The Art, Science, and Technology of Charcoal Production[†]

Michael Jerry Antal, Jr.*

Hawaii Natural Energy Institute, University of Hawaii at Manoa, Honolulu, Hawaii 96822

Morten Grønli

SINTEF Energy Research, Thermal Energy, 7465 Trondheim, Norway

In this review, we summarize the knowledge of the production and properties of charcoal that has been accumulated over the past 38 millenia. The manipulation of pressure, moisture content, and gas flow enables biomass carbonization with fixed-carbon yields that approach—or attain—the theoretical limit after reaction times of a few tens of minutes. Much of the heat needed to carbonize the feed is released by vigorous, exothermic secondary reactions that reduce the formation of unwanted tars by augmenting the charcoal yield in a well-designed carbonizer. As a renewable fuel, charcoal has many attractive features: it contains virtually no sulfur or mercury and is low in nitrogen and ash; it is highly reactive yet easy to store and handle. Carbonized charcoal can be a good adsorbent with a large surface area and a semimetal with an electrical resistivity comparable to that of graphite. Recent advances in knowledge about the production and properties of charcoal presage its expanded use as a renewable fuel, reductant, adsorbent, and soil amendment.

Contents

Introduction

Magnificent charcoal drawings in the Grotte Chauvet (see Figure 1), which are over 38 000[1] years old, bear witness to Cro-Magnon man's artistic creativity and native chemical engineering talents.[2,3] The antiquity of this breathtaking artwork suggests that charcoal was

Figure 1. Charcoal mounds on the floor of the Grotte Chauvet with charcoal drawings on the wall above. Similar drawings have been dated at ~30 000[2] to 38 000[1] years B.P. Photo courtesy of Prof. Jean Clottes.

the first synthetic material produced by man.[2,3] Many millennia thereafter, but still before the dawn of recorded history, man employed shallow pits of charcoal

---

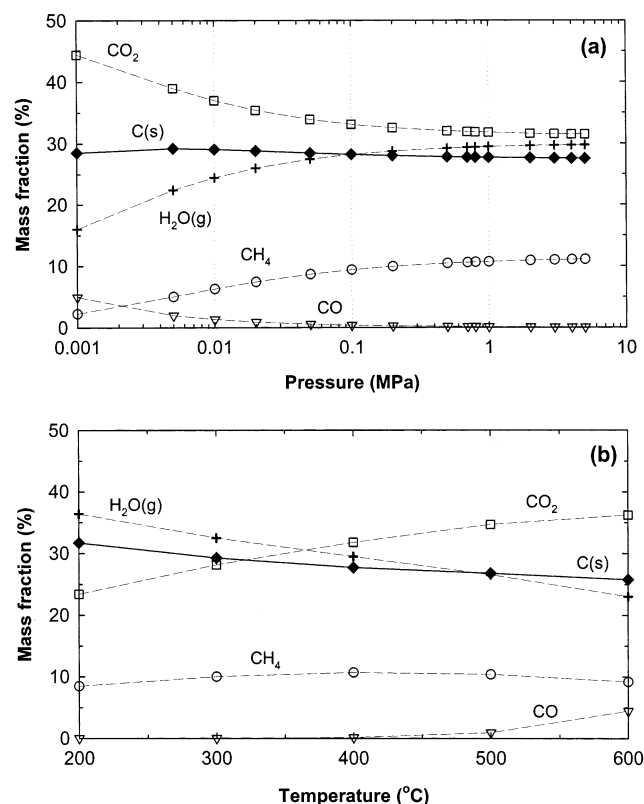* To whom correspondence should be addressed.

Figure 2. (a) Effects of pressure on the products of cellulose pyrolysis following the attainment of thermochemical equilibrium at 400 °C. (b) Effects of temperature on the products of cellulose pyrolysis following the attainment of thermochemical equilibrium at 1 MPa [◆, C(s); □, CO_2; ▽, CO; ○, CH_4; +, $H_2O(g)$].

to smelt tin needed for the manufacture of bronze tools.[4] Charcoal has always been a favorite fuel for cooking. Even today, there is near universal agreement that charcoal is preferred to kerosene as a cooking fuel.[5] Likewise, charcoal is still the most valued reductant of the metallurgical industry: in 1998, the Norwegian ferrosilicon industry imported between 70 000 and 100 000 tonnes of wood charcoal to reduce silica to silicon.[6] And artists still display their creative talents using charcoal: among the most beautiful of impressionist drawings are the charcoal sketches of Degas.

Why was it possible for Cro-Magnon man to discover the technology of manufacturing charcoal at such an early stage of his development? Thermodynamics offers an explanation. Thermochemical equilibrium calculations[7] 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 2a 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. We emphasize that the major trends displayed in Figure 2 are unchanged when the exact C, H, O compositions of particular biomass species are employed in the thermochemical equilibrium calculations. Thus, Figure 2 is a representative example of product compositions after the attainment of thermochemcial equilibrium. Detailed calculations based on the measured composition of selected species will be presented later in this review. The equilibrium data displayed in Figure 2 at 1 MPa can be represented by the approximate stoichiometric equation

$$C_6H_{10}O_5 \rightarrow 3.74C + 2.65H_2O + 1.17CO_2 + 1.08CH_4 \quad (1)$$
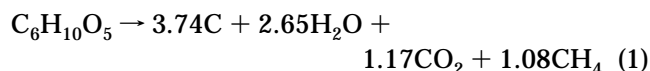
In this equation, the yield of carbon from cellulose is 27.7 wt % (i.e., 62.4 mol % of cellulose carbon is converted into biocarbon) and is not significantly affected by pressure. The scientific literature concerning biomass carbonization contains no record of a carbon yield from biomass that exceeds 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. Figure 2b displays the effects of temperature on thermochemical equilibrium product yields at 1.0 MPa. Temperatures below 400 °C are primarily of theoretical interest, as the rates of biomass carbonization are very slow in this regime. At higher temperatures, the yields of carbon, water, and methane decrease with increasing temperature, whereas those of carbon monoxide increase. The energy balance of the reaction at 400 °C and 1.0 MPa is particularly interesting: 52.2% of the higher heating value (HHV) of the cellulose (17.4 MJ/kg) is retained in the carbon, and 36.2% is captured by the gas products (primarily methane). For the sake of comparison, in 1909, Klason and co-workers[8] represented their experimental measurements of the products of cellulose pyrolysis at 400 °C by the approximate stoichiometric equation

$$C_6H_{10}O_5 \rightarrow 3.75CH_{0.60}O_{0.13} + 2.88H_2O + 0.5CO_2 + 0.25CO + C_{1.5}H_{1.25}O_{0.38} \quad (2)$$
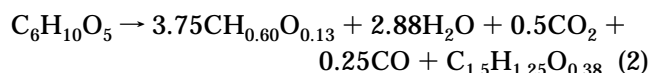
where the first product is charcoal and the last is tar. Using thermodynamic data available at that time, Klason estimated the heat release associated with eq 2 for cotton cellulose to be 3.6% of its heat of combustion. Since then, the highest measured value for the exothermic heat of pyrolysis of cellulose—in a closed crucible that developed considerable pressure within a differential scanning calorimeter (DSC)—was 0.66 MJ/kg (i.e., 3.8% of the HHV of cellulose).[9] 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 thermochemical equilibrium strongly favors the formation of product carbon and byproduct gases. Thus, a theoretical analysis implies that it should be possible to trigger the immediate, efficient transformation of biomass into carbon and gas by merely heating the biomass to a temperature where pyrolysis occurs.

Despite the promising yields predicted by thermochemical equilibrium calculations, current industrial technologies for producing charcoal are not efficient.[10] Traditional kilns in Madagascar and Rwanda realize efficiencies (see below) of only 8−9%, while elsewhere, efficiencies in the range of 8−36% have been reported.[11−16] The low efficiency of charcoal production causes it to be a principal cause of the deforestation of many tropical countries and a contributor to global warming.[15−17] Reflecting on the wasteful use of wood to manufacture charcoal, many environmentalists feel that charcoal production should be banned![11,13] An explanation for the low efficiency of conventional charcoal kilns and retorts is given in Figure 3a. Pyrolysis abruptly transforms wood into a tarry vapor containing a complex soup of organic compounds mixed with
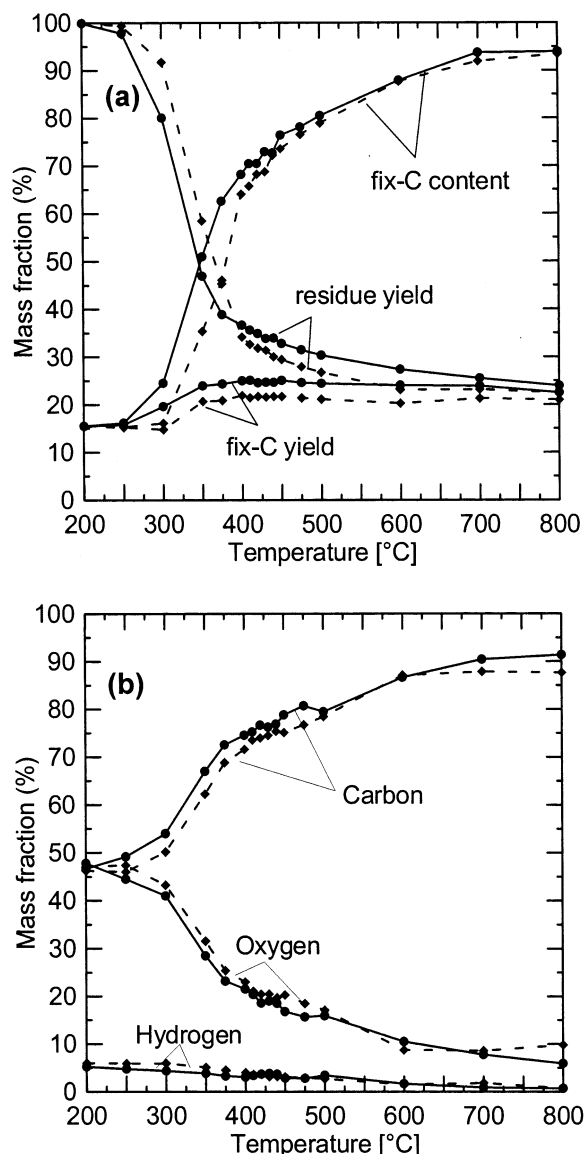
Figure 3. Effects of temperature and heating rate on (a) yields and (b) CHO contents of beech chars.[90] The solid and dashed lines represent heating rates of 2 and 10 °C/min, respectively.

noncondensable gases (including CO_2, CO, H_2, CH_4, and heavier hydrocarbons) between 250 and 400 °C. The tarry vapors quickly escape the heated region of the reactor without establishing equilibrium and without forming charcoal. Klason and co-workers[18,19] represented these observations in the following approximate stoichiometric reaction for the carbonization of "wood" at 400 °C

$$2C_{42}H_{60}O_{28} \rightarrow 3C_{16}H_{10}O_2 + 28H_2O + 5CO_2 + 3CO + C_{28}H_{34}O_9 \quad (3)$$
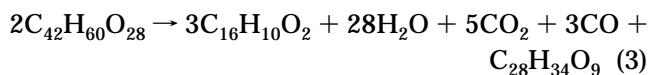
Note that the yield of charcoal ($C_{16}H_{10}O_2$) in this equation is 36.7 wt %, and that the tarry vapors ($C_{28}H_{34}O_9$) constitute a significant loss of carbon. Because the cost of the wood feedstock comprises 50% or more of the cost of producing charcoal in a conventional kiln,[14,20] there is great economic incentive to transform these tarry vapors into charcoal and thereby reduce the consumption of biomass. Moreover, a high carbonization efficiency reduces the amount of feedstock consumed,[14,21] the transportation costs of the feedstock to the kiln,[14]

and the release of the tarry vapors into the environment with their serious impacts on air and water quality.[13]

We hesitate to offer a true estimate of the amount of charcoal produced in the world. Deglise and Magne[22] cited a value of 5.5 million tonnes in 1981, an estimate for charcoal production in Brazil (alone) during 1989 was 9.3 million tonnes,[23] the FAO offered a worldwide value of 3.8 million tonnes in 1991[24] and 26 million in 1995[25] (that was later reduced to 21 million), and an authoritative estimate for 1996 tallied 100 million tonnes.[26] These variations mirror estimates of the annual per capita charcoal consumption in Tanzania, which ranged from 170 to 353 kg per head.[13] The price of charcoal also varies widely.[27] In developing countries, it ranges from $90 to $180 per tonne, but it can be as high as $400 per tonne in Africa.[10] Dry to wet seasonal variations can cause a 300% increase in price.[13] The value of charcoal sales in 26 sub-Saharan African countries exceeds $1.8 billion per year, and the total charcoal consumption (as energy) in these countries often surpasses their gross consumption of electric power.[11] In the Cote d'Ivoire, as many as 90 000 people are engaged in the woodfuels sector.[11] Recently, the wholesale price of wood charcoal in the U.S. was about $200 per tonne, and the Norwegian ferrosilicon industry paid about $440 per tonne of fixed carbon.[28] Note that the U.S. price of $200 per tonne is about $6.30 per GJ (or about $36 per bbl of oil equivalent).

Why is the Norwegian ferrosilicon industry willing to pay $440 per tonne (fixed carbon) for imported wood charcoal, when it can obtain washed coal and coke at only $140−270 per tonne (fixed carbon)?[28] Charcoal and other biocarbons contain virtually no sulfur or mercury. Relative to their fossil fuel cousins, biocarbons are very low in nitrogen and low in ash. Consequently, many carbonized charcoals are purer forms of carbon than most graphites. Unlike graphite, however, biocarbons are extremely reactive. Consider that the transformation of biomass to charcoal involves the loss of 60% or more of the substrate's mass with the evolution of nearly 4 mol of gas per mole of monomer (see eq 2). During this transformation, the molecular framework of the sugar moieties composing biomass is grossly rearranged to form aromatic structures. Because the transformation does not involve a liquid phase, many bonds are left dangling, giving rise to a carbonaceous solid that is inherently porous at the molecular level and highly reactive. The purity and reactivity of charcoal enable it to command a premium price as a metallurgical reductant. Other properties cause charcoal to find applications in a surprisingly wide range of fields. Because of their inherent porosity, biocarbons manufactured from charcoal often have high surface areas. These carbons are preferred adsorbents for air and water treatment. Biocarbons are also amorphous (i.e., there are only hints of a turostratic structure in their X-ray diffraction spectra). Nevertheless, a packed bed of carbonized charcoal conducts electricity nearly as well as a packed bed of graphite particles. Consequently, biocarbons can be used to form electrodes.[29−31] In contrast with other renewable fuels (e.g., hydrogen and ethanol), charcoal is easy to store and cheap to produce. Similarly, when compared with other conventional fuels, biocarbons are surprisingly benign. Charcoal crusts on toasted bread in soupe à l'oignon gratinée are served to discriminating diners in the finest French restaurants. Pills of charcoal[32] are swallowed by health food enthusiasts "after

every meal". Charcoal has been injected into the intestines of poison victims to save their lives by adsorbing fatal toxins.

From a different perspective, charcoal is carbon stolen from the atmosphere by photosynthesis. Consequently, the widespread use of charcoal as a soil amendment sequesters carbon and reduces the greenhouse gas effect. The remarkable discovery of terra preta do Indio ("Indian dark earth") in Amazonia sheds light on the utility of charcoal as a soil amendment. The prehistoric Amazonians added large amounts of charcoal to their wet desert soil (i.e., "oxisol") to render it fertile.[33,34] Terra preta soil may occupy 10% of Amazonia (an area the size of France), and it sustained large settlements there for 2 millenia. Today, terra preta is mined and sold as potting soil.[35] In our experience, most potting soils available in local garden shops contain charcoal as a cofactor. Herbicides also employ charcoal in standard carbon-based formulations. Activated carbons are routinely added to tissue culture media formulations. Remarkably, the scientific rationale for these applications is absent. A Japanese patent[36] speculated that the electrical properties of carbon soil amendments help to condition the soil and improve plant growth. Finnish fire researchers described the effects of charcoal on the pH of humus and its influence on the growth rate of microbial communities within the humus.[37] Many researchers believe that the ability of charcoal soil amendments to adsorb toxic substances in the soil improves plant survival, health, and productivity.[38]

In his classic textbook (translated from German to English in 1970), Hermann F. J. Wenzl offers the following insight.[39] "Since the chemical industry today can produce the by-products obtained from the pyrolysis of wood, with the exception of charcoal, more cheaply than the pyrolysis process, the main emphasis in the latter is on the production of charcoal. For this reason, simple carbonization methods, similar to the original charcoal piles but in an improved form, are likely to be more economical than more complicated plants that place emphasis on the isolation and processing of byproducts." We agree with Wenzl's opinion that charcoal is the preferred product of biomass pyrolysis, and that carbonization reactors should be designed to maximize the production of charcoal and minimize the formation of byproducts. Consequently we focus this review on the charcoal product of biomass pyrolysis. Readers interested in the formation of gases, "oils", tars, pyroligneous acids, and the other byproducts of biomass pyrolysis have an ample literature available to them.[39–44] One goal of this review is to summarize knowledge of the reaction conditions that maximize the yields of charcoal from biomass and minimize the reaction times. Another goal is to detail what is known about the unique and extraordinary properties of biocarbons. We begin with a concise discussion of the key properties of charcoals that are used to define the charcoal yield (y_{char}) and fixed-carbon yield (y_{fC}) of a carbonization process. Following this, we discuss the effects of thermal pretreatments, heating rate, and peak temperature on charcoal properties and yields. Of these parameters, the peak temperature is the key determinant of a charcoal's properties. We show that the gas environment, particularly the pressure, exerts a strong influence on charcoal yields. The composition of biomass feedstocks varies greatly and significantly affects both the properties and the yields of product charcoals. As discussed above, the

reactivity of charcoal causes it to command a high value in the marketplace; consequently, we offer a detailed discussion of this property. Finally, we summarize the current status of industrial technologies for biomass carbonization.

Charcoal Properties and Yields

Because the carbon content of charcoal approaches an asymptote with increasing peak temperature, the limiting asymptotic value is an important property of the material. An approximation of this value is given by proximate analysis according to ASTM D 1762-84. Essentially, in this analysis, the charcoal is heated ("carbonized") in a covered crucible to 950 °C and held at this temperature for 6 min. The measured weight loss is defined to be volatile matter (VM), and the residual solid is carbonized charcoal, i.e., % VM = 100 × (m_{char} − m_{cc})/m_{char}, where m_{char} is the initial dry mass of charcoal and m_{cc} is the dry mass of the carbonized charcoal that remains after heating. The ash content of a charcoal is also important. Ash content is determined by heating the carbonized charcoal residue of the VM determination in an open crucible to 750 °C with a "soak" at this temperature for 6 h. The material that remains in the crucible is defined to be ash, i.e., % char ash = 100 × m_{ash}/m_{char}, where m_{ash} is the dry mass of ash that remains following combustion of the carbonized charcoal. The fixed-carbon content of the charcoal is defined as % fC = 100 − % VM − % char ash. The Norwegian ferrosilicon industry employs the same procedures in its proximate analyses, except that the sample is held at 950 °C for 7 min during carbonization.

The volatile matter content of a "good-quality" charcoal depends on its use. Charcoal intended for domestic cooking typically contains 20−30% VM (with a value of 40% being marginally acceptable), whereas metallurgical charcoal often contains 10−15% (or less) VM.[13] The ash content of a good-quality charcoal typically lies between 0.5 and 5%, resulting in a range of calorific values between 28 and 33 MJ/kg.[13] An insightful description of good-quality charcoal was given by Chaturvedi as follows:[13,45] "Charcoal of good quality retains the grain of the wood; it is jet black in color with a shining luster in a fresh cross-section. It is sonorous with a metallic ring, and does not crush, nor does it soil the fingers. It floats in water, is a bad conductor of heat and electricity, and burns without flame."

The charcoal yield y_{char} provided by a kiln is given by $y_{char} = m_{char}/m_{bio}$, where m_{char} is the dry mass of charcoal taken from the kiln and m_{bio} is the dry mass of the feedstock loaded into the kiln. Unfortunately, this representation of the efficiency of the carbonization process is intrinsically vague because it does not reflect the fixed-carbon content of charcoal product, which varies widely. As early as the 1850s, Violette,[46] who was Commissioner of Gunpowder Production in France (the same post that was held earlier by Lavoisier prior to his execution), called attention to this problem. More recently, Aucamp[47] observed that: "Extremely good charcoal yields are commonly claimed by South American charcoal producers. In practice, these claims are seldom related to the moisture content of the wood, the fixed-carbon content of the charcoal, ...". A more meaningful measure of the carbonization efficiency is given by the fixed-carbon yield $y_{fC} = y_{char}$ × [% fC/(100 − % feed ash)], where % feed ash is the percentage ash content of the feed.[6] This yield represents the efficiency

realized by the pyrolytic conversion of the ash-free organic matter in the feedstock into a relatively pure, ash-free carbon. If chemical equilibrium is attained in the kiln, the fixed-carbon yield should approximate the theoretical carbon yield that results from a thermo-chemical equilibrium calculation, such as those displayed in Figure 2 for cellulose. For example, Girard and co-workers presented a particularly detailed study of the products and mass and energy balances associated with charcoal production from oak,[48] meranti, spruce, and chestnut woods.[49] Their measured values of the fixed-carbon yields ranged from 21.4% (chestnut) to 29.5% (oak), which are 57 and 80%, respectively, of calculated theoretical carbon yields based on the reported chemical compositions of the feedstocks. In our experience, these values are close to the maximum that can be obtained from a kiln operating at atmospheric pressure. Occasionally, a "charcoal carbon yield", y_C, is reported in the literature,[16] where $y_C = y_{char} \times$ (% charcoal C/% feed C), % charcoal C is the % carbon content of the dry charcoal, and % feed C is the % carbon content of the dry feed. Because CO_2 and CO are evolved during the fixed-carbon analysis of charcoal, there is no simple relationship between y_{fC} and y_C. In light of the facts that the metallurgical industry employs the fixed-carbon content of charcoal to determine its price and y_{fC} can be compared to the theoretical thermochemical equilibrium yield of carbon from feedstock, we emphasize y_{fC} in this paper. Gaur and Reed in their *Atlas of Thermal Data for Biomass and Other Fuels* present measurements of the yields and fixed-carbon contents of charcoals produced from a variety of biomass feedstocks at atmospheric pressure.[50] These data can be used to estimate realistic atmospheric-pressure fixed-carbon yields for these feedstocks. Finally, we define the energy conversion efficiency of a kiln as $\eta_{char} = y_{char} \times$ (HHV_{char}/HHV_{bio}), where HHV_{char} is the HHV of the charcoal and HHV_{bio} is the HHV of the feedstock.

Beyond its proximate analysis, the quality of a charcoal can be represented by a great many other properties. These include moisture content, calorific value, elemental composition, hardness (abrasion resistance), compressive strength, bulk and true densities, surface area, porosity and pore volume distribution, electrical resistivity, and reactivity. Klar,[19] Hawley,[41] Cheremisinoff,[51] Bhattacharya,[12] Gaur and Reed,[50] and others[52−54] provide extensive tables listing the properties of biomass-derived chars. The discussion below offers examples of typical values of these properties.

Effects of Thermal Pretreatments, Heating Rate, and Final (Peak) Temperature

The following discussion presumes the ability of the experimentalist to measure accurate values of the temperature of the biomass substrate. Unfortunately, large thermal gradients are often present when biomass is subjected to high heat fluxes or when large samples are employed. Our readers are cautioned to keep these difficulties in mind as they read the literature of the field.[55,56]

Thermal Pretreatments. Over 25 years ago, thermal pretreatments of cellulose at temperatures between 230 and 275 °C at 0.1 MPa were reported to increase the cellulosic char yield from 11.0 to 27.6%.[57] Although more recent work[58] has called into question some aspects of the kinetic model for cellulose pyrolysis that Broido and co-workers[57,59,60] developed to describe this phenomenon, there is no doubt that a thermal pretreatment can augment the char yield from cellulose. Unfortunately, thermal pretreatments have little effect on the amount of charcoal that can be obtained from lignocellulosic biomass substrates.[10,61,62]

Heating Rate. In 1851, Violette[46] reported a charcoal yield of 18.87 wt % from wood heated slowly over a 6-h period. This charcoal was described as very hard, well-cured, sonorous, and heavy with a dense structure and a carbon content of 82.1%. The charcoal yield decreased to 8.96 wt % when the wood was heated quickly, and the product was light and friable with a carbon content of 79.6%. Years later, Klar[19] presented a table of wood distillation products (attributed to Senff[63]) that displayed the effects of heating rate on yields. A change from "slow" to "rapid" carbonization decreased measured charcoal yields from 2 to 10 wt %, depending on the species. For example, the yield of charcoal from "sound, peeled Alder trunkwood" decreased from 31.56 to 21.11 wt % with increased heating rate. Likewise, Goos observed that short carbonization times, realized by sudden exposure of the biomass feed to a high temperature (e.g., 953 °C), gave low carbon yields.[44] Brunner reported a log−linear relationship between the heating rate and the char yield from cellulose.[64] Recently, Lédé and co-workers described the complete vaporization of cellulose at high heat flux densities.[65−68] In accord with these observations, the kinetic models for cellulose pyrolysis of Broido and co-workers,[10,57,59,60] Shafizadeh et al.,[69] and Varhegyi et al.[58,70,71] all predict an improvement in char yield as the heating rate of the substrate is reduced. Moreover, MacKay and Roberts[72] reported an increase from 22 to 32% in the yield of charcoal from redwood when the heating rate was reduced from 200 to 1 °C/min. However, other workers, who emphasized lignocellulosic substrates (not pure cellulose) and lower heating rates, observed no significant improvement as the heating rate was reduced.[10,61,62,73] It appears that, as the heating rate is decreased, an asymptote in the char yield is reached.[10] Furthermore, it is simply not practical to employ very low heating rates because the required reaction times are uneconomical.

It is well-known that large wood particles shrink and often crack during pyrolysis and that these cracks can confound studies of pyrolysis kinetics.[74] Byrne and Nagle[75] showed that monolithic wood particles do not crack when the heating rate is restricted to 15 °C/h or less.

Peak Temperature. The peak temperature is the highest temperature reached during the carbonization process. This temperature largely controls the quality (i.e., the volatile matter content) and other properties of the charcoal product.[10] In Figure 4, Wenzl[39] has compiled a succinct summary of the trends (if not the exact values) of many important properties of charcoal with increasing peak temperature. Our discussion below offers more details for cellulosic and lignocellulosic chars subjected to increasing temperature.

At temperatures below 220 °C, cellulose loses weight mainly by the formation of water,[76] but at higher temperatures (up to 250 °C), CO_2 and CO are also evolved.[42,43] Boon and co-workers identified three distinct stages in the formation of char from microcrystalline cellulose at low temperatures. Below 250 °C, the oligosaccharides were preserved, but the color of the char and its FTIR spectra indicated the formation of unsaturated C−C bonds and carbonyl groups, probably
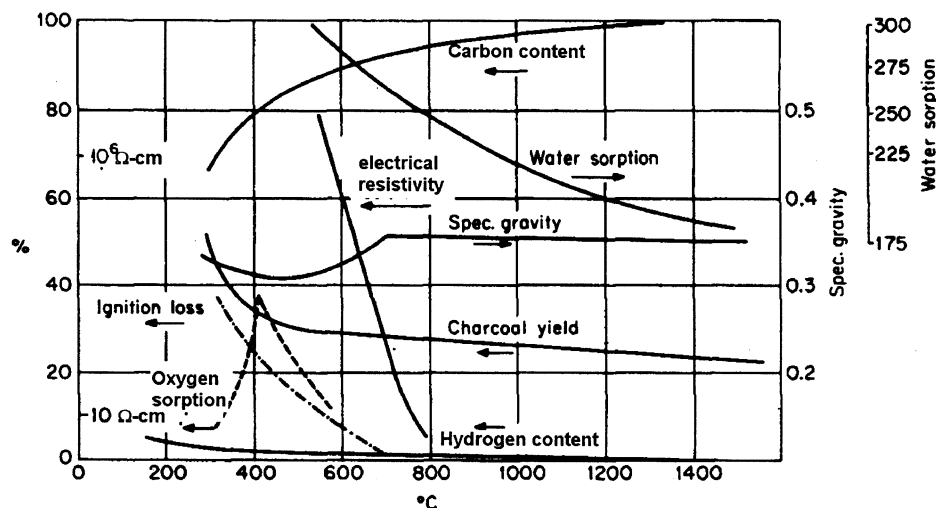
Figure 4. Effect of temperature on the properties of charcoal. In this figure, we have corrected translation errors by Wenzl[39] of the original figure (in Swedish) due to Bergström and Wesslen.[93,94] All values are approximate.

by the elimination of water.[77] Remarkably, after a 20–30% weight loss at temperatures below 250 °C, the solid residue from cellulose pyrolysis was composed primarily of oligosaccharides.[78] Between 220 and 270 °C, the acid hydrolyzable content of the char declined from 90 to 35%.[79] The PYMS spectrum of the hydrolysis residue of the 250 °C char revealed the nascent presence of a char composed mainly of phenols, furans, and aromatic hydrocarbons. During the second stage (above 250 °C), phenol and furan structures appeared.[77] In the case of a microcrystalline cellulose, anhydroglucooligosaccharides were present in chars after heating at 270 °C for 2 h, and acid hydrolysis of the cellulosic char revealed the presence of glucose even at temperatures as high as 310 °C.[76] During the third stage (above 290 °C), the composition of the cellulosic char was dominated by the presence of alkyl furans, benzenoid aromatics, and condensed aromatics.[77,80] Boon and co-workers[79] hypothesized that nonvolatile carbohydrate fragments, which are byproducts of the formation of volatile levoglucosan and glycolaldehyde, act as aldol condensation sites for the reactive soup of volatile species that are released during pyrolysis. The condensed light pyrolysis products (e.g., glycolaldehyde, ketene, enolic furans, etc.) serve as a molecular glue that prevents the remaining carbohydrate structural elements from volatilizing.

The chemical changes that occur during the low-temperature pyrolysis of whole biomass materials are not as well characterized. As the peak temperature increases, the solid pyrolytic residue of a woody material progresses through several stages. Wood "retification" is said to occur at temperatures from 230 to 250 °C.[81] The color of wood heated to this temperature becomes reddish brown or chocolate,[44] and the material is said to be resistant to biological attack. Torrefaction[82–84] occurs at temperatures between 250 and 280 °C at low heating rates, and creates a brown or black product with little strength. Yields of torrefied wood range from 84% at 250 °C to 67% at 270 °C, with energy yields of 90–77%, respectively.[85] "Pyrochar",[86] conventional charcoal, and "carbonized" charcoal,[87] each with successively less volatile matter, are formed at increasingly higher peak temperatures. The soak time at peak temperature is also important, but the Arrhenius behavior of the pyrolysis kinetics establishes temperature as the controlling variable.

Almost 150 years ago, Violette[41,46,88] described detailed measurements of the residues of the destructive distillation of wood at temperatures above 150 °C. Two generations later, Chorley and Ramsay[41,89] reported similar measurements, including the observation that wood pyrolysis is exothermic above 280 °C. Modern studies of the effects of peak temperature on the character and evolution of the carbonaceous residue are well represented by the work of Schenkel,[90] who detailed measurements of the effects of heating rate and soak time on charcoal formation from European beech wood at 0.1 MPa. Figure 3a displays his measured values of the solid residue, its fixed-carbon content, and the fixed-carbon yield at two heating rates, following a soak time of 15 min at each temperature. Note the dramatic increase in the fixed-carbon content of the residue between 300 and 500 °C and the related decrease in the oxygen content over the same temperature range. Pyrolysis at 10 °C/min causes the fixed-carbon yield of the solid residue to increase from 15% (at 200 °C) to about 21%. A decrease in heating rate from 10 to 2 °C/min causes a further increase in the fixed-carbon yield to 23%. At low heating rates, the carbon content of the residue (see Figure 3b) steadily increases to values exceeding 90%. Note that % fC < % C at 450 °C, whereas % fC > % C at 800 °C in Figure 3. A comparison of Schenkel's data with Violette's measurements reveals greater carbonization at lower temperatures in Violette's work. For example, Violette[19,46,88] measured a charcoal yield of 29.66 wt % with a carbon content (not fixed carbon) of 76.6% at 350 °C, whereas Schenkel observed values between 46 and 58 wt %. This discrepancy can be explained by the limited knowledge of the temperature scale in 1850: Violette believed the melting point of antimony to be 432 °C, whereas the true value is 630.7 °C. Bergström's early (1904) measurements of the carbon content of kiln charcoal (84.18% at 500 °C)[91] agree remarkably well with Schenkel's fixed-carbon value of 80% at 500 °C.

Table 1 displays elemental analyses of representative carbonized charcoals. Because the composition of charcoals varies widely according to their volatile matter content, we have omitted them from this table. Representative analyses of many charcoals are available in the literature.[12,19,41,50–54] Carbonized charcoals are rich in carbon (typically 90 wt % or more on an ash-free

Table 1. Elemental Analyses of Carbonized Charcoals

feed	C (wt %)	H (wt %)	O (wt %)	N (wt %)	S (wt %)	ash (wt %)
coconut shell	92.28	1.09	3.08	0.47	0.04	2.78
corncob	86.38	1.20	5.34	0.56	0.05	4.31
kukui nut shell	90.31	1.03	4.31	0.42	0.02	3.27
leucaena wood	85.41	1.27	6.37	0.53	0.04	4.62
macadamia nut shell	94.58	0.97	2.93	0.47	0.03	1.04
oak board	91.50	1.22	3.55	0.18	0.01	1.04
oak slabs	92.84	1.09	3.49	0.24	0.04	1.46
pine wood	94.58	1.06	3.09	0.11	0.04	0.69
rice hulls	52.61	0.82	3.87	0.57	0.06	41.34

basis), with oxygen contents below 6 wt % and hydrogen contents near 1 wt %. Both charcoal and carbonized charcoal contain virtually no sulfur or mercury. Relative to their fossil fuel cousins, these biocarbons are very low in nitrogen (typically <0.6 wt %) and low in ash (often <3 wt %). The high ash content of carbonized rice hull charcoal in Table 1 merely reflects the high ash content of rice hulls. Many carbonized charcoals are purer forms of carbon than most natural graphites.

Considerable shrinkage of wood particles occurs during pyrolysis. In 1860, Von Berg[19,92] reported bulk volumetric "yields" of charcoal from wood ranging between 42% (oak branchwood) and 78% (spruce split billets). This shrinkage partially counteracts pyrolytic weight loss and results in charcoal bulk densities ranging between 106 kg/m^3 (Scotch pine branchwood) and 190 kg/m^3 (Birch).[19] Some woods (e.g., spruce) swell during pyrolysis.[74,93,94] McGinnes and co-workers[95] observed shrinkages of 26% in the tangential direction, 15% in the radial direction, and 11% in the longitudinal direction during the pyrolysis of oven-dried white oak wood cubes in a Missouri kiln. The average volumetric shrinkage of the white oak cubes was 45%. The volatile matter contents of these charcoals, which were not reported, must have been high because the maximum temperatures were low (280−400 °C). Further work[96] with oven-dry white oak and hickory cubes offered very detailed dimensional shrinkage measurements for temperatures ranging from 250 to 800 °C.[96] Similar results were described by Grønli,[74] Beall et al.,[97] and Connor et al.[98] Conner and co-workers[98] reported a linear dependence of char density on sample weight loss during carbonization at temperatures as high as 420 °C. McGinnes et al.[96] and Blankenhorn et al.[99] observed a curious minimum in density for several wood species at 600 °C: the density at 800 °C slightly increased relative to values at lower temperatures. Subsequently, McGinnes et al.[100] and Beall et al.[97] described SEM and shrinkage studies of southern pine and yellow poplar wood during pyrolysis. This work revealed that the disappearance of discrete cell wall layers was both temperature-dependent and time-dependent. Later, Conner et al.[98] observed the disappearance of the middle lamella at temperatures between 300 and 400 °C. Nevertheless, Klar[19] emphasized that charcoal retains the form and structure of the wood from which it is produced to such an extent that the appearance of the charcoal can be used to identify its origin.

Reported values of the specific heat of charcoal at room temperature span a range of 670−1350 J/kg·K.[74] Correlations for the temperature dependence of the specific heat of charcoal predict values that range from 1000 to 3000 J/kg·K at 800 °C, and attempts to improve the accuracy of the correlations failed because of uncertainties in the measurements of temperature profiles

during the heating of charcoal cylinders.[74,101,102] A careful modeling study by Larfeldt and co-workers[102] concluded that the use of a constant thermal diffusivity to describe the heating of charcoal to temperatures as high as 700 °C is recommended. This simplification reflects the fact that the temperature dependencies of the specific heat and thermal conductivity approximately cancel each other, as well as the experimental difficulties associated with accurate measurements of these properties.[102]

Blankenhorn and co-workers reported measurements of some mechanical properties of wood charcoals.[103,104] They observed a decrease in the dynamic elastic modulus of black cherry wood by a factor of 10 to a minimum near 330 °C, after which the modulus increased to regain its initial value for carbonization temperatures near 900 °C.[104] Grønli[74] measured compressive strengths parallel to the grain that were 3−4 times greater than those perpendicular to the grain. He also found that the compressive strength of the charcoal decreased as the peak temperature and heating rate increased and that charcoal from softwoods (e.g., spruce and pine) was more fragile than that from hardwoods (e.g., alder and birch).[74]

The peak temperature has a strong influence on the pore structure, surface area, and adsorption properties of the charcoal. Shafizadeh et al.[105] described the influence of temperature on the development of surface area and the concentration of free radicals in a cellulose char. Both values peaked at temperatures between 500 and 600 °C. On the other hand, Marsh and co-workers observed a maximum in the surface area (500 m^2/g) of a cellulose char that was carbonized at 900 °C.[106] Masters and McEnaney[107] reported a strong falloff in the open micropore volume of carbons derived from cellulose at heat-treatment temperatures (HTTs) above 1000 °C. Raw biomass charcoal prepared at a low temperature (~400 °C) has a negligible surface area and an iodine number below 50.[108] Baileys and Blankenhorn[109] reported an increase in total porosity with increasing peak temperatures up to 500 °C (the highest temperature studied). On the other hand, Khalil[110] observed very low surface areas and iodine numbers for carbons from a wide variety of lignocellulosic materials charred at 550 °C. Without specific references to the literature, Wenzl stated that the micropore volume reached a maximum at relatively high temperatures (800−850 °C), whereas the mesopore volume did not increase at temperatures above 550 °C.[39] MacKay and Roberts[72] found that microporosity was established near 500 °C and further heating volatilized residual material that blocked micropores,[41] thereby increasing the micropore volume somewhat. Blankenhorn and co-workers[99] observed a maximum in the total porosity of black cherry wood near 700 °C. In the case of redwood, MacKay and Roberts[72] reported pore volumes in the range of 0.18−0.23 mL/g. Corn stover char evidenced lower micropore volumes because its high content of inorganic materials partially filled or blocked access to the micropores. At temperatures near 900 °C, McKay and Roberts[72] observed shrinkage of the micropore structure leading to a reduction in open porosity. Precursor composition and heating rate had little influence on char microporosity.[72] Corroborating these findings, Dai and Antal[108] reported a decrease in iodine number from 181 to 129 for macadamia nut shell ("macshell") charcoal carbonized at 750 and 900 °C,

respectively. They attributed this decrease to the loss of free sites, defects, and edges that results from thermal annealing.[107,111] The 900 °C carbonized charcoal had a surface area of about 100 m^2/g and a pore volume of 0.06 mL/g. Using the same macshell charcoal carbonized at 950 °C, Conesa et al. measured an iodine number of 154 and a surface area of 193 m^2/g. De-ashing of the biomass feedstock often increases the surface area of its carbon derivative.[53] In our experience, the surface area and pore properties of a carbon can be dramatically affected by the presence or absence of gas flow during carbonization and any inadvertent exposure of the carbon to air during carbonization.

A menagerie of chemical functionalities inhabits the surfaces of most charcoals. Neither pressure nor feedstock identity greatly affects the FTIR spectra of charcoals.[9,112] These spectra reveal the presence of alkyl aromatic units with a variety of oxygen-containing functional groups, including hydroxyl, carboxyl, carbonyl, ether, and lactone structures.[9,112−114] As the peak temperature increases, these functional groups are gradually lost. At 650 °C, the OH, C=O, and aliphatic C−H groups are largely gone, and by 750 °C, most of the aromatic C−H groups have decomposed. By 950 °C, the spectra of many carbonized charcoals resemble that of graphite. Lee and Reucroft[115] reported similar observations using X-ray photoelectron spectroscopy.

Shafizadeh's CP/MAS ^{13}C NMR studies of the carbonization of cellulose revealed the loss of paraffinic carbons as the char was heated: the paraffinic carbon content was reduced from 27% at 400 °C to 12% at 500 °C.[116] The residual carbon at 500 °C was highly aromatic.

The electrical resistivity of charcoal is also strongly influenced by temperature: it decreases by 6 orders of magnitude to attain values below 1 Ω·cm at temperatures above 900 °C.[39] Consequently, carbonized charcoal can be used to fabricate electrodes. As early as 1830, charcoal was used as an electrode for primary batteries. These electrodes were made from powdered charcoal or coke bonded with sugar syrup or coal tar, pressed, and carbonized.[117] Coutinho, Luengo, and their co-workers[29−31] have described extensive studies of biocarbon electrodes. Their X-ray diffraction (XRD) studies of Eucalyptus wood charcoal carbonized at 900 °C revealed the early stages of development of a turbostratic (i.e., microcrystalline) structure in the carbon.[29,31] The measured electrical resistivity fell to 10^{-2} Ω·cm for carbonization at >900 °C. Packed beds of carbonized charcoal also have potential electrical applications. Espinola et al. reported resistivities of 1.24 Ω·cm for a packed bed of Babacu nut coke compressed at 19.6 MPa and 0.272 Ω·cm for the same packed bed at 98 MPa.[118] Likewise, they reported resistivity values of 0.92 Ω·cm at 19.6 MPa and 0.19 Ω·cm at 98 MPa for a compressed packed bed of Eucalyptus lignin carbon. Bamboo charcoal has attracted special interest in the Japanese patent literature because of its low resistivity.[119]

Carbonization. The volatile matter content of charcoal lies in a range of about 40−10%. When subjected to higher peak temperatures (i.e., carbonized), the remaining volatile matter of the charcoal is driven off, leaving a nearly pure carbon product (see Table 1). Varhegyi and co-workers reported detailed studies of the carbonization of macshell charcoal using thermogravimetry and mass spectrometry (TG−MS).[112,120] They observed two well-separated regions of species evolu-

tion.[112] Below 600 °C, weight loss occurred by the evolution of light organic species and gases. Above 600 °C, weight loss was dominated by multiple overlapping peaks related to the evolution of H_2O, CO_2, CO, CH_4, and H_2 at increasing temperatures. Surprisingly, measured differential thermogravimetric (DTG) curves of charcoals with different volatile matter contents, derived from the same substrate, were remarkably similar.[112]

An increase in particle size delays the escape of volatiles from the carbon matrix. This delay offers additional opportunities for residual tarry vapors to suffer secondary reactions with the solid carbon and increases the yield of fixed carbon. For example, Varhegyi et al.[112] reported an increase in residue yield during carbonization of macshell charcoal from 20 to 29% as the particle size increased from <120 μm to a single 2-mg particle, but this effect was incurred at temperatures below about 520 °C. Above 550 °C, the DTG curves of samples with different particle sizes were identical, indicating that volatiles, which evolve at high temperatures, do not form fixed carbon by secondary reactions.

Effects of the Gas Environment

Much can be deduced about charcoal production from the thermochemical equilibrium calculations displayed in Figure 2. As emphasized earlier in this discussion, cellulose serves as a representative model compound for whole biomass. The trends displayed in Figure 2 remain the same when the exact C, H, O compositions of particular biomass species are employed in the calculations. At temperatures between 400 and 500 °C, the carbon yield from cellulose improves slightly as pressure is increased from vacuum to 0.1 MPa, but not thereafter. High pressures are not needed to secure a high yield of carbon from cellulose after equilibrium is established. Water, carbon dioxide, and methane are the only significant byproducts of cellulose carbonization. Note that water will be present during carbonization, even when a dry biomass feedstock is employed. Unfortunately, biomass feedstocks do not easily reach thermochemical equilibrium in a pyrolytic reactor. The chief obstacle is the formation of tarry vapors that can quickly escape from the hot reaction zone. As discussed below, the performance of a carbonizer is strongly influenced by its ability to control the gas-phase conditions in its interior.

Moisture. In a conventional kiln, the moisture content of the feed strongly affects the reaction time and charcoal yield. More feed must be burned to dry the remainder (prior to carbonization) when the feed is very wet. Hawley[41] remarks that moisture contents of 15−20% are satisfactory for most wood kilns, which often require drying of the wood feed for 6−18 months. The Stafford process[121] employed a very dry wood (moisture content < 0.5%)[39] to reduce its energy input requirements effectively to zero, but such dry feedstocks are not economical today. Usines Lambiotte, which operates one of the largest plants in Europe (25 000 tonnes per year in France), uses two shaft furnaces for drying of the feedstock. The optimum moisture content is 10%, but the average over the year is between 15 and 20%.[122]

The literature concerning the effects of moisture on biomass pyrolysis chemistry illustrates the important influence of pressure on the pyrolysis chemistry. At low temperatures (i.e., 100−150 °C), Shimazu and Ster-
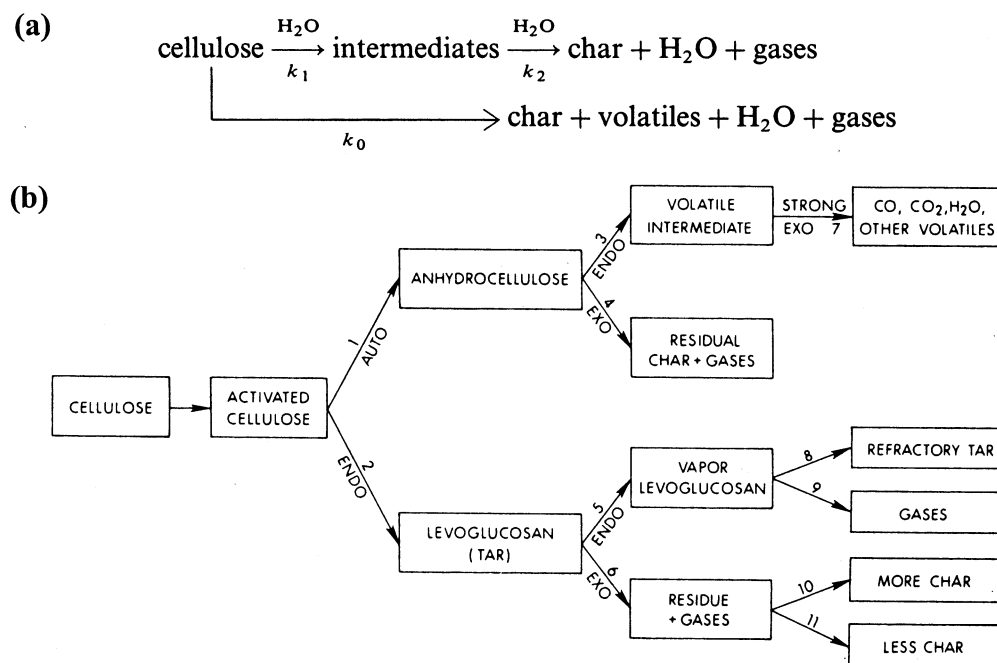
(a)

$$\text{cellulose} \xrightarrow[k_1]{H_2O} \text{intermediates} \xrightarrow[k_2]{H_2O} \text{char} + H_2O + \text{gases}$$

$$\xrightarrow{k_0} \text{char} + \text{volatiles} + H_2O + \text{gases}$$

(b)

Figure 5. (a) Kinetic model for char formation from cellulose at high pressures.[130] (b) Detailed mechanism of cellulose pyrolysis at elevated pressures.[171]

ling[123] found that moist cellulose (i.e., cellulose immersed in liquid water at an elevated pressure) breaks down less rapidly than dry cellulose. At higher temperatures, Hawley[41] speculated that wood pyrolysis in flowing steam resembles that in a vacuum. Stamm[124] also noted the favorable effect of steaming conditions on wood pyrolysis. His interpretation of the data of MacLean[125] led him to conclude that the apparent activation energy for wood pyrolysis in steam below 180 °C is about half that observed under dry heat. Darmstadt and co-workers[126] observed only a slight influence of moisture content on the charcoal yield from maple bark under vacuum, but a decrease in bark moisture caused the charcoal surface to become more graphite-like. An analysis of product yields from the Poore carbonization process by Klar[19] led him to conclude that pyrolysis in the presence of flowing steam at atmospheric pressure has "practically no effect on the yield of the (charcoal) product". Likewise, at atmospheric pressure and temperatures between 320 and 460 °C, Antal and co-workers[127] observed no influence of flowing steam on the kinetics of cellulose pyrolysis or the yields of char. Recently, Gergova, Petrov, and Eser[128] reported the synthesis of activated carbons with large BET surface areas (as high as 820 m²/g) by a steam pyrolysis of apricot, cherry, and grape seeds and almond shells at atmospheric pressure and temperatures ranging from 600 to 700 °C. Alaya, Girgis, and Mourad obtained similar results.[129] Burnoffs due to the water–gas reaction (i.e., steam gasification of carbon) were not large at these temperatures. Evidently, steam pyrolysis at high temperatures preferentially removes highly reactive carbon that blocks the intrinsic pore structure of the biocarbons.

In an externally heated, sealed crucible (that developed considerable internal pressure), Mok and co-workers showed that an increase in the moisture content of the cellulose substrate systematically enhanced the charcoal yield at high temperatures from 36% (dry cellulose substrate) to 40% (45% moisture, dry basis) while decreasing the onset temperature of py-

Table 2. Effects of Moisture Content (MC) on the Fixed-Carbon (fC) Yield from Eucalyptus Wood at 1 MPa

MC (wt %)	mass (kg)	charcoal yield (wt %)	fC content (wt %)	fC yield (wt %)
0.0	1.79	43.0	65.5	28.4
16.2	1.08	41.8	69.6	29.3
29.0	0.86	42.2	71.4	30.4
56.9	1.63	46.1	71.6	33.3

rolysis by more than 25 °C.[9] Varhegyi and co-workers[130] were able to simulate the data of Mok et al.[9] using the kinetic model displayed in Figure 5a. In this model, water plays the role of an autocatalytic agent for charcoal formation via reactions 1 and 2.[130] Results from both a pilot plant and a laboratory-scale reactor were consistent with the sealed crucible data. In the electrically heated pilot plant, air-dried Eucalyptus wood with a moisture content of 15% offered charcoal yields of 28–35%. Using the same wood and the same conditions, higher yields (i.e., 40–45%) were obtained when liquid water was pumped into the pilot plant during heatup and pyrolysis.[131] Similarly, in the electrically heated laboratory-scale reactor operating at 1 MPa, an increase in the moisture content of the Eucalyptus wood from 0 to 57% increased the fixed-carbon yield from 28.4 to 33.3% (see Table 2).[21] The consistency of these results clearly indicates that moisture content can improve the yield of charcoal from biomass at elevated pressures in situations where the flow of gas through the externally heated retort is small or negligible. Beyond the modeling work of Varhegyi et al.[130] and (more recently) Ball et al.,[132] the details of the chemistry that underlies the improved yields are not understood.

Vapor-Phase Residence Time. Although Klason established the key role of secondary (vapor-phase) pyrolytic reactions in the formation of charcoal 88 years ago;[40,41] today, many researchers still assume that charcoal is solely a product of primary (solid-phase) pyrolytic reactions. In reality, charcoal contains both "primary" charcoal and "secondary" charcoal that is a coke derived from the decomposition of the organic
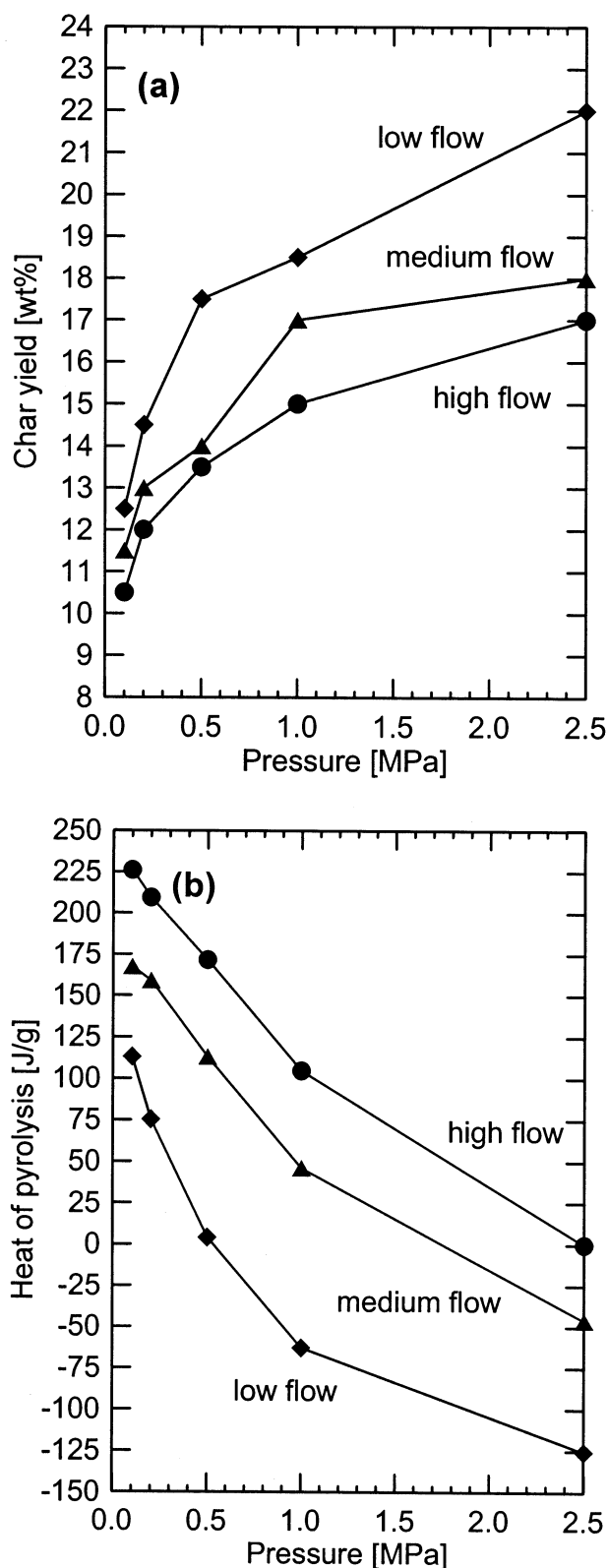
Figure 6. Effects of pressure and gas flow on the (a) yield of char and (b) heat of pyrolysis from cellulose.[138,171]

vapors ("tars") onto the solid carbonaceous solid.[41] This decomposition is probably catalyzed by the charcoal.[133–136] Remarkably, secondary charcoal is as reactive as primary charcoal.[137] The role of vapor-phase reactions in the formation of charcoal is well illustrated in Figure 6, which displays the effects of gas flow at various pressures on the yield of char derived from cellulose.[138] Plainly, low gas flows provide increased opportunities

for reactive volatile matter to interact with the solid carbonaceous residue of pyrolysis and produce more charcoal. Additional evidence supporting the impact of gas flow on charcoal production was reported by Varhegyi et al.,[61] who conducted TG studies of Avicel cellulose pyrolysis in open and covered sample pans. The char yield in the open sample pan was typically about 7%. When pyrolysis was conducted in a covered pan with a pinhole, the char yield dramatically increased to 19%. These striking results clarify the beneficial effects of both prolonged vapor-phase residence times and increased concentrations of vapors on the carbonization chemistry. Varhegyi's findings were corroborated by Suuberg and co-workers,[139] who varied the char yield from 4 to 20% by pyrolyzing cellulose samples of 1–30 mg in open pans or closed pans with 2–10 holes. Similar, but less dramatic, observations have been reported by coal researchers. Kamashita et al.[140] and Anthony et al.[141] both observed increases in the char yield from coal when the transport of reactive volatile products out of the coal particle was hindered.

Pressure. In 1914, Klason showed that charcoal yields are minimal when pyrolysis is conducted in a vacuum.[40,41,142] Instead of charcoal, Klason[19,40] reported that vacuum favors the formation of tars (which Bergström[93,94] designated as "B-tars"), with yields as high as 43.6 wt % from birch wood. More recently, Shafizadeh and Fu[143] and Broido and Nelson[57] reported lower char yields from cellulose under vacuum.

Violette's visionary work included a remarkable study of biomass carbonization at very high pressures.[46] Violette heated wood samples weighing about 1 g in sealed glass tubes to temperatures that caused some of the tubes to explode. When a tube did not explode, Violette was able to use a clever procedure to recover the products for analysis. At the highest temperature employed in his work, Violette reported a charcoal yield of 79.1 wt % with a carbon content of 77.1%. The charcoal was shiny and brittle and had undergone fusion similar to coking coal. Although the yield and carbon content data of these experiments appear to be impossibly high, Violette's observations are intriguing, and his experiments remain novel even today. Bergström[93,94] recognized that elevated pressures increase charcoal yield at the expense of the formation of B-tars. Sixty years after Violette's work, Palmer presented the first thorough study of the effects of elevated pressures on wood distillation in this journal.[144] Influenced by the strong interest that existed in optimizing the yield and quality of distillate at the turn of the century, Palmer reported yields of "charcoal" formed at temperatures below 338 °C with no analysis of its fixed-carbon content. Very small improvements in the charcoal yields were observed (e.g., 39–42% for maple sawdust) at elevated pressure together with some improvement in alcohol yields and a decrease in pyroligneous acid and tar formation. Palmer's observation that "Distillations were made at pressures as high as 450 lbs. (sic), but the exothermic reaction was so violent that it was not advisable to continue the experiments" was a prescient harbinger of later work. Shortly thereafter, Frolich et al.[145] at MIT reported a study of the effects of pressure on the destructive distillation of wood and cellulose within a pressure vessel that permitted high flows of hydrogen and other sweep gases. No effect of pressure on the yield of charcoal heated to 500 °C was detected. It appears that Palmer and Frolich overlooked the

Table 3. Effects of Pressure on the Fixed-Carbon (fC) Yield from Air-Dry Macadamia Nut Shells

pressure (MPa)	mass (kg)	charcoal yield (wt %)	fC content (wt %)	fC yield (wt %)
0.4	0.92	40.5	78.6	32.0
0.7	0.92	40.2	81.5	32.9
1.0	0.73	44.4	73.9	32.9
1.1	2.76	50.8	70.4	35.9
3.3	2.69	51.0	69.9	35.8

effects of pressure on biomass carbonization because of their focus on wood distillation, that caused them to employ high gas flow rates and low reaction temperatures.

Five decades later, using tubular flow reactors embedded in a differential scanning calorimeter (DSC), Mok and Antal[138] observed an increase from 12 to 22% in the yield of char from cellulose with an increase in pressure from 0.1 to 2.5 MPa at low gas flow (see Figure 6). The improved yield of char was accompanied by the formation of additional CO_2, H_2, and C_2H_6 and lesser quantities of CO, CH_4, and C_2H_4. A methodical study of the effects of pressure, gas flow, and thermal pretreatments on the products and heats of cellulose, anhydrocellulose, and levoglucosan pyrolysis led Mok and Antal to associate the pathways displayed in Figure 5b with the observed reaction chemistry. The pathways associated with the formation and decomposition of anhydrocellulose are not of great practical importance, since they are evoked by slow heating that is uneconomical. At high flow rates and pressures below 1 MPa, Mok and Antal observed the endotherm associated with the phase change of levoglucosan (reaction 5). But at low flow rates the endotherm was replaced by a strong exotherm. This change was due to the in situ carbonization of levoglucosan (reaction 6). Mok and Antal found that the carbonaceous residue of reaction 6 decomposed via competing reactions (10 and 11), with higher heating rates favoring the formation of less char (reaction 11). Unfortunately, the reaction network displayed in Figure 5b was not reduced to a kinetic model; furthermore, no kinetic models that embody the complex effects of pressure, vapor-phase residence time, and thermal pretreatments have been reported in the literature. Consequently, our understanding of the important but subtle effects of pressure and flow rate remains largely qualitative.

Other workers have corroborated many of the observations of Mok and Antal. In a pressurized TGA instrument Blackadder and Rensfelt[146] observed the char yield from cellulose pyrolysis to increase from 6% at 0.1 MPa to 15% at 4 MPa. Likewise, the char yield from wood increased from 21 to 28% over the same pressure range. Richard and Antal[147] reported an increase from 19 to 41% in the char yield from cellulose when the pressure was increased from 0.1 to 2.0 MPa with constant purge gas velocity. On the other hand, Kandiyoti and co-workers[148] observed little influence of pressure on char yields from Eucalyptus sawdust in a hot-rod reactor wherein the volatiles were quickly removed from the reaction zone. When examined in terms of fixed-carbon yields, the data of Antal et al.[21] (see Table 3) show a clear trend of increasing yields (i.e., from 31.9 to 35.7%) from macshells as the pressure increased from 0.4 to 3.3 MPa. Recently, we compared the fixed-carbon yields and reaction times realized by pyrolysis of various wood species in a conventional muffle furnace at atmospheric pressure with those

Table 4. Comparison of Charcoal and Fixed-Carbon Yields Realized at Atmospheric Pressure (0.1 MPa) under Different Heating Conditions with Those Obtained at 1.0 MPa

feed	0.1 MPa charcoal yield (wt %)	0.1 MPa fC content (wt %)	0.1 MPa fC yield (wt %)	1.0 MPa charcoal yield (wt %)	1.0 MPa fC content (wt %)	1.0 MPa fC yield (wt %)
alder wood[a]	30.2	71.7	21.7			
alder wood[b]	30.5	76.2	23.3			
alder wood[c]	29.8	78.4	23.4			
alder wood[e]				35.9	70.7	25.4
birch wood[a]	29.5	72.5	21.4			
birch wood[b]	28.8	77.2	22.3			
birch wood[c]	28.8	79.1	22.8			
birch wood[e]				34.6	78.5	27.2
oak wood[b]	31.2	76.9	24.0			
oak wood[e]				39.8	75.0	29.9
pine wood[a]	28.9	69.6	20.2			
pine wood[b]	32.1	74.6	24.0			
pine wood[c]	31.8	78.6	25.0			
pine wood[d]	28.8	86.6	25.0			
pine wood[e]				35.2	79.6	28.1
spruce wood[a]	33.0	69.1	22.9			
spruce wood[b]	32.2	74.7	24.1			
spruce wood[c]	31.7	78.7	25.0			
spruce wood[e]				37.5	76.7	28.8

[a] Rapid heating to 450 °C (within 90 min), followed by 10 min of soaking at 450 °C (0.1 MPa). [b] Slow heating to 450 °C (within 240 min), followed by 60 min of soaking at 450 °C (0.1 MPa). [c] Slow heating to 450 °C (within 240 min), followed by 240 min of soaking at 450 °C (0.1 MPa). [d] Slow heating to 550 °C (within 300 min), followed by 60 minof soaking at 550 °C (0.1 MPa). [e] Rapid heating to 450 °C (within 70 min), with no soaking time (1.0 MPa).

achieved in a pressurized retort (see Table 4).[6] Fixed-carbon yields at atmospheric pressure fell in the range of 20.2−25.0 wt %. As expected, slow heating, prolonged holding times at the peak temperature, and an increase in peak temperature from 450 to 550 °C improved the fixed-carbon yields somewhat. At 1 MPa, the fixed-carbon yields increased to 25.4−29.9 wt %. Reaction times were reduced from 300 min in the muffle furnace to 70 min in the pressurized retort. In light of these findings, there can be no doubt that elevated pressures improve charcoal fixed-carbon yields (at the expense of tar production). Concerning the importance of processing time, Foley[13] makes the following insightful observation. "For many charcoal makers, the question of yields is not one to which they give a great deal of attention. Provided the wood is plentiful, the question of labor costs and the length of time taken for carbonization can be far more important." In light of this observation, the reduction in processing time realized by pyrolysis at elevated pressure may be more important than improvements in charcoal yields.

In 1892, Chorley and Ramsay[41,89] first reported the exothermic release of heat during wood pyrolysis at temperatures above 280 °C. Klason and co-workers[8,18,41,149] both confirmed the exothermicity of the reaction and actually measured the heat evolved. Their value (6% of the HHV of wood) agrees well with modern measurements associated with high charcoal yields. Klason also discovered that the exotherm results from the decomposition of primary tar into coke and secondary tar.[40] Other workers[19,150−152] reported similar findings at about the same time as Klason. Much later, Roberts reported that the exotherm can release as much as 8−10% of the heat content of a feed.[153] This exotherm is so important that Hawley[41] was of the opinion that, without it, wood distillation would not be practical!

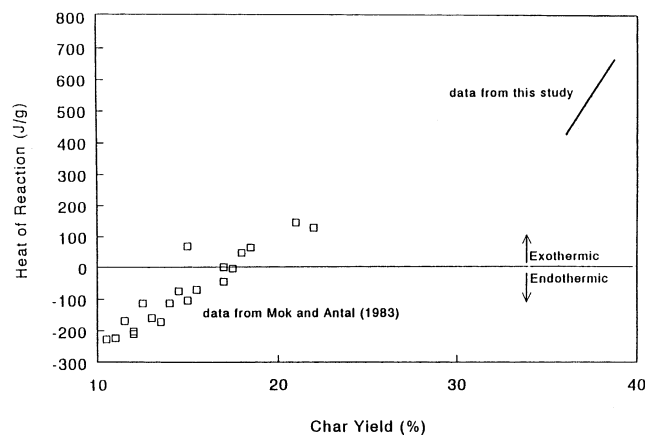Nevertheless, recent workers found that the pyrolytic

Figure 7. Values measured by Mok et al.[9,10] for the pyrolytic heat of reaction vs char yield over a wide range of pressures.

reactions of biomass can be exothermic or endothermic depending on reaction conditions.[56] For example, in their TGA/DSC study of wood pyrolysis in flowing nitrogen, Havens et al. reported endothermic heat of reaction of 200 and 110 J/g for pine and oak, respectively.[154] Likewise, in his numerical study of the pyrolysis of wood slabs, Kung[155] remarked that the effects of the *endothermic* pyrolysis reaction were "evidently an important matter". The varied, contradictory reports of endothermicity and exothermicity in the modern literature could easily confound a student, or amuse a seasoned researcher. Tang and Neil,[156] Kung,[155] Kung and Kalelkar,[157] Lee et al.,[158] Kansa et al.,[159] and Bennini et al.[160] reported pyrolytic endotherms, whereas Bamford et al.,[161] Akita,[162] Roberts and Clough,[163] Tinney,[164] and Roberts[165] observed exotherms. Recognizing the unresolved nature of the heat of reaction, some recent workers utilized variable or multiple values for the heat of reaction according to the situation.[166-170]

In his MSE thesis at Princeton, Mok was the first to clarify the conundrum.[171] He showed that increasing pressure causes the total heat of cellulose pyrolysis to shift (see Figure 6) from values near 230 J/g (endothermic) to values near −130 J/g (exothermic). Furthermore, in a sealed crucible (no gas flow), the heat of cellulose pyrolysis reached −600 J/g (exothermic) with a charcoal yield of 40%.[9] Figure 7 displays the linear relationship that exists between the pyrolytic heat of reaction and the observed char yield.[9,56,138] Recently, Milosavljevic et al.[139] reported similar findings from experiments conducted at atmospheric pressure. An increase in pressure also affects the pyrolysis of hemicellulose: Mok[138] observed one broad exotherm within a temperature range of 195−235 °C during the pyrolysis of a xylan extract in a flowing inert gas at 0.1 MPa. This exotherm shifted to lower temperatures at higher pressures. Increasing pressure at low flow rates also causes lignin to undergo exothermic pyrolysis with a small increase in yield, but the rates of reaction are low.[138] Mok's study of oak wood pyrolysis revealed a 60% increase in char yields when a low-pressure, high-flow condition was altered to a high-pressure, low-flow condition (see Figure 8). The measured exothermicity of the reaction also increased.[138] Increasing pressure lowered the onset of pyrolysis from 360 to 350 °C. Corn cob evidenced similar behavior: elevated pressures favored exothermicity and a reduction in the onset temperature, but the effects were reduced relative to those observed for oak wood and cellulose.[138] In sealed crucibles, the
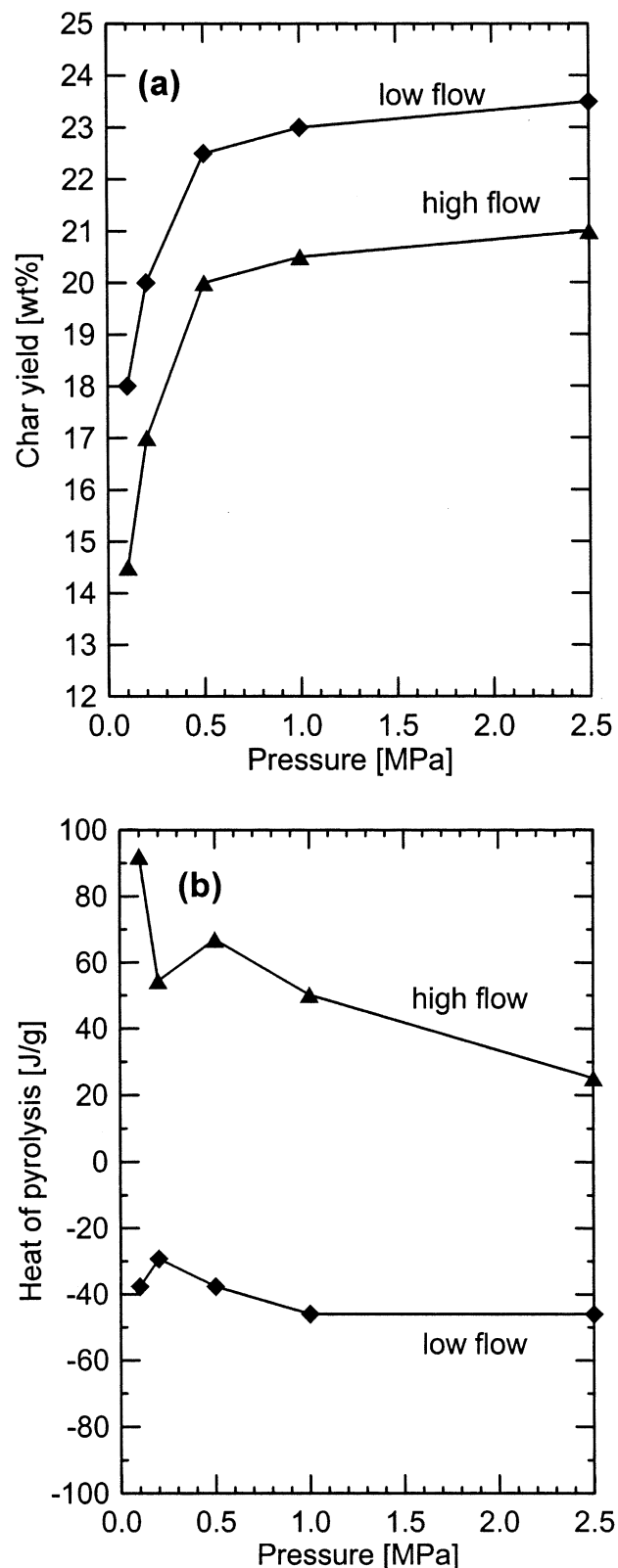

Figure 8. Effects of pressure and gas flow on the (a) yield of char and (b) heat of pyrolysis of oak wood.[171]

reaction exotherms due to hemicellulose decomposition exhibited peaks between 273 and 285 °C for woody species and between 244 and 246 °C for herbaceous species.[9] Cellulose decomposition occurred between 312 and 332 °C for woody species and between 291 and 299 °C for herbaceous species.[9] There was no peak associated with lignin decomposition.

Because thermochemical equilibrium calculations predict that elevated pressure should have no effect on the yields of carbon from biomass, the influence of pressure on fixed-carbon yields demands an explanation. As mentioned earlier, 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 solid.[41] Under pressure, the highly reactive, tarry vapors have a smaller specific volume; consequently, their intraparticle 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 reaction.[9] These effects can be magnified when the flow of gas through the particle bed is small,[130,139] as is the case at elevated pressure.[138,146,147] Furthermore, the formation of secondary carbon from the tarry vapor is catalyzed by the charcoal,[133−136] and water vapor or chemisorbed moisture can act as an autocatalytic agent for carbon formation at elevated pressures.[9,21,130,131] Molecular diffusivities are also affected by increasing pressure and can influence the escape of the tarry vapor from the solid particle.[172] Finally, we remark that equilibrium will be established between water's liquid and vapor phases at elevated pressures. It is well-known that steam and liquid water can soften, degrade, and extract lignin at temperatures near 100 °C.[173−175] Furthermore, formic and acetic acids are early products of biomass pyrolysis; consequently, an acid-catalyzed hydrolysis of the wet holocelluose fraction of the feed can occur at elevated pressures and somewhat higher temperatures when liquid water is present. All these phenomena can contribute to the improved fixed-carbon yields that are obtained by carbonization at elevated pressure.

Effects of Feedstock Properties

The size of a particle undergoing pyrolysis has a considerable effect on the decomposition chemistry. In an elegant paper pregnant with insights, Arseneau[176] used TGA and DSC to detect the appearance of a high-temperature exotherm during the pyrolysis of samples of cellulose with increasing thickness. He attributed this exotherm to the formation of secondary char that resulted from the decomposition of volatile matter (levoglucosan) that was unable to rapidly escape from the thicker cellulose samples. Usually, larger particles are associated with higher charcoal yields that are the result of these secondary reactions.[42,43] The performance of industrial-scale kilns and retorts that carbonize wood chips and other large biomass particles is influenced by the strong exotherm associated with charcoal formation. As noted by Palmer,[144] it can be difficult to measure the peak temperature of these reactors and to control it.[82,86] The exothermic release of heat during pyrolysis was the foundation of the commercial Stafford process[121,177] for charcoal production from very dry wood that realized a charcoal yield of 30%.[39]

Although some lore in the field suggests that charcoal yields are related to the density of the feedstock,[10] Byrne and Nagle[75] demonstrated that the yield of charcoal from various wood species is independent of the bulk wood density. On the other hand, Byrne and Nagle[75] showed that the bulk density of the charcoal is linearly proportional to the feedstock's bulk density with a proportionality constant of 0.82. Byrne and Nagle's

results were corroborated by Teixeira do Vale et al.[178] and Connor et al.[179]

Hawley[41] divided his presentation of wood distillation into sections concerning hardwoods and resinous woods, but this division was made to focus on the extraction of resinous products from softwoods. Hawley noted no difference, apart from coking of the resins that can lead to a higher charcoal density, between charcoals produced from softwoods and hardwoods. Wenzl[39] observed that the charcoal yield is sometimes considerably lower from deciduous than from coniferous woods, and Pontinha et al.[180] reported that several Brazilian pine species are better suited for charcoal production than *Eucalyptus grandis* when dense charcoal is not needed. On the other hand, Foley[13] voiced the opinion that hardwood charcoal is dense and resists breakage and burns cleanly and slowly, whereas softwood charcoal is soft and friable and burns quickly. Foley also cautioned against the use of bark in the production of charcoal. For whatever reason, hardwoods are the usual feedstock for charcoal production in the U.S.

Not unexpectedly, the charcoal yield from biomass is influenced by its lignin, holocellulose, and extractives contents.[44,181] Biomass species with high lignin contents offer higher charcoal yields,[9,181] reflecting the fact that lignin preferentially forms char during pyrolysis.[182−184] However, the claim by MacKay and Roberts[181] that the carbon yield of a lignocellulosic material can be predicted by a simple model that sums the yields of the substrate's cellulose, hemicellulose, and lignin components is misleading, because the carbon yield is strongly dependent on the vapor-phase conditions present in the pyrolytic reactor. Recently, Di Blasi and co-workers reported higher yields of charcoal from extractive-rich woods (e.g., chestnut) than from those with lower extractives content.[185] Corroborating this insight, Gaur and Reed realized a remarkable 44% fixed-carbon yield from Wattle tannin.[50] On the other hand, Roy and co-workers[186] obtained higher charcoal yields (under vacuum) from extractive-free wood. Their findings might be unique to vacuum pyrolysis technology. In any case, at elevated pressure, a great variety of biomass feedstocks offer attractive yields of charcoal. For example, in a pressurized retort, the fixed-carbon yields from bamboo, leucaena wood, and kukui nut shells all attained the theoretical values predicted to exist when thermochemical equilibrium is established at 1 MPa (see Figure 9).[6] High fixed-carbon yields were also realized in a pressurized retort from other feedstocks, including oak and eucalyptus wood, rice and oat hulls, macshells, and garlic wastes. Note that each theoretical yield value displayed in Figure 9 reflects the elemental composition of each feedstock (including its lignin content).

The composition of the feedstock also affects the ash, nitrogen, and sulfur contents of the charcoal. For example, Olsson et al.[187] observed little release of alkali metals during pyrolysis of wheat straw below 500 °C. Corroborating this result, Jensen et al.[188] detected no release of potassium during the pyrolysis of straw at temperatures below 700 °C. On the other hand, 60% of the chlorine was released (probably as HCl) in a temperature range of 200−400 °C and the remainder between 700 and 900 °C.[188,189] Olsson et al.[187] also observed enhanced alkali emissions from feeds with a chlorine-rich ash. To the best of our knowledge, no comparable studies have been reported on the distribu-
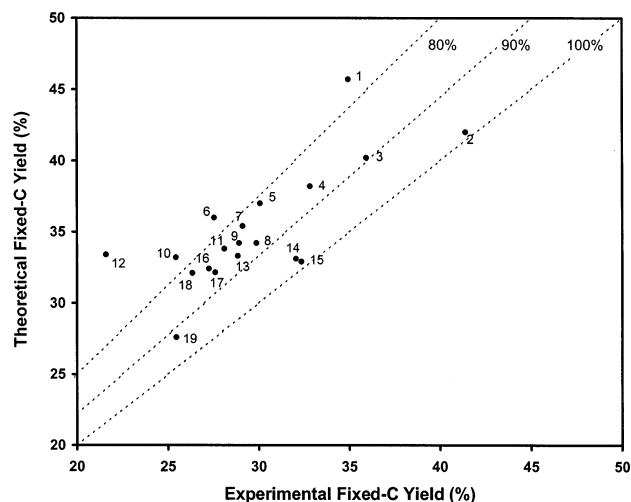
Figure 9. Parity plot of fixed-carbon yield (theoretical vs experimental at 1.0 MPa):[6] (1) pecan shell, (2) kukui nut shell, (3) macadamia nut shell, (4) eucalyptus wood, (5) coconut shell, (6) sunflower seed hull, (7) walnut shell, (8) oak wood (results from PDU), (9) almond shell, (10) alder wood, (11) pine wood (results from PDU), (12) corn cob, (13) spruce wood, (14) bamboo, (15) leucaena wood, (16) birch wood, (17) rice hull, (18) oat hull, and (19) garlic waste.

tions of sulfur and nitrogen species between the charcoal and volatile pyrolysis products. Although the sulfur and nitrogen contents of most biomass feedstocks and their charcoal derivatives are low, it is uncertain how much sulfur and nitrogen may be carried away in the off-gases of a pyrolytic reactor.

Philpot[190] completed an extensive study of the influence of mineral matter on the pyrolysis of various plant materials. In general, higher charcoal yields were obtained from feedstocks with higher ash contents, but the effect was less strong above 5% ash content. He found that only some of the mineral elements present in plant ash affect the pyrolysis reactions (e.g., silica has little influence). Richards and Zheng noted higher charcoal yields from cottonwood when potassium, lithium, or calcium ions were incorporated into the substrate by ion exchange.[191] Furneaux and Shafizadeh[192] removed the mineral matter from ivory-nut meal by acid washings and observed a decrease in the char yield from 33 to 22%. Raveendran et al.[53] also reported an increase in volatile yields as a result of de-ashing in some cases, but in the case of rice hulls and groundnut shells, the char yield increased after de-ashing. Recently, Radlein and co-workers[193] described a study of demineralization by a dilute HNO_3 treatment of the feedstock prior to pyrolysis. This pretreatment removed alkali and alkali earth metals that serve as catalysts for char formation. Fast pyrolysis produced high yields of anydrosugars from the pretreated herbaceous biomass materials.

Remarkably, a simple hot water wash can effectively remove the ash from many biomass feedstocks.[71] For example, Teng and Wei[194] showed that the char yield decreased and the volatile yield increased when rice hulls were washed in hot water prior to pyrolysis. These findings suggest that the results of Ravendreen et al.[53] (see above) might have been influenced by their de-ashing method. Jensen et al.[188] realized nearly quantitative removal of postassium from straw by a hot water wash after only 30 min of treatment at 80 °C. De-ashing can have the undesired effect of increasing the pyrolysis temperature by as much as 50 °C.[71] Unfortunately, hot water washes are less effective at removing minerals from charcoal.[195]

Reactivity

Unlike coal and other aromatic fossil fuels, biomass chars are notoriously reactive. The following subsections review the reactivity of charcoal in air at increasing temperatures.

Pyrophoricity. A recent article in the Honolulu Advertiser entitled "Charcoal Confirmed as Source of Blaze" described the spontaneous ignition of a bucket of wet charcoal briquettes that was left to dry.[196] This problem is unpleasantly familiar to skippers bound for Norway who often extinguish fires in shiploads of wet wood charcoal that self-ignite on the high seas. The handbook *Industrial Charcoal Making* offers the following caution:[14] "Tightly packed masses of charcoal fines and charcoal with a high content of volatiles are more subject to spontaneous combustion than larger pieces of lump charcoal. Self ignition may even occur if charcoal has been water-sprayed for better cooling." These observations are in accord with an early report by Ranke[197] and with Shafizadeh's findings[105,198] concerning the pyrophoric nature of biomass chars. Bergström[93,94] noted that oven-dry charcoal (<5 wt % moisture) evolves heat when adsorbing water, but not in sufficient quantity to cause autoignition. He believed that oxygen chemisorption is the root cause of autoignition, which he reported to occur at temperatures as low as 150 °C (spruce) and 170 °C (aspen) for charcoals prepared at 430 °C. On the other hand, Brocksiepe[199] reported that the ignition point of charcoal "ranges between 200 and 250 °C, depending on the content of volatile compounds". Brocksiepe's values are in excellent agreement with the low-temperature ignition measurements of Di Blasi and co-workers,[200] Dai and Antal,[108] and Tam and Antal.[201] In any case, we have not observed any pyrophoric behavior of charcoal in our research. We believe that a search for pyrophoric carbons, followed by the development of an understanding of their pyrophoricity, could be quite fruitful.

Chemisorption. Biomass carbonization involves the fracture of most of the chemical bonds initially present in the biomass feedstock. The product carbon does not go through a fluid state; consequently, many of these bonds are left "dangling". These dangling bonds give rise to the chemisorption properties of charcoal.

Significant amounts of oxygen and moisture can be chemisorbed by charcoal during storage.[72] The German Regulation for Dangerous Goods requires a storage (equilibration) period before shipment of 4 days after production for lump charcoal and 8 days for charcoal dust or granulated charcoal.[199] Wenzl[39] reported a maximum in oxygen chemisorption on charcoals carbonized at about 430 °C. This value agrees with the findings of Richards and co-workers, who observed a maximum level of oxygen chemisorption on cellulose[202] and wood[203] chars pyrolyzed at 450–500 °C, and Bradbury and Shafizadeh[204] who reported a maximum at 550 °C for cellulose char. Higher peak temperatures reduced the amount of oxygen chemisorbed on the chars. Oxygen chemisorption involves the formation of oxides and peroxides on the charcoal surface at temperatures as high as 250 °C, until it becomes saturated with oxygen and stabilization of weight occurs.[39] The carbon–oxygen complex can act as a Lewis base, and considerable work has been done in characterizing the oxygen functional

groups by means of titrations[205] and FTIR spectroscopy. Chemisorbed oxygen causes the carbon to become hydrophilic, thereby influencing its ability to chemisorb water. Oxygen chemisorption also affects the electrical resistivity of carbon particles: increased oxygen content greatly increases the electrical resistivity of the carbon.[205] An increase in chemisorbed oxygen to 4% increased the electrical resistance of a powdered carbon by a factor of 100. Richards and co-workers[202] observed the formation of CO_2 and H_2O (little CO) during temperature-programmed desorption (TPD) of oxidized cellulose char. Their results show that oxygen associates with both carbon and hydrogen atoms on the surface of the char. Using an oxidized macshell carbonized charcoal, Dai and Antal[108] reported the evolution of both CO and CO_2 by TPD with an increasing CO/CO_2 ratio at higher carbonization temperatures.

As mentioned earlier, Antal and co-workers[108,206] measured iodine numbers in the range of 130–180 for macshell charcoal carbonized at temperatures between 750 and 900 °C. They were able to increase the iodine number to 260 by merely exposing carbonized macshell charcoal to air at 100 °C for 2 h and then performing a second carbonization at 950 °C.[206] The second carbonization served to drive off the chemisorbed species and thereby greatly magnified the microporosity of the carbon. Remarkably, Richards and co-workers[202] observed that the rates and extents of oxygen chemisorption on chars derived from Whatman #41 filter paper were much lower than those reported by Bradbury and Shafizadeh[204] on chars derived from cotton cellulose. These results point to the ability of carbonized charcoal to aggressively chemisorb oxygen present in the environment and the unusual sensitivity of the chemisorption process to the nature of the carbon.

Foley notes that the volatile matter content of charcoal affects its uptake of moisture.[13] Typical charcoals adsorb 3–8 wt % moisture, but a high-VM-content charcoal can take on 15 wt % moisture. Klar[19] cautions that a period of 3 weeks is needed to fully equilibrate charcoal with a mass gain of 8%, but 72 h is sufficient for the charcoal to realize a 4% weight gain. Antal and co-workers[206] washed a carbonized macshell charcoal in compressed liquid water at 150 °C for 2 h and then carbonized the washed product at 950 °C. The iodine number increased from about 180 to 330 because of the loss of carbon bound to chemisorbed water during the second carbonization. The aggressive nature of the chemisorption process is further illustrated by the evolution of carbon dioxide when water contacts clean commercial activated nutshell charcoal at 25 °C.[207,208] At 200 °C, Smith et al.[207] observed the formation of hydrogen in addition to much larger quantities of carbon dioxide during the chemisorption of water on the same carbon. These authors proposed a mechanism that involved the initial adsorption of a water molecule onto a carbon oxygen complex site and the existence of a stable CO complex and a less stable CO_2 complex on the surface of the carbon. In agreement with Smith et al., Lee and Reucroft[115] showed that an increase in water vapor adsorption onto wood-based activated carbons was correlated with higher concentrations of functional groups that contained oxygen on the carbon's surface. Shadle and co-workers[209] described an equilibrium model for water adsorption and desorption on coal chars. If the effects of variable surface areas and other surface properties were to be included in this model, it may also prove useful for predicting the adsorption properties of biomass charcoals.

Ignition. Both the feedstock and the carbonization temperature affect the ignition properties of charcoal. For example, Hshieh and Richards[203] could not ignite a charcoal produced from an acid-washed cottonwood (i.e., neither temperature runaway nor incandescence was observed during heating in air). Likewise, a charcoal made from ash-free cellulose required a temperature of 400 °C to sustain a measurable reaction rate in air.[210] Also, Richards and co-workers found that a preadsorption of oxygen on charcoal elevated the observed ignition temperature by 73–130 °C. Ward and Rideal[211] found that the amount of oxygen adsorbed (per gram of charcoal) was proportional to the partial pressure of oxygen, except at very low pressures. The initial adsorption of oxygen on outgassed samples, however, evidenced an extraordinary exotherm, exceeding values of 5 kJ per mole of oxygen adsorbed. Ward and Rideal[211] observed the greatest heat evolution from oxygen adsorption on an activated charcoal with an ash content of 9.6%. The addition of cobalt or potassium by ion exchange to acid-washed cottonwood lowered the ignition temperature of its oxygenated charcoal (i.e., charcoal with substantial amounts of chemisorbed oxygen), whereas the addition of calcium increased the ignition temperature.[203] Thus, the presence of chemisorbed oxygen and the makeup of the mineral matter content of the charcoal strongly influence its ignition behavior.

Combustion. Shafizadeh's laboratory was among the first to initiate chemical studies of the smoldering combustion of cellulosic chars. His CP/MAS ^{13}C NMR analyses of cellulosic chars and partially oxidized chars revealed the preferential attack at low temperatures of oxygen on paraffinic carbons present in the chars. At higher temperatures, the aromatic carbons were oxidized.[212]

Both the heating rate and the peak temperature can affect the reactivity of biocarbons. Chen et al.[137] observed a 140–230% increase in the reactivity (with steam and carbon dioxide) of birch wood charcoal produced at high heating rates. One "normal" effect of increasing peak temperature (i.e., HTT) is a reduction in char reactivity. In the case of wheat straw, a large drop in reactivity occurs at HTT between 1000 and 1200 °C.[213] This "thermal annealing" process can result from a loss of surface area, a reduction in the concentration of active sites on the char's surface,[214] a decrease in the H/C ratio as the charcoal composition becomes increasingly aromatic, or a loss of catalytic activity of minerals present in the char.[213] Richards, Kannan, and their co-workers observed departures from the normal thermal annealing behavior when chars with significant amounts of potassium[214,215] or copper[216] in their ash were gasified in air at 400 °C. In both cases, elevated heat-treatment temperatures (400 °C for copper and above 650 °C for potassium) reduced the oxidation states of these ions (in the presence of carbon) to elemental metals. The greatly enhanced reactivity of these chars was ascribed to the unusual catalytic activity and mobility of the elemental metal in the char.[214–216] Similar effects were not observed with calcium, because its oxides cannot be reduced by carbon at peak temperatures below about 2000 °C.[210,214,215] Recently, Jensen and co-workers[213] also described the considerable influence of potassium as a catalytic agent for the oxidation of wheat straw

chars subjected to various HTTs below 1200 °C, but the catalytic effect was lost at 1200 °C and above.[213]

The extraordinary reactivity of charcoal[217] sets pitfalls for researchers attempting to measure reaction rates. Underestimates of the apparent activation energy of biomass pyrolysis at high heating rates—due to thermal lag that results in part from the pyrolytic endotherm—are well-known.[42,56,70,71,218,219] Likewise, oxygen chemisorption and gasification are accompanied by a vigorous reaction exotherm that can cause an overestimate of the apparent activation energy associated with measurements of charcoal reactivity in air. Thus, Richards and his colleagues reported a "jump phenomenon" in the air-gasification rate of biomass charcoals at low temperatures,[216] which they later attributed to temperature runaway. Despite the small samples employed in their TGA studies, during runaway, the actual sample temperature greatly exceeded the "sample temperature" reported by the TGA device, leading to a gross overestimate of the reactivity of the charcoal.[210,220] The temperature range where runaway occurred (255–340 °C) is in good agreement with measured ignition temperatures of charcoal. In some cases (e.g., calcium-doped cellulose chars), Richards and co-workers found that presorption of oxygen on the char below the gasification temperature eliminated the runaway,[210] whereas in other cases (e.g., copper-doped cellulose chars), the runaway could not be eliminated.[220]

Both Dai[108,221] and Tam[201] studied the low-temperature combustion of carbonized macshell charcoal in a thin packed bed. The charcoal substrate of Dai[108,221] was carbonized at 750 °C, whereas the substrate of Tam[201] was carbonized at 900 °C. Despite these relatively high heat-treatment temperatures, Dai[108,221] observed steady combustion (after a transient peak) at about 285 °C in air–helium mixtures with an oxygen partial pressure of about 10 kPa. Tam[201] reported similar results at constant combustion temperatures of 177, 277, 327, and 387 °C. Both workers observed a strong, transient combustion peak whose reaction rate declined by a factor of 2 or more to a relatively steady value after some tens of minutes. During the transient, the temperature of the bed varied by less than 10 °C. Using calculated values of the Weisz–Prater criteria, they concluded that the measured combustion rate was not affected by extraparticle or intraparticle mass-transfer limitations at 285 °C, but Tam[201] inferred intraparticle mass-transfer limitations within the carbon's micropores at higher temperatures. These results are important because they provide a benchmark for the rate of carbonized charcoal combustion at low temperatures.

Several research teams have reported studies of charcoal combustion by thermogravimetry at constant heating rates.[200,213,222–227] The chief purpose of these studies was the development of engineering rate laws that could be used to design a charcoal combustor. In all cases, the simple rate equation

$$r = k_0 \exp(-E_A/RT)P_{O_2}{}^n(1 - x)^m$$

afforded a good fit to the weight-loss curves. In this equation, r is the rate of weight loss, k_0 is the preexponential constant, E_A is the apparent activation energy, R is the gas constant, T is the temperature, P_{O_2} is the partial pressure of oxygen, x is the fractional conversion of the carbon substrate, and n and m are apparent orders of reaction. For biomass chars the reported values of E_A range from 71 to 162 kJ/mol with fractional values of n (0.5–0.9) and m (0.5–1). Cozzani[226] and Janse et al.[225] offer clear comparisons of the reported rate laws in the form of Arrhenius plots (see Figure 7 of Cozanni and Figure 11 of Janse et al.). These plots reveal a considerable range in the predicted reaction rates at any given temperature. This range may reflect catalytic effects of minerals present in each individual char, or it may reflect the heat-treatment temperature of the char; or the heating rate employed to produce the char, which influences the H/C ratio of the char; or the pore volume distributions of the chars; or some other property of each individual char. Although each team took care to eliminate heat- and mass-transfer limitations, such intrusions might have influenced the some of the rate data.

We feel some concern that thermogravimetric studies might gloss over the strong influence of oxygen chemisorption at low temperatures. In theory, the simple rate law mentioned above captures some of the features of the chemisorption process. Usually, this process is represented by the following three reactions[228,229]

$$\text{(i) } 2C + O_2 \rightarrow 2C(O)$$

$$\text{(ii) } C(O) \rightarrow CO$$

$$\text{(iii) } C(O) + C(O) \rightarrow CO_2 + C$$
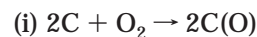
These equations do not represent the interaction of oxygen atoms with hydrogen atoms present in the char,[202] nor do they represent the presence of multiple, different carbon sites for oxygen chemisorption as revealed by TPD of oxidized chars.[120] Nevertheless, the low-temperature reaction rates derived from thermogravimetric data agree well with the values of Dai and Tam mentioned above.

Industrial Processes

Modern industrial processes for charcoal production employ either internal heating (e.g., a Missouri kiln), external heating (e.g., a VMR retort), or heating by gas recirculation (e.g., the Degussa process) to carbonize the feedstock. All commercial processes operate at near-atmospheric pressure, and most use wood as the feedstock. Often, the reported charcoal yield of the process is not defined. Usually, the values of the moisture contents of the feed and the charcoal are not reported. The fixed-carbon yield of these processes is never reported and is difficult to estimate without a representative proximate analysis of the charcoal product and the moisture and ash contents of the feed. The following paragraphs are a summary of a recent survey by Grønli[230] that also includes examples of continuous processes (e.g., those of Lambiotte in France and Lurgi in Australia).

Missouri kilns, Argentine kilns, and Brazilian "beehive" kilns employ internal heating based on the partial combustion of the feedstock to manufacture charcoal. The Missouri kiln is a large (ca. 180-m³) rectangular structure of poured concrete that is filled with wood slabs by front-end loaders. Following ignition, air entry into the kiln is regulated, and emissions are directed to afterburners. In the U.S., many Missouri kilns have ceased to operate because they have not been able to meet emissions regulations. Operating on a 7–30-day cycle, the charcoal yield of a Missouri kiln is reported to vary between 20 and 30%.

The VMR oven consists of two horizontal cavities and a central combustion chamber that provides external heating to canisters full of wood that are loaded into the cavities by forklifts. Operating in a cyclic manner, combustible vapors evolved during the exothermic pyrolysis reaction in one canister are burned in the oven to deliver heat to the other canister full of fresh wood. This heat dries the wood and initiates pyrolysis and the evolution of combustible vapors. At this point, the first canister (full of hot charcoal) is removed, and a new canister full of fresh wood is loaded in its place. The canisters are airtight and are set aside to cool before the charcoal is removed. The carbonization time for a 4.5-m^3 canister is 8−12 h, and the charcoal yield is reported to be 30−32%.

The Degussa (Reichert) process employs a batch-fed retort to generate a pyrolysis gas. Condensables are removed from the gas, after which the gas is heated in a heat exchanger and returned to the retort. Excess gas is burned to drive the heat exchanger and predry the feedstock. Acetic acid and smoke flavoring compounds are recovered from the condensables and marketed. A batch cycle in the 100-m^3 retort requires 16−20 h and is said to offer a charcoal yield of 34% from beech wood.

Conclusions

Research findings during the past decade have kindled a renewed interest in charcoal. Initially, some experts opined that little could be done to improve a technology that had been in continuous use since prehistoric times. Shortly thereafter, researchers described the development of pressurized equipment that improved the yields of charcoal and dramatically reduced the needed reaction times. A few years later, thermochemical equilibrium calculations were used to show that the improved yields actually approach—and in some cases attain—the theoretical limit. Researchers also made considerable progress in understanding the properties of charcoal, including the evolution of its chemical composition, its electrical properties, and its surface properties.

The emphasis during the preceding 20 years (1972−1992) was the minimization of charcoal yields. Because of the "energy crisis", researchers around the world focused their attention on maximizing the production of pyrolytic liquid fuels (i.e., "biocrude oil") by minimizing byproduct gases and char.[231,232]

During the four decades that preceded the energy crisis of 1972, because of the rapid growth of the oil industry, charcoal research lay dormant. Knowledge about biocarbons reflected the rapid advances that had occurred during the preceding eight decades (1852−1932), when the wood distillation industry was a major source of chemicals and solvents. It was during this era that scientists first defined the chemical composition of charcoal. They explored the effects of process conditions on charcoal formation and byproduct yields. It was an exciting time when man first began to comprehend the science underlying the art of charcoal production that skillful colliers had developed by trial-and-error methods over the preceding 38 millenia.

Our review of the literature offers the following conclusions:

1. Thermochemical equilibrium predictions set meaningful limits on the maximum ("theoretical") yield of carbon that can be obtained from a particular biomass feedstock. The measured fixed-carbon yield of charcoal derived from a feedstock can be compared to the calculated theoretical yield of carbon for the feedstock. This comparison is a measure of the efficiency of the carbonization process.

2. Carbonization at elevated pressure improves the yield of charcoal from biomass particles. Under pressure, the tarry pyrolytic vapors have a smaller specific volume; consequently, their residence time within the particle and in the near vicinity of the particle increases. Also, the partial pressure of the tarry vapor within and in the vicinity of the particle is higher. These effects are magnified when the flow of gas through the particle bed is small. The tarry vapor is composed of a complex reactive mixture of organic compounds—including vapor-phase sugars, and anhdyrosugars and their oligomers, fragments of sugars, and lignin moieties—that are highly unstable at elevated temperatures. These tarry vapors rapidly decompose on the surface of charcoal, producing secondary charcoal and a gas composed primarily of water, carbon dioxide, methane, hydrogen, and carbon monoxide.

3. The presence of water in the feedstock can either decrease or increase the yield of charcoal from the dry fraction of the feed material. Obviously, when carbonization is conducted in an air-blown kiln, more feedstock must be burned to supply heat to dry the moist feed before pyrolysis can commence. On the other hand, at elevated pressure, an increase in the moisture content of the feed increases the yield of charcoal produced by an externally heated retort. There is some evidence that moisture acts as a catalytic agent for the formation of charcoal.

4. The heat evolved by pyrolysis is proportional to the amount of charcoal produced by the primary and secondary carbonization reactions. When the yield of charcoal is high, the pyrolysis chemistry is strongly exothermic. If the feedstock is dry and the yield is high, the exothermic evolution of heat can elevate the temperature of incoming feedstock sufficiently to initiate the carbonization reactions.

5. Components of the mineral matter naturally present in biomass (e.g., potassium) are "built-in" catalysts for charcoal formation, oxygen chemisorption on charcoal, and charcoal combustion.

6. Charcoal is a renewable, highly reactive, truly "clean coal". Relative to fossil fuels, charcoal contains virtually no sulfur or mercury and very little nitrogen and ash. Carbonized charcoal can conduct electricity nearly as well as a metal, and it can have a high surface area. This extraordinary combination of properties causes charcoal to be the carbon of choice for applications ranging from potting media to the production of pure silicon for the semiconductor industry.

Much remains to be learned before a modern kiln can be optimally designed by numerical simulations. Little knowledge of the kinetics of secondary char formation exists. Coking studies are exacerbated by difficulties associated with capturing and analyzing the complex reacting soup of organic compounds present in the vapor phase. A kinetic model that described coking chemistry and the oxidation chemistry of the vapors, including the effects of the vapor-phase concentrations of water, oxygen, and organic species, would be a real boon. Such a model would enable the design of reactors with improved throughputs that would minimize labor inputs and maximize the efficient use of the renewable biomass feed. Little is known about the disposition of fuel-bound nitrogen and mineral matter between the products of

pyrolysis. Knowledge about this distribution is needed to predict the properties of charcoal and the effluents of the carbonization process. Also, carbonization evokes the development of surface area and electrical conductivity, but a good understanding of the materials science that underlies these changes—especially the 6 orders of magnitude increase in electrical conductivity—is lacking. The pyrophoric nature of wet charcoal is a real mystery. Despite our 38 000 years of experience with charcoal, its secrets continue to captivate us.

Acknowledgment

Literature Cited

(1) Bard, E. Extending the Calibrated Radiocarbon Record. *Science* **2001**, *292*, 2443.

(2) Clottes, J. *Direction Des Antiquités Préhistoriques De Midi-Pyrenees*; Foix, France. Personal communication, 2002.

(3) Clottes, J., Ed., *La Grotte Chauvet. l'Art des Origines*; Seuil: Paris, 2001.

(4) Agricola, G. *De Re Metallica*; Dover Publications: New York, 1950.

(5) http://www.shellfoundation.org/sep/, Shell Foundation, 2001.

(6) Antal, M. J.; Allen, S. G.; Dai, X.; Shimizu, B.; Tam, M. S.; Grønli, M. G. Attainment of the theoretical yield of carbon from biomass. *Ind. Eng. Chem. Res.* **2000**, *39*, 4024.

(7) Reynolds, W. C. *STANJAN Thermochemical Equilibrium Software*, version 3.91; Stanford University: Stanford, CA, 1987.

(8) Klason, P.; Heidenstam, G.; Norlin, E. Untersuchungen zur Holzverkohlung. I. Die trockene Destillation der Cellulose. *Z. Angew. Chem.* **1909**, *25*, 1205.

(9) Mok, W. S. L.; Antal, M. J.; Szabo, P.; Varhegyi, G.; Zelei, B. Formation of Charcoal from Biomass in a Sealed Reactor. *Ind. Eng. Chem. Res.* **1992**, *31*, 1162.

(10) Antal, M. J.; Mok, W. S. L.; Varhegyi, G.; Szekely, T. Review of Methods for Improving the Yield of Charcoal from Biomass. *Energy Fuels* **1990**, *4*, 221.

(11) van der Plas, R. *Burning Charcoal Issues. Energy Issues*; FPD Energy Note No. 1; The World Bank Group: Washington, DC, 1995.

(12) Bhattacharya, S. C.; Shrestha, R. M.; Sivasakthy, S. *State of the Art for Biocoal Technology*; Asian Institute of Technology: Bangkok, Thailand, 1988.

(13) Foley, G. *Charcoal Making in Developing Countries*; Earthscan: London, 1986.

(14) *Industrial Charcoal Making*; FAO Forestry Paper 63; FAO, United Nations: Rome, 1985.

(15) Lacaux, J.-P.; Brocard, D.; Lacaus, C.; Delmas, R.; Brou, A.; Yoboue, V.; Koffi, M. Traditional charcoal making: An important source of atmospheric pollution in the African Tropics. *Atmos. Res.* **1994**, *35*, 71.

(16) Pennise, D. M.; Smith, K. R.; Kithinji, J. P.; Rezende, M. E.; Raad, T. J.; Zhang, J.; Fan, C. Emissions of greenhouse gases and other airborne pollutants from charcoal making in Kenya and Brazil. *J. Geophys. Res.* **2001**, *106*, 24143.

(17) Smith, K. R.; Pennise, D. M.; Khummongkol, P.; Chaiwong, V.; Ritgeen, K.; Zhang, J.; Panyathanya, W.; Rasmussen, R. A.; Khalil, M. A. K. *Greenhouse Gases from Small-Scale Combustion Devices in Developing Countries: Charcoal-Making Kilns in Thailand*; Report EPA-600/R-99-109; Office of Air and Radiation

and Policy and Program Evaluation Division, U.S. Environmental Protection Agency: Washington, DC, 1999.

(18) Klason, P.; Heidenstam, G. V.; Norlin, E. Teoretiska undersokningar rorande kolning af ved. I. Om torrdestillation of cellulosa. *Ark. Kemi, Mineral. Geol.* **1908**, *3*, 1.

(19) Klar, M. *The Technology of Wood Distillation*; Chapman & Hall: London, 1925.

(20) *Charcoal: Production, Marketing, and Use*; U.S. Department of Agriculture Forest Service Report #2213; U.S. Department of Agriculture: Washington, DC, 1961.

(21) Antal, M. J.; Croiset, E.; Dai, X. F.; DeAlmeida, C.; Mok, W. S. L.; Norberg, N.; Richard, J. R.; Majthoub, M. A. High-Yield Biomass Charcoal. *Energy Fuels* **1996**, *10*, 652.

(22) Deglise, X.; Magne, P. Pyrolysis and Industrial Charcoal. In *Biomass*; Hall, D. O., Overend, R. P., Eds.; J. Wiley: New York, 1987; p

(23) Vegetal, A. B. d. C. *Statistical Yearbook*; 1990.

(24) *Quarterly Bulletin of Statistics*; FAO, United Nations: Rome, 1992.

(25) *Yearbook of Forest Products 1995*; FAO, United Nations: Rome, 1997.

(26) Rosilo-Calle, F.; De Rezende, M. A. A.; Furtado, P.; Hall, D. O. *The Charcoal Dilemma*; Intermediate Technologies Publications: London, 1996.

(27) Shingi, P. M.; Seetharaman, S. P. *Charcoal Production and Marketing in Gujarat*; GCP/RAS/131/NET, Field Document 36; FAO, United Nations: Bangkok, Thailand, 1993.

(28) Eikeland, I. J. Elkem, Oslo, Norway. Personal communication, 2002.

(29) Coutinho, A. R.; Luengo, C. A. Preparing and Characterizing Electrode Grade Carbons from Eucalyptus Pyrolysis Products. In *Advances in Thermochemical Biomass Conversion*; Bridgwater, A. V., Ed.; Blackie Academic & Professional: London, 1993; p 1230.

(30) Coutinho, A. R.; Luengo, C. A. Mass Balance of Biocarbon Electrodes Obtained by Experimental Bench Production. In *Developments in Thermochemical Biomass Conversion*; Bridgwater, A. V., Boocock, D. G. B., Eds.; Blackie Academic & Professional: London, 1997; p 305.

(31) Coutinho, A. R.; Rocha, J. D.; Luengo, C. A. Preparing and characterizing biocarbon electrodes. *Fuel Process. Technol.* **2000**, *67*, 93.

(32) Kramer Laboratories, Miami, FL, 2002.

(33) Glaser, B.; Haumaier, L.; Guggenberger, G.; Zech, W. The 'Terra Preta' phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften* **2001**, *88*, 37.

(34) Glaser, B.; Lehmann, J.; Zech, W. Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—A review. *Biol. Fertil. Soils* **2002**, *35*, 219.

(35) Mann, C. C. The Real Dirt on Rainforest Fertility. *Science* **2002**, *297*, 920.

(36) Ueda, R.; Miyakawa, K. Plant growth-supporting agents comprising activated carbon and method to support plant growth. Japanese Patent JP 2001122712, 2001.

(37) Pietikainen, J.; Kiikkila, O.; Fritze, H. Charcoal as a habitat for microbes and its effect on the microbial community of the underlying humus. *Oikos* **2000**, *89*, 231.

(38) Van Winkle, S. C.; Pullman, G. S. The Role of Activated Carbon in Tissue Culture Medium. *Energeia* **1995**, *6*, 1.

(39) Wenzl, H. F. J. *The Chemical Technology of Wood*; Academic Press: New York, 1970.

(40) Klason, P. Versuch einer Theorie der TrockenDestillation von Holz. *J. Prakt. Chem.* **1914**, *90*, 413.

(41) Hawley, L. F. *Wood Distillation*; Chemical Catalog Co.: New York, 1923.

(42) Antal, M. J. Biomass Pyrolysis: A Review of the Literature. Part 1. Carbohydrate Pyrolysis. In *Advances in Solar Energy*; Boer, K. W., Duffie, J. A., Eds.; American Solar Energy Society: New York, 1982; p 61.

(43) Antal, M. J. Biomass Pyrolysis: A Review of the Literature. Part 2. Lignocellulose Pyrolysis. In *Advances in Solar Energy*; Boer, K. W., Duffie, J. A., Eds.; Plenum Press: New York, 1985; p 175.

(44) Goos, A. W. The Thermal Decomposition of Wood. In *Wood Chemistry*; Wise, L. E., Jahn, E. C., Eds.; Rheinhold Publishing Co.: New York, 1952; p 826.

(45) Chaturvedi, M. D. The Chinese Charcoal Kiln. *Indian For.* **1943**, *69*, 75.

(46) Violette, M. Memoire sur les Charbons de Bois. *Ann. Chim. Phys.* **1853**, *32*, 304.

(47) Aucamp, H. L. Large Scale Charcoal Technology. V Encontro Nacional de Florestadores, Gramado/Canela, 1979; p 1.

(48) Shah, N.; Girard, P.; Capart, R. Carbonization of Wood: Product Analysis and Energy Assessment. *Appl. Energy* **1989**, *34*, 223.

(49) Shah, N.; Girard, P.; Mezerette, C.; Vergnet, A. M. Wood-to-charcoal conversion in a partial-combustion kiln: An experimental study to understand and upgrade the process. *Fuel* **1992**, *71*, 955.

(50) Gaur, S.; Reed, T. B. *An Atlas of Thermal Data for Biomass and Other Fuels*; report NREL/TP-433-7965; National Renewable Energy Laboratory (NREL): Golden, CO, 1995.

(51) Cheremisinoff, P. N. *Biomass: Applications, Technology, and Production*; Marcel Dekker: New York, 1980.

(52) Demirbas, A. Carbonization ranking of selected biomass for charcoal, liquid and gaseous products. *Energy Convers. Manage.* **2001**, *42*, 1229.

(53) Raveendran, K.; Ganesh, A.; Khilar, K. C. Influence of mineral matter on biomass pyrolysis characteristics. *Fuel* **1995**, *74*, 1812.

(54) Di Blasi, C.; Signorelli, G.; Di Russo, C.; Rea, G. Product Distribution from Pyrolysis of Wood and Agricultural Residues. *Ind. Eng. Chem. Res.* **1999**, *38*, 2216.

(55) Lede, J. Reaction Temperature of Solid Particles Undergoing an Endothermal Volatilization. *Biomass Bioenergy* **1995**, *7*, 49.

(56) Narayan, R.; Antal, M. J. Thermal Lag, Fusion, and the Compensation Effect during Biomass Pyrolysis. *Ind. Eng. Chem. Res.* **1996**, *35*, 1711.

(57) Broido, A.; Nelson, M. Char Yield on Pyrolysis of Cellulose. *Combust. Flame* **1975**, *24*, 263.

(58) Varhegyi, G.; Jakab, E.; Antal, M. J. Is the Broido–Shafizadeh Model for Cellulose Pyrolysis True? *Energy Fuels* **1994**, *8*, 1345.

(59) Broido, A. Kinetics of Solid-Phase Cellulose Pyrolysis. In *Thermal Uses and Properties of Carbohydrates and Lignins*; Shafizadeh, F., Sarkanen, K., Tillman, D. A., Eds.; Academic Press: New York, 1976; p 19.

(60) Broido, A.; Weinstein, M. Low-Temperature Isothermal Pyrolysis of Cellulose. In *Proceedings of the 3rd International Conference on Thermal Analysis*; Birkhèauser: Basel, Switzerland, 1971; p 285.

(61) Varhegyi, G.; Antal, M. J.; Szekely, T.; Till, F.; Jakab, E. Simultaneous Thermogravimetric–Mass Spectrometric Studies of the Thermal Decomposition of Biopolymers. 1. Avicel Cellulose in the Presence and Absence of Catalysts. *Energy Fuels* **1988**, *2*, 267.

(62) Varhegyi, G.; Antal, M. J.; Szekely, T.; Till, F.; Szabo, P. Simultaneous Thermogravimetric-Mass Spectrometric Studies of the Thermal Decomposition of Biopolymers. 2. Sugar Cane Bagasse in the Presence and Absence of Catalysts. *Energy Fuels* **1988**, *2*, 273.

(63) Senff, M. Uber die trockene Destillation des Holzes. *Ber. Dtsch. Chem. Ges.* **1885**, *18*, 60.

(64) Brunner, P. Examination of the pyrolysis of cellulose for the production of activated carbon from wastes. *Int. Solid Wastes Assoc. Bull.* **1977**, *23*, 2.

(65) Lede, J.; Li, H. Z.; Villermaux, J. Fusion-like Behaviour of Wood Pyrolysis. *J. Anal. Appl. Pyrol.* **1987**, *10*, 291.

(66) Boutin, O.; Ferrer, M.; Lede, J. Radiant Flash Pyrolysis of Cellulose. Evidence for the Formation of a Short Life Intermediate Liquid Species. *J. Anal. Appl. Pyrol.* **1998**, *47*, 13.

(67) Boutin, O.; Ferrer, M.; Lede, J. Flash Pyrolysis of Cellulose Pellets Submitted to Concentrated Solar Radiation: Experiments and Modelling. *Chem. Eng. Commun.* **2002**, *57*, 15.

(68) Lede, J.; Blanchard, F.; Boutin, O. Radiant Flash Pyrolysis of Cellulose Pellets: Products and Mechanisms Involved in Transcient and Steady-State Conditions. *Fuel* **2002**, *91*, 1269.

(69) Bradbury, A. G. W.; Sakai, Y.; Shafizadeh, F. A Kinetic Model for Pyrolysis of Cellulose. *J. Appl. Polym. Sci.* **1979**, *23*, 3271.

(70) Antal, M. J., Jr.; Varhegyi, G.; Jakab, E. Cellulose Pyrolysis Kinetics: Revisited. *Ind. Eng. Chem. Res.* **1998**, *37*, 1267.

(71) Antal, M. J.; Varhegyi, G. Cellulose Pyrolysis Kinetics: The Current State of Knowledge. *Ind. Eng. Chem. Res.* **1995**, *34*, 703.

(72) MacKay, D. M.; Roberts, P. V. The Influence of Pyrolysis Conditions on Yield and Microporosity of Lignocellulosic Chars. *Carbon* **1982**, *20*, 95.

(73) Chan, W. R.; Kelbon, M.; Krieger-Brockett, B. Single-particle biomass pyrolysis: Correlations of reaction products with process conditions. *Ind. Eng. Chem. Res.* **1988**, *27*, 2261.

(74) Grønli, M. G. A theoretical and experimental study of the thermal degradation of biomass. Ph.D. Dissertation, NTNU, Trondheim, Norway, 1996. See also Grønli, M. Charcoal Production – Laboratory Experiments; TR F5603 SINTEF: Trondheim, 2002.

(75) Byrne, C. E.; Nagle, D. C. Carbonization of Wood for Advanced Materials Applications. *Carbon* **1997**, *35*, 259.

(76) Pastorova, I.; Arisz, P. W.; Boon, J. J. Preservation of D-glucose-oligosaccharides in cellulose chars. *Carbohydr. Res.* **1993**, *248*, 151.

(77) Pastorova, I.; Botto, R. E.; Arisz, P. W.; Boon, J. J. Cellulose Char Structure: A Combined Analytical Py–GC–MS, FTIR, and NMR Study. *Carbohydr. Res.* **1994**, *262*, 27.

(78) Patai, S.; Halpern, Y. Pyrolytic Reaction of Carbohydrates. Part IX. The Effect of Additives on the Thermal Behavior of Cellulose Samples of Different Crystallinity. *Israel J. Chem.* **1970**, *8*, 655.

(79) Boon, J. J.; Pastorova, I.; Botto, R. E.; Arisz, P. W. Structural Studies on Cellulose Pyrolysis and Cellulose Chars by PYMS, PYGCMS, FTIR, NMR, and by Wet Chemical Techniques. *Biomass Bioenergy* **1994**, *7*, 25.

(80) Smith, R. C.; Howard, H. C. Aromatization of Cellulose by Heat. *J. Am. Chem. Soc.* **1937**, *59*, 234.

(81) Nebesarova, I.; Guyonnet, R. Improvement of the Dimensional Stability and Preservation Properties by Thermochemical Densification Treatment: Retified Wood Plastic Composite. In *IUFRO World Congress, Proceedings*; International Union of Forest Research Organizations: Vienna, Austria, 1995; p 1.

(82) Bourgeois, J. P.; Doat, J. Torrefied Wood from Temperate and Tropical Species. In *Bioenergy 84*; Egneus, H. Ellegard, A. Eds.; Elsevier Applied Science: London, 1984; Vol. III Biomass Conversion, p 153.

(83) Schwob, Y. U.S. Patent 4,553,978, 1985.

(84) Bourgeois, J. P.; Guyonnet, R. Thermal Treatment of Wood. *Wood Sci. Technol.* **1989**, *23*, 303.

(85) Pentananunt, R.; Rahman, A. N. M. M.; Bhattacharya, S. C. Upgrading of Biomass by Means of Torrefaction. *Energy* **1990**, *15*, 1175.

(86) Pyle, O. U.S. Patent 3,950,143, 1976.

(87) Koppelman, E. U.S. Patent 4,129,420, 1978.

(88) Violette, M. Memoire sur les Charbons de Bois. *Ann. Chim. Phys.* **1855**, *39*, 291.

(89) Chorley, J. C.; Ramsay, W. On the Destructive Distillation of Wood. *J. Soc. Chem. Ind.* **1892**, *11*, 395.

(90) Schenkel, Y. Modelisation des Flux Massiques et Energetiques dans la Carbonisation du Bois en Four Cornue. Ph.D. Dissertation, Université des Sciences Agronomiques de Gembloux, Gembloux, Belgium, 1999.

(91) Bergstrom, H. *Om Kolning af Barved*; Jernkontoret: Stockholm, Sweden, 1904.

(92) Berg, C. H. E. *Anleitung zum Verkohlen des Holzes: Ein Handbuch fur Forstmanner*; *und Hüttenbeamte*. Second edition, Zernin: Darmstadt, Germany, 1860.

(93) Bergström, H.; Wesslen, G. *Om Träkolning*; Jernkontoret: Stockholm, Sweden, 1915.

(94) Bergström, H. *Handbok for Kolare*; Fourth edition, Jernkontoret: Uppsala, Sweden, 1947.

(95) McGinnes, E. A.; Kandeel, S. A.; Szopa, P. S. Some Structural Changes Observed in the Transformation of Wood into Charcoal. *Wood Fiber* **1971**, *3*, 77.

(96) Slocum, D. H.; McGinnes, E. A.; Beall, F. C. Charcoal Yield, Shrinkage, and Density Changes During Carbonization of Oak and Hickory Woods. *Wood Sci.* **1978**, *11*, 42.

(97) Beall, F. C.; Blankenhorn, P. R.; Moore, G. R. Carbonized Wood-Physical Properties and Use as an SEM Preparation. *Wood Sci.* **1974**, *6*, 212.

(98) Connor, M. A.; Daria, V.; Ward, J. Changes in Wood Structure During the Course of Carbonisation. In *Advances in Thermochemical Biomass Conversion*; Bridgwater, A. V., Ed.; Blackie: London, 1994; p 846.

(99) Blankenhorn, P. R.; Barnes, D. P.; Kline, D. E.; Murphey, W. K. Porosity and Pore Size Distribution of Black Cherry Carbonized in an Inert Atmosphere. *Wood Sci.* **1978**, *11*, 23.

(100) Cutter, B. E.; Cumbie, B. G.; McGinnes, E. A. SEM and Shrinkage Analyses of Southern Pine Wood Following Pyrolysis. *Wood Sci. Technol.* **1980**, *14*, 115.

(101) Fredlund, B. A. A model for heat and mass transfer in timber structures during fire. Ph.D. Dissertation, Lund University, Lund, Sweden, 1988.

(102) Larfeldt, J.; Leckner, B.; Melaaen, M. C. Modelling and measurements of heat transfer in charcoal from pyrolysis of large wood particles. *Biomass Bioenergy* **2000**, *18*, 507.

(103) Blankenhorn, P. R.; Jenkins, G. M.; Kline, D. E. Dynamic mechanical properties and microstructure of some carbonized hardwoods. *Wood Fiber* **1972**, *4*, 212.

(104) Blankenhorn, P. R.; Kline, D. E.; Beall, F. C. Dynamic Mechanical Behavior of Carbonized Black Cherry Wood. *Carbon* **1973**, *11*, 603.

(105) Shafizadeh, F.; Bradbury, A. G. W.; DeGroot, W. F. Univ. Montana, Missoula, MT. Personal communication.

(106) Czechowski, F.; Jankowska, A.; Marsh, H.; Siemien-iewska, T.; Tomkow, K. The development of porosity in group components of brown coals on carbonisation and activation. In *Characterisation of Porous Solids*; Gregg, S. J., Sing, K. S. W., Stoeckli, H. F., Eds.; Society of Chemical Industry: London, 1979; p 67.

(107) Masters, K. J.; McEnaney, B. The development of the structure of microporous carbons. In *Characterisation of Porous Solids*; Gregg, S. J., Sing, K. S. W., Stoeckli, H. F., Eds.; Society of Chemical Industry: London, 1979; p 79.

(108) Dai, X.; Antal, M. J., Jr. Synthesis of a High-Yield Activated Carbon by Air Gasification of Macadamia Nut Shell Charcoal. *Ind. Eng. Chem. Res.* **1999**, *38*, 3386.

(109) Baileys, R. T.; Blankenhorn, P. R. Calorific and Porosity Development in Carbonized Wood. *Wood Sci.* **1982**, *15*, 19.

(110) Khalil, L. B. Porosity Characteristics of Chars Derived from Different Lignocellulosic Materials. *Adsorpt. Sci. Technol.* **1999**, *17*, 729.

(111) Shim, H.-S.; Hurt, R. H. Thermal Annealing of Chars from Diverse Organic Precursors under Combustion-like Conditions. *Energy Fuels* **2000**, *14*, 340.

(112) Varhegyi, G.; Szabo, P.; Till, F.; Zelei, B.; Antal, M. J.; Dai, X. TG, TG−MS, and FTIR Characterization of High-Yield Biomass Charcoals. *Energy Fuels* **1998**, *12*, 969.

(113) Fitzer, E.; Kochling, K. H.; Boehm, H. P.; Marsh, H. Recommended Terminology for the Description of Carbon as a Solid. *Pure Appl. Chem.* **1995**, *67*, 473.

(114) Sekiguchi, Y.; Shafizadeh, F. The Effect of Inorganic Additives on the Formation, Composition, and Combustion of Cellulose Char. *J. Appl. Polym. Sci.* **1984**, *29*, 1267.

(115) Lee, W. H.; Reucroft, P. J. Vapor adsorption on coal- and wood-based chemically activated carbons (I) Surface oxidation states and adsorption of H2O. *Carbon* **1999**, *37*, 7.

(116) Sekiguchi, Y.; Frye, J. S.; Shafizadeh, F. Structure and Formation of Cellulosic Chars. *J. Appl. Polym. Sci.* **1983**, *28*, 3513.

(117) Ford, A. R.; Greenhalgh, E. Industrial Applications of Carbon and Graphite. In *Modern Aspects of Graphite Technology*; Blackman, L. C. F., Ed.; Academic Press: London, 1970; p 258.

(118) Espinola, A.; Miguel, P. M.; Salles, M. R.; Pinto, A. R. Electrical Properties of Carbons−Resistance of Powder Materials. *Carbon* **1986**, *24*, 337.

(119) Okada, J.; Maeda, J. Conductive Bamboo Charcoal and Its Production. Japanese Patent JP 2000104076, 2000.

(120) Tam, M. S.; Antal, M. J.; Jakab, E.; Varhegyi, G. Activated Carbon from Macadamia Nut Shell by Air Oxidation in Boiling Water. *Ind. Eng. Chem. Res.* **2001**, *40*, 578.

(121) Nelson, W. G. Waste-Wood Utilization by the Badger−Stafford Process. *Ind. Eng. Chem.* **1930**, *22*, 312.

(122) Mares, J. G., Usines Lambiotte, Premery, France. Personal communication, 1999.

(123) Shimazu, F.; Sterling, C. J. Effect of Wet and Dry Heat on Structure of Cellulose. *J. Food Sci.* **1966**, *31*, 548.

(124) Stamm, A. J. Thermal Degradation of Wood and Cellulose. *Ind. Eng. Chem.* **1956**, *48*, 413.

(125) MacLean, J. D. Forest Products Laboratory Report R1471; Forest Products Laboratory: Madison, WI, 1945.

(126) Darmstadt, H.; Pantea, D.; Summchen, L.; Roland, U.; Kaliaguine, S.; Roy, C. Surface and bulk chemistry of charcoal obtained by vacuum pyrolysis of bark: influence of feedstock moisture content. *J. Anal. Appl. Pyrol.* **2000**, *53*, 1.

(127) Antal, M. J.; Friedman, H. L.; Rogers, F. E. Kinetics of Cellulose Pyrolysis in Nitrogen and Steam. *Combust. Sci. Technol.* **1980**, *21*, 141.

(128) Gergova, K.; Petrov, N.; Eser, S. Adsorption Properties and Microstructure of Activated Carbons Produced from Agricultural By-Products by Steam Pyrolysis. *Carbon* **1994**, *32*, 693.

(129) Alaya, M. N.; Girgis, B. S.; Mourad, W. E. Activated Carbon from Some Agricultural Wastes Under Action of One-Step Steam Pyrolysis. *J. Porous Mater.* **2000**, *7*, 509.

(130) Varhegyi, G.; Szabo, P.; Mok, W. S.-L. Kinetics of the thermal decomposition of cellulose in sealed vessels at elevated pressures. Effects of the presence of water on the reaction mechanism. *J. Anal. Appl. Pyrol.* **1993**, *26*, 159.

(131) Antal, M. J.; DeAlmeida, C.; Mok, W. S.-L. A New Technology for Manufacturing Charcoal from Biomass. In *Proceedings of the IGT Conference on Energy from Biomass & Wastes XV*; Klass, D. E., Ed.; Institute for Gas Technology: Chicago, IL, 1991; p 521.

(132) Ball, R.; McIntosh, A. C.; Brindley, J. The role of char-forming processes in the thermal decomposition of cellulose. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5035.

(133) Xu, X.; Matsumura, Y.; Stenberg, J.; Antal, M. J. Carbon-Catalyzed Gasification of Organic Feedstocks in Supercritical Water. *Ind. Eng. Chem. Res.* **1996**, *35*, 2522.

(134) Brandt, P.; Larsen, E.; Henriksen, U. High Tar Reduction in a Two-Stage Gasifier. *Energy Fuels* **2000**, *14*, 816.

(135) Radovic, L. R.; Sudhakar, C. Carbon as a Catalyst Support: Production, Properties, and Applications. In *Introduction to Carbon Technologies*; Marsh, H., Heintz, E. A., Rodriguez-Reinoso, F., Eds.; Universidad de Alicante: Alicante, Spain, 1997; p 103.

(136) Cookson, J. T. Physicochemical Changes of Substances By or Within Carbon Adsorption Beds. In *Activated Carbon Adsorption of Organics from the Aqueous Phase*; Suffet, I. H., McGuire, M. J., Eds.; Ann Arbor Science: Ann Arbor, MI, 1980; p 379.

(137) Chen, G.; Yu, Q.; Sjostrom, K. Reactivity of char from pyrolysis of birch wood. *J. Anal. Appl. Pyrol.* **1997**, *40–41*, 491.

(138) Mok, W. S. L.; Antal, M. J. Effects of Presure on Biomass Pyrolysis. II. Heats of Reaction of Cellulose Pyrolysis. *Thermochim. Acta* **1983**, *68*, 165.

(139) Milosavljevic, I.; Oja, V.; Suuberg, E. M. Thermal Effects in Cellulose Pyrolysis: Relationship to Char Formation Processes. *Ind. Eng. Chem. Res.* **1996**, *35*, 653.

(140) Kamashita, M.; Mahajan, O. P.; Walker, P. L. Effect of Carbon Deposition on Porosity and Reactivity of a Lignite Char. *Fuel* **1977**, *56*, 444.

(141) Anthony, D. B.; Howard, J. B.; Hottel, H. C.; Meissner, P. Rapid Devolatilization and Hydrogasification of Bituminous Coal. *Fuel* **1976**, *55*, 121.

(142) Klason, P. Försök Tillen Teori fr̊ Torrdestillation of Trä. *Uppsala Archiv. för Kemi, Mineral. Geol.*; Vol.5, No. 7, Svenska Vetenskapsakademien: 1913.

(143) Shafizadeh, F.; Fu, Y. L. Pyrolysis of Cellulose. *Carbohydr. Res.* **1973**, *29*, 113.

(144) Palmer, R. C. Effect of Pressure on Yields of Products in the Destructive Distillation of Hardwood. *J. Ind. Eng. Chem.* **1914**, *6*, 890.

(145) Frolich, P. K.; Spalding, H. B.; Bacon, T. S. Destructive Distillation of Wood and Cellulose under Pressure. *J. Ind. Eng. Chem.* **1928**, *20*, 36.

(146) Blackadder, W.; Rensfelt, E. A. Pressurized Thermo Balance for Pyrolysis and Gasification Studies of Biomass, Wood, and Peat. In *Fundamentals of Thermochemical Biomass Conversion*; Overend, R. P., Milne, T. A., Mudge, L. K., Eds.; Elsevier Applied Science: London, 1985; p 747.

(147) Richard, J.-R.; Antal, M. J. Thermogravimetric Studies of Charcoal Formation from Cellulose at Elevated Pressures. In *Advances in Thermochemical Biomass Conversion*; Bridgwater, A. V., Ed.; Blackie Academic & Professional: London, 1994; p 784.

(148) Pindoria, R. V.; Megaritis, A.; Messenbock, R. C.; Dugwell, D. R.; Kandiyoti, R. Comparison of the pyrolysis and gasification of biomass: effect of reacting gas atmosphere and pressure on Eucalyptus wood. *Fuel* **1998**, *77*, 1247.

(149) Klason, P.; Heidenstam, G.; Norlin, E. Untersuchungen zur Holzverkohlung. II. Die trockene Destillation des Holzes von Kiefer, Fichte, Birke und Buche. *Z. Angew. Chem.* **1910**, 1252.

(150) Juon, E. Gasverhaltnisse bei der Holzverkohlung. *Stahl Eisen* **1907**, *27*, 733.

(151) Juon, E. Wood Charcoal: Examination of gases evolved in the preparation of charcoal. *J. Soc. Chem. Ind.* **1907**, *26*, 677.

(152) Buttner, G.; Wislicenus, H. Versuche zur trocknen Destillation des Holzes mit uberhitztem Dampf. *J. Prakt. Chem.* **1909**, *79*, 177.

(153) Roberts, A. F. The Heat of Reaction During the Pyrolysis of Wood. *Combust. Flame* **1971**, *17*, 79.

(154) Havens, J. A.; Welker, J. R.; Sliepcevich, C. M. Pyrolysis of Wood: A Thermoanalytical Study. *J. Fire Flammability* **1971**, *2*, 321.

(155) Kung, H.-C. A Mathematical Model of Wood Pyrolysis. *Combust. Flame* **1972**, *18*, 185.

(156) Tang, W. K.; Neill, W. K. Effect of Flame Retardants on Pyrolysis and Combustion of Alpha Cellulose. *J. Polym. Sci. C* **1964**, *6*, 65.

(157) Kung, H.-C.; Kalelkar, A. S. On the Heat of Reaction in Wood Pyrolysis. *Combust. Flame* **1973**, *20*, 91.

(158) Lee, C.; Chaiken, R. F.; Singer, J. M. Charring Pyrolysis of Wood in Fires by Laser Simulation. In *Sixteenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1976; p 1459.

(159) Kansa, E. J.; Perlee, H. E.; Chaiken, R. F. Mathematical Model of Wood Pyrolysis Including Internal Forced Convection. *Combust. Flame* **1977**, *29*, 311.

(160) Bennini, S.; Castillo, S.; Traverse, J. P. Effects of an Intense Thermal Flux on a Lignocellulosic Material. *J. Anal. Appl. Pyrol.* **1991**, *21*, 305.

(161) Bamford, C. H.; Crank, J.; Malan, D. H. The Combustion of Wood. *Proc. Cambridge Philos. Soc.* **1945**, *42*, 166.

(162) Akita, K. *Rept. Fire Res. Inst. Jpn.* **1959**, *9*, 10.

(163) Roberts, A. F.; Clough, G. Thermal Decomposition of Wood in an Inert Atmosphere. In *Ninth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1963; p 158.

(164) Tinney, E. R. The Combustion of Wooden Dowels in Heated Air. In *Tenth Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, PA, 1963; p 925.

(165) Roberts, A. F. A Review of Kinetics Data for the Pyrolysis of Wood and Related Substances. *Combust. Flame* **1970**, *14*, 261.

(166) Chan, R. W. C.; Kelbon, M.; Krieger, B. B. Product Formation in the Pyrolysis of Large Wood Particles. In *Fundamentals of Thermochemical Biomass Conversion*; Overend, R. P., Milne, T. A., Mudge, L. K., Eds.; Elsevier: London, 1985; p 219.

(167) Chan, R. W. C.; Kelbon, M.; Krieger, B. B. Single-Particle Biomass Pyrolysis: Correlations of Reaction Products with Process Conditions. *Ind. Eng. Chem. Res.* **1988**, *27*, 2261.

(168) Pyle, D. L.; Zaror, C. A. Heat Transfer and Kinetics in the Low-Temperature Pyrolysis of Solids. *Chem. Eng. Sci.* **1984**, *39*, 147.

(169) Capart, R.; Falk, L.; Gelus, M. Pyrolysis of Wood Macrocylinders under Pressure: Application of a Simple Mathematical Model. *Appl. Energy* **1988**, *30*, 1.

(170) Alves, S. S.; Figueiredo, J. L. A Model for Pyrolysis of Wet Wood. *Chem. Eng. Sci.* **1989**, *44*, 2861.

(171) Mok, W. S. L. The Effects of Pressure on Biomass Pyrolysis and Gasification. MSE Thesis, Princeton University, Princeton, NJ, 1983.

(172) Hajaligol, M. R.; Howard, J. B.; Peters, W. A. An Experimental and Modeling Study of Pressure Effects on Tar Release by Rapid Pyrolysis of Cellulose Sheets in a Screen Heater. *Combust. Flame* **1993**, *95*, 47.

(173) Goring, D. A. I. Thermal softening of lignin, hemicellulose, and cellulose. *Pulp Pap. Magn. Can.* **1963**, *64*, T517.

(174) Koser, H. J. K.; Schmalstieg, G.; Siemers, W. Densification of Water Hyacinth—Basic Data. *Fuel* **1982**, *61*, 791.

(175) Ando, H.; Sakaki, T.; Kokusho, T.; Shibata, M.; Uemura, Y. l.; Hatate, Y. Decomposition Behavior of Plant Biomass in Hot-Compressed Water. *Ind. Eng. Chem. Res.* **2000**, *39*, 3688.

(176) Arseneau, D. F. Competitive Reactions in the Thermal Decomposition of Cellulose. *Can. J. Chem.* **1971**, *49*, 632.

(177) Stafford, O. F. Destructive Distillation Process. U.S. Patent 1,380,262, 1921.

(178) Teixeira do Vale, A.; Florian da Costa, A.; Gonsalez, J. C.; Nogueira, M. Correlation between wood basic density and the yield and quality of charcoal from stunted trees from grazing land. *Rev. Arvore* **2001**, *25*, 89.

(179) Connor, M. A.; Viljoen, M. H.; Ilic, J. Relationships Between Wood Density, Wood Permeability and Charcoal Yield. In *Developments in Thermochemical Biomass Conversion*; Bridgwater, A. V., Boocock, D. G. B., Eds.; Blackie: London, 1997; p 82.

(180) Pontinha, A. D. A. S.; Veiga, R. A. D. A.; Leao, A. L. Charcoal Production Using Tropical Pine Thinnings. *Energy* **1992**, *17*, 757.

(181) MacKay, D. M.; Roberts, P. V. The Dependence of Char and Carbon Yield on Lignocellulosic Precursor Composition. *Carbon* **1982**, *20*, 87.

(182) Antal, M. J. Effects of Reactor Severity on the Gas-Phase Pyrolysis of Cellulose- and Kraft Lignin-Derived Volatile Matter. *Ind. Eng. Chem. Prod. Res. Dev.* **1983**, *22*, 366.

(183) Gillet, A.; Urlings, J. Comparative pyrolysis of wood, cellulose, lignin and coal. I. Stepwise pyrolysis of wood. *Chim. Ind.* **1952**, *67*, 909.

(184) Raveendran, K.; Ganesh, A.; Khilar, K. C. Pyrolysis characteristics of biomass and biomass components. *Fuel* **1996**, *75*, 987.

(185) Di Blasi, C.; Branca, C.; Santoro, A.; Hernandez, E. G. Pyrolytic Behavior and Products of Some Wood Varieties. *Combust. Flame* **2001**, *124*, 165.

(186) Roy, C.; Pakdel, H.; Brouillard, D. The Role of Extractives during Vacuum Pyrolysis of Wood. *J. Anal. Appl. Pyrol.* **1990**, *41*, 337.

(187) Olsson, J. G.; Jaglid, K.; Pettersson, J. B. C. Alkali Metal Emission during Pyrolysis of Biomass. *Energy Fuels* **1997**, *11*, 779.

(188) Jensen, P. A.; Frandsen, F. J.; Dam-Johansen, K.; Sander, B. Experimental Investigation of the Transformation and Release to Gas Phase of Potassium and Chlorine during Straw Pyrolysis. *Energy Fuels* **2000**, *14*, 1280.

(189) Bjorkman, E.; Stromberg, B. Release of Chlorine from Biomass at Pyrolysis and Gasification Conditions. *Energy Fuels* **1997**, *11*, 1026.

(190) Philpot, C. W. Influence of Mineral Content on the Pyrolysis of Plant Materials. *For. Sci.* **1970**, *16*, 461.

(191) Richards, G. N.; DeGroot, W. F. Influence of Metal Ions and Salts on the Products from Pyrolysis of Wood. *J. Anal. Appl. Pyrol.* **1991**, *21*, 133.

(192) Furneaux, R.; Shafizadeh, F. Pyrolytic Production of 1,6-Anhydro- -D-mannopyroanose. *Carbohydr. Res.* **1979**, *74*, 354.

(193) Brown, R. C.; Radlein, D.; Piskorz, J. Pretreatment processes to increase pyrolytic yield of levoglucosan from herbaceous feedstocks. In *Chemicals and Materials from Renewable Resources*; ACS Symposium Series 784; American Chemical Society: Washington, DC, 2001; p 123.

(194) Teng, H.; Wei, Y.-C. Thermogravimetric Studies on the Kinetics of Rice Hull Pyrolysis and the Influence of Water Treatment. *Ind. Eng. Chem. Res.* **1998**, *37*, 3806.

(195) Jensen, P. A.; Sander, B.; Dam-Johansen, K. Removal of K and Cl by leaching of straw char. *Biomass Bioenergy* **2001**, *20*, 447.

(196) In *Honolulu Advertiser*, Honolulu, HI, 2000, p B4.

(197) Ranke, H. Experimentelleer Beweis der Moglichkeit der Selbstentzundung des Heues. *Liebig's Ann. Chem. Pharm.* **1873**, *167*, 361.

(198) Bradbury, A. G. W.; Shafizadeh, F. Role of Oxygen Chemisorption in Low-Temperature Ignition of Cellulose. *Combust. Flame* **1980**, *37*, 85.

(199) Brocksiepe, H.-G. Charcoal. In *Ullmann's Encyclopedia of Industrial Chemistry*; Gerhartz, W., Ed.; VCH: Weinheim, Germany, 1986; p 157.

(200) Di Blasi, C.; Buonanno, F.; Branca, C. Reactivities of some biomass chars in air. *Carbon* **1999**, *37*, 1227.

(201) Tam, M. S.; Antal, M. J., Jr. Preparation of Activated Carbons from Macadamia Nut Shell and Coconut Shell by Air Activation. *Ind. Eng. Chem. Res.* **1999**, *38*, 4268.

(202) DeGroot, W. F.; Osterheld, T. H.; Richards, G. N. Chemisorption of Oxygen and of Nitric Oxide on Cellulosic Chars. *Carbon* **1991**, *29*, 185.

(203) Hshieh, F. Y.; Richards, G. N. Factors Influencing Chemisorption and Ignition of Wood Chars. *Combust. Flame* **1989**, *76*, 37.

(204) Bradbury, A. G. W.; Shafizadeh, F. Chemisorption of Oxygen on Cellulose Char. *Carbon* **1980**, *18*, 109.

(205) Golden, T. C.; Jenkins, R. G.; Otake, Y.; Scaroni, A. W. Oxygen Complexes on Carbon Surfaces. In *Proceedings of the Workshop on the Electrochemistry of Carbon*; Sarangapani, S., Akridge, J. R., Schumm, B., Eds.; The Electrochemical Society: Pennington, NJ, 1983; p 61.

(206) Conesa, J. A.; Sakurai, M.; Antal, M. J. Synthesis of a High-Yield Activated Carbon by Oxygen Gasification of Macadamia Nut Shell Charcoal in Hot, Liquid Water. *Carbon* **2000**, *38*, 839.

(207) Smith, R. N.; Pierce, C.; Joel, C. D. The Low-Temperature Reaction of Water with Carbon. *J. Phys. Chem.* **1954**, *58*, 298.

(208) Waters, P. L. Semiconduction Properties of Carbonized Coal. In *Proceedings of the Fifth Conference on Carbon*; Mrozowski, S., Ed.; Pergamon Press: New York, 1963; p 131.

(209) Monazam, E. R.; Shadle, L. J.; Evans, R.; Schroeder, K. Water Adsorption and Desorption by Coals and Chars. *Energy Fuels* **1998**, *12*, 1299.

(210) Devi, T. G.; Edye, L. A.; Kannan, M. P.; Richards, G. N. Univ. Montana, Missoula, MT, Personal communication, 1992.

(211) Ward, A. F. H.; Rideal, E. K. The Heat of Adsorption of Oxygen on Charcoal. *J. Chem. Soc.* **1927**, 3117.

(212) Shafizadeh, F.; Sekiguchi, Y. Oxidation of chars during smoldering combustion of cellulosic materials. *Combust. Flame* **1984**, *55*, 171.

(213) Zolin, A.; Jensen, A.; Frandsen, F. J.; Dam-Johansen, K. The Influence of Inorganic Materials on the Thermal Deactivation of Fuel Chars. *Energy Fuels* **2001**, *15*, 1110.

(214) Kannan, M. P.; Richards, G. N. Potassium Catalysis in Air Gasification of Cellulosic Chars. *Fuel* **1990**, *69*, 999.

(215) Devi, G. T.; Kannan, M. P. Gasification of Biomass Chars in Air—Effect of Heat Treatment Temperature. *Energy Fuels* **2000**, *14*, 127.

(216) Devi, T. G.; Kannan, M. P.; Richards, G. N. Copper catalysis in the air gasification of cellulosic chars. *Fuel* **1990**, *69*, 1440.

(217) Henrich, E.; Burkle, S.; Meza-Renken, Z. I.; Rumpel, S. Combustion and gasification kinetics of pyrolysis chars from waste and biomass. *J. Anal. Appl. Pyrol.* **1999**, *49*, 221.

(218) Grønli, M.; Antal, M. J., Jr.; Varhegyi, G. A Round-Robin Study of Cellulose Pyrolysis Kinetics by Thermogravimetry. *Ind. Eng. Chem. Res.* **1999**, *38*, 2238.

(219) Antal, M. J., Jr.; Varhegyi, G. Impact of Systematic Errors on the Determination of Cellulose Pyrolysis Kinetics. *Energy Fuels* **1997**, *11*, 1309.

(220) Edye, L. A.; Richards, G. N. Univ. Montana, Missoula, MT, Personal communication, 1992.

(221) Dai, X. Pyrolytic and Oxidative Syntheses of High-Yield Carbons from Biomass. Ph.D. Thesis, University of Hawaii at Manoa, Honolulu, HI, 1998.

(222) McCarthy, D. J. Changes in Oxyreactivity of Carbons due to Heat Treatment and Prehyudrogenation. *Carbon* **1981**, *19*, 297.

(223) Kashiwagi, T.; Nambu, H. Global Kinetic Constants for Thermal Oxidative Degradation of a Cellulosic Paper. *Combust. Flame* **1992**, *88*, 345.

(224) Magnaterra, M. R.; Cukierman, A. L.; Lemcoff, N. O. Kinetic study of the reaction of different hardwood sawdust char with oxygen. In *Advances in Thermochemical Biomass Conversion*; Bridgwater, A. V., Ed.; Blackie Academic and Professional: London, 1992; p 116.

(225) Janse, A. M. C.; de Jonge, H. G.; Prins, W.; van Swaaij, W. P. M. Combustion Kinetics of Char Obtained by Flash Pyrolysis of Pine Wood. *Ind. Eng. Chem. Res.* **1998**, *37*, 3909.

(226) Cozzani, V. Reactivity in Oxygen and Carbon Dioxide of Char Formed in the Pyrolysis of Refuse-Derived Fuel. *Ind. Eng. Chem. Res.* **2000**, *39*, 864.

(227) Adanez, J.; de Diego, L. F.; Garcia-Labiano, F.; Abad, A.; Abanades, J. C. Determination of Biomass Char Combustion Reactivities for FBC Applications by a Combined Methodology. *Ind. Eng. Chem. Res.* **2001**, *40*, 4317.

(228) Laurendeau, N. M. Heterogeneous Kinetics of Coal Char Gasification and Combustion. *Prog. Energy Combust. Sci.* **1978**, *4*, 221.

(229) Lin, L. C.; Deo, M. D.; Hanson, F. V.; Oblad, A. G. Nonisothermal analysis of the kinetics of the combustion of coked sand. *Ind. Eng. Chem. Res.* **1991**, *30*, 1795.

(230) Grønli, M. G. Charcoal Production—A Technology Review; TR F5061; SINTEF: Trondheim, Norway, 1999 (in Norwegian).

(231) Soltes, E. J., Milne, T. A., Eds. *Pyrolysis Oils from Biomass*; American Chemical Society: Washington, DC, 1988.

(232) Bridgwater, A. V.; Cottam, M.-L. Opportunities for Biomass Pyrolysis Liquids Production and Upgrading. *Energy Fuels* **1992**, *6*, 113.