

# PRODUCTION OF ACTIVATED CARBON FROM BIOCHARS OF MALLEE BIOMASS PYROLYSIS

Yanwu Yang<sup>1</sup>, H- Ming Ang<sup>1</sup>, Hongwei Wu<sup>\*1,2</sup>

1 Department of Chemical Engineering, Curtin University, GPO Box U1987, Perth, WA 6845, Australia

2 Fuels and Energy Technology Institute, Curtin University, GPO Box U1987, Perth WA 6845, Australia; \*Email: h.wu@curtin.edu.au

## ABSTRACT

Biochar was prepared from low-temperature pyrolysis of mallee biomass and then activated using steam for activated carbon production. The results show that via steam activation, production of activated carbon with a high surface area can be achieved at a low conversion ~5%. During steam activation, the biochar specific reactivity initially decreases with conversions. Analysis of the gas product also shows that during steam activation, the primary product is CO and the formation of CO<sub>2</sub> is more likely from water-gas-shift reaction.

Key words: Activated carbon, steam gasification, specific reactivity

## 1 INTRODUCTION

Activated carbon (AC) is widely applied in many industrial applications such as gas purification and water treatment. Recent statistics (Group, 2008) forecast that the world consumption of virgin activated carbon expand 5.2% per year through 2012 to 1.15 million metric tons. The most common feedstock (Nowicki, 2008, Srinivasakannan, 2004, Kawano, 2008, Bagheri, 2009) for AC preparation is plants (e.g. wood, nut-core), coal (e.g. anthracite), petroleum (petroleum asphalt), waste materials (e.g. sewage sludge, used tyre) and plastics materials.

In Western Australia, mallee planting is a key strategy for managing dry land salinity and preventing the loss of fertile agriculture land (Bartle). Therefore, it does not compete with food production and can be regarded as by-product of dry salinity management so that complement food production (Ridley and Pannell, 2005). Mallee biomass production is of large scale (Bartle, 2007) and has small energy and carbon footprints (Wu, 2008, Yu, 2009) so that it is an ideal secondary generation feedstock for the production of energy, chemicals and other value-added products such as AC.

However, little work has been done so far on AC production from mallee biomass. Tancredi (Tancredi, 1996) used *Eucalyptus grandis* to prepare AC via steam activation but applied extensive carbonization at the pyrolysis temperature (2 hours) and a high burn-off (>25%) during steam activation. Arriagada (Arriagada, 1994) compared the performance of AC production via CO<sub>2</sub> and steam activation. However, little is known

on the structure development of AC during mallee pyrolysis and activation, yet such data are essential to practical applications.

Therefore, this study aims to investigate AC production at short low-temperature carbonization time and minimal conversion of the char for AC preparation during steam activation. To gain a fundamental understanding on the mechanism of steam activation, this study also analyses the gas products during the course of steam activation.

## 2 EXPERIMENTAL SECTION

The mallee wood sample in this study was prepared and used in a previous study(Yip et al., 2010) Briefly, green mallee trees (*E.loxophleba lissophloia*) were harvested from farms in Narrogin, Western Australia and then separated into leaf, wood and bark. This study only used mallee wood which was dried in a large lab oven at 40 °C, cut then sieved into the size fraction of 150~250 µm. The properties of the mallee wood sample are listed in Table 1. The contents of alkali and alkaline earth metallic species (AAEM) like Na, K, Mg, and Ca were tested by Dionex ICS-3000 ion chromatography. Other inorganic species of sample like Al, P, and Si were determined by an inductively coupled plasma-atomic emission spectroscopy (ICP-AES).The detailed procedure of inorganic species testing can be found elsewhere (Gao and Wu).

Table1: Properties of mallee wood used in the present study

Proximate analysis, wt% db				Ultimate analysis, wt% daf					
Moisture, wt% ad	Ash, wt%db	Volatile Matter, wt%db	Fixed Carbon, wt%db	C	H	N	S	O (by difference )	
5.3	0.4	80.7	18.9	49.0	6.7	0.19	0.02	44.1	
Inorganic species (wt% db)									
Element	Na	K	Mg	Ca	Cl	P	N	Al	Si
(wt%)	0.0212	0.0744	0.0364	0.1236	0.0323	0.0182	0.191	0.0025	0.0026

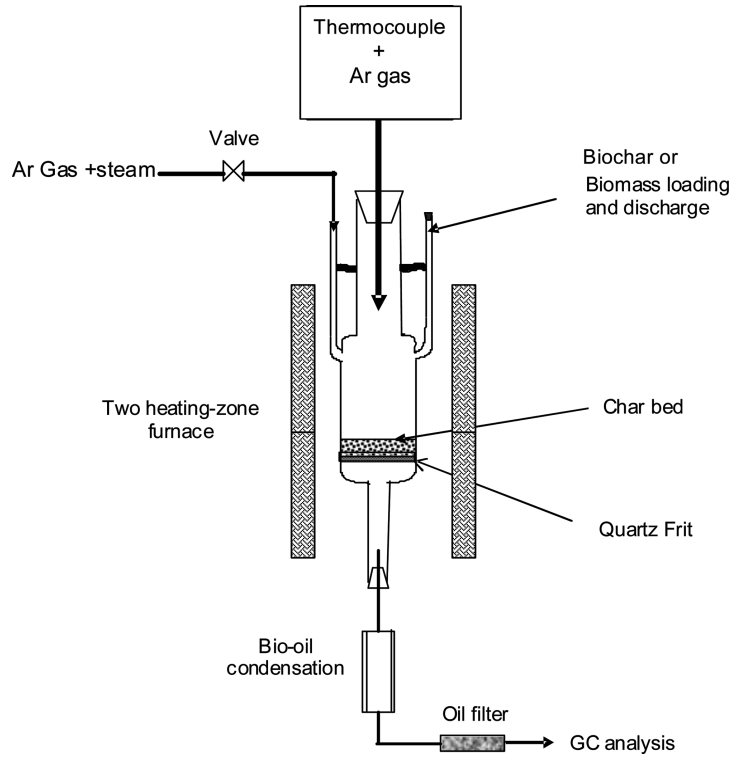


Figure 1: Steam gasification system used in present experiment(Yip et al., 2010)

A fixed-bed reactor with 40mm diameter of quartz frit shown in Figure 1 was used in present study. Biochar samples were prepared from mallee wood using a fixed-bed reactor under slow pyrolysis at 540 °C and 750 °C with 10 K/min and 15 mins holding time. Activation of the biochar samples were carried out in the same reactor via steam activation. In each steam gasification experiment 0.1 g biochar sample was used. As for biochar produced at 540°C, after biochar preparation is completed, the reactor was then heated up to 750 °C for steam activation via replacing argon with a steam-argon mixture. As for biochar obtained at 750 °C, steam was switched on immediately after pyrolysis. After experiments were finished, reactor was lift out of furnace immediately and cooling down naturally with inert gas going through. The total gas flow rate was controlled at 3 L/min by mass flow controls and the steam concentration is 8.2%vol. The steam was produced from evaporation of Milli-Q water pumped by an HPLC pump (Alltech Model 626). The relative standard deviation of AC yield was found in the range of 2~3%. Preliminary experiments were carried out to carefully choose conditions under which the reactor can be regarded as a differential reactor. The product gas ( $H_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ) were analysed by two PERKIN-Elmer gas chromatographs (GCs). The biochar specific reactivity ( $R$ ) during steam activation can be calculated by:

$$R = -\frac{1}{C} \frac{dC}{dt}$$

Where,  $C$  is the instantaneous amount (mol) of carbon remaining in the reacting biochar at any time  $t$ . The total carbon of a biochar sample was determined by the combustion of biochar then analysing the  $CO_2$  and  $CO$  in the gas.  $N_2$  adsorption-desorption isotherm at 77K of activated carbon was carried out using a Quantachrome Autosorb AS-1 instrument. Apparent surface area (SBET  $m^2/g$ ) was calculated by Stephen Brunauer, Paul Hugh Emmett, and Edward Teller equation (BET). Pore volume of micropore

(cc/g) and average half pore width (A) was calculated by Dubbin-Radushkevich (DR) plot. Total volume was obtained at around  $p/p_0=0.9998$  (cc/g). All these data analysis were completed by ASWIN software. The relative standard deviations of SBET, total volume and AHPW are 0.8~2.2%, 0.8~2.1% and 1.4~3.2% respectively.

## RESULTS AND DISCUSSION

### AC characteristics under different temperature

Figure 1 presents the  $N_2$  adsorption-desorption isotherm of the biochar produced from mallee wood pyrolysis at 540 °C and the AC produced from the biochar after steam activation at 750 °C. It should be noted that there is only 5 mins activation. Figure 1 clearly shows that the adsorption capability has been increased substantially after steam activation of the biochar. The adsorption capacity of AC increases to be >100 cc/g, suggesting that the AC has abundant micropores. It is also clearly seen that hysteresis loop appears after steam activation, indicating the AC also has abundant mesopores. As is shown in Table 2, the steam activation process has substantially increased the BET surface of the sample from 19 m<sup>2</sup>/g of the biochar to 435 m<sup>2</sup>/g of the AC after activation.

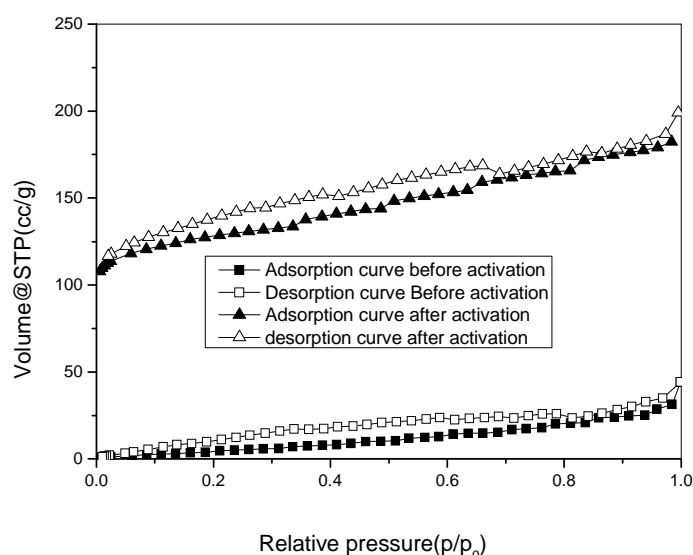


Figure 2:  $N_2$  adsorption-desorption isotherm at 77K of biochar and AC produced from steam activation of the biochar

Table 2: Characteristics of raw biochar and AC prepared from steam activation of the biochar

Samples	SBET (m <sup>2</sup> /g)	DR		Total volume (cc/g)
		V <sub>d</sub> (cc/g)	AHPW(A)	
Biochar produced from mallee wood (540 °C; 10 K/min; 15 mins holding)	19	0.006	22.81	0.0685
Activated Carbon (750 °C; 5 min steam activation)	435	0.193	6.475	0.193

### Evolution of AC Structure during Biochar Steam Activation

Practically, a minimal conversion of the biochar is desired during steam activation in order to maximize the productivity of AC. A series of experiments are then carried out to study the properties of AC produced from biochar produced at steam activation with various conversions 2~ 15%. Pyrolysis temperature and steam gasification temperature are the same as 750 °C. Figures 2 and 3 present the adsorption-desorption isotherm and the BET surface area of various AC produced, respectively. Figure 3 clearly shows that the adsorption curves of all ACs are of type II according to the classification by Brunauer, Deming, Deming and Teller (BDDT) (S. Brunauer, 1940) suggesting that the ACs consist of a wide range of micro-, meso- and macro-pores, as also evident by the data listed in Table 3.

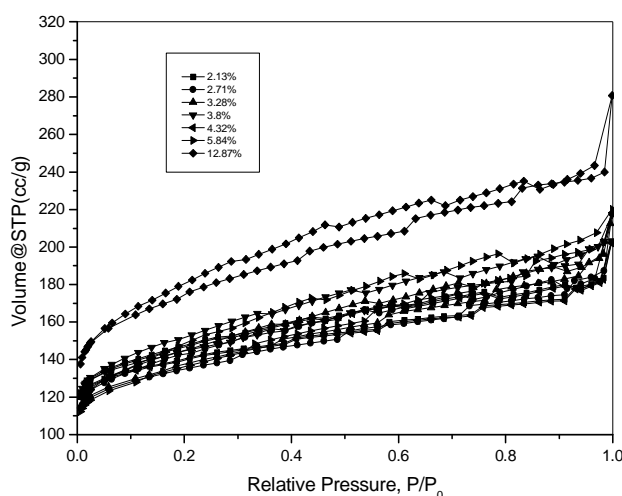


Figure 3: N<sub>2</sub> adsorption-desorption isotherm at 77K of AC produced from biochar via steam activation with various conversion

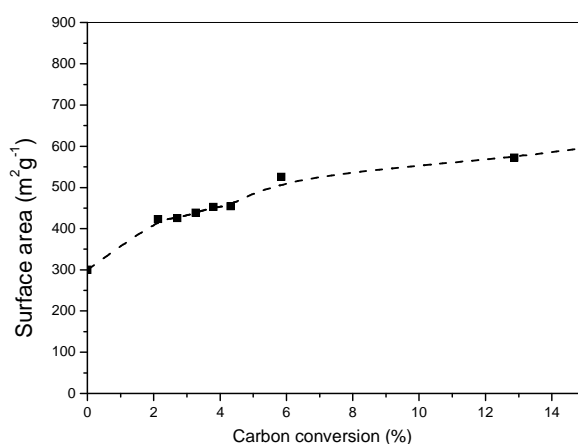


Figure 4: Surface areas as the function of carbon conversion during the course of steam gasification

It is also clear that the adsorption ability generally increases with biochar conversion but only in the early stage up to ~5% carbon conversion. Longer time of activation leads to

only limited further increase in opening more pores and generating more surface area within the biochar, as shown in Table 3. Therefore, the data clearly suggest that only a short period of steam activation is needed to produce AC from the biochar. In this case, a very low carbon conversion of ~5% is required to produce ACs with an SBET surface area high up to 526m<sup>2</sup>/g and a maximised AC yield as 12.1% db from biomass. This is desirable for practical applications.

Table 3: Characteristics of AC produced from steam activation of biochar

Carbon Conversion (%)	SBET (m <sup>2</sup> /g)	DR		Total volume (cc/g)	AC yield (%) (dry basis)
		Vd (cc/g)	AHPW( A)		
2.13	423	0.211	5.811	0.3142	
2.71	425	0.201	6.042	0.3367	
3.28	439	0.203	6.089	0.3287	15.3
3.8	452	0.217	6.046	0.3364	14.1
4.32	454	0.21	5.811	0.3126	
5.54	526	0.236	7.533	0.4155	12.1
12.87	572	0.264	7.468	0.4342	11.4

### Evolution of biochar reactivity and Instantaneous gas products during steam activation

Figure 5a presents biochar specific reactivity as a function of conversion during steam activation. It can be clearly seen that the reactivity of biochar decreases as carbon conversion increases up to 10%. It should be noted that the activation reactions take place under chemical-reaction-controlled regime, where mass transport effects are minimized. As evidenced in Figure 5b, steam consumption is small so that the steam partial pressure is kept constant. Therefore, a substantial decrease in biochar specific reactivity during the early conversion of biochar during steam activation (see Figure 4a) suggests a decrease in the density of reactive sites within the biochar. The exact reasons are unknown at present, although there are two possible reasons. One is the removal of a proportion of very reactive carbon materials in the biochar; the other is a change in the form of inherent catalytic species within the biochar that leads to the deactivation of catalytic active sites.

Efforts were then made to study the gas evolution during biochar steam activation, with the specific gas formation rates being presented in Figure 6. It is clearly seen in the figure that the formation rates of H<sub>2</sub>, CO and CO<sub>2</sub> decreases with conversion initially, in consistence with the reactivity data presented in Figure 5a. Furthermore, it should be noted that the formation of CH<sub>4</sub> is thermodynamically negligible under the reaction conditions(Walker Jr et al., 1959) Therefore, the overall reaction can be written as:



Where X = CO<sub>2</sub>/CO is determined by was-gas-shift reaction



$$K_{eq} = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{H_2O}}$$

Where,  $p$  is partial pressure. So the ratio of  $H_2/CO$  and  $CO_2/CO$  at equilibrium can be calculated by equation  $\frac{p_{CO_2}}{p_{CO}} = K_{eq} \frac{p_{H_2O}}{p_{H_2}}$  and  $\frac{p_{H_2}}{p_{CO}} = K_{eq} \frac{p_{H_2O}}{p_{CO_2}}$ . (Yip et al., 2010)

Figure 7 presents the actual ratios of  $H_2/CO$  and  $CO_2/CO$  based on the experimental data, benchmarking against the equilibrium ratios calculated under the same steam activation conditions. It is obvious that the actual ratio of  $CO_2/CO$  is lower than the equilibrium values, suggesting that during steam activation, the primary product is  $CO$  and the formation of  $CO_2$  is more likely from water-gas-shift reaction. This is clearly shown in Figure 8 in which  $H_2/(CO+CO_2)$  ratio is  $\sim 1.5$  at various conversions during the early stage of steam activation.

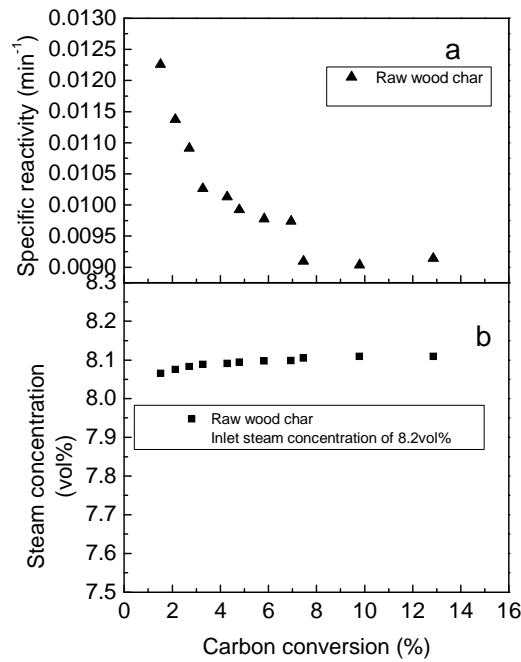


Figure 5: Biochar specific reactivity and steam concentration in the reactor as a function of carbon conversion during biochar steam activation (temperature: 750 °C; inlet steam concentration: 8.2% vol)

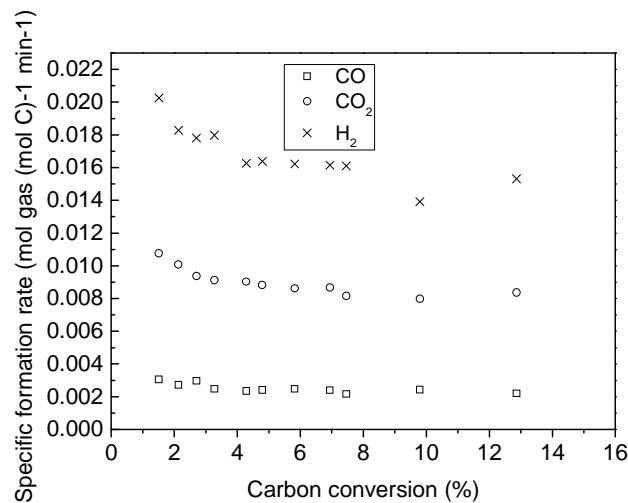
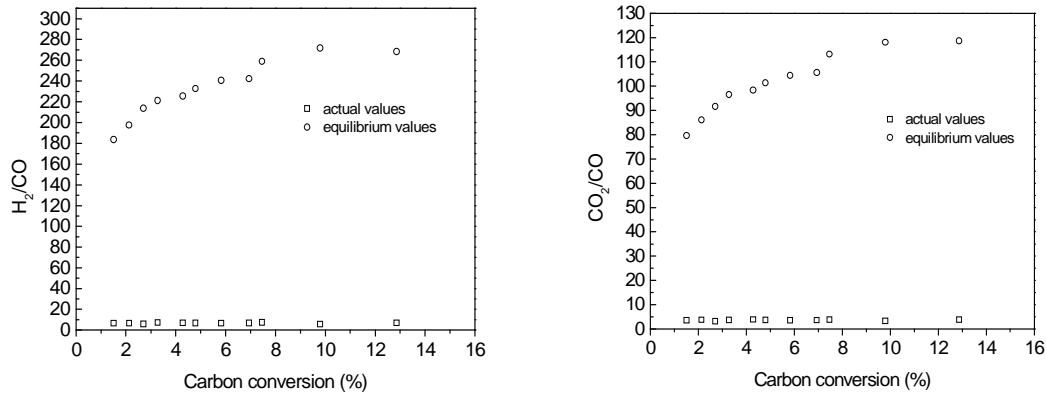
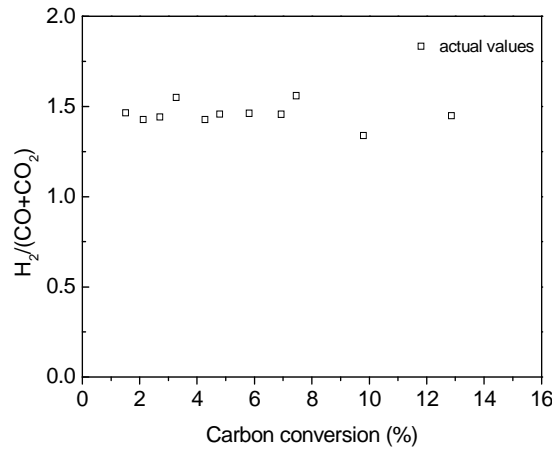


Figure 6: Specific formation rates of CO, CO<sub>2</sub>, and H<sub>2</sub> during biochar steam activationFigure 7: Actual values and theoretical equilibrium values of H<sub>2</sub>/CO and CO<sub>2</sub>/CO as function of carbon conversion during steam activationFigure 8: Actual values of H<sub>2</sub>/ (CO+ CO<sub>2</sub>) vs. carbon conversion during steam activation

## CONCLUSION

In this study, biochar was prepared at slow pyrolysis of mallee wood at two temperatures 540 °C and 750°C then steam activated at the same temperature 750 °C for activated carbon production. The results demonstrate that via steam activation, production of activated carbon with surface area 435 m<sup>2</sup>/g and 526m<sup>2</sup>/g (low conversion ~5%) can be achieved within 5 minutes activation. During steam activation, the biochar specific reactivity initially decreases with conversions. It is also shown that during biochar steam activation, the primary gaseous product is CO and the formation of CO<sub>2</sub> is more likely from water-gas-shift reaction.



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**BRIEF BIOGRAPHY OF PRESENTER**

Yanwu Yang received his M.E degree from China University of Mining Technology (CUMT) in 2004. She then became a lecturer at CUMT for 5 years till 2009 when she started her PhD study in Chemical Engineering of Curtin University. Her research interests include biomass utilisation, waste water treatment and reuse.