Pore Development during CO₂ and Steam Activation of a Spent Tyre Pyrolysis Char

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Abstract

The activation of a spent tyre pyrolysis char using CO₂ and steam was experimentally investigated, focusing on the pore development of the char during activation. The pyrolysis char, produced in an industrial scale retort process, was ground and sieved to a particle size fraction <150 µm, and activated in a fixed bed reactor under CO₂ and steam, respectively. The effect of temperature (750 to 1050 °C), reaction time (0.5 to 4 h for steam activation, 1 to 6 h for CO₂ activation) and activation agent concentration (33.3 to 66.7 vol% of CO₂ or steam in N₂) on the carbon conversion and reaction rate was measured. The activated chars were characterised for the BET surface area, pore volume and average pore size of the activated chars using N₂ adsorption and morphology using SEM. Higher temperature and activation agent concentration, and longer reaction time led to higher carbon conversion. As the carbon conversion increased, the BET surface area initially increased linearly and then decreased, reaching a maximum surface area of 666.6 m²g⁻¹ (0.60 conversion) for steam and 434.5 m²g⁻¹ (0.52 conversion) for CO₂. Micropores were created in the early stage of activation, increasing first until carbon conversion reaching *ca.*0.30. Steam-activated chars showed higher BET surface areas than CO₂-activated chars at the same carbon conversion. Steam was found to generate both greater microporosity and mesoporosity than CO₂.

Keywords: Activation; Pore Development; Pyrolysis char; Spent tyres

Statement of Novelty

Spent tyre is an industrial waste which can cause huge health and environmental hazard if not properly handled. Pyrolysis of spent tyres to produce solid char and then converting the char to activated carbon is a sustainable and environmental friendly method to valorize spent tyres. This work evaluates feasibility of producing activated carbon from a spent tyre pyrolysis char from an industrial scale retort process. A correlation between pore characteristics (BET surface area, pore size and volume, microporosity) and activation conditions (temperature, time and activation agent) was established. Due to its unique structure of the spent tyre pyrolysis char, the activated carbon produced is dominated by mesopores after *ca.*0.30 carbon conversion and the BET surface area and mesoporosity increased almost linearly with carbon conversion. The scientific knowledge shed a new insight on development and utilization of activated carbon from spent tyres.

1. Introduction

Approximately 17 million tonnes of spent tyres were produced in 2017 worldwide and this number is expected to increase due to growing global automobile industry [1]. Over 70 % of spent tyres were landfilled and stockpiled [2]. By their very nature, spent tyres represent both health and environmental hazards as they are non-biodegradable, sulphur-rich, highly flammable, and, when ignited, they release toxic, carcinogenic and mutagenic pollutants [3-6]. There are some available thermochemical conversion processes to deal with the current challenges in spent tyre accumulation such as pyrolysis, gasification, hydrothermal liquefaction and incineration [7,8]. Pyrolysis, which involves the decomposition of organic compounds in an inert atmosphere or absence of oxygen at 400 – 700 °C and low pressure, is an attractive option for the disposal of spent tyres and production of valuable chemicals and fuels [9-12]. During pyrolysis, spent tyres thermally decompose to pyrolysis gas (non-condensable low molecular weight pyrolysis products), oil (condensable high molecular weight compounds), and char (remained pyrolysis solid) [13].

Spent tyres pyrolysis char is a carbon-rich material, which mainly consists of carbon and other inorganic compounds used in tyre manufacturing, such as Zn, Ca, Si and S. The pyrolysis char can be used to produce fuel for energy [14], gasified to produce syngas [15], or converted to high value-added carbonaceous materials, such as carbon black or activated carbon [16,17]. San Miguel et al. [18] reported the activation of spent tyre rubber with CO₂ and steam and obtained activated carbon samples with BET surface area ranging from 90 to 1070 m² g⁻¹. Betancur et al. [19] studied the activation of a spent tyre pyrolysis char under CO₂ atmosphere at 900 °C, producing an activated carbon with a maximum BET surface area of 414.5 m² g⁻¹. López et al. [20] investigated steam activation of spent tyre pyrolysis chars at 850 and 950 °C and obtained activated carbon with BET surface area greater than 500 m² g⁻¹. Choi et al. [21] attained a BET surface area of 437 m² g⁻¹ and total pore volume 1.33 cm³ g⁻¹ by using CO₂ activation at 950 °C for 3h. The variation in the literature is mainly attributable to the difference in experimental conditions and initial feedstock properties.

Most researchers examining the CO₂ and steam activation of spent tyre pyrolysis char focused on the preparation of activated carbon and optimisation of the activation conditions to achieve highest BET surface area or adsorption properties [22-26]. The porosity is a very important indicator of quality and usefulness of activated carbon with significant implication in its applications such as wastewater treatment, gas adsorption and dye adsorption [16,22,27,28]. However, there is very limited research directly examining pore development (micro-, meso- and macroporosity) during the activation process.

It has been shown that the activation agent plays a significant role in the development and size distribution of pore structures during the activation of carbon materials [29-31]. Some studies found that steam activation generated activated carbons with narrower pore size distribution and larger surface area and total pore volume than CO₂ activation [23,27,32], which was believed to be caused by higher activation rates in char-steam [20,33,34]. However, the activation rate of char also heavily depends on the activation temperature and concentration of the activation agent, regardless of which activation agent is used [35-38]. So far, very few literature reports have examined the effects of the concentration of the activation agent on the development of pore structure during the activation process, although it has been demonstrated to play a significant role in activation [35,37]. Literature reports on the effect of the concentration of activation agent are relatively few. Therefore, further detailed research is required to better understand the effect of steam and CO₂ on the properties and pore characterisation of the activated carbon from spent tyre pyrolysis chars. This contribution specifically examined the effect of the activation conditions, including temperature, time and the activation agent and its concentration, on the development of pores in activated carbon from spent tyre pyrolysis char. Converting spent tyre pyrolysis char to activated carbon will not only minimise the environmental and health problems associated with spent tyre accumulation but also provide a cleaner, sustainable and more cost effective method of activated carbon production. As the structure of the pores is considered one of the most important aspects of activated carbon utilisation, it is

imperative to understand the effect of activation conditions on the development of pores during the activation of spent tyre pyrolysis char.

In this study, a spent tyre pyrolysis char produced from an industrial kiln reactor was activated in a fixed-bed reactor using steam and compared to the activation of the same char in CO₂ [39]. Meanwhile, the effects of temperature (750 to 1050 °C), activation agent concentration (33.3 to 66.7 vol% of CO₂ or steam using N₂ as a carrier gas) and activation time (0.5 to 4 h for steam activation, 1 to 6 h for CO₂ activation) on the carbon conversion, reaction rate, BET surface area, and the development of micropore, mesopore structure of the activated chars were investigated and discussed.

2. Experimental

2.1 Materials

A pyrolysis char obtained in an industrial scale retort process operating in the absence of air at 550 °C was used for the activation experiments. Considering that the operating pyrolysis conditions in industrial-scale processes can have a significant effect on the properties of the pyrolysis char, the as-received sample was ground and sieved to a particle size fraction <150 µm and thermally treated in N₂ at 550 °C for 1h in a fixed-bed reactor with a heating rate of 5 °C min⁻¹. The unified pyrolysis char was then used for the experimental work.

2.2 Experimental Equipment and Facilities

Table 1 Activation conditions in the experiments

	Steam activation	CO ₂ activation
Temperature (°C)	750, 850, 950, 1050	
Activation time (h)	0.5, 1, 2, 3, 4	1, 2, 3, 6
Concentration	33.3, 50.0 and 66.7 vol% in N ₂	

Activation experiments were carried out in a vertical fixed-bed reactor (Fig. 1) at set reaction temperatures (750 – 1050 °C), times (0.5 – 4 h for steam activation and 1 – 6 h for CO₂ activation), and gas environments (CO₂ or steam at 33.3, 50.0 and 66.7 vol% in N₂), summarised in Table 1.

Fig. 1. Schematic diagram of the experimental activation system

The flow of N₂ and CO₂ was controlled by a rotameter and the flow of steam was controllable by an HPLC pump injecting ultra-pure water through a preheater set at 200 °C during steam activation. To ensure stable temperature control, a thermocouple protected by a quartz sheath was placed in the reactor bed. Approximately 5g of unified pyrolysis char was loaded into a quartz sample holder and heated to the desired temperature, during which the atmosphere was kept inert by continuously flowing nitrogen (N₂) through the reactor at 150 mL min⁻¹. Once the reactor reached the desired temperature, the gas was switched to the activation gas, a mixture of CO₂ or steam and N₂, at a flow rate of 150 mL min⁻¹. A cold trap was placed at the outlet of the reactor to collect condensates for steam activation. Once the set duration was reached the gas was switched to N₂ and the reactor cooled to room temperature. After activation, the mass of the activated char was measured and the mass loss was determined. The carbon conversion (X) and reaction rate (R) [40] were calculated using the following equations:

$$X = \frac{m_1 - m_{vol} - m_2}{m_1 - m_{vol} - m_{ash}} \quad (1)$$

$$R = \frac{X}{t} \quad (2)$$

where m_1 (g) is the mass of loaded unified pyrolysis char, m_2 (g) is the mass of obtained activated char sample after activation, m_{vol} (g) is the volatile matter of the unified pyrolysis char, and m_{ash} (g) is the ash of unified pyrolysis char, and t (s) is the activation time. Note that the volatile matter of the unified pyrolysis char (m_{vol} (g)) was determined using a muffle furnace following the ASTM standard D5832-98 at 950 °C. Although the temperature has an impact on the content of volatile matter, it was found that the volatile content in N₂ gasification at temperatures between 750 – 1050 °C showed marginal difference (3 – 5 wt.%), comparable to that of the unified pyrolysis char (4.5 wt.%). Therefore, the content of the volatile matter of the unified pyrolysis char was used for the calculation of carbon conversion, which did not affect the overall trend of carbon conversion.

2.3 Analysis and Characterisation

Table 2 Proximate and ultimate analysis of unified pyrolysis char

Proximate analysis (wt.%)		Ultimate analysis (wt.%)	
Moisture	1.12	C	78.22
Volatile matter	4.46	H	0.55
Ash	16.66	N	1.61
Fixed carbon	77.76	S	1.93

The proximate analysis of the unified pyrolysis char was performed using a muffle furnace following the ASTM standards D2867-17 for moisture, D5832-98 for volatile matter and D2866-11 for the ash content, and the fixed carbon was calculated by difference. The ultimate analysis was conducted using a ThermoFisher Scientific FlashSmartTM CHNS/O elemental analyser. The proximate and ultimate analysis results of the unified pyrolysis char are shown in Table 2. The samples of activated char (0.2 g) were degassed at 200 °C overnight for nitrogen adsorption and then characterised for surface area by the Brunauer-Emmett-Teller (BET) and pore size distribution by the Barrett-Joyner-Halenda (BJH) at -196°C using Micromeritics TriStar II [41]. The total pore volume was defined by the volume of nitrogen molecule adsorbed at a relative pressure $P/P_0 = 0.97$. The micropore surface area and micropore volume were calculated by the t-plot method [22,42]. The mesopore volume and mesopore surface area were calculated by BJH method [43]. The average micropore size and average

mesopore size were calculated by $4V/A$, where V is the pore volume and A is the surface area. The surface morphology of raw and activated char samples were examined using on a Zeiss 1555 Variable Pressure Field Emission Scanning Electron Microscope (VP-FESEM) mounted with an in-lens detector operating at 3 kV and a 30 μm aperture at a ~ 5 mm working distance. The samples for the VP-FESEM were all coated with platinum to avoid activated chars charging.

3. Results and Discussion

Fig. 2. Carbon conversion of spent tyre pyrolysis char under different conditions by CO_2 [39] and steam activation: effect of (a) 33.3 vol% activation agent; (b) 50.0 vol% activation agent; (c) 66.7 vol% activation agent. N_2 was used as the carrier gas

Fig. 2 shows the carbon conversion during the CO_2 and steam activation, respectively, of the unified pyrolysis char under different conditions. The results were extremely repeatable, with the average of three repeats under each condition producing a standard deviation within ± 0.02 . The results show an

increase in carbon conversion with increasing activation temperature, activation time and activation agent concentration under the conditions tested. The carbon conversion of steam-activated char was higher than those activated with CO₂ under the same test conditions, which is more apparent at higher temperatures. For example, at 950 °C and 1050 °C the carbon conversion of the steam-activated char was *ca.* 30 – 70% higher than the CO₂-activated char. It is known that steam is more reactive than CO₂ towards carbon [44-46], suggesting that CO₂ activation requires longer activation times than steam activation to achieve the same level of conversion. The reaction rates also increased with increasing activation temperature and concentration of the activation agents (Fig. 3). Note that the reaction rate was not significantly affected by the duration of the activation.

Fig. 3. Reaction rate of spent tyre pyrolysis chars at different conditions by CO₂ and steam activation: effect of: (a) 33.3 vol% activation agent; (b) 50.0 vol% activation agent; (c) 66.7 vol% activation agent. N₂ was used as the carrier gas

Fig. 4. N_2 adsorption and desorption isotherms of spent tyre pyrolysis chars at different conditions by CO_2 and steam activation: (a) activation agent concentration at 50.0 vol% and activation time at 3 h, (b) activation agent concentration at 50.0 vol% and activation temperature at 950 °C, (c) activation time at 3 h and activation temperature at 950 °C, (d) activation time at 3 h and activation temperature at 1050 °C

The pore structure and adsorption capacity are amongst the most important characteristics of activated chars during utilisation. The size and distribution of pores were determined by examining the N_2 adsorption and desorption isotherm curves of activated chars produced under different conditions by CO_2 and steam activation, shown in Fig. 4. The activated chars produced by steam and CO_2 in this study all exhibit a type IV curve (IUPAC classification) [47], defined by a sharp increase in N_2 adsorption at low relative pressure ($P/P_0 < 0.1$) and a hysteresis loop at medium relative pressure ($0.4 < P/P_0 < 1.0$). Type IV curves are characteristic of materials with high mesoporosity

relative to microporosity [18-20,40]. The hysteresis loop becomes wider as the activation temperature and activation agent concentration increased (Fig. 4a and d), indicating that more mesopores were generated at higher temperature and activation agent concentration [48]. The sharp increase in N_2 adsorption at a relative pressure (P/P_0) close to 1.0 in all activated chars indicates the presence of large mesopores (> 20 nm) or macropores [49]. Comparing the steam-activated chars and CO_2 -activated chars, steam-activated char exhibited higher N_2 adsorption than CO_2 -activated chars under the same activation conditions and thus has higher total porosity.

Fig. 5. Pore size distributions of CO_2 and steam activated spent tyre pyrolysis chars at: (a) activation agent concentration at 50.0 vol% and activation time at 3 h, (b) activation agent concentration at 50.0 vol% and activation temperature at 950 °C, (c) activation time at 3 h and activation temperature at 950 °C, and (d) activation time at 3 h and activation temperature at 1050 °C

In order to confirm the type of porosity (micro-, meso- and macropore), Fig. 5 shows the pore size distributions of the unified pyrolysis chars activated by CO₂ and steam activation under different conditions. The pore size ranged from 0 to 102 nm for all the samples, with the bulk of the pores less than 25 nm, suggesting the development of more micropores (0 – 2 nm) and mesopores (2 – 50 nm) than macropores (50 – 100 nm). From 750 to 950 °C pore size distributions were similar but shifted to larger pore size at 1050 °C (Fig. 5a). The duration of the activation also did not have a substantial effect on pore size distribution for either steam or CO₂-activated chars if the temperature and gas environment were the same (950 °C, 50.0 vol% agent concentration; Fig. 5b). The activation agent concentration had a negligible effect on the pore size distribution at 950 °C (Fig. 5c), while showed a significant impact at 1050 °C (Fig. 5d). The pore size distribution shifted to larger size with the increase of activation agent concentration for both CO₂- and steam-activated chars at 1050 °C, indicating that the generation of mesopores was enhanced with increasing the activation agent concentration at 1050 °C, as discussed below. The increase in mesoporosity at higher activation agent concentration is consistent with the observations shown in Fig. 4d, where pore size was significantly enlarged at 1050 °C.

Fig. 6. BET surface area of the activated chars as a function of the carbon conversion

To understand the function between BET surface area and carbon conversion, Fig. 6 shows the BET surface area of the activated char samples at different carbon conversions. For both CO₂ and steam

activation, the BET surface area of the activated char initially increased, reaching a maximum for both CO₂ (434.5 m²g⁻¹ at 0.5 conversion) and steam (666.6 m²g⁻¹ at 0.6 conversion), and then gradually decreased. This overall trend of initially increasing then decreasing BET surface area with increasing carbon conversion has also been described in studies that examine the activation of other carbonaceous materials [50,51]. As the carbonisation reaction proceeds at the early stage of activation, both new micropores and mesopores were generated and increased the BET surface area. The decrease of the BET surface area after carbon conversion reaches 0.5 for CO₂ activation and 0.6 for steam activation implies consumption of the char and the formation of larger pores. The evolution of the BET surface areas of the activated carbon as a function of carbon conversion was very similar under 750 – 950 °C, which suggests that while temperature mainly affected the reaction rate, it had little impact on the development of the porous structure. However, at a higher temperature (1050 °C) BET surface areas were lower than that at lower temperatures (750 – 950 °C) due to the higher conversion, which is more pronounced for the steam activation. The smaller BET surface areas at 1050 °C may be due to the increase in mesopores relative to micropores as the carbon conversion increases, which is consistent with the pore size distribution as shown in Fig. 5 [32]. Steam-activated char also had 20 – 50% higher BET surface areas than those activated with CO₂ at the same carbon conversion, due to the higher reactivity of steam over CO₂ (Fig. 3).

Fig. 7 shows the total pore volumes of the activated chars at different carbon conversion. The evolution of the total pore volume as a function of carbon conversion was similar under different temperatures, for both CO₂ and steam activation. With the consumption of carbon, total pore volume increased with the carbon conversion due to the generation and enlargement of existing pores [51]. As observed in Fig. 7, steam-activated chars displayed higher total pore volumes than CO₂-activated chars, which was more noticeable when the carbon conversion was higher than 0.3. This is mainly because the steam activation produced more mesopores than CO₂ activation, which contributes largely to the total pore volume [33,39].

Fig. 7. The total pore volume of prepared activated chars at different carbon conversion

Fig. 8. The micropore volume (a) and mesopore volume (b) of prepared activated chars at different carbon conversion

The micropore and mesopore volume are shown in Fig. 8. It can be seen that the micropore volume of the activated char increased first, and then decreased when the carbon conversion level was higher than *ca.* 0.30 for both steam and CO₂ activation. The decrease in the micropore volume after a certain level of carbon conversion was due to the widening of micropores and the collapse of walls between pores as the carbon is consumed by activation reactions of the char with steam or CO₂. This is supported by an accompanying increase in mesopore volume. Activation at 1050 °C resulted in consistently smaller micropore volumes than the lower temperature range (750 – 950 °C) at the

similar conversion for both steam and CO₂ activation because of pore widening, merging and collapsing [23,34,52]. This further explains why the BET surface areas at 1050 °C were smaller than those at temperatures of 750 – 950 °C (Fig.6). Steam-activated chars showed higher micropore volume to CO₂-activated chars at low carbon conversion, suggesting that the development of micropores for steam activation was faster than CO₂ at the same temperature. The micropore volume of steam activated chars was lower than that of CO₂ activated chars at high carbon conversion, particularly at higher temperatures, which was due to the greater reactivity of steam with carbon at higher temperatures, as shown in Fig. 8 (a). Steam-activated chars had slightly higher mesopore volumes than the CO₂-activated chars until *ca.* 0.30 carbon conversion, above which mesopore volumes were notably higher for steam-activated char. Given the mesopore volume (Fig. 8b) against the total pore volume (Fig. 7), the total pore volume is largely attributable to mesopores regardless of the activation agent.

Fig. 9. The average pore size of prepared activated chars at different carbon conversion

Fig. 9 shows the average micropore size and average mesopores size of the activated chars at different carbon conversion level. The range of average micropore size was from 1.3 nm to 1.9 nm and the average mesopore size was between 4 nm to 16 nm. The average micropore size presents a consistent size around 1.8 nm until *ca.* 0.30 carbon conversion, above which it decreased. This agrees with the decreased micropore volume after *ca.* 0.30 carbon conversion (Fig. 8). The average mesopore size decreased until *ca.* 0.50 carbon conversion and then increased afterwards, which is due to the dominance of micropores during the first stage of activation and the widening of micropores to produce mesopores at a later stage. The average micropore and mesopore sizes of the steam-activated chars are initially similar to the CO₂-activated chars, but the average sizes decrease when the carbon conversion is higher than *ca.* 0.30 for micropores and *ca.* 0.20 for mesopores.

Fig. 10. SEM of the activated chars: (a) unified spent tyre pyrolysis char under N₂, 550 °C, 1h; steam-activated chars at the carbon conversion of (b) 0.1 (850 °C, 2 h, 33.3 vol% of steam) and (c) 0.5 (950 °C, 4 h, 50.0 vol% of steam); and CO₂-activated chars at the conversion of (d) 0.1 (950 °C, 1 h, 66.7 vol% of CO₂) and (e) 0.5 (950 °C, 6 h, 66.7 vol% of CO₂). N₂ was used as the carrier gas

The SEM images of the spent tyre unified pyrolysis char and activated chars produced under various conditions are shown in Fig. 10 to further understand the morphological development of the surface during activation. The spent tyre unified pyrolysis char and activated chars showed a similar carbon-black like surface morphology with disordered carbon particles forming aggregates. Nonetheless, there is a significant difference in surface structures among activated chars with different carbon conversions. It was observed that the activated chars, produced under both steam and CO₂, have larger pores as carbon conversion increased. Under the conditions studied, the reaction agent (either steam or CO₂) penetrates the pores and reacts with char on the surface, which gives rise to the enlargement of pores and an increase of meso- and macropores at the expense of micropores. These phenomena are in agreement with the observations of the BET surface area and pore volume discussed previously (Fig. 6 and 8). The steam-activated chars showed more and larger pores than CO₂-activated chars at the same carbon conversion level. This was due to higher reactivity of steam under the conditions studied which gives rise to a greater pore enlargement.

4. Conclusions

It was found that higher activation temperature, longer activation time and higher activation agent concentration led to higher carbon conversions. The carbon conversion of the steam activation was *ca.* 30 – 70% higher than CO₂ under the same activation condition of temperature, activation time and agent concentration. The generation of micropores occurred at the early stage of the activation for both steam and CO₂ activation and micropore volume increased linearly with the carbon conversion. However, when the carbon conversion was higher than *ca.* 0.30, mesopores were dominant in the activated chars and increased almost linearly with carbon conversion. As the carbon conversion increased, the BET surface area increased almost linearly first and then decreased, reaching a maximum for CO₂ (434.5 m²g⁻¹) and steam (666.6 m²g⁻¹) under the conditions studied. The pore size distributions were similar at 750 – 950 °C but shifted to larger pore sizes at 1050 °C, which was more pronounced for the steam activation. Steam-activated chars displayed higher BET

336 surface areas, microporosity and mesoporosity than CO₂-activated chars.

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