Mechanochemical approach in the synthesis of activated carbons from waste tyres and its hydrogen storage applications

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Abstract

The increase in waste tyres has led scientist in the quest for finding various ways for minimizing problems associated with their disposal. The sought solutions are not only meant to be environmentally friendly but also be able to boost the economy. Pyrolysis of waste tyres is one of the preferred ways of recycling waste tyres since it gives valuable products such as pyrolysis oil, gas and solid char. Solid char has low surface area and contains inorganic traces that disadvantage it from competing with commercial carbon black. The aim of this study was to apply the mechanochemical approach, which is the compaction of the solid char with an activating agent before the activation process in order to increase reactive sites. The solid char was initially treated with water, HF and HNO_3 prior to the mechanochemical approach. The obtained materials were analysed using EDS, XRD and FTIR. The textural properties were also studied using N_2 sorption isotherms. The HNO_3 washed and compactivated CB had the highest surface area of 955.20 m^2/g and also the highest H_2 storage capacity of 1.4 wt. % at 1 bar.

Keywords: Waste tyres; Solid char; Mechanochemical; Compactivation

1. Introduction

The automobile industry increases in production each year. In 2016 alone, approximately 80 million cars were produced world-wide and approximately 400 000 cars were produced in South Africa (SA) [1]. With such a large number of cars produced in SA there are a lot of waste tyres generated and around 60 million of the waste tyres are in stock piles [2]. As a result, there has been an initiative branded as Recycling and Economic Development Initiative of South Africa (*REDISA*) that has been implemented to minimize the problem of waste tyres. The disposal of waste tyres poses a major environmental predicament worldwide. As a means of disposal, waste tyres are dumped in landfills and end up occupying large tracks of land. These landfills serve as a breeding ground for disease carrying organism which in turn affects the population health. These dumping grounds could also pose uncontrollable fire hazard which leads to air pollution, danger to human settlement and destruction of vegetation [3]. To minimize or eradicate this problem, governments world-wide have come with initiatives such as repurposing and various methods of waste tyres recycling. Repurposing is an alternative route of transforming the use of waste tyres to a much useful function such as modification of children's playground, making of chairs, table and shoes.

Recycling consist of methods such as retreading, separation by mechanical milling, separation by cryogenic milling, reclaiming, incineration and pyrolysis [4-6].

Pyrolysis is a process of breaking down the waste tyres into its various organic components at high temperatures in an oxygen free environment. The process gives useful by-products such as pyrolysis oil, pyrolysis gas and the solid char which are widely used in the industry [7, 8]. The solid char from pyrolysis of waste tyres consist of other contaminants that are as result of decomposition of other additives included during the tyre manufacturing process. Even though there are other elements (Ca, Fe, and Si) present in waste tyres, the most abundantly are S and Zn [9-11]. The two can react together to form Zinc sulphide (ZnS). To enable the solid char to be desirable in the market it needs to be treated thoroughly in order for it to have the same properties as a virgin carbon black. Thus, the solid char is usually treated with acids to enable removal of the inorganic elements. In most cases, the treated waste tyre solid char is often used in industrial rubber product as a reinforcement agent and also as a coat in automotive, marine and aerospace industry due to its ability to offer protection from UV rays. The treated solid char can also be used in inks in providing pigmentation. Additionally, it can also be used as an adsorbent however due to its low surface area of around 30-90 m^2/g there is always a need for activation in order to enhance its porosity and increase the surface area [4, 12-13]. Due to the high porous nature and adsorption capacity, activated carbons have been used in supercapacitors, gas separation, and separation of toxic metals in water [4, 13]. The activation parameters such as the type of carbon precursor, method of activation and activation time play an important role in determining the resulting properties of the activated carbons.

Conventionally, activated carbons are often prepared using two different methods that are; physical and chemical activation [12, 13, 15]. Physical activation is a two-step process involving carbonization of the carbon precursor and gasification in the presence of CO_2 or steam. During gasification, the unreacted carbon atoms are eradicated and thus generating porosity [16-18]. In the chemical activation process, an activating agent is introduced to the carbon precursor and pyrolyzed in an inert gas. Chemical activation method is a highly favored route because of its advantages such as (i) low temperatures of activation, (ii) higher yield compared to physical activation, (iii) control of porosity of the product by variation of activation parameters and (iv) delivers high surface area and large pore volumes. Activating agents such as phosphoric acid (H_3PO_4), zinc chloride (ZnCl) and potassium hydroxide (KOH) have been extensively investigated [15, 19]. From the above-mentioned activating agents, KOH is effective in generating high surface areas and pore volume amongst its peers. KOH has low reacting temperature during the activation process and have a high yield of carbon [20]. In general, chemical activation depends on the carbon precursor and the hydroxide compound. During the heat treatment stage which is often below 500 °C, hydrogen is produced as a result of the solid-hydroxide reaction and metal carbonates are formed. There is evolution of CO_2 at high temperatures of 800 °C as a result of carbonates decomposition and hence resulting in porosity. The above-mentioned process can be described by equation (1) and (2) below [15, 21, 22].

$$6KOH + 2C \rightarrow 2K + 2H_2 + 2K_2CO_3 \tag{1}$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \tag{2}$$

Most studies on activation of waste tyres char have mainly focused on the conventional chemical activation although there are still other studies that have adopted the physical activation route. For example, Stavropoulos [35] conducted chemical activation using KOH and obtained surface area of 758 m^2/g, with a pore volume of 0.43 cm^3/g. LÓpez et al [36] showed that the surface area of the tyre char could be improved from 38 m^2/g to 242 m^2/g upon chemical activation and the total pore volume improved from 0.30 cm^3/g to 0.44 cm^3/g. Many other studies and results are reported by other researchers [14, 32, 33]. Recent studies by Robert Mokaya's group at the University of Nottingham [23, 31, 42] reported that the application of a mechanochemical/compactivation approach to sawdust and zeolite templated carbon feedstock prior to activation presented a promising route for increasing the surface area of the resulting activated carbon. Based on the promising findings from Mokaya's group, the current study adopted the mechanochemical/compactivation strategy to improve the properties of the activated carbons obtained from the waste tyres solid char.

2. Experimental

2.1. Materials and reagents

The waste tyres solid char was supplied by the International Rubber Recycling Company based in Pretoria, South Africa. Potassium hydroxide (KOH) pellets were supplied by LabChem. 37% Hydrochloric acid (HCl), 60 % Nitric acid (HNO_3) and 40% Hydrofluoric acid (HF) were supplied by Associated Chemical Enterprises (South Africa). Argon (Ar), Hydrogen (H_2) and Ethylene (C_2H_4) were supplied by Afrox.

2.2. Pre-treatment of waste tyres solid char

For the removal of inorganic elements present in the solid char, the solid chars were initially washed with water and various acids by magnetic stirring. In the first instance, the solid char was washed with deionized water and vacuum filtered. A different solid char sample was washed with HF by stirring for 3 hours at room temperature, vacuum filtered and the resulting solid char was washed again thoroughly with deionized water. The obtained HF-washed solid char was then refluxed in 10% HCl at 70 ℃ for 24 hours and thereafter washed thoroughly with deionized water. A third solid char sample was washed with 60% of HNO_3 for 24 hours at room temperature, vacuum filtered and washed again thoroughly with deionized water. All the resulting washed samples were further dried in the oven at 90 ℃ for 24 hours.
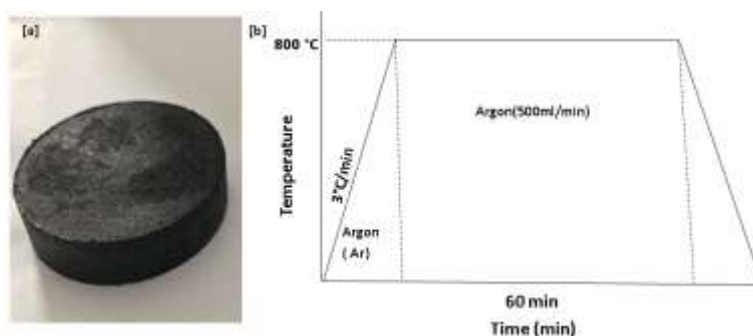
2.3. Compactivation process

Fig. 1. (a) A pellet of compacted mixture of waste tyre solid char and KOH (b) The CVD temperature heating profile and synthesis conditions.

The as-received and washed solid chars (4 g) were individually thoroughly mixed with KOH (16 g) using a mortar and pestle to obtain the ratio of 4:1 (KOH:CB). The resulting powder mixture was then compacted using a hydraulic press at a pressure of 10 Mpa for 15 minutes, resulting in pellets. The compacted pellets were then transferred into a ceramic boat and placed inside a tube furnace. The temperature was set to 800 ℃ at the ramping rate of 3 ℃/min under argon (500 ml/min). The activation temperature remained at 800 °C for 1 hour and the system was cooled to room temperature. The choice of KOH:CB mass ratio and activation conditions were based on optimal conditions reported elsewhere [36,23, 31, 42]. A picture of the resulting compacted pellet together with the CVD heating profile is shown in Fig. 1. The raw waste tyre solid char was denoted CB. The conventionally activated mixture of as-received CB and KOH was denoted as Conv_AC whereas the water washed compacted sample was denoted as W_COMP. The HF/HCL washed compacted sample was denoted as HF_COMP whereas the HNO_3 washed compacted sample was denoted as HNO_3_COMP.

2.4. Materials characterization

The morphology and the elemental composition of the obtained carbonaceous materials were analysed using an Auriga Cobra Focused-Ion Beam Scanning Electron Microscope (FIB-SEM). X-ray diffraction (XRD) patterns were obtained using a PANalytical X'Pert Pro powder diffractometer with Pixcel detector using Ni-filtered Cu-Kα radiation (0.154 nm) in the range of 2θ = 1–60°, and scanning rate of 0.1°s−1. BET surface area measurements and H_2 uptake were conducted by volumetric analysis at liquid nitrogen temperature (77 K) using Micromeritics ASAP 2020. The BET surface areas of the carbon materials were calculated in the region 0.01< P/P0 <0.25 and the H2 uptake measurement were conducted at 1 bar at 77 K. Before each gas sorption analysis, samples were degassed under vacuum at 200 °C for 8 hours. Pore size distribution of the materials was obtained using non-local density functional theory (NLDFT). The micropore volume was determined using the t-plot and the pore volume using the Horvath-Kawazoe (HK).

3. Results and Discussions

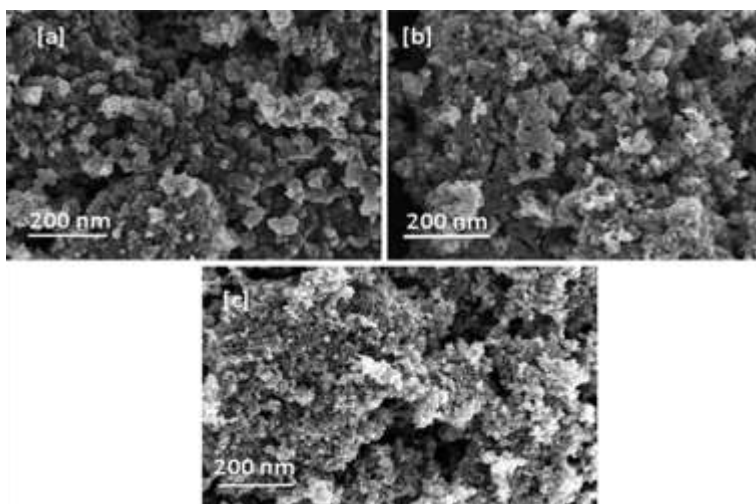### 3.1. Scanning Electron Microscopy (SEM)

Fig. 2. SEM images of (a) Raw waste tyre; (b) Conv_AC and C) HNO$_3$_COMP

Fig. 2a shows that the raw waste tyre CB consists of aggregates that are in a form of spheres with grape shaped clusters which is in agreement with previous reports [25, 34]. The larger aggregates are also due to the fact that the raw CB has impurities, high ash content and carbon [34]. The activated carbons were found to also consist of these globular aggregates but smaller in particle sizes and much finer as was also reported elsewhere [41]. Even though not shown here, there were no observable differences in morphology for the compactivated carbons resulting after the washing with HF when compared to HNO$_3$ washed sample.

3.2. Elemental analysis of CB and activated carbons

Table 1: Chemical composition of and activated carbons.

Composition	CB (wt. %)	W_COMP (wt. %)	HF_COMP (wt. %)	HNO$_3$_COMP (wt. %)
C	95.3	99.7	99.9	99.6
S	1.6	0.1	0.1	0.1
Zn	3.0	0.0	0.0	0.0

Table 1 presents the chemical composition of the raw tyre solid char, water washed as well as the acid treated compactivated carbons. The raw CB had a relatively larger quantity of S (1.6 wt. %) and Zn (3 wt. %) which are mostly found on tyres as additives during the tyre manufacturing process. All the compactivated carbons did not have any Zn traces which suggested thorough washing of the carbons and therefore the pores were unclogged and were available for adsorption studies [24]. Interestingly, there were still traces of S (<0.1) which could be due to the inability of its eradication during the CVD process because it could be chemically bonded to the carbon atoms.

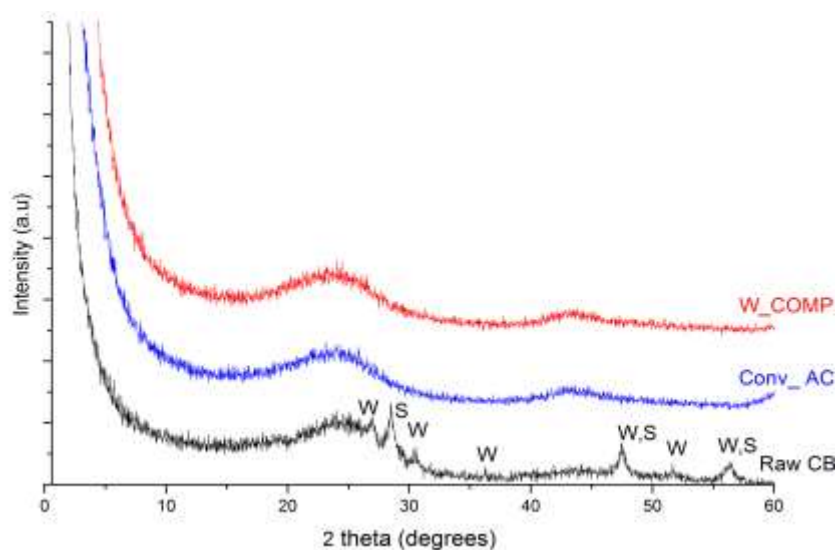## 3.3. Structural analysis

3.3.1. X-ray Diffraction (XRD)

Fig. 3. XRD patterns of raw CB, conventionally activated carbon (Conv_AC) and water-washed compactivated carbon (W_COMP). W=Wurtzite (α-ZnS) and S-Sphalerite (β-ZnS).

The XRD pattern of the as-received CB (Fig. 3) shows the presence of various inorganic compounds. These impurities are mainly zinc sulphides that are wurtzite (α-ZnS) and sphalerite (β-ZnS) which occur as a result of a reaction between zinc oxide (ZnO) and hydrogen sulphide (H_2S) which is produced during tyre vulcanization. This observation also corresponds with results from previous reports [32, 36]. After the water and acid washings, it is seen that the impurities of Zn-based minerals disappeared as was also confirmed by EDS analysis. Similar observations were also reported by Chaala et al [37] where waste tyre carbon black was treated in an acid-basic media. Both the conventional and compactivated carbons show a broad peak at around $2\theta= 25°$ which is an indication of the amorphous nature of the activated carbons and is associated with the (002) plane. The patterns also consist of a broad band at 42.5° which is associated with the (101) of the graphite structure and is also consistent with previous reports [25, 43, 44].

3.4. Physical properties and hydrogen uptake
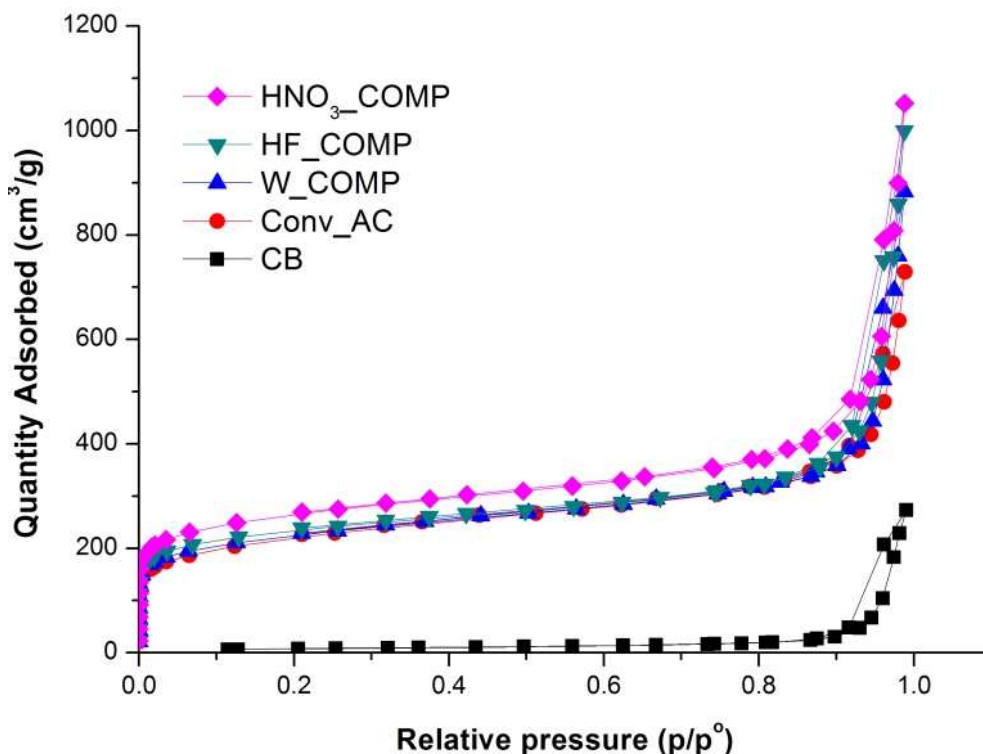
3.4.1. N$_2$ sorption isotherm

Fig. 4. N$_2$ sorption isotherms of raw solid char; conventionally activated carbon and the pre-treated compactivated carbons.

N$_2$ sorption isotherms shown in Fig. 4 were used to analyse the porous properties of the obtained carbons. All the carbon materials exhibited type IV isotherms (according to the IUPAC classification). The steep N$_2$ uptake at the lower partial pressures (p/p$_0$ <0.01) for the conventional and compacted carbons suggests micropore filling. The observed hysteresis loop at about p/p$_0$ >0.8 was due to capillary condensation and signifies the presence of mesoporosity. Since the raw solid char had relatively low surface area of 38 m^2/g (Table 2) and is known to lack internal porosity, the observed hysteresis loop could be associated with the interparticle voids.

Table 2: Textural properties and H$_2$ uptake for activated carbons.

Sample	BET SA (m^2/g)	Micropore Vol (cm^3/g)	Pore Vol (cm^3/g)	Pore size (Å)	H$_2$ Uptake (wt. %)
CB	38				
Conv_AC	775.41	0.062	0.412	5.8	1.1
W_COMP	801.95	0.095	0.414	8.2	1.2
HF_COMP	842.28	0.109	0.420	8.5	1.3
HNO$_3$_COMP	955.20	0.145	0.479	8.6	1.4

The compactivated carbons adsorbed relatively large amounts of nitrogen at low partial pressures. Contrary to the expected high surfaces areas that had been obtained by Mokaya's group [23, 31, 42] who had reported increases of over 25% when conventional activation was compared to compactivation strategy, the increase obtained in this study was between the 3 and 24%.

From Table 1, HNO_3_COMP carbon had the highest specific surface area of 955.20 m^2/g with micropore volume of 0.145 cm^3/g followed by HF_COMP which had a surface area of 842.28 m^2/g and micropore volume of 0.109 cm^3/g.The Conv_AC showed the surface area of 775.41 m^2/g which lies in the range of other previously reported conventionally activated carbons [14, 32-33]. Other textural properties (shown in Table 1) were also found to increase from raw CB to compactivated carbons. The inability to obtain the exceptional high surface areas, as high as >3000 m^2/g, as was reported by other researchers [23, 31, 42] could be ascribed to the differences in morphologies of the used carbon feedstock.

The waste tyre solid char unlike the other reported carbon materials consists of aggregates that are spherical in nature [25, 34]. Since the mechanochemical strategy is aimed to assists in the reduction of the interparticle voids between the carbon precursor and the activating agent and thus generating more reactive sites, the spherical morphology of the waste tyre solid char disadvantages its intended intimate interaction with the KOH activating agent. This could explain the relatively low surface areas obtained from the compacted carbons as compared to previous reports by Mokaya's group [23].
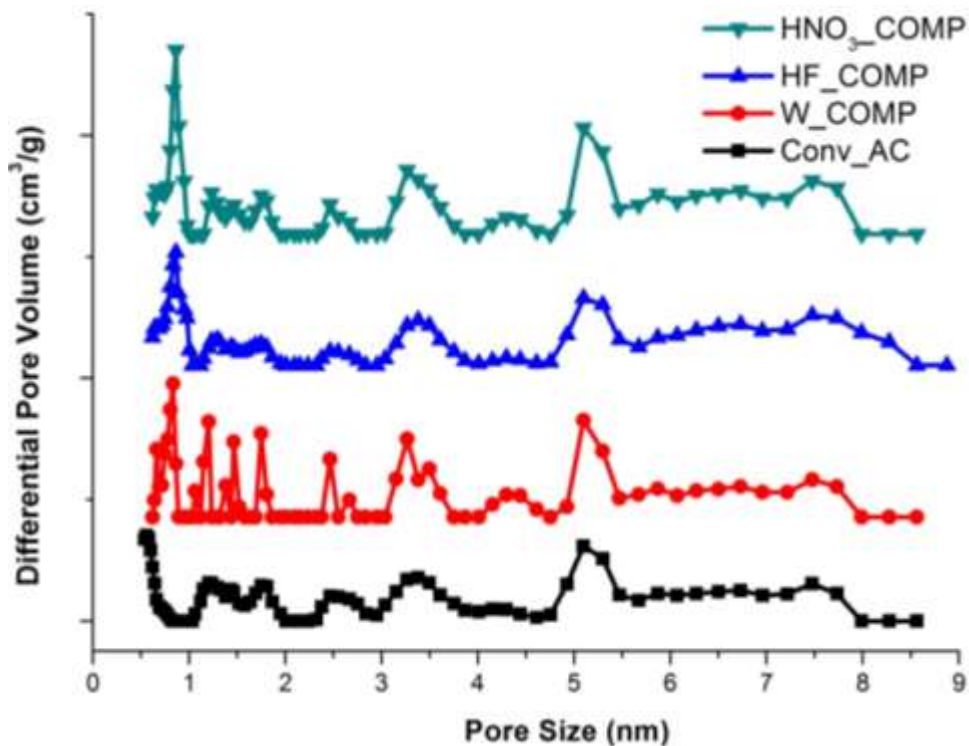
3.4.2. Pore Size Distribution(PSD)

Fig. 5. Comparison of PSD of conventionally activated carbon and the pre-treated compactivated carbons.

The PSD distribution of the obtained carbons is presented in Fig 5. The conventional activated carbon consists of mesopores which are randomly distributed in the same range as the compacted carbons which are consistent with reports from Mokaya's group [23, 31, 42]. However, the pore sizes of the acid washed samples (HNO_3_COMP and HF_COMP) are well defined both at the micropore (< 2 nm) and mesopore (2 − 50 nm) range. This observation further confirms the improvements caused by the acid washing. The result suggests that the removal of inorganic elements by acid treatment generated more pores which were also enhanced by the compacting process. The micropore volume was also noted to increase from 0.06 to 0.145 cm^3/g and was consistent with the type of washing which indicates that the acid treatment had an effect in the porosity of the obtained carbons [30].

3.4.3. H₂ Uptake

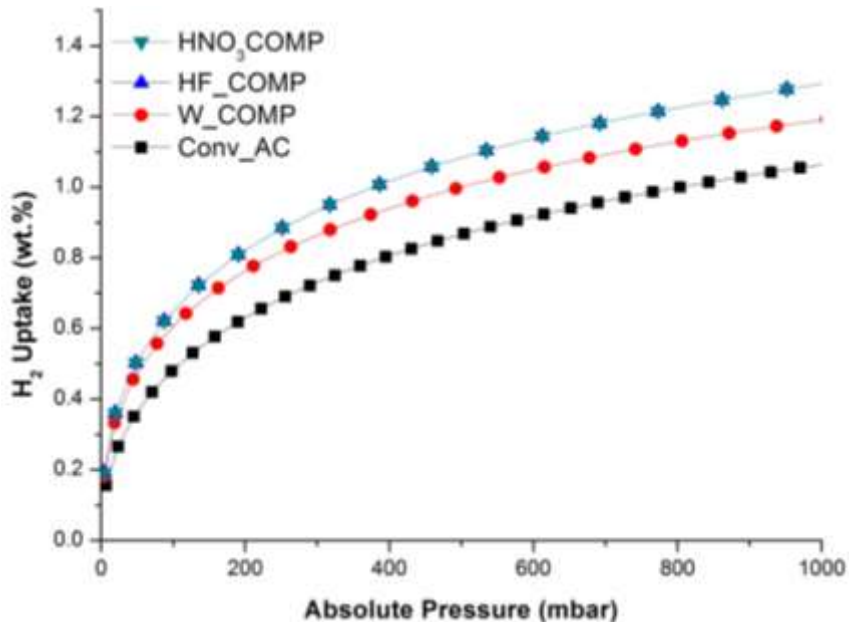Fig. 6. The H₂ uptake isotherms of conventionally activated carbon and the pre-treated compactivated carbons.

The hydrogen measurements were done on all activated carbons (Fig. 6). All the obtained isotherms did not indicate any hysteresis loop meaning that the adsorption process is reversible. The H_2 uptake was noted to increase proportionally with the observed increase in the textural properties of the respective activated carbons (Table 2). This trend has been observed by other researchers [38-40]. The HNO_3_COMP sample had the highest H_2 uptake (1.4 wt. %) due to its high surface area. Importantly, the H_2 uptake isotherms were found not to reach saturation at 1 bar indicating that these activated carbons can adsorb more H_2 at high pressures.

4. Conclusions

In conclusion, the synthesis of carbon materials from waste tyre solid char following the mechanochemical strategy was successful. Compared to the conventional activation method, the application of the compactivation method was observed to lead to an increase in surface area between 3 and 24%. The failure to obtain the exceptional high surface areas that was reported by other researchers [> 25%] was ascribed to the morphological difference of the used carbon feedstock. Since the carbon char used in this study was spherical in nature, it disadvantaged it from the intended intimate interaction with the KOH activating agent that is associated with application of the compactivation strategy. Additionally, the type of washing prior to the compactivation was observed to have an effect on the porosity of the obtained carbons with the acid washing seen to lead to well defined pores both at the micropore and mesopore range. This observation suggested that the removal of inorganic elements by acid treatment generated more pores which were also enhanced by the compactivation process. Hydrogen uptake measurement showed that the highest the surface area carbon (HNO_3_COMP) had the best H_2 storage capacity of 1.4 wt. % at 1 bar.

Acknowledgements

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