Characterization of Rice Husk-Based Catalyst Prepared via Conventional and Microwave Carbonisation

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Abstract

Carbon-based sulphonated catalysts (CBSCs) were made from rice husk for biodiesel production. The CBSCs were prepared by microwave (MW) and conventional heating processes from the same feedstock. In both heating systems, the preparation was a two-step process: carbonisation and sulphonation. The aim of this study was to use MW heating to reduce the conventional CBSC preparation time and enhance the $–SO_3H$ group attachment to the solid catalyst. The biomass based solid acid catalysts from the two systems were characterised and compared in terms of physicochemical properties including: sulphonation, morphology, surface area and structure. The reaction times for MW assisted carbonisation and for sulphonation were significantly reduced compared to the conventional heating system; these were 30 min vs 4 h and 20 min vs 12 h, respectively. The MW prepared catalyst showed higher sulphur content (4.91%) as compared to the conventional catalyst (2.10%). The FTIR analysis showed well distinguished peaks for $–SO_3H$ for the MW prepared catalyst suggesting the solid catalyst was successfully sulphonated, while these peaks were very weak for the conventional catalyst. SEM analysis revealed a highly porous structure in the MW prepared catalyst, whilst a denser solid resulted for its conventionally prepared analogue, owing to the higher temperatures applied and longer sulphonation time. The surface area for the MW was higher than the conventionally prepared catalysts (43.63 m^2/g and 37.01 m^2/g, respectively). The structure of the samples was identified as amorphous for both catalysts as confirmed by XRD. The prepared CBSC is expected to catalyse biodiesel production reaction as evidenced by its total acidity and surface area.

Keywords: biomass, carbonisation, solid acid catalyst, rice husk, microwave energy.

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Abbreviations:

MW: microwave, CBSC: carbon-based sulphonated catalyst, RH: rice husk, CRH: carbonised rice husk, FFA: free fatty acid.

1. Introduction

In recent years, the industrial use of agricultural waste has gained attention, due to advantages such as low cost, lack of competition with food supply, reduced dependence on non-renewable energy/material source and its potential to reduce greenhouse gas emission [1-4]. Various agricultural wastes have been explored, including rice husk (RH), sugarcane bagasse, coconut husk, rice straw, wheat straw, and so forth [2-7]. RH is a major agricultural by-product in several parts of Asia; mainly in China and India, which have 33% and 22% of the global rice harvest, respectively [1]. RH is a promising feedstock for industrial application, due to its wide abundance and composition[1, 6, 8, 9]. Similar to other lignocellulosic materials, RH is composed of cellulose, hemicellulose, lignin and ash. More importantly, this biomass waste possesses unique properties, such as high silica content, high porosity, light weight and high external surface area [1, 10]. These properties makes it an ideal biomass waste for use as a potential metal adsorbent, a ligand in construction material, a silica source in ceramics, a catalyst or a catalyst support for other applications [11, 12]. Transesterification reactions for long chain esters (biodiesel) production are usually catalysed by homogenous or heterogeneous catalysts. Most common homogeneous catalysts are liquid acids. Acid assisted transesterification has been widely used for long chain ester production [14-15]. Acids such as sulfuric acid, hydrochloric acid and sulphonic acid are common catalysts with an effective catalytic performance [14, 15]. However, there are some drawbacks of these liquid acid catalysts, such as environment pollution, equipment corrosion, product separation issues and successive reaction operation is also not practical [16]. Solid acid materials, eco-friendly and reusable heterogeneous catalysts have gained increasing attention and are favoured over homogenous acid catalysts. Since, solid acid catalysts can be easily separated from reaction systems, so they can be recovered and reused.

An ideal solid acid catalyst for biodiesel production should have a high density of strong acidic sites, excellent stability, high porosity, low cost and hydrophobic surfaces so the catalyst is not deactivated [17]. Among the most promising solid catalysts are the carbon- based sulphonated catalysts (CBSCs). CBSCs possess a carbon supporting framework and can provide a high density of strong acid sites ($-SO_3H$ group); they also resist water deactivation during the transesterification reaction. Furthermore, CBSCs have other acid groups such as the carboxylic group (-COOH) and hydroxyl group (–OH), thus differing from conventional solid acids bearing a single functional group [18, 19]. Owing to the extensive sources of raw material, cheap price and simple preparation, biomass material is widely used for catalyst preparation [16, 20-26]. Different catalyst preparation methods have been developed, such as hydrothermal conversion and pyrolysis, followed by sulphonation [16, 21, 26]. Several highly efficient solid acid catalysts prepared by these methods have been reported [16, 20, 26]. However, the conventional biomass derived solid acid catalyst preparations were generally performed under high temperature (400-800 ^{o}C) and long reaction time (4-15 hours), suggesting the conventional catalyst preparation processes are time consuming and energy intensive. Microwave (MW) energy has become a widely accepted alternative energy source. Since this form of energy is faster, more uniform than conventional heating and is widely applied to assist biomass pyrolysis, hydrolysis and pre-treatment [27-30]. RH has been used as a biomass waste for several applications as mentioned above. However, MW assisted RH based catalyst preparation was only reported under alkaline conditions [31]. As far as we are aware, MW facilitated RH based solid acid catalyst under acid conditions has not been reported before. In the present study, RH derived CBSC (RH CBSC) were prepared using two heating systems for comparison purposes: a) conventional heating to induce pyrolysis, followed by sulphonation and b) MW assisted carbonisation and sulphonation. The aim of the current study is two fold: 1) to prepare RH based CBSCs using the two heating systems; 2) to characterise and compare the MW assisted RH CBSC and the conventional heating facilitated RH CBSC made from the same feedstock.

Experimental

1.1 Conventional CBSC catalyst preparation

Conventional CBCS was prepared by a two-step process: carbonisation and sulphonation. Rice husk was supplied from a rice mill, Kilang Seri Padi Dusun Sdn. Bhd., located in Kota Belud, Sabah, Malaysia. The RH was pyrolysed in a tube furnace (Eurotherm 2116) under nitrogen flow of 100 ml min^{-1} at 400 °C for 4 h. The resultant char was ground using a pestle and mortar into fine powder. 20 g of the RH biochar was sulphonated in a 3-necked round bottom flask, using 74.0 mL of fuming sulfuric acid (H_2SO_4) (20 wt.% free SO_3) at 160 °C for 12 h under nitrogen flow [32]. After cooling to room temperature, the sulphonated rice husk was heated to 80 °C in 1000 mL distilled water, and stirred using a magnetic bar for 1h. The char was filtered for further washing. The washing was repeated until no sulphate ion was detected in the washed water, and the pH was close to neutral. Then, the sample was dried overnight in an oven at 104 °C [32].

1.2 Microwave CBSC catalyst preparation

RH was supplied from a rice mill, Kilang Seri Padi Dusun Sdn. Bhd., located in Kota Belud, Sabah, Malaysia, following the milling process. The sample particles were 8 to 10 mm long, 2.0 to 2.5 mm wide and 0.1 to 0.15 mm thick. The RH was blended before use. Rice husk samples each of 3 g were mixed with 3 ml or 4 ml of 1 M or 2 M H_2SO_4, followed by microwave incomplete carbonisation under the conditions of 200 ^{o}C for 30 min in a PTFE reactor (ETHOS

EX, Microwave Extraction System, Milesone, US). The temperature in the MW was monitored using an IR temperature probe. The carbonised biomass material was then dried overnight in an oven (50 ^{o}C), followed by hand milling into fine powder. Black fine powder (2 g) was mixed with 20% SO_3 fuming sulfuric acid (8 ml) in the microwave reactor. The sulphonation was performed in the microwave between 5 min and 20 min. The carbonisation and sulphonation conditions can be found in Table S1. After cooling to room temperature, the mixture was washed with deionized water to neutrality. The resulting black solid was dried overnight at 100 ^{o}C.

1.3 Characterisation of RH-CBSCs

1.3.1 FTIR spectroscopy

The chemical composition of the CBSC solid residues before and after the pre-treatments were analysed by attenuated total reflection–Fourier transformed infrared spectroscopy (ATR-FTIR). ATR-FTIR was conducted using a Thermo scientific PIKE Nicolet IS5 with built-in diamond-germanium ATR single reflection crystal. Samples were pressed firmly against the diamond surface using a screw-loaded anvil. Sample spectra were obtained using 32 scans in the wave number range of 650 to 4000 cm^{-1} at a spectral resolution of 4 cm^{-1}.

1.3.2 Total acidity

Total acidity of the CBSC was measured by acid-base back titration. 60 ml of NaOH (8 mM) was added to 0.1g of the catalyst in a conical flask and stirred for 30 minutes at room temperature. Then the mixture was titrated with HCl (20 mM) and the changes in the acidity was measured by pH meter (Mettler Toledo, UK). When the pH reached 7.00 it indicated the end point of the titration.

1.3.3 Scanning electron microscopy (SEM)

Morphological characteristics of CBSC were studied using a scanning electron microscope fitted with a tungsten filament cathode (Stereoscan 360, Cambridge Instruments). The samples were sputter-coated with 7 nm Au to enhance the conductivity for better SEM images. Images were obtained under vacuum at 10-15 kV acceleration voltage.

1.3.4 X-ray diffraction (XRD)

XRD analysis of the catalysts was made on a Philips Diffractometer (model PW 3710) with X'Pert PRO graphics software package. An aluminium-glass composite sample holder with a circular slot of 1 cm diameter was filled with the powdered sample using the front loading method. The samples were analysed using monochromated cobalt radiation (λ =1.540Å) with a nickel filter. The Bragg angle was in the 2θ angle range of 10-80° and a scan speed of 0.72° per minute with a step-size of 0.015°was used. The Philips diffractometer was operated at 40 kV and 40 mA.

1.3.5 Elemental analysis and Inductively Coupled Plasma-Mass Spectrometry (ICP)

CHNS content of the RH and the CBSC were determined using a Carlo Erba EA 1108 Fisons instrument. The ICP analysis were performed following aqua regia acid digestion. The aqua regia acid digestion was carried out using 3 ml nitric acid (HNO_3), 1 ml hydrofluoric acid (HF) and 1 ml hydrochloric acid (HCl) at 170 °C. The digestion was followed by ICP analysis.

1.3.6 Brunauer- Emmett-Teller (BET) analysis

The specific surface area and pore volume were determined by nitrogen adsorption and desorption isotherms measured at 77 K using a Micromeritics Surface Area and Porosity Analyzer. The isotherms were analysed to obtain the specific surface area according to the BET model. The pore volume within the solid acid catalysts were evaluated from the isotherms using the BJH (Barrett-Joyner-Halenda) model.

2. Results and Discussion

Since the first reported highly efficient carbon-based solid acid catalyst preparation [22], the incomplete carbonisation reaction using H_2SO_4 has been widely adopted to produce aromatic carbon sheets as a catalyst support [16, 17, 33, 34]. The incomplete carbonisation is followed by a sulphonation reaction, that is, SO_3H group attachment to the carbon sheets. Herein, the incomplete carbonisation was performed at 200 ^oC using different ratios of RH to H_2SO_4 (Supplement information, Table S1). The carbon-based solid was sulphonated using a fixed ratio of RH to fuming sulfuric acid (20%) and different reaction times (Supplement information, Table S1). The ratio of the RH to H_2SO_4 for the carbonisation step was investigated along with the sulphonation time. Furthermore, the MW prepared CBSC and the conventionally prepared CBSC are compared in terms of their properties.

2.1 Elemental analysis and total acidity of RH and RH CBSCs

The CHNS content of RH and CBSC prepared by MW and conventional heating systems are presented in Table 1. The RH feedstock was mainly composed of 36.6 wt.% C, 4.7 wt.% H, 0.4 wt.% N, 54.1 wt.% O and 4.15 wt. % ash (with 3.94 wt. % Si). The amounts of C and N in the prepared CBSCs did not vary significantly compared to those in the RH feedstock. However, the H content was remarkably reduced (ca. 50 %) following the carbonisation and sulphonation reactions as compared to the feedstock. The reduced amount of H, suggests its covalent binding with sulphur -SO_3H presumably exchanged in CH bonds [36]. Moreover, the O content was reduced by 20 % most likely due to the dehydration and condensation reactions [35, 36]. Sulphur was detected with 0.03 wt. % in the raw material. The conventional and MW catalyst sulphonation processes resulted in S content of 1.11 wt. % and 2.52- 4.91 wt. % respectively (Table 2). These results were confirmed by ICP heavy metal analysis (see Supplement Information, Table S1). The sulphur content in the MW sulphonated catalysts increased by two orders of magnitude as compared to the sulphur originally found in the raw RH (Table 2), while the conventionally prepared catalyst resulted in only 30-fold increase of sulphur content relative to the feedstock. The ratio of RH to acid showed no effect in terms of the sulphur content in the range investigated. Similarly, the MW sulphonation for 20 min seemed slightly better than for shorter times. The sulphur content is slightly higher as can be seen for samples CBSC-1-3-5 and CBSC-1-3-20 sulphonated at 5 min and 20 min respectively (Table 1). The sulphonation time effect can be seen in Supplement Information, Table S1.

Table 1. C, H, N, S content in RH feedstock and MW & Conv. CBSC

Entry	Elemental component (wt. %)					
	C	H	N	S	O^a	Ash
RH	36.56	4.66	0.40	0.03	54.23	4.15
CBSC-1-3-5	39.21	2.68	0.40	4.22	43.33	10.16
CBSC-1-3-20	38.71	2.27	0.46	4.91	44.22	9.43
CBSC-2-4-20	33.63	2.30	0.28	3.85	49.80	10.14
Conv. CBSC	31.29	1.53	0.40	1.11	49.75	15.92

* Conv. CBSC: Conventional carbon based solid catalyst. CBSC-1-3-5: the first number designates the acid concentration, the second number is the acid volume and the third number is the sulphonation time. The elemental composition was calculated on a dry-weight basis (oxygen was determined by difference)

In order to investigate the relationship of the sulphur content with the total acidity of the prepared catalysts, the samples with higher sulphur content (CBSC-1-3-5, CBSC-1-3-20 and CBSC-2-4-20) and the samples with lower sulphur content (CBSC-1-4-5 and CBSC-1-4-10) were chosen for the total acid density test (Table 2). Total acidity comprises the sulphonic acid group (SO_3H), carboxylic group (COOH) and hydroxyl group (OH). High acid sites in solid catalysts are known to promote high catalytic acidity [37]. Strong acidity is usually attributed to the sulphonic acid group (SO_3H), high loading of the sulphonic acid group was shown to increase the catalytic activity [37]. The total acidity increases almost proportionally with the sulphur content, indicating that part of the acidity is due to SO_3H group attachment. The total acidity of the MW prepared catalysts achieved in this work is around twice that of their conventionally prepared analogues (Table 2). Liu *et al*. prepared carbon-based solid catalyst by sulfonating activated carbon (AC-SO_3H) which resulted in only 1.01 mmol H^+ /g total acid density (Table 2) [38]. The same group also prepared corn straw based sulphonated catalysts using conventional heating (carbonisation: ≥ 250 ºC, 1 h; sulphonation: 80 ºC, 4 h). Their results showed 2.64 mmol H^+/g total acid density [20]. Another reported study on different feedstock carbon-based sulphonated catalysts showed higher S content and relatively lower total acidity [39] (see Table 2). The MW prepared catalysts in this work showed the highest sulphur content and total acidity compared to the above-mentioned conventionally prepared biomass based catalysts. Furthermore, the MW catalysts showed comparable total acid density to the commercial Amberlyst-15 (avr. MW CBSC 3.85 mmol H^+ /g vs 4.20 mmol H^+ /g) [20].

Table 2 Total acid density of MW CBSC and Conv. CBSC

Sample	S content (%)	Total acidity mmol H^+/g
CBSC-1-3-5[a]	4.22	3.90
CBSC-1-3-20[a]	4.91	4.24
CBSC-2-4-20[a]	3.85	4.36
CBSC-1-4-5[a]	2.52	3.54
CBSC-1-4-10[a]	2.54	3.20
AC-SO_3H [38]	0.90	1.01
Corn straw [20]		2.64
D glucose derived catalyst [39]	4.70	1.60
Cellulose derived catalyst [39]	5.40	1.82
Starch derived catalyst [39]	5.90	1.97
Amberlyst 15	-	4.20
Conv. CBSC[a]	1.11	2.10

[a] *denotes this work*

2.2 FT-IR absorption spectra and analysis

The RH feedstock chemical changes upon carbonisation and sulphonation were qualitatively analysed by ATR-FTIR spectroscopy. RH is mainly composed of cellulose, hemicellulose, lignin and waxes. The lignocellulosic stucture consists of alkenes, esters, aromatics, ketones and alcohols. Figure 1a shows the rice husk feedstock spectrum. A sharp peak at 792 cm^{-1} related to O-Si-O stretching vibrations of silica group is observed [4]. The silica related peak remained following both the microwave and the conventional carbonisation and sulphonation processes as expected (Figure 1). It is important to note that the silica was not removed from the carbon based materials in both processes. Since, silica proved to maintain the mesoporous structure which otherwise will cause the carbon composites to collapse [40, 41]. The RH spectrum shows a broad band of a peak at 1030 cm^{-1} and a shoulder at 1054 cm^{-1} (Figure 1a). These peaks are attributed to C-O stretching in the C-OH and C-O-C stretching between the sugar units in celluose [42]. The peak at 1030 cm^{-1} related to cellulose disappeared upon carbonisatation of the RH (Figure 1b and c), this indicated its degradation by the two heating systems. Following the carbonisation and sulphonation, new peaks around 1040 cm^{-1} and 1080 cm^{-1} appear clearly in the MW prepared catalyst (Figure 1b), but are less distinguished in the conventional catalyst (Figure 1c). These newly appearing absorption bands at 1040 cm^{-1} and 1080 cm^{-1} represent the asymmetric and asymmetric stretching respectively of S=O bonds of sulphonic acid (SO_3-H) [43]. The sulphonation process was achieved in this case by a covalent attachment of $-SO_3H$ to the carbon framework through substitution of hydrogen in the C-H bond [16]. The attachment of sulphur groups is further confirmed by the elemental analysis (Table 1) and the acidity test (Table 2). The C-H vibration in cellulose and C1-O vibration in the syringyl ring derivatives at 1330 cm^{-1} and the CH_2 cellulose plane bending vibrations at 1430 cm^{-1} are clearly visible in the RH FTIR spectrum (Figure 1a) [44]. Besides the peak at 1371 cm^{-1} that corresponds to the C-H deformation in cellulose and hemicellulose. The C-H related peaks (1330 cm^{-1} and 1370 cm^{-1}) wither after the carbonisation process indicating the degradation of cellulose/hemicellulose [45], while the C-H deformation in cellulose and hemicellulose at 1430 cm^{-1} band appears visibly broader and weaker in both the MW and conventionally heated solid acid catalysts. This is not surprising since the heating applied was higher than 200 °C in both systems and the decomposition of the cellulose in this case is significant. Furthermore, the lignin absorption band in the RH spectrum, at 1460 cm^{-1} ascribed to lignin methoxy groups (-OCH$_3$), the bands at 1510 cm^{-1} and 1600 cm^{-1} related to the phenolic ring vibrations of lignin and the peak at 1731 cm^{-1} representing the ester bond (C=O) between hemicelluloses and lignin also disappear after the two different carbonisation processes [29, 45]. This reflects the destruction of the lignin aromatic system and formation of a new broad band at 1614 cm^{-1} after both MW and conventional heating processes (Figure 1b and c). The 1614 cm^{-1} band is attributed to a C=C stretching of alkenes and some newly formed aromatics [47]. The disappearance of the peak at 1731 cm^{-1} in the RH and the appearance of the peak at 1710 cm^{-1} that is related to C=O suggests that the sulphonation process also produces a certain amount of weak acid, such as carboxylic acid. Hence, the low temperature MW assisted carbonisation and sulphonation process of RH feedstock produced both strong and weak acid groups on the surface of the catalyst.

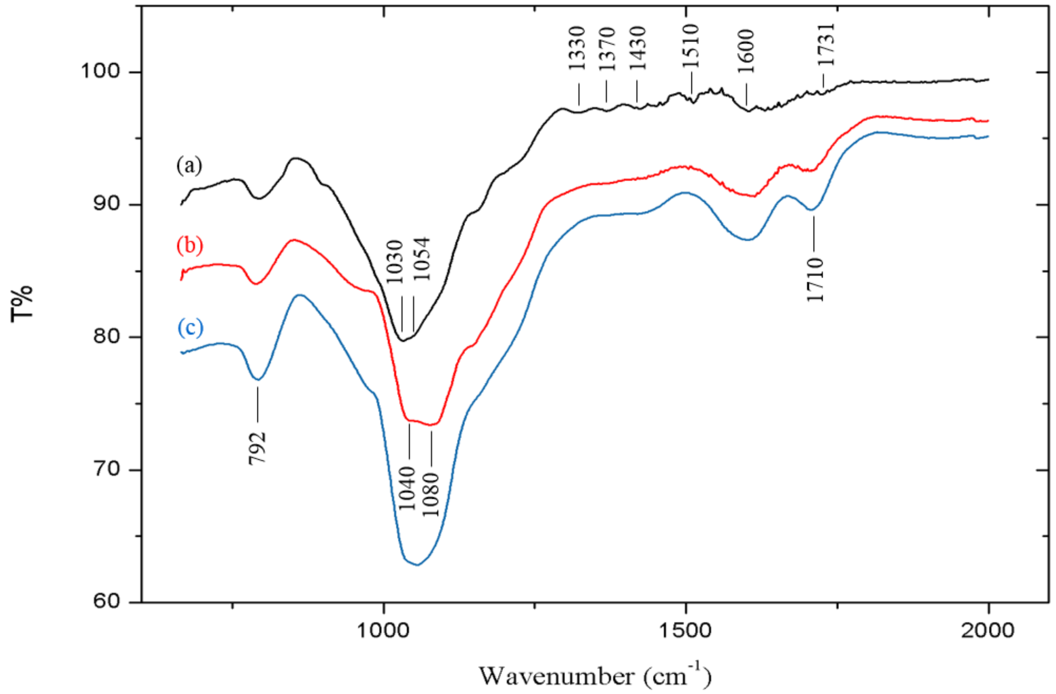

Figure 1 FTIR spectra of (a) RH feedstock, (b) MW CBSC and (c) Conv. CBSC

2.3 SEM Morphological analysis

The morphology of the RH feedstock shows macrostructural aggregates with a size range 6-10 mm (Figure S1 d and e, Supplement Information). The RH particles (Figure 2a) consist of an external surface with a corrugated structure similar in nature to references [31, 32]. The external walls are supported by an inherent longitudinal mesoporous layer with ca. 20 µm pore height supported by a transversal porous layer (ca. 10 µm length). This feature is seen as 90º crossed longitudinal/transversal channels (cross section view, Figure 2a). The channels are covered by a featureless layer. Figure 2a bottom shows the featureless biomass surface with some bundles.

The MW carbonisation process decomposes the organic components of the rice husk leading to induced cracks (Figure S1 d). In Figure 2c, the RH self-construction was preserved in the carbonised samples. While, this process induced cracks in the external walls of the particles (Figure S1 d) and probably removed the underneath covering layer (Figure 2b), it also formed porous structure in the internal walls with average pore size ca. 2µm. The vascular bundles of

RH were still maintained after sulphonation. Furthermore, a large amount of micropores and mesopores with pore diameters of 1-10 µm and 5-20 nm can be clearly observed in Figure 2b and Figure S1b, Supplement Information, respectively. The acid addition was demonstrated to induce the porosity of carbon materials with high surface area and large pore volume [31]. Figure 2c shows the morphology of CBSC prepared by the conventional heating method. The CBSC surface seems denser than the MW CBSC. It also appears damaged and covered with seemingly solid biomass fragments. By comparison with the conventional heating preparation method, the MW prepared CBSC led to a highly porous structure. The acid induced meso-porosity is further confirmed by the BET surface area measurements described in the following section.

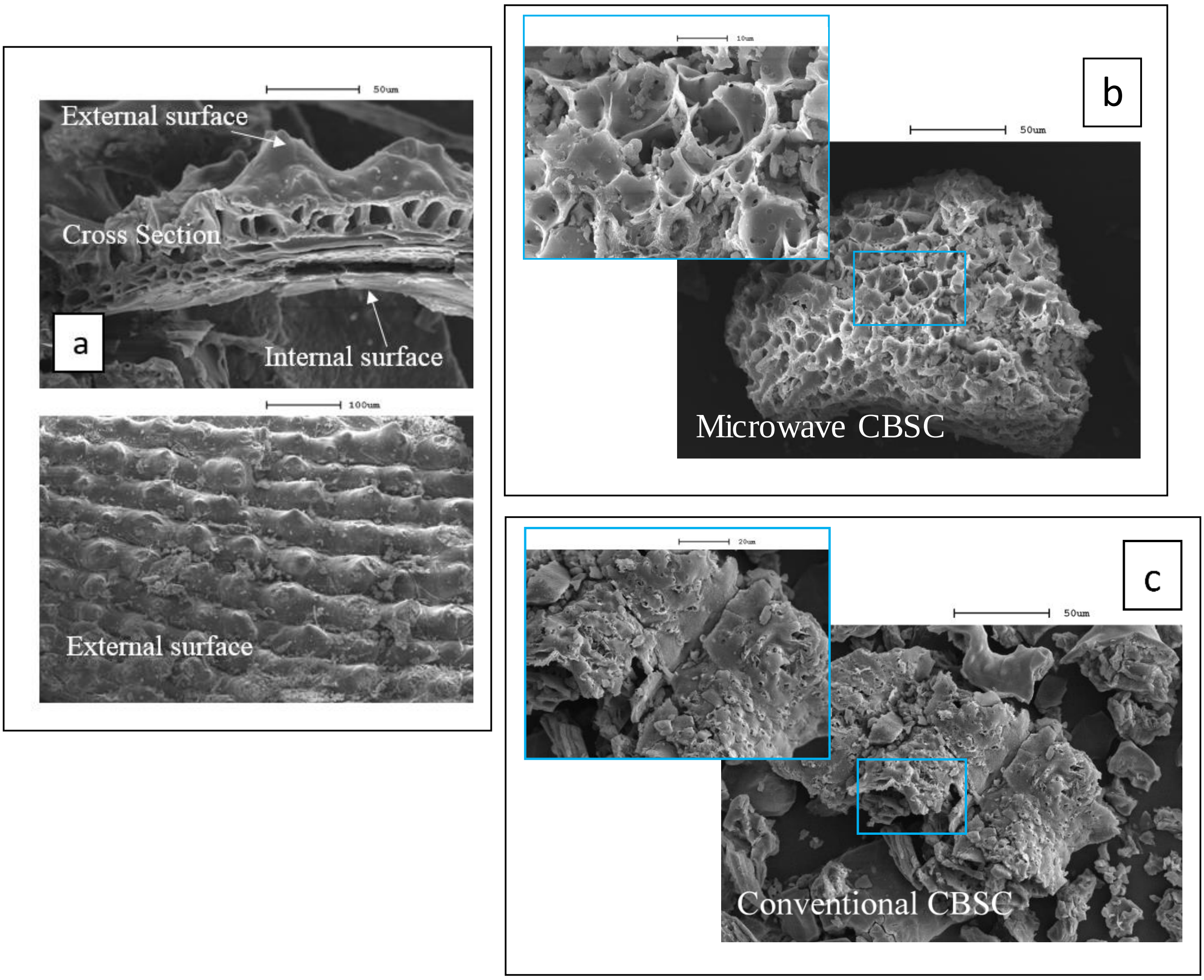

Figure 2 SEM of RH feedstock and CBSC samples (a) RH feedstock. Top: cross section. Bottom: external surface, (b) MW CBSC and (c) Conv. CBSC

2.4 Surface characterization

In order to gain further insight into structural changes the carbonised RH (CRH) and the CBSC porosity was analysed using the BET method. The surface area, pore volume and pore diameter for RH, carbonised samples and CBSC are shown in Table 3. The surface area and pore volume data reported herein was taken from Barrett-Joyner-Halenda (BJH) desorption cumulative surface area and volume measured between 17 Å and 3000 Å. The CBSC show microporosity with a pore size ranging from ca. 5 nm to ca. 10 nm (Table 3). The RH shows surface area of 10.43 m^2/g, this has increased at least 4-fold after carbonisation (not shown); following the sulphonation a further increase of 10-21% is observed. The catalysts sulphonated for 20 min showed the largest surface area of 43-48 m^2/g. The data at hand indicate that the microwave treatment has promoted the porosity; this is further observed from 60-80% increase of the pore volume for microwave prepared catalysts as compared to the raw RH. No correlation was observed between the microwave sulphonation time and the surface area of the CBSCs. However, the pore volume seems to increase with longer sulphonation time. This is illustrated by the 60% increase of pore volume upon 25 min additional sulphonation time in agreement with reference [48]. The conventionally prepared catalyst exhibited 15 % lower surface area than the microwave prepared analogues (Table 3). Surprisingly, the pore volume of the Conv. CBSC reduced to 28% lower than the raw rice husk. This suggests the collapse of the carbon based structure resulting in elongated and nearly closed pores as shown in SEM images

(Supplement Information, Figure S1). Lou *et al.* used different feedstock to make CBSC under conventional heating methods (Table 3). In contrast with their results, the catalyst in the current study presents a larger surface area and similar pore diameter. However, the pore volume of our catalysts is lower. Further investigation and study are needed to improve the pore volume in this study.

Table 3. BET characteristics of RH, CRH and CBSC samples

Sample	Surface Area (m^2/g)	Pore Diameter (nm)	Pore Volume (cm^3/g)
RH	10.43	5.71	0.025
CBSC-1-3-5	42.81	4.85	0.062
CBSC-1-3-20	40.41	4.89	0.078
CBSC-2-4-20	47.69	6.46	0.103
Conv. CBSC	37.01	6.44	0.018
Glucose derived catalyst*	4.10	4.00	0.440
Cellulose derived catalyst*	5.70	5.10	0.520
Starch derived catalyst*	7.20	8.20	0.810
Amberlyst-15 [9]	45.00	-	-

* Lou *et al. catalyst [26]*

Figure 3 highlights the effect of different heating systems on the surface properties of the mesoporous carbon materials. The microwave and the conventional CBSC samples show a slightly different N_2 adsorption-desorption isotherm but relatively similar pore size distribution.

However, the conventional CBSC catalyst shows an isotherm of type IV with a larger hysteresis loop than the microwave CBSC catalyst, which has type II isotherm. Isotherms of type II are theoretically assigned to non-porous solids but in practice are often applicable equally to porous solids [50]. Hence, the microwave CBSC catalyst is considered porous as shown previously from SEM images. In addition, the distinction between isotherm II and IV is without practical significance in the low pressure range which is the case herein. At high relative vapour pressures, the adsorption-desorption isotherms of a given material is dependent on the restrictions of adsorption by the pore width. At low pressure range, materials such as microwave CBSC have such a great volume of relatively large pores (2-50 nm) that this restriction is negligible. Therefore, the isotherm of type II obtained at such low pressure is effectively not different from the conventional CBSC catalyst isotherm. The effect of the microwave preparation time is shown in the Supplement Information, Figure S2. The microwave catalyst is mesoporous, with pore sizes in the 2-50 nm range, while the conventional catalyst is similarly mesoporous but with a narrower range of pore sizes, < 20 nm.

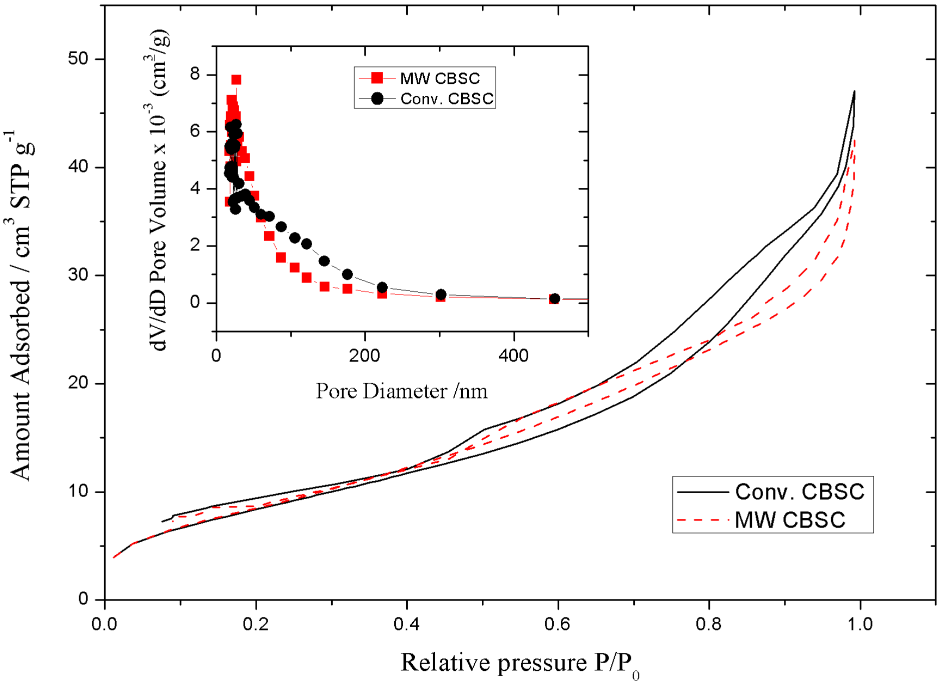

Figure 3 N_2 adsorption-desorption isotherm and pore size distribution of conventional and microwave CBSC

2.5 XRD analysis

The XRD of the RH feedstock and CBSC are illustrated in Figure 4. No crystalline structures are observed. Instead strong broad peaks are observed at Bragg 2θ angle of 20° and a weak peak at 35° can be assigned to reflections from (002) and (100) planes of graphite, implying an amorphous structure of silica in the RH [31, 36] . The broad nature of the peak was also attributed to hydrogen bond transformation in cellulose during the heat treatment and acid addition [49]. Furthermore, the low crystallinity is believed to be due to the large amount of amorphous cellulose in the catalysts [49]. The XRD analysis before and after the carbonisation and sulphonation shows a significant reduction of the intensity in the RH as compared to the CBSC samples between ca. 20° to 30°. The decrease and the broadening of the CBSC XRD peak is attributed to the amorphous nature of carbon composed of aromatic carbon sheets oriented in a random manner [37].

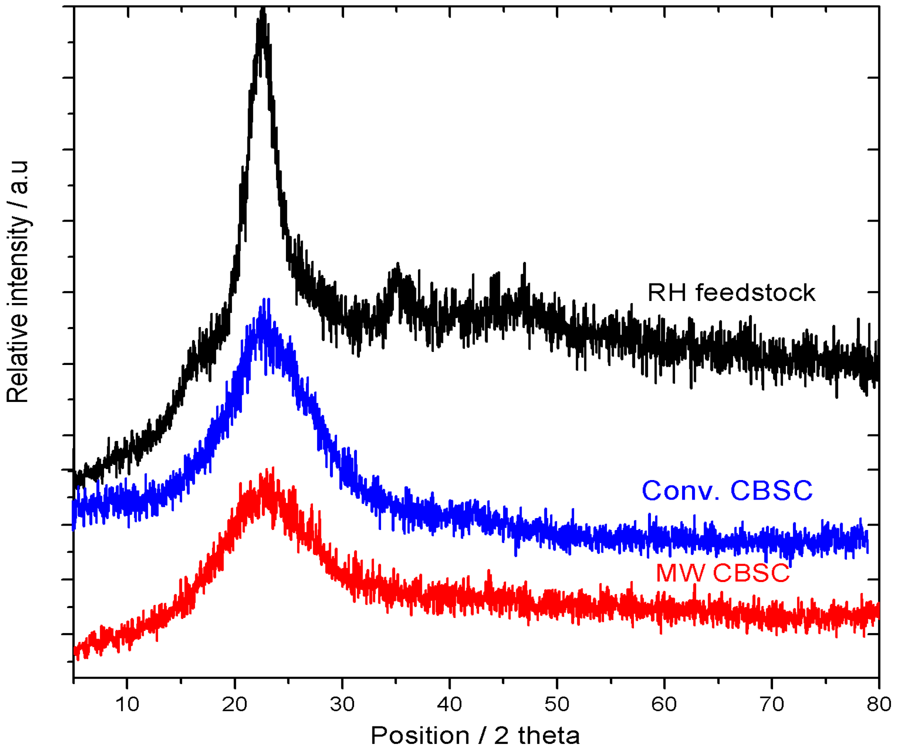

Figure 4 XRD of RH and CBSC-1-3-10 and CBSC-1-4-10

3. Conclusion

RH derived CBSC were prepared using conventional and MW heating systems. The results showed that MW prepared CBSC exhibited high acidity, high sulphur content and high porosity. This was achieved at significantly shorter reaction times (5-20 min vs 12 h) and lower temperatures (200 °C vs 400 °C) than the conventional carbonisation. The sulphur content of MW CBSC was much high than that of CBSC prepared by conventional heating (4.91% and 1.11%, respectively). The microwave prepared CBSC also showed higher total acid density. An average total acidity of 4.16 mmol H^+/g was achieved as compared to the commercial analogue (4.60 mmol H^+/g), which was itself better than for catalysts made by conventional heating (1.76 mmol H^+/g). FTIR studies confirmed the successful attachment of sulphonic acid groups. The morphological study showed that microwave CBSC presented a highly porous structure, whilst conventional CBSC catalysts showed a dense biomass surface covered with some fragments. The current study presents a promising preparation method for making carbon based solid acid catalyst from biomass material in a time-saving and energy efficient manner. The catalysts' activity in transesterification reactions remains to be assessed.

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Appendix A:

Supplement Information

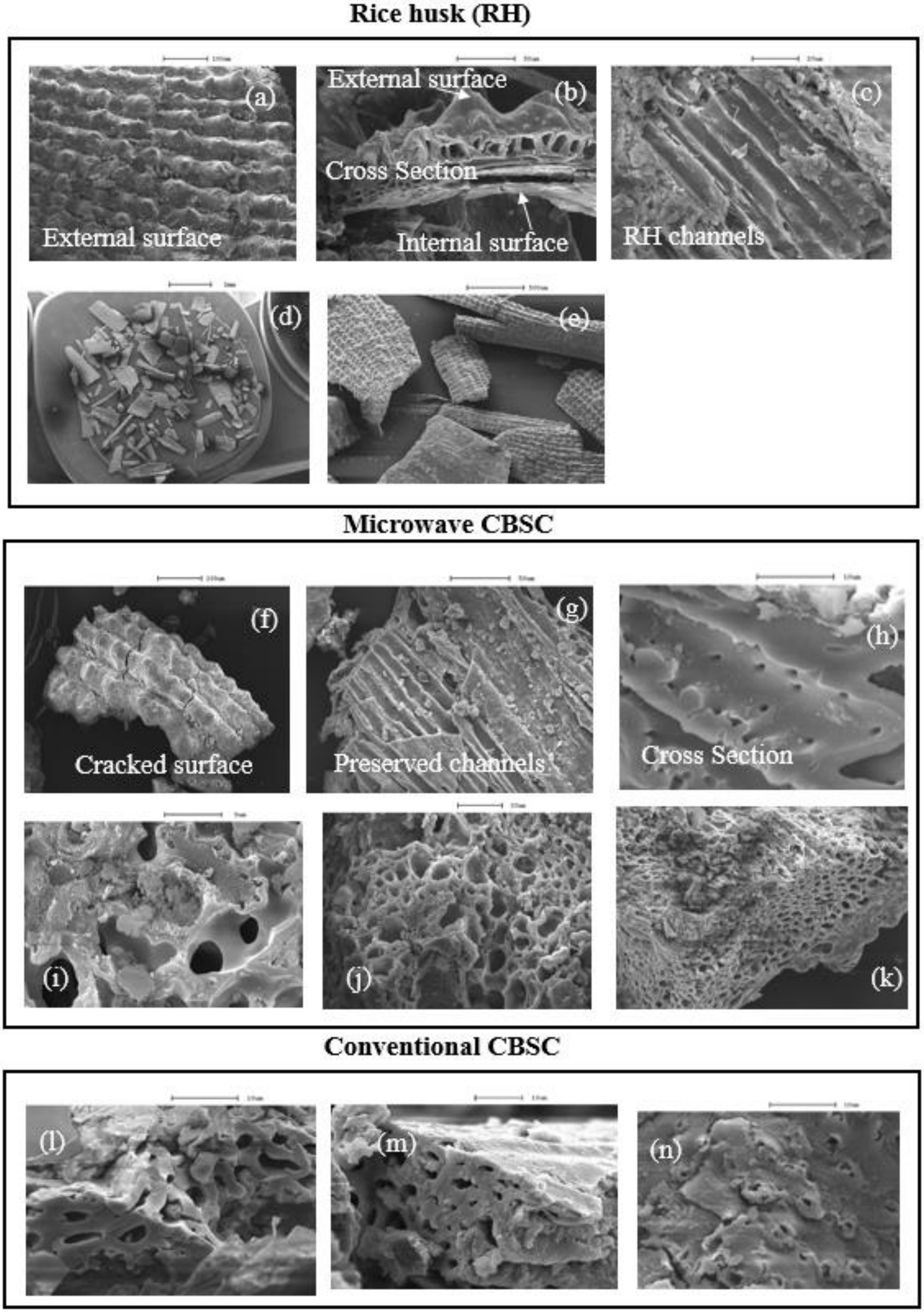

Figure S1 SEM images of RH feedstock, MW and Conv. CSBC samples

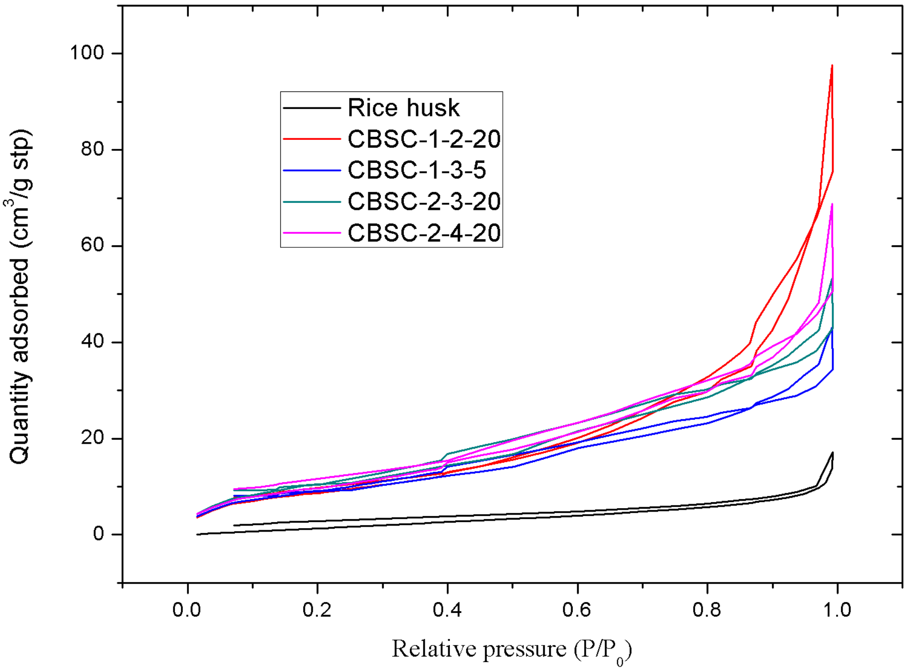

Figure S2 N$_2$ adsorption-desorption isotherm and pore size distribution of microwave CBSC

Table S1. Reaction conditions for MW CBSC

Sample name	Carbonisation conditions (200°C, 30min)	Char yield(g)	Sulphonation time (min)	Elemental component (wt.%)			
	Ratio of Rice Husk to H_2SO_4			C	H	N	S
CBSC-1-3-5	1: 0.294	2.12	5	39.21	2.68	0.40	4.22
CBSC-1-3-10		1.98	10	38.32	2.71	0.40	3.06
CBSC-1-3-20		2.05	20	38.71	2.27	0.46	4.91
CBSC-1-4-5	1: 0.392	2.12	5	37.44	2.19	0.38	2.52
CBSC-1-4-10		2.12	10	32.69	1.98	0.38	2.54
CBSC-1-4-20		2.01	20	33.92	2.28	0.46	4.12
CBSC-2-3-5	1: 0.588	2.04	5	38.08	2.41	0.37	3.63
CBSC-2-3-10		2.09	10	33.60	2.14	0.34	2.69
CBSC-2-3-20		2.11	20	37.90	2.48	0.32	3.74
CBSC-2-4-5	1: 0.784	2.12	5	36.44	2.10	0.40	2.56
CBSC-2-4-10		2.33	10	36.18	1.85	0.41	3.20
CBSC-2-4-20		2.08	20	33.63	2.30	0.28	3.85