 12–18 h. Subsequent esterification cycles were carried out with each run having 1 less replicate owing to losses in the amount of catalyst during the recovery process. As much as possible, the amount of catalyst used and reactants were maintained the same during each subsequent cycle. However, when the recovered catalysts are not enough to meet the required quantities for at least 2 replicates of a given reuse cycle, the reaction mixture is scaled down proportionately as needed until only one trial is possible with the amount of catalyst

recovered.

2.4.3. Gas chromatography

Gas chromatographic (GC) analysis was carried out using Shimadzu GC-2010 Plus equipped with a split injector, Rxi-5HT column (15 m × 0.32 mm x 0.1 μm), and flame ionization detector, to quantify the amount of fatty acid methyl ester (FAME) generated. The crude product (125 mg) was dissolved in ethyl acetate (5 mL), and filtered through 0.20-μm PTFE membrane filters (13-mm syringe filters) before subjecting to gas chromatography analysis adopting a previously established analysis program from earlier studies [30,31], and peaks quantified using with an external calibration curve prepared using methyl oleate obtained from Sigma-Aldrich as standard.

3. Results and discussions

The collected, dried (5.46 ± 0.68 wt% moisture), and milled (0.335 ± 0.030 mm) SCB contains water extractives at 48.48 ± 5.98 wt% while having ethanol extractives of about 2.29 ± 1.05 wt% on a moisture-free basis. Compared to values reported in the literature, where the total extractives are less than 15 wt% [32,33], the extractive content of the collected SCB and used in this work is higher since the SCB was collected from a commercial source than that of an industrial source. In view of sugar content, 54.40 ± 7.17 wt% total sugar on a moisture-free basis, with ~69% structural sugars (37.06 ± 4.86 wt%), and ~31%, soluble sugars (14.39 ± 2.23 wt%). The high soluble sugar content is consistent with the fact that samples were of commercial source, where the extraction of soluble sugar is not as efficient as those in sugar mills. Compared to reports from the literature, where structural sugar (holocellulose) in SCB typically ranges from 60 to 80 wt% [18,32,33], the holocellulose content of the collected SCB is much lower. However, holocellulose content (75.48 ± 3.78 wt%) expressed in extractive-free and moisture-free basis is within ranges reported in the literature. In addition, extractive-free and moisture-free SCB contains at least 19.5 wt % lignin, based on material balance. With the collected SCB from a commercial source, it may be easier to recover the sugars in the form of reducing sugars owing to the lower lignin content relative to the native SCB. Moreover, it may be more practical to process such residue to obtain products of higher value owing to limitations in collecting the commercially generated SCB. Thus, the following section details an attempt to valorize SCB from a commercial source through DAH to generate sugar-rich hydrolysate and subsequent synthesis or generation of SAC.

3.1. Dilute acid hydrolysis of sugarcane bagasse

As mentioned earlier, two main variables considered in the hydrolysis of SCB explored in this work include acid concentration and SSR. Summarized in Fig. 1 is the concentration profile of the total reducing sugar and furans in the hydrolysate, over the course of the hydrolysis reaction. The increase of acid concentration from 2 wt% to 6 wt% resulted in a shorter time to reach the maximum sugar concentration (~70 g/L), from 180 to 30 min (Fig. 1a). In such a short period a total sugar yield of ~0.54 g/g with respect to moisture-free SCB processed

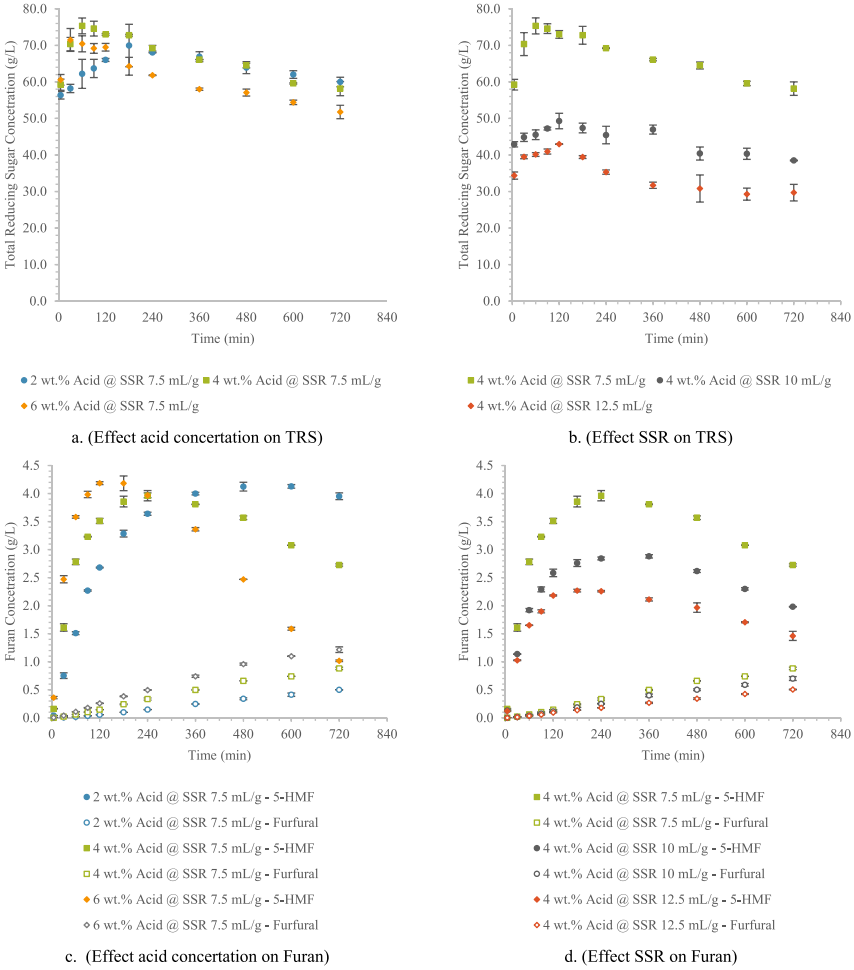

Fig. 1. Total reducing sugar and furan concentrations in the hydrolysate over the course of the 12-h dilute acid hydrolysis at 100 °C with different solvent-to-solid ratios (7.5, 10.0, and 12.5 mL/g) and using a sulfur acid solution of different concentrations (2, 4, and 6 wt%).

could be achieved, which translates to almost complete dissolution and breakdown of available sugars. In a separate work by Lavarack et al. [34] where the kinetics on the hydrolysis of hemicellulose fraction of SCB was investigated, a similar trend of decreasing hydrolysis time required, from ~150 to 20 min, to reach the optimum yield in xylose (0.22 g/g) as acid concentration was increased from 1 to 4 wt% was also observed. However, only about 80% of the available xylose was released into the hydrolysate. The difference observed is most likely because the SCB used in the current work is obtained from a commercial source as compared to those reported in the literature. With commercial SCB containing more soluble sugar, which is more easily hydrolyzed there is more hydrolyzing medium and catalyst available for the hydrolysis of the available structural sugar, which results in a much higher overall sugar yield. In view of increasing SSR (Fig. 1b), the increase in SSR from 7.5 mL/g resulted in a slightly longer time to reach the maximum sugar concertation in the hydrolysate which would range somewhere between 30 and 120 min. However, the increase in SSR resulted in a large decrease in the sugar concentration. Despite this, the overall maximum sugar yield remained at the range of 0.50–0.54 g/g (Table 1). The observed decrease in sugar concentration in the hydrolysate may be mainly attributed to the dilution of the system, while still liberating the same total amount of sugars.

In a separate work reported by Tizazu and Moholkar [33], increasing the temperature beyond 100 °C was found to favor the oxidative degradation of reducing sugars like xylose to furfural even within a period of less than 2 h. To minimize possible degradation, a fixed temperature of 100 °C was adopted in this work. Despite such precautions, higher acid concentrations and prolonged hydrolysis time, still promoted the degradation of the generated reducing sugars (Fig. 1a), regardless of the SSR adopted (Fig. 1b). The degradation of the reducing sugars is further supported by the generation of furans (Fig. 1c and d). Compared to earlier reports on the hydrolysis of SCB [33,34], where furfural is generated in larger quantities compared to 5-HMF, the opposite is observed in this work. The generation of higher 5-HMF is indicative that the collected SCB is comprised of hexoses and may be attributed to the higher soluble sugars, which are primarily of sucrose as compared to industrially sourced SCB where the hemicellulose fraction is generally hydrolyzed and degraded first. From another kinetic study which focused on the conversion of sucrose to levulinic acid [35], sucrose is almost instantly hydrolyzed into glucose and fructose in the presence of H_2SO_4 even at a temperature of 100 °C, with fructose more easily dehydrated to 5-HMF than glucose and is subsequently degrade to form levulinic acid. The subsequent degradation of 5-HMF was also observed in the current work with the decrease in 5-HMF in more acid environment (Fig. 1c) and prolonged hydrolysis time (Fig. 1d). Although production of platform chemicals like furans and levulinic acid are also of interest, this work is focused on the generation of sugar-rich hydrolysates, and thus a catalyst concentration of 4 wt% and reaction time of about 2 h would be most favorable.

3.2. Direct sulfonation of post-hydrolyzed sugarcane bagasse

Most works on the hydrolysis of SCB and other biomass are often carried out at a high SSR of ≥20 mL/g and usually assume that the solubilized sugars are recovered in the collected hydrolysates. For practical reasons, the hydrolysis reaction was scaled up 64 times using about 32 g of SCB and at a low SSR of 7.5–12.5 mL/g. Generally, an increase in SSR results in higher hydrolysate yields and subsequently higher sugar recoveries, but concentrations decrease with the increase in SSR as having been observed from the small-scale experiments (Table 2). Compared to small-scale experiments, the overall process yields, and recoveries are less than what is expected since not all the hydrolyzing medium is recovered, with 20–30% entrained in the residual solids. Although washing of the residual solid would enable the recovery of all the sugars solubilized and generate, it will result in hydrolysates of lower concentration, and thus, this was avoided in the current work. For furan concentrations, these are also found to be in the same magnitude as the small-scale experiments. Furan aldehydes have been found to have inhibitory effects on yeast growth during fermentation, however, the concertations obtained are below the critical inhibitory concentrations of ~3.8 g/L for 5-HMF and ~2.9 g/L for furfural based on recent reports in the fermentation of sugars in hydrolysates to ethanol using *Saccharomyces cerevisiae* [36] or some alcohol yeast [37]. Apart from ethanol production, prior works have also shown the use of hydrolysates obtained from DAH of various biomass to be a good carbon source for oleaginous yeast for lipid accumulation, with *Yarrowia lipolytica, Cryotoccoccus curvatus, Rhodotorula glutinis, Lipomyces starkeyi, and Rhodosporidium fluvial* species and strains having good tolerance to the presence of 5-HMF (<4 g/L) and furfural (<1 g/L) [38,39].

With about 48 wt% of the SCB being soluble in water, and about 37 wt% of hydrolysable structural sugars, the least amount of residue recoverable would amount to 15 wt%. However, with only 70–85% of hydrolysates recovered, the potential residue would at least range from 27 to 44 g per 100 g of SCB processed. The solid yield after drying (Table 2) of the collected wet residue at 100 °C coincides with these estimates, with the slightly higher values obtained owing to the residual H_2SO_4 that is not vaporized at the said temperature. In view of the drying temperature, the solid yield ranged from 28 to 50 g per 100 g moisture-free SCB, with yields decreasing as the temperature was increased from 100 to 150 °C (Table 2), which may have resulted due to the further hydrolysis, carbonization, sulfonation, and subsequent evaporation of volatile components or products. The solid yields, hereinafter referred to as catalyst yield, obtained in this work is within the same range (20–50 g per 100 g moisture-free SCB) as that of simultaneously carbonized and sulfonated commercially-sourced SCB with concentrated H_2SO_4 carried out at a synthesis temperature of 150–250 °C [21]. The lower temperature required in the proposed synthesis process to achieve the same catalyst yields is owing to the DAH step adopted before the simultaneous carbonization and sulfonation process. Despite the use of lesser H_2SO_4 than conventional approaches, the residues after DAH were carbonized and potentially sulfonated as indicated by the change in its color to black.

To confirm the carbonization and sulfonation of SCB residues after hydrolysis, FTIR analysis was carried out, with results presented in Fig. 2. Absorption bands at 3332 cm^{-1} (–OH), 2929 cm^{-1} (C–H), and 1051 cm^{-1} (C–O–H), corresponding to cellulosic components (hemicellulose, cellulose, and lignin) of SCB [17,19], are observed to have diminished with after the hydrolysis and subsequent drying process

Table 1
Influence of solvent-to-solid ratio (SSR) during small-scale dilute acid hydrolysis of sugarcane bagasse with acid solution containing 4 wt% H_2SO_4 for 2 h.

SSR (mL/g)	10-mL Scale (0.5 g SCB)				
	Sugar Yield, Y_s (g/g, dry basis)	Sugar Concentration, C_s (g/L)	Sugar Recovery, R_s (%)	5-HMF Concentration, $C_{5\text{-HMF}}$ (g/L)	Furfural Concentration, $C_{furfural}$ (g/L)
7.5	0.55 ± 0.02	2.74 ± 0.04[a] (72.98 ± 1.05)[b]	101.08 ± 1.35	0.13 ± 0.00[a] (3.51 ± 0.05)[b]	0.01 ± 0.00[a] (0.14 ± 0.00)[b]
10.0	0.50 ± 0.02	2.46 ± 0.11[a] (49.29.01 ± 2.12)[b]	91.37 ± 4.02	0.13 ± 0.00[a] (2.58 ± 0.07)[b]	0.01 ± 0.00[a] (0.11 ± 0.00)[b]
12.5	0.54 ± 0.01	2.68 ± 0.01[a] (42.96 ± 0.06)[b]	98.40 ± 0.30	0.14 ± 0.00[a] (2.18 ± 0.01)[b]	0.01 ± 0.00[a] (0.09 ± 0.00)[b]

[a] Values obtained from the analysis of collected hydrolysates and diluted to 100 mL.
[b] Values expressed relative to the initial volume of the acid solution added to the reaction system.

Table 2
Influence of solvent-to-solid ratio (SSR) during large-scale hydrolysis and subsequent simultaneous drying, carbonization, & sulfonation on the catalyst yield.

SSR (mL/g)	Hydrolysis with 4 wt% H_2SO_4 acid solution at 100 °C for 2 h (32 g dry SCB)*						Simultaneous Drying, Carbonization, and Sulfonation for 36 h		
	Sugar Yield, Y_s (g/g, dry basis)	Sugar Concentration, C_s (g/L)	Hydrolysate Yield, mL	Sugar Recovery, R_s (%)	5-HMF Concentration, $C_{5\text{-}HMF}$ (g/L)	Furfural Concentration, $C_{furfural}$ (g/L)	Temperature (°C)	Moisture or Volatilized Fraction (g/100 g, wet basis)	Average Solid or Catalyst Yield (g/100 g, dry basis)
7.5	0.37 ± 0.02	64.29 ± 1.77	183 ± 7 (~70.4%)[a]	67.77 ± 4.17	3.05 ± 0.19	0.07 ± 0.01	100	81.74 ± 1.35	49.79 ± 2.47
							125	85.99 ± 0.69	40.71 ± 1.44
							150	87.68 ± 0.28	36.43 ± 0.73
10.0	[a].40 ± 0.03	48.20 ± 1.57	272 ± 6 (~80.3%)[a]	72.91 ± 5.02	2.63 ± 0.21	0.06 ± 0.00	100	86.17 ± 1.32	45.86 ± 4.63
							125	86.49 ± 0.52	35[a]22 ± 0.91
							150	87.90 ± 0.72	32.89 ± 0.69
12.5	0.48 ± 0.02	42.27 ± 1.26	364 ± 8 (~86.7%)[a]	88.57 ± 3.52	2.34 ± 0.20	0.05 ± 0.01	100	84.69 ± 0.78	38.37 ± 0.51
							125	87.20 ± 0.48	28.89 ± 0.59
							150	88.52 ± 0.40	28.56 ± 0.57

b Fraction lost during simultaneous drying, carbonization, and sulfonation expressed relative to the amount of wet residue obtained after hydrolysis.
c Amount of dry residue obtained after simultaneous drying, carbonization, and sulfonation.
*A total of 12 re[a]licates were carried out for each SSR and 4 replicates were taken each time for simultaneous carbonization and sulfonation at a given temperatura.
[a] Hydrolysate yield expressed relative to the initial volumes of acid solution used for the reaction and the wash water.

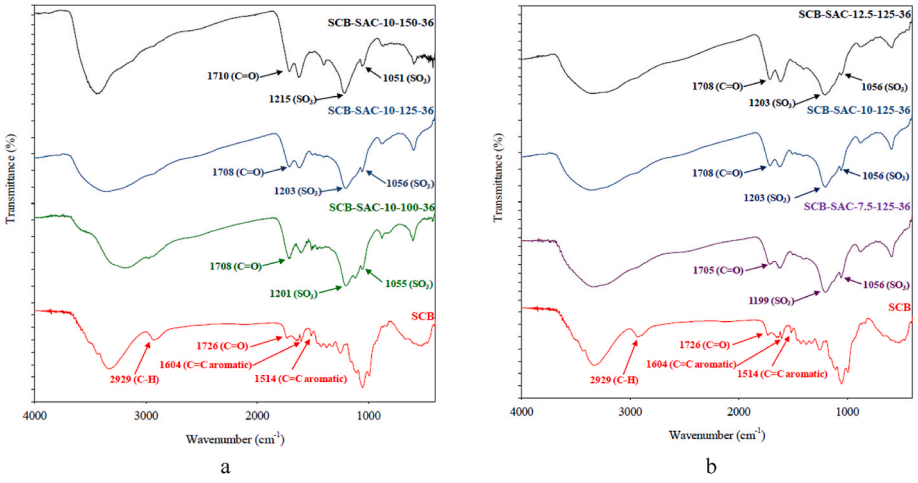

Fig. 2. FTIR spectra of raw sugarcane bagasse and derived catalysts at different hydrolysis SSR (a) and drying temperature (b).

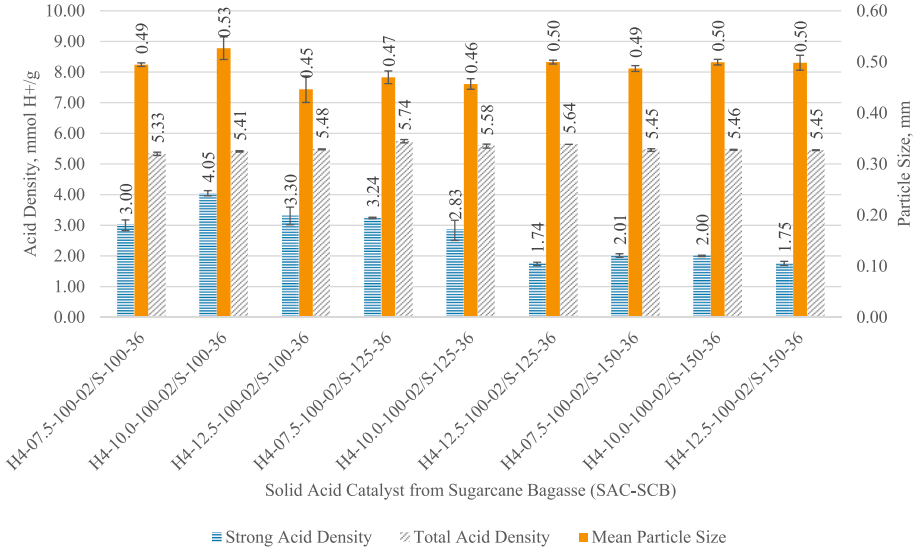

Fig. 3. Acid density and particle size of SAC-SCB synthesized under different SSR during hydrolysis and simultaneously carbonized and sulfonated under different temperatures.

(Fig. 2a). In addition, after the treatment, adsorption bands at 1726 cm^{-1} (C═O) of hemicellulose [17] have shifted to 1708–1710 cm^{-1} (C═O), which may be owing to the breakdown of the polymeric network of hemicellulose and lignin and exposing more carboxylic sites. The increase in SSR during hydrolysis results in the higher intensity of the carbonyl group (C═O) (Fig. 2b), which may have resulted in the higher extent of breakdown of lignin's polymeric network, exposing more carboxylic groups. In view of drying temperature, increasing from 100 to 150 °C resulted in the demising intensity of the C═O and the aromatic stretching (C═C) of lignin at 1514 cm^{-1} [17,19], while sulfonic and sulfone or sulfoxide groups represented by 1199–1215 cm^{-1} and 1051–1056 cm^{-1} [17–19], respectively (Fig. 2a), are observed to have increased in intensity. Further, a sharp absorbance peak at 600 cm^{-1} (C–S) confirms the attachment of sulfur to the carbon matrix [18,21]. As a quantitative basis, acid sites were also determined via neutralization and ion exchange to determine the total and strong acid sites, respectively (Fig. 3). In view of total acid sites (–SO_3H, –COOH, and –OH), all catalysts generated were not significantly different (5.33–5.44 mmol H^+/g, $p > 0.05$). However, higher SSR and temperatures result in catalysts with lesser strong acid sites, which is owing to lesser residual sulfuric acid left with higher SSR and volatilization components at higher temperatures. In consideration of the residual H_2SO_4 after hydrolysis, the maximum sulfonic sites expected 1.8–2.0 mmol H^+/g. With the native SCB having a strong acid density of only 0.012 mmol H^+/g, and the synthesized catalyst having at least 1.75 mmol H^+/g, this supports the successful formation of carboxylic sites and attachment of sulfonic acid moieties. Elemental analysis of catalyst (H4-10.0-100-02-S-125-36) also resulted in significant amounts of sulfur (5.03 wt%) as compared to the native SCB which had no detectable sulfur present in the biomass. Apart from the surface chemistry, the particle size of the resulting catalyst (0.45–0.53 mm) is larger than the native SCB (0.335 ± 0.030 mm). The increase in particle size may be indicative of the formation of carbon sheets from the dehydration of residual sugars and their subsequent carbonization and sulfonation. However, the particle size as determined under different synthesis conditions was not significantly different.

3.3. Catalytic activity of sulfonated sugarcane bagasse residue

Although functionalization of SCB residues after DAH has been confirmed, their performance as catalysts is best confirmed with its intended application. Fig. 4 is a summary of the esterification performance of SAC-SCB synthesized under different conditions when used as a catalyst in the esterification of oleic acid and methanol. As could be observed from Fig. 4a, the resulting product after a reaction time of 1 h contains 78 to 86 wt% FAME and are generally found higher as SSR used during the hydrolysis of SCB is increased, and decreases as the temperature for drying or curing (direct carbonization and sulfonation), was increased beyond 125 °C. Although the SAD of the SAC-SCBs synthesized from lower SSR (<10 mL/g) and lower curing temperatures (100 °C) tend to be significantly higher than other catalysts synthesized (Fig. 4b), their performance was not significantly higher. This may be because SAD is a measure of strong acids sites including –COOH, which does not have strong catalytic activity for esterification as compared to –SO_3H under the esterification conditions carried out. The increase in SSR during hydrolysis and curing temperature may have facilitated the removal of organic components during hydrolysis and volatile organic acids, which decreased the overall SAD but improved the catalytic activity relative to the available acid sites (Fig. 4a–d). Higher curing temperatures also tend to result in a decrease in SAD, which may be observed due to the transformation of sulfonic sites into inactive sulfone or sulfate groups apart from the volatilization of volatile acidic components. A similar observation was observed by Flores et al. [21] in the direct sulfonation of SCB with concentrated H_2SO_4, where the catalytic activity decreased from achieving a conversion of ~60% to <10% as the sulfonation temperature was increased from 150 °C to 250 °C.

Although the derived catalysts had a similar performance for esterification of oleic acid and methanol, those derived from residues obtained after hydrolysis at an SSR 10 mL/g were found to be more stable, retaining higher activity after the first cycle (Fig. 4a and b). The use of lower SSR may have resulted in poorer stability owing to the removal of functionalized unrecovered soluble sugar molecules, which are not bound to the solid matrix, after the first cycle of using the synthesized catalyst while higher SSR might have facilitated a greater extent of breaking down of the solid matrix of SCB and removal of components, where the sulfonic groups could be incorporated during curing. Although these are difficult to support with direct quantitative proofs, catalysts derived from residues obtained adopting SSR 10 mL/g during hydrolysis were found to consistently have better catalytic performance. From a practical perspective, adopting an SSR of 10 mL/g also provides a good balance in the quality of hydrolysate and sugar yield during hydrolysis (Table 2).

In view of curing time at a fixed SSR and different temperatures (Fig. 4c and d), it can be observed that prolonged time resulted in higher SAD and correspondingly better catalytic performance during esterification. This is also because prolonged curing time results in the complete

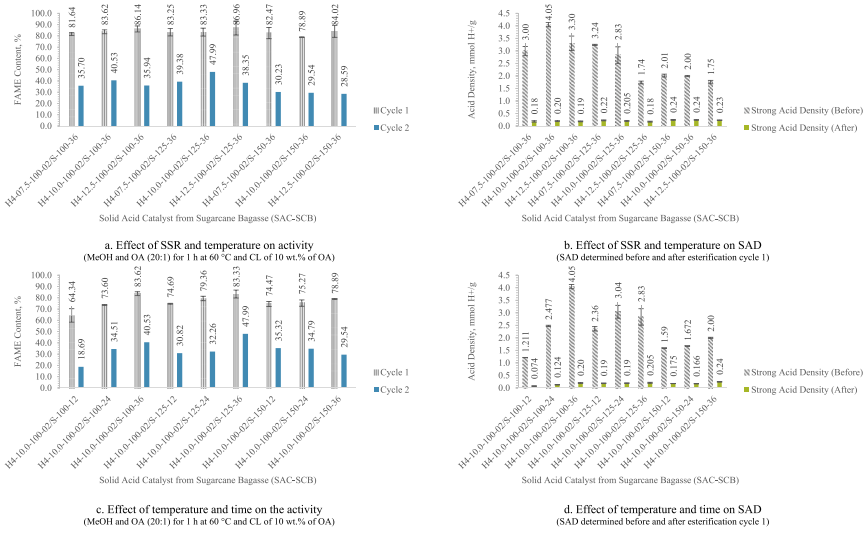

Fig. 4. Catalytic activity and strong acid sites of synthesized SAC-SCB under different SSR during hydrolysis and drying temperature with a fixed simultaneous carbonization & sulfonation time of 36 h (a & b), and at different simultaneous carbonization & sulfonation time at a fixed SSR of 10 mL/g during hydrolysis (c & d).

removal of moisture. A curing time of 24–36 h may at first seem to be a very long period, but compared to conventional synthesis of SAC-SCB which requires, high temperatures (350–400 °C) for 0.5–4 h to facilitate partial carbonization, and sulfonation with concentrated sulfuric acid at 150 °C for 15 h to achieve a TAD and SAD of 1.68–5.49 mmol H^+/g and 0.55–1.49 mmol H^+/g, respectively [17–19], the current process may be comparable in terms of the magnitude of acid density achieved (Figs. 3 and 4), and may be less energy-intensive and would not require specialized equipment for processing. Regardless of the curing time investigated, the temperature of 125 °C consistently results in better catalytic performance both in the fresh catalysts and those recovered and reused. In related works using cacao shell as a carbon source, its sulfonation after carbonization [40] or simultaneous sulfonation and carbonization [41] with concentrated H_2SO_4, was found to be best carried out 120 °C. The observed favorable temperature (125 °C) for curing to induce simultaneous carbonization and sulfonation falls within the range typically adopted in other published works on sequential or direct synthesis of SAC-SCB, which ranges from 120 to 150 °C [18,19,21,41]. The better performance of catalyst synthesized at 125 °C may also be because of its textural properties (Table 3), having a larger pore diameter (18.1 nm) and relatively higher surface area (1.6 m^2/g). Although the surface areas obtained are much less than those conventionally prepared via two-step carbonization and sulfonation which are around 3.01–54.74 m^2/g, it has a comparable pore diameter compared to those reported in the literature (2.7–48.97 nm) [16,19]. When compared to the specific surface area of the native or original SCB which was determined to be only 0.88 m^2/g the synthesis process was able to increase the specific area of material by at least twice its original. The lower surface areas of the resulting catalyst may have resulted as there is no dedicated carbonization step and that the synthesized catalysts were not further washed after the curing process to minimize the generation of waste. However, when compared to direct sulfonation of SCB using concentrated sulfuric acid, the obtained surface area and specific pore volumes (Table 3) are much larger than those reported by Savaliya and Dohlakiya [20], which were 1.268 cm^2/g and 0.0033 cm^3/g, respectively. The larger pore volume may have also enhanced the overall performance of the obtained catalysts. Comparing the catalyst synthesized at 12, 24, and 36 h of curing under 125 °C, those synthesized at 12 h have smaller pore volumes (0.005 cm^3/g) and performed relatively poorer as compared to those synthesized at 24 and 36 h (Fig. 4c). In general, the increase in surface area, pore diameter, and pore volume improve the catalytic activity of the resulting catalyst owing to improved availability and accessibility of the catalytic sites by the reactants.

Table 3
Influence of drying/curing time and temperature on textural properties* of synthesized catalyst from SCB pretreated with 4 wt% H_2SO_4 at an SSR of 10 mL/g for 2 h at 100 °C.

Catalyst	Drying/ Curing Temperature (°C)	Drying/ Curing Time (h)	Specific surface area (m^2/g)	Pore size or diameter (nm)	SpecificPore volume (cm^3/g)
H4-10.0-100-02-S-100-36	100	36	1.640	17.868	0.0[a]7
H4-10.0-100-02-S-125-12	125	12	1.247	17.044	0.005
H4-10.0-100-02-S-125-24	125	24	1.515	19.003	0.007
H4-10.0-100-02-S-125-36	125	36	1.603	18.128	0.007
H4-10.0-100-02-S-150-36	150	36	1.502	17.942	0.007

*Results are from a single analysis of representative samples of a given catalyst taken from the pooled synthesized materials collected owing to constraints and availability of the analyzer.

In comparison with the conventional simultaneous carbonization and sulfonation of SCB by Savaliya and Dohlakiya [20] and later revisited by Flores et al. [21], the current process avoids the direct use of concentrated sulfuric acid and the generation of acid waste. Instead, through the hydrolysis step, the sugar-rich hydrolysate is generated, and the generation of acid waste could be avoided. Like SAC-SCB synthesized through the conventional approach, catalysts that are not exhaustively washed are observed to have decreased activities by about half. In the work reported by Flores et al. [21], fresh catalyst without exhaustive washing could achieve about ~89% conversion of oleic acid to methyl oleate at a catalyst loading of 10 wt% and methanol to oil molar ratio of 20. However, washed catalyst only allowed conversion of 44–53% of the oleic acid. Likening to the washed catalyst previously reported, under the same reaction conditions, the catalyst (H4-10.0-100-02-S-125-36) as synthesized in the current approach only allowed conversion of 47% of the available oleic acid at most, after the first cycle. Compared to the original conversion of 83%, using a fresh catalyst, the relative decrease is about 43%. The observed decrease may be large at first glance but compared to the decrease in the SAD from 2.82 to 0.21 mmol H^+/g, with a relative decrease of ~93% in acid sites, the catalyst remained highly active. To better understand the performance of the synthesized SAC-SCB, subsequent experiments adopt the use of H4-10.0-100-02-S-125-36 as the catalyst for the esterification of oleic acid under different reaction conditions.

3.4. Performance and reusability of H4-10-100-02/S-125-36 SAC-SCB

To better assess the performance of H4-10.0-100-02-S-125-36 as the catalyst, reactions were carried out under different solvent-to-oil ration (SOR), catalyst loading (CL), reaction temperature, over a period of 24 h. Moreover, its reusability was also looked into along with its residual acid sites in terms of SAD after each reuse. A summary of the results is presented in Figs. 5–8.

3.4.1. Solvent-to-oil ratio (SOR)

Reactions catalyzed using fresh catalyst rapidly reach a FAME content in the product over ~85% in a short period within 0.5 h (Fig. 5a) or even as short as 5 min (Fig. S1a). The rapid increase in the conversion or yield was also observed by Akinfalabi et al. [42] when using SAB-SAC derived from two-step carbonization and sulfonation process, where the FAME yield of almost 80% was attained at 0.5 h even when the catalyst loading was only 2 wt%. However, the reaction tends to be erratic over the first 4 h probably owing to the loosely bound or soluble components of the catalyst, resulting in certain competition between the main esterification reaction and solubilization of organic components. Another possibility would be owing to the excess amount of methanol present. Although excess methanol ensures the forward reaction is favored, it could also result in better miscibility of the by-product water, which may result in the reverse reaction. To better understand the influence of SOR, the reactions were prolonged for 24 h for comparison. After 24 h (Fig. 5b), it is more evident that the increase in SOR beyond

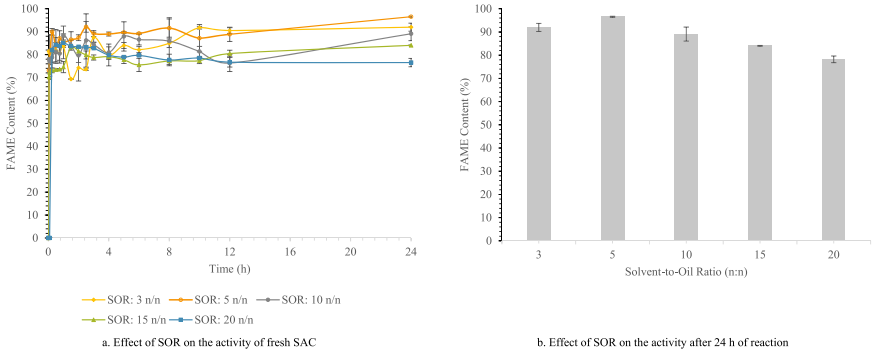

Fig. 5. Performance of H4-10-100-02/S-125-36 SAC-SCB as the catalyst for the esterification of oleic acid with methanol at various solvent-to-oil ratios (SOR), constant temperature of 60 °C, CL of 10 wt% of OA and agitated at a fixed shaking speed of 200 rpm.

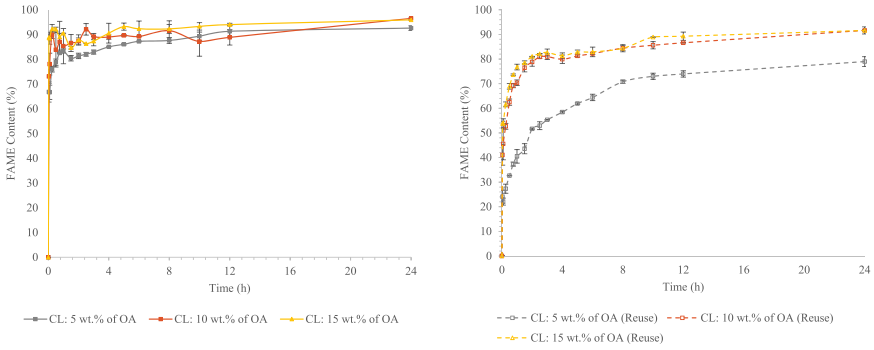

Fig. 6. Performance of H4-10-100-02/S-125-36 SAC-SCB as the catalyst for the esterification of oleic acid with methanol at various catalyst loadings (CL), constant temperature of 60 °C, SOR of 5 n/n and agitated at a fixed shaking speed of 200 rpm.

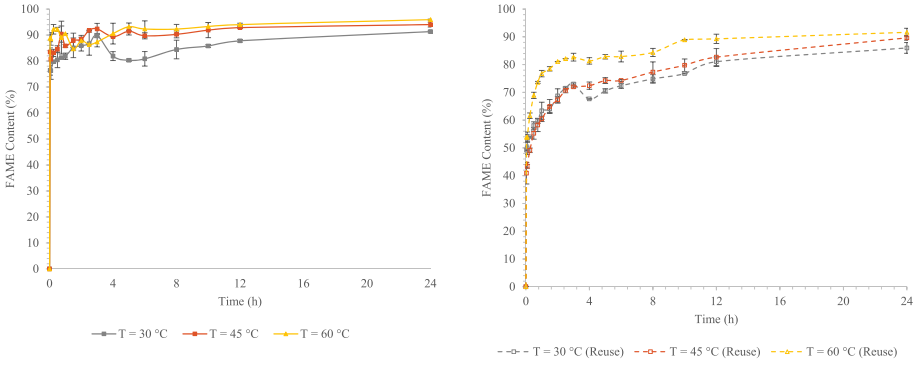

Fig. 7. Performance of H4-10-100-02/S-125-36 SAC-SCB as the catalyst for the esterification of oleic acid with methanol at various temperatures, SOR of 5 n/n, CL of 15 wt% of OA, and agitated at a fixed shaking speed of 200 rpm.

certain optimum results in lower final yields or conversions, with SOR of 5:1 being favorable. A closer inspection at the first few minutes of the reaction (Fig. S1) also reveals the same tendencies with higher SOR resulting in s slower reaction rate and a significant lag in the conversion could be observed at an SOR of 20:1. At an SOR of 5:1, the amount of methanol added is already 5 times the stoichiometric requirement, which not only favors the forward reaction but minimizes the required methanol to be recovered while allowing more fatty acid to be processed for a given reactor volume. This phenomenon has also been observed with SAC-SCB previously reported in the literature. In the study reported by Ezebor et al. [17], palmitic acid to methanol molar ratio beyond 1:18 was also observed to result in decreased FAME yield. The decreased yield was attributed to the shielding of palmitic acid by excess methanol, minimizing its contact with the catalyst. A more physically correct explanation would be the dilution of the overall oleic acid and catalyst in the reaction system since these two components are held constant while the amount of methanol is increased. A lower optimum ratio is observed for oleic acid in this study may be owing to the higher acid density (~3.1 mmol H^+/g) as compared to the catalyst reported by Ezebor et al. [17], which only had ~1.5 mmol H^+/g sulfonic sites, or could also be owing to the better solubility of oleic acid in methanol than palmitic acid.

3.4.2. *Catalyst loading (CL)*

Apart from SOR, which influences the effective amount of catalyst present, the amount of catalyst loaded also influences the overall catalytic sites available to facilitate the reaction. However, a good balance between the amount of catalyst loaded and the amount of reactants is of

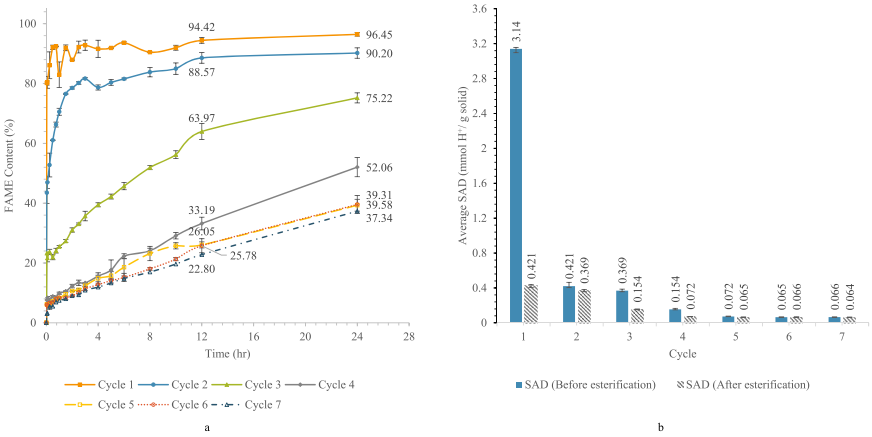

Fig. 8. Reusability of H4-10-100-02/S-125-36 SAC-SCB as the catalyst for the esterification of oleic acid with methanol at SOR of 5 n/n, CL of 15 wt% of OA, and temperature of 60 °C: Product purity in 24 h reaction cycle (a), and acid density of spent catalyst (b).

importance to avoid possible mass transfer limitations [43]. As could be observed from Fig. 6a and b as well as in Figs. S1c and S1d, the rate of increase in the FAME content increased as the CL was increased from 5 to 15 wt% relative to the oleic acid in the reaction system. Although a CL of 15 wt% has a relatively higher initial rate (Figs. S1c and S1d) the difference in yield was marginal for 10 and 15 wt% CL at prolonged reaction time (Fig. 6a). The observed trend is similar to the observation reported by Ezebor et al. [17] carrying out esterification of palm fatty acid distillate with SCB-SAC at 65 °C, where an increase in catalyst loading beyond 9 wt% do not result in improved yields. However, an initial reusability test of spent catalyst resulted in a decrease in FFA conversion (Fig. 6b), which is indicative that higher loading would be required to anticipate possible losses in the active sites in subsequent reuse. Another observation made is the fact that lower SOR, also potentially minimizes leaching of active sites given that spent catalyst achieved higher conversions when reused at the same CL of 10 wt% (Figs. 4c and 6b). Given that 15 wt% CL does not result in observable mass transfer limitations, this was adopted in subsequent experiments. In general, higher catalyst loading provided more acid sites or catalytic sites (sulfonic acid groups) available to interact with the available oleic acid and methanol which improves the reaction yield if no mass transfer limitation occurs.

3.4.3. Reaction temperature

Another important parameter in any reaction is the reaction temperature. In most cases, conventional esterification of FFA favors temperatures near the boiling point of the alcohol used. As could be observed from Fig. 7a and Fig. S1e, the increase in FAME content in the reaction mixture is faster when carried out at 60 °C as compared to lower temperatures of 30 and 45 °C. Generally, an increase in temperature lowers the viscosity of the liquid reactants and provides the needed energy to push the reaction forward. These are also observed by other researchers adopting the use of SAC derived from SCB [42]. When compared to other SAC derived from SCB, the fresh catalyst synthesized in this work is generally more active as it requires less methanol and achieves higher conversions within a shorter time when esterification is carried out at around 60 °C as compared to other SAC derived from SCB reported in the literature. For instance, the SAC-SCB synthesized via a 2-step process involving separate carbonization and sulfonation step, required a methanol-to-palmitic acid molar ratio of 18 and achieves a yield of 96% after 6 h under continuous reflux (~65 °C) [17]. In a separate work also involving a two-step process for SAC-SCB synthesis, an SOR of 10 was required for the esterification system involving methanol and oleic acid, while requiring a reaction temperature of 80 °C to achieve a yield of 95% in 6 h [18]. The primary difference in performance is the SAD of the derived catalyst with H4-10.0-100-02-S-125-36 having almost 3 times as many strong acid sites. When compared to a SAC-SCB synthesized via a simultaneous carbonization and sulfonation process (1-step process) which required 24 h to reach a conversion of 89% at an SOR of 20 for the esterification of methanol and oleic acid [21], H4-10.0-100-02-S-125-36 still outperforms previously reported SAC-SCB when based on the performance of the fresh catalyst. One major difference in the synthesis process as compared to previously derived SAC from SCB is the exclusion of a washing step after synthesis. This was not necessary for the SAC-SCB synthesized in the current work since the catalyst obtained afterward was not anymore immersed in a bath of concentrated acid and other degraded organic material. Thus, incorporating a washing step with hot or warm water would not be practical. When reusing the catalyst, it is expected that a fraction of the available active sites may be leached out which results in decreased activity as evidenced by the decrease in conversion. However, adopting a reaction temperature of 60 °C also compensates for the loss in activity (Fig. 7b).

3.4.4. Reusability

A more detailed investigation on the reusability of H4-10.0-100-02-S-125-36 with no complex regeneration step required apart from washing the catalyst with methanol and subsequent drying to remove the residual FAME and methanol, respectively. As indicated from the reusability study, there is a loss in activity after each cycle and is primarily owing to the decrease in SAD of the recovered catalyst (Fig. 8). However, after multiple recoveries and reuse of the catalyst, a stable activity is eventually approached and does not necessarily lead to the total loss in the activity of the catalyst. This tendency is similar to previously reported sulfonated carbon-based SAC derived from other biomass [40,44–46]. As could be observed from Fig. 8a, there is a continuous decrease in the conversion achieved after 24 h as the cycle number was increased from 1 to 5. The decrease in the achieved conversion at a fixed time is indicative of the loss in catalytic power/activity of the catalyst, which could be corroborated by the decrease in the SAD after each cycle (Fig. 8b). Interestingly similar conversions and rates were achieved from cycles 5 to 7, and correspondingly the SAD remained relatively the same (Fig. 8). Apart from the leaching of the sites, blockage or deactivation may have also occurred owing to the attachment of entrainment of fatty acids or the esters. An FTIR analysis of the spent catalyst after the 7th cycle indicates the presence of alkyl groups (–CH–) at 2920 and 2853 cm^{-1} when compared to simply washing the catalyst with methanol (Fig. S2). Future developments may have to look into practical and effective stabilization of active sites and regeneration processes. Nevertheless, regardless of the synthesis method adopted in the synthesis of SAC-SCB the decrease in activity after each reuse has been observed, be it in a 2-step [16–18] or 1-step [21] process.

However, compared to the work reported by Flores et al. [21], on a single step synthesis of SAC-SCB, where the SAC-SCB ultimately had an activity of ~1.95 mmol FAME/mmol SO_3H•h after 4 cycles, the catalyst in this work still has an activity of ~5.38 mmol FAME/mmol SO_3H•h, both compared at a 24-h cycle.

4. Conclusions

From the results of the study, a new approach in the processing of SCB to produce raw materials for biofuel production was successfully carried out. Rind-free SCB from a commercial source could be subjected to dilute acid hydrolysis at 100 °C for 2 h at an SSR of 10 mL/g with the hydrolyzing solution containing 4 wt% of sulfuric acid to generate hydrolysates with a reducing sugar content of 48 g/L, which translates to a sugar recovery of 73%. Subsequent drying of collected residue after hydrolysis at 125 °C for 36 h induces simultaneous carbonization and sulfonation owing to the residual acid left after separating the hydrolysates and the SCB residues. Post-hydrolysis SCB yield under the favorable condition is about 35 wt% of the initial SCB processed and is not partially carbonized with sulfonic groups attached. The obtained PHSCB was successfully used as a catalyst for the esterification of oleic acid with methanol, achieving high conversions of over 95% using the freshly synthesized catalyst and requiring low SOR of 5:1 (oleic acid to methanol) and with the reaction carried out at 60 °C. The SAC-SCB synthesized using the current approach is generally reusable. Although active sites were observed to diminish with subsequent reuse, the catalytic activity and the SAD eventually reaches a stable value, which could be maintained for subsequent 3 cycles tested, with a final activity of ~5.38 mmol FAME/mmol SO_3H•h at 60 °C in a 24-h cycle. The synthesis and use of the SAC-SCB synthesized via dilute acid hydrolysis and subsequent simultaneous carbonization and sulfonation upon drying of post-hydrolysis residue are yet to be fully optimized, the initial results presented in this work provide proof that the theorized approach works and could well be explored in view of maximizing the use of SCB to produce sugar-rich hydrolysates for possible use in bioethanol production and the subsequent generation of catalyst useful in the conversion of free fatty acids into FAME via esterification with methanol. The current approach could potentially be adopted as a new route for the synthesis of SAC from biomass to avoid the generation of waste and maximized use of raw material but would require further investigation to elucidate the functionalization mechanism and ways to improve stability and reusability of the synthesized catalyst.

Declarations of interest

None.

Authors contribution

Alchris Woo Go – Writing-Original Draft, Writing-Review & Editing, Supervision, Conceptualization, Project Administration, Formal Analysis, Funding Acquisition, Methodology, Visualization, Data Curation.

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Appendix A. Supplementary data

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