

HIGH YIELD CARBONS FROM EUCALYPTUS WOOD AT ELEVATED PRESSURES

G. Bezzon, C. A. Luengo

*Group Alternative Fuels, University of Campinas
Cx. P. 6165, Campinas, SP, 13083-970, Brazil*

X. Dai, and M. J. Antal, Jr.

*Hawaii Natural Energy Institute, University of Hawaii at Manoa
Homes Hall 246 - 2540 Dole St., Honolulu, HI, 96822, USA*

Introduction

The controlled pyrolysis of biomass at elevated pressures results in high yields of a good quality charcoal with a cycle of two hours or less and a reduced energy consumption. Due to the high yields, this process minimizes gases and liquids production, diminishing the pollutants generated by the conventional biomass pyrolysis [1-3]. Further oxidation under controlled conditions, can activate the charcoal obtained in the pyrolysis step, increasing its internal surface area and pore volume. Depending on the burn-off and the reaction time, high yields of activated carbon in a short period can be achieved. For a good pore development the oxygen diffusion and the reaction must have compatible rates otherwise, only the external surface is consumed and the pores are not formed.

Experimental

The pyrolysis of Eucalyptus wood at elevated pressures and the oxidation of the remaining charcoal were studied using a pressurized batch reactor designed to operate under pressures up to 3 MPa and temperatures up to 600°C. This reactor was configured to convert up to 2 kg of biomass to high yield charcoal and subsequently conduct a partial oxidation of the remaining charcoal. A detailed description of this equipment is reported elsewhere [4]. The pyrolysis occurs under constant pressure in a self-generated gaseous atmosphere. For the measurement and temperature control, thermocouples connected to a computer and a temperature controller were used. The pyrolysis gases and liquids are burnt in an atmospheric flare and a dry charcoal is obtained in the end of the experiment. For the oxidation step, a mixture of air (oxygen) with superheated steam or nitrogen (N₂) is used as oxidizing agent. Since the reaction of oxygen with carbon is highly exothermic, the steam (or N₂) is used as a thermal ballast and dilutant, decreasing the

oxygen partial pressure in the mixture and keeping a constant temperature in the charcoal bed.

To evaluate the reaction and diffusion rates, some thermogravimetric analysis of the Eucalyptus charcoal oxidation and the determination of the charcoal pore distribution using a Hg porosimeter were conducted. Through the devoping of a numerical model based on the theory of heterogeneous catalysis, an estimate of the Thiele Modulus and effectiveness factor for the charcoal particle was calculated [5]. The main parameters considered in the model, which directly affect the whole process are temperature, oxygen partial pressure, total pressure, burn-off, particle size and shape.

Results and Discussion

The pyrolysis of 100g of Eucalyptus wood (6 mm cubic particles) with 13% moisture (dry basis) was conducted at 1 MPa and final temperature 450°C. The pyrolysis yield was 42% and the charcoal presented a high heating value of 30 MJ/kg, 77% of fixed carbon content, BET surface area of 15 m²/g and iodine number less than 50. The pyrolysis step was repeated with a good reproducibility before each oxidation experiment. After the pyrolysis, the reactor was set to the oxidation temperature and the mixture of air and N₂ (or steam) was flushed using a mass flow controller. In some experiments, two different particle sizes were used: small (2 mm) and large (6 mm). The iodine number and BET surface area of the final carbon were measured. Table 1 describes the oxidation parameters and results.

We can note that the effectiveness factor for larger particles is relatively low, decreasing with the increase of temperature. For the smaller particles, the effectiveness factor becomes higher and the diffusion through the particle is more efficient. Despite the effectiveness factor decreases with temperature, the iodine number and BET surface area increase. An explanation for this observation is the stability of some oxygen complexes resulting from the oxidation reaction.

Experiment #	1	2	3	4	5	6	7	8
Dilutant	Steam	Steam	N ₂	N ₂	N ₂	N ₂	Steam	Steam
Average Temp. (°C)	378	382	401	450	450	424	442	410
Pressure (MPa)	1	0.3	0.1	0.1	0.1	0.1	0.5	0.5
O ₂ Part. Press. (kPa)	21	7.0	4.2	4.2	4.2	4.2	6.6	6.5
Activation Time (min)	80	120	80	60	33	45	50	90
Burn-off (%)	48	50	28	44	24	32	43	45
Overall yield (%)	22	21	30	24	32	29	24	23
Iodine Number *	182	231	260	269	228/191	265/255	264/194	261/238
BET Surf. Area (m ² /g)*	108	143	237	332	235/208	249/204	285/186	270/155
Thiele Modulus*	4.1	4.6	6.6	9.7	3.3/9.8	3.2/9.5	2.9/8.7	2.2/6.5
Effectiveness Factor*	0.55	0.51	0.39	0.27	0.64/0.27	0.65/0.28	0.68/0.31	0.78/0.39

* Two numbers denote small/large particles (2/6 mm). The same burn-off was found for small and large particles

Table 1. Oxidation parameters and results.

At low temperatures, the oxygen complexes formed in the pores are stable and few free active sites are left for further activation. As temperature increases, the complexes become unstable and the reaction into the pores takes place, increasing the internal surface area. Otherwise, at high temperatures (more than 450°C), the reaction becomes very fast, the effectiveness factor is low, and most of the external surface is consumed.

The results from table 1 show that lower oxygen partial pressures under a N₂ environment develop higher iodine number and BET surface area (see exp. #3 and 4). According to Radovic et. al. [6], the oxygen complexes are less stable at lower oxygen partial pressures. So, there are more free active sites in the pores that help the development of the internal surface area. The application of elevated pressures have not indicated good improvements in the iodine number and surface area (see exp. # 6 and 8). Increasing pressure will increase the oxygen partial pressure and as discussed previously, lower partial pressures give better results. The use of smaller particles results in higher iodine number and surface area (see exp. # 5 to 8). The diffusion is facilitated into small particles because the oxygen molecules can easily penetrate the internal pores, and the concentration gradient through the particle is not so severe as in large particles. The overall yield was relatively high, depending on the burn-off, varying from 21 to 30% in the experiments.

The use of oxygen to increase the internal surface area of biomass carbons is strongly influenced by the oxidation temperature. The reaction of oxygen with carbon is highly exothermic and starts at relatively low temperatures where the oxygen complexes are stable. For the Eucalyptus charcoal used in the experiments, the evolution of these complexes begins at 400°C and the rate of desorption increases with a peak at 700°C. The oxidation rate at this peak temperature is very fast

and most of the oxygen reacts before entering the pores. Thus, only a narrow temperature range (which is typically from 400°C to 450°C) can be used to improve the internal surface area. The carbons obtained from these experiments did not present high active surface areas compared to commercial activated carbons, mainly because of the oxygen complexes chemisorbed into the pores. Relatively high yields of carbons were obtained in the pyrolysis and oxidation experiments.

Acknowledgment

The authors wish to thank Dr. Gabor Várhegyi with the Hungarian Academy of Sciences for the TGA measurements of the Eucalyptus charcoal oxidation.

References

1. Antal Jr., M. J., Mok, W. S., Várhegyi G. and Szekely T., *Energy&Fuels*, 1992, 4, 3, p. 221.
2. Mok, W. S., Antal Jr., M. J., Szabo, P., Várhegyi, G. and Zelei, B., *Ind&Eng.Chem.Res.*, 1992, 31, 1, 162.
3. Antal Jr., M. J., Croiset, E., Dai, X., DeAlmeida, C., Mok, W. S., Norberg, N., Richard, J. R. and Majthoub, M. A., *Energy&Fuels*, 1996, 10, 3, p. 652.
4. Dai, X., Norberg, N. and Antal Jr., M. J., *Proceedings of the Symposium on Materials and Chemicals Synthesis from Fossil Fuels and Biomass*, 1995 Anaheim, CA.
5. Fogler, H. S., *Elements of Chemical Reaction Engineering*, 1992 (Ed. by PTR Prentice-Hall).
6. Radovic, L. R., Lizzio, A. A. and Jiano, H., in *Fundamental Issues in Control of Carbon Gasification Reactivity*, 1991 (Ed. by Kluwer Academic Publishers), p. 235.