Flash Carbonization of Biomass

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Abstract: This paper describes a quick and efficient carbonization technology that converts biomass into biocarbon with yields that can equal the thermochemical equilibrium limit after a few tens of minutes of reaction time. Our work emphasized the ignition and control of a flash fire within a packed bed of biomass at an elevated pressure. Biomass feedstocks included woods (e.g., leucaena and oak) and agricultural byproducts (e.g., corncob, and rice hulls). In a typical experiment, the system was pressurized to 1 MPa by air and electric power was delivered to heaters at the bottom of the reactor. Ignition occurred after a few minutes under pressure, and the resultant flash fire triggered the conversion of biomass to biocarbon. In the case of corncob, the fixed-carbon yield attained the theoretical limit, and the reaction was complete after 20 min.

Introduction

Biocarbons (e.g. charcoal and carbonized charcoal) have been manufactured by man for more than 38,000 years [1] and are among the most important renewable fuels in use today. Nevertheless, commercial technologies that carbonize biomass are remarkably slow and inefficient. A typical yield of charcoal manufactured from hardwoods in a Missouri kiln operated on a 7 to 12 day cycle is about 25 wt % [2]. This charcoal has a fixed-carbon content of about 80 wt%; therefore the process offers a fixed-carbon yield of about 20 wt % [3]. Less efficient carbonization processes are widely employed in the developing world [4-7] and are a principal cause of the deforestation of many tropical countries. Also, because of pollution associated with inefficient carbonization processes, the charcoal fuel cycle is among the most greenhouse-gas intensive energy sources employed by mankind [4]. Here we show how to ignite and control a flash fire at 1 MPa within a packed bed of biomass that triggers its transformation to carbon with yields that can reach the thermochemical equilibrium "limit" in less than 30 min of reaction time.

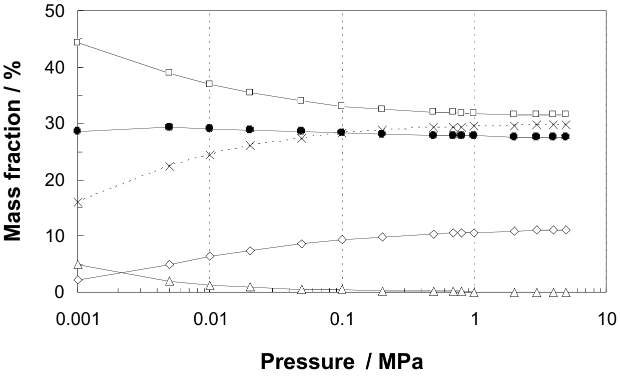

Figure 1 Effects of pressure on the products of cellulose pyrolysis following the attainment of thermochemical equilibrium at 400 °C (●: C (solid), ◇: CH_4, △: CO, □: CO_2, ×: H_2O)

From a theoretical perspective, biomass carbonization should be quick and efficient. Thermochemical equilibrium calculations [8] indicate that carbon is a preferred product of biomass pyrolysis at moderate temperatures, with byproducts of carbon dioxide, water, methane, and traces of carbon monoxide. To illustrate this result we display in **Figure 1** the products of cellulose pyrolysis in thermochemical equilibrium as a function of pressure at 400 °C. Cellulose is the dominant component of most biomass, and serves as a representative model compound in this discussion. At 1 MPa the yield of carbon from cellulose is 27.7 wt% (i.e. 62.4 mol% of cellulose carbon is converted into biocarbon), and is not significantly affected by pressure. The scientific literature concerning biomass carbonization spans 150 years [9,10] and stands on a foundation developed over 38 millenia1. No record exists of a carbon yield from biomass that exceeds the thermochemical equilibrium value. Evidently, the pyrolytic yield of carbon from biomass approaches the equilibrium value from below; consequently, we refer to this value as the thermochemical equilibrium "limit" for the carbon yield. An energy balance on the equilibrium product mixture from the model compound cellulose at 400 °C and 1 MPa indicates that the carbon product retains 52.2% of the higher heating value (HHV) of the cellulose (17.4 MJ/kg), and 36.2% is captured by the gas products (primarily methane). The remaining 2.0 MJ/kg is released as heat by the exothermic pyrolysis reaction. For the sake of comparison, the highest measured value for the exothermic heat of pyrolysis of cellulose - in a closed crucible that developed considerable pressure - was 0.66 MJ/kg [11]. In light of the fact that the exothermic pyrolysis reaction proceeds with a large increase in entropy (due to the formation of gas), it is clear that equilibrium strongly favors the formation of product carbon and byproduct gases.

Experimental

Biomass feedstocks employed in this study are listed in **Table 1**. Waste oak (Quercus spec.) wood floorboards used as a feedstock for the commercial production of charcoal were supplied by the Cowboy Charcoal Co. Air dried, debarked Leucaena leucocephela logs and corncob grown on Oahu were provided by Prof. J. Brewbaker (U. Hawaii). Rice hulls from Arkansas were supplied by the ConAgra Corp. The sample standard deviation of the measured fixed carbon yield realized in our equipment is about 1% (i.e. for corncob $y_{fc} = 0.28 \pm 0.01$) [3]. To estimate the HHV of some of the biocarbons produced in this work we employed a correlation [26] that offers a good fit ($R^2 = 0.938$) to measured HHV data for a representative selection of our biocarbons. In a typical experiment a measured amount (0.5 to 1.4 kg) of feedstock, divided into three sections, is placed inside a cylindrical canister and loaded into a vertical pressure vessel (autoclave), which is subsequently pressurized to 1.1 MPa (150 psig) by air. Electric power (0.2 kWh) is delivered to two heaters at the bottom of the autoclave. Ignition occurs after a few minutes and the heaters are turned off. The total specific power consumption (ca. 0.4 kWh per kg of charcoal) is almost a factor of ten less than that employed in our earlier work [12], and will be reduced further when larger autoclaves enable the same power input to ignite a flash fire within a much larger bed of biomass. Then air is delivered to the autoclave and the flash fire spreads throughout the bed, triggering the conversion of biomass into carbon. When sufficient air has been delivered to assure carbonization of the bed, the airflow is halted, the autoclave is depressurized and permitted to cool. Subsequently, each section is equilibrated in the open air, weighed, and a representative carbon sub-sample taken from each section is subjected to proximate analysis according to ASTM D1762-84.

Table 1 Feedstock analysis: leucaena wood (LW), oak wood (OW), corncob (CC), and rice hull (RH)

ID	MC [a] (%)	Ash [b] (%)	Ultimate analysis [c] (%)						HHV [c] (kJ/g)
			C	H	O	N	S	Ash	
LW	13.1	2.34	48.47	5.90	42.41	0.51	0.08	3.49	18.1
OW	8.67	0.27	46.44	6.45	47.42	0.10	0.02	0.39	17.7
CC	13.9	1.17	43.42	6.32	46.69	0.67	0.07	2.30	17.4
RH	9.70	17.2	38.38	5.47	39.46	0.37	0.06	16.01	15.5

[a] ASTM E 1756-95, [b] ASTM E 1755-95, [c] commercial analytical service (Huffman Labs, Inc., USA).

Results and Discussion

Table 2 summarizes results of the flash carbonization of biomass materials tested. We define the charcoal yield $y_{char} = m_{char}/m_{bio}$, where m_{char} the dry mass of product charcoal and m_{bio} is the dry mass of the feedstock. Unfortunately, this representation of the efficiency is intrinsically vague because the chemical composition of charcoal is not defined. A more meaningful measure of the carbonization efficiency is given by the fixed-carbon yield $y_{fC} = y_{char} \times \{\%\ fC / (100 - \%\ \text{feed ash})\}$, where % fC is the percentage fixed-carbon content of the charcoal, and % feed ash is the percentage ash content of the feed [3]. This yield represents the efficiency realized by the pyrolytic conversion of ash-free organic matter in the feedstock into a relatively pure, ash-free carbon. Likewise, we define the energy conversion efficiency $\eta_{char} = y_{char} \times (HHV_{char}/HHV_{bio})$, where HHV_{char} is the HHV of the charcoal and HHV_{bio} is the HHV of the feedstock.

Table 2 Results of flash carbonization (weighted average values of the three sections)

ID	Proximate analysis (%)			y_{char} (%)	y_{fC} (%)	HHV (MJ/kg)	η_{char} (%)
	VM	FC	Ash				
LW-moist	24.7	72.5	2.9	40.0	29.7	29.9	66.1
LW-dried	15.8	80.6	3.6	36.8	30.4	31.2	63.6
OW	20.0	79.5	0.5	35.1	28.0	31.6	62.5
CC	13.6	83.7	2.7	33.1	28.0	32.0	60.7
RH	23.8	43.2	33.0	46.1	24.0	19.4	57.7

Figure 2 displays a parity plot comparison of measured, mass-average fixed-carbon yields with the calculated equilibrium limit. Oak and Leucaena (a nitrogen fixing tree) are popular feedstocks for the production of biocarbons. At 1.5 MPa the oak ignited after 5 min of heating, and airflow to the autoclave was halted after 25 min. Based on the C, H, O composition of the oak (Table 1), the thermochemical equilibrium limit for the fixed carbon yield is 29.6 wt% [3]. The experimental mass-weighted average value of this yield was 95% of the thermochemical equilibrium limit, and the charcoal product retained 62.2% of the energy of the dry wood feed. This result represents a significant improvement over our earlier work that employed an externally heated pressure vessel and achieved only 88% of the limit value for the fixed-carbon yield from oak after 300 min of reaction time from cold start [3]. The Leucaena wood offered high yields of charcoal (40.0%) and fixed-carbon (29.7%) with $\eta_{th} = 66.3\%$. Remarkably, the use of oven-dry Leucaena as a feedstock had little effect on the measured fixed-carbon yield (30.4%), and the energy conversion efficiency (62.6%). This result shows that high carbonization efficiencies can be achieved without substantial drying of the feedstock. Corncob and rice hulls are among the most plentiful agricultural residues in the USA. The cob is a particularly attractive feedstock for carbonization: at 1.2 MPa it ignited after 2 min of heating, and airflow to the autoclave was halted after 18 min. The fixed-carbon yield was 100% of the thermochemical equilibrium limit with $\eta_{th} = 59.5\%$. This remarkable result represents a substantial improvement over our earlier work that realized less than 70% of the limit value for the fixed-carbon yield from cob after more than 300 min of reaction time [3]. The disposal of rice hulls is a vexing problem. Although the rice hull ash content is very high, this ash is high-purity silica that has many potential metallurgical uses [13]. Like corncob, rice hulls burn easily in air at elevated pressure, but airflow and heat transfer is inhibited in a packed bed of hulls. As a result of these idiosyncrasies the fixed-carbon yield (24%) was only 82% of the limit value and the fixed-carbon content of the charcoal was less uniform. We anticipate that this yield and the uniformity of the biocarbon product can be substantially improved by minor modifications to the equipment and operating procedures.

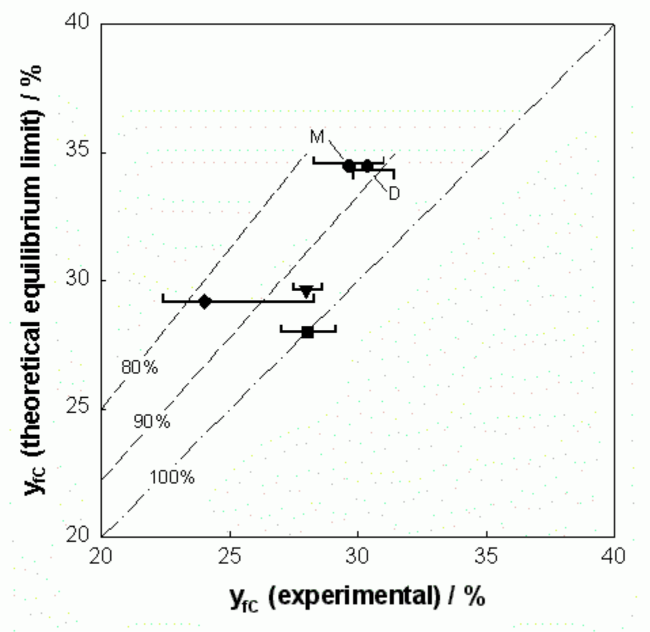

Figure 2 Parity plot displaying the experimental, mass-average value and the associated range of fixed-carbon yields vs. the theoretical thermochemical equilibrium value ("limit") for all feedstocks (●: leucaena, ▼: oak, ■: corncob; ◆: rice hull; M: moist, D: oven-dry).

The extraordinary yields of biocarbons reported above are a result of a flash carbonization process that occurs at elevated pressure, yet thermochemical equilibrium calculations predict that elevated pressure should have no effect on the yields of carbon from biomass. There are several explanations for this seeming contradiction. Biocarbons are composed of both a "primary" and a "secondary" carbon that is a coke derived from the decomposition of the tarry organic vapors onto the carbonaceous solid14. Under pressure the highly reactive, tarry vapors have a smaller specific volume; consequently, their intra-particle residence time is prolonged, increasing the extent of their decomposition as they escape the biomass particle. Also the concentration (partial pressure) of the tarry vapor is higher, increasing the rate of the decomposition reaction11. These effects are magnified when the flow of gas through the particle bed is small [15,16] – as is the case at elevated pressure [17-19]. Furthermore, the formation of secondary carbon from the tarry vapor is catalyzed by the charcoal [20-23], and water vapor or chemisorbed moisture may act as an autocatalytic agent for carbon formation at elevated pressures [11,15,24,25].

Conclusion

Biomass materials can be converted to biocarbons quickly and efficiently. The remarkable ease with which a flash fire at elevated pressure triggers the transformation of biomass to carbon augurs well for the expanded production of biocarbons as a substitute for coal.

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