LITERATURE REVIEW Self-Heating In Yard Trimmings: **Conditions Leading To Spontaneous Combustion**

Richard Buggeln¹ and Robert Rynk²

1. The University of Tennessee Center for Industrial Services, Knoxville, Tennessee 2. Senior Technical Editor, The JG Press, Emmaus, Pennsylvania

Spontaneous combustion (SC) is defined as combustion of material in the absence of "forced ignition", that is, an externally applied spark or flame. This paper describes how SC occurs in piles of yard trimmings, starting with chemical and physical events that initiate heat-producing reactions via biotic and abiotic processes involving oxygen and a little water. The accumulation of heat generated within a pile depends on the balance between rate of internal heat production and rate of heat loss to the external environment. When the former rate is higher than the latter, a "critical" internal temperature may be reached at which time run away ignition, i.e., SC, is unavoidable. Water plays the interesting role of "governor" of temperature change and heat exchange within a pile of yard trimmings as well as heat loss from a pile. While heat, in the form of water vapor, is being lost from a self-heating pile, the pile temperature does not rise above 70 -90°C until all free water has been removed. An analogy is potatoes in a pot of boiling water that only start to burn after the water has boiled off. Important experiments with Eucalyptus leaves, sawdust, and other types of plant material demonstrate the inverse relationship between mass of material and ambient temperatures than can lead to SC. That is, the bigger the pile, the lower the ambient temperature at which SC may occur. SC has been studied most intensively in coal. The roles of particle size, pile compaction, and other potentially catalytic phenomena observed in coal may have application to the propensity of SC to occur in piles of yard trimmings. Finally, several incendiary experiences at composting and mulching operations will be described together with guidelines on the prevention of costly fires that are very hard to extinguish.

Introduction

Spontaneous combustion (SC) is an infrequent but real phenomenon during storage and composting of the mixed vegetative and woody materials collectively referred to as yard waste, green waste or yard trimmings. On one hand, it is surprising that SC fires are not more common given that these materials are combustible, amassed in large quantities, and deliberately managed at temperatures well above ambient. On the other hand, it is curious to composters that fires occur at all since the biological processes responsible for the heat of composting cease below 80°C.

If woody materials have ignition temperatures in the range of 120 - 145° C (248 – 293°F) and higher, what are the factors or conditions occurring in piles of ground leaves and woody materials that may lead to SC? In his scholarly treatise on SC, Bowes (1984) opined: "With coal, perhaps to a much greater extent than with any other system with which we shall be concerned, we are faced with a large number of variables whose relative importance can differ widely from one situation to another. Any simple theoretical model is likely to be applicable only to rather narrowly defined cases." Given an opportunity to revisit this statement today, might the author supplant coal with a heterogeneous assemblage of vegetation, the predecessor of coal in the first place, and find it even more complex?

The goal of this paper is to develop a picture of the chemical and physical factors and processes that culminate in incendiary activity in piles of vegetative material at com-

Self-Heating In Yard Trimmings: Conditions Leading To Spontaneous Combustion

posting and mulching facilities. In pursuing this goal, we have relied on work by other authors who have examined SC relationships for several materials including vegetation, hay, wood and coal. References are cited for the reader to obtained additional details.

Table 1 lists organic materials in which SC has been reported (adopted from Kayser & Boyars 1975). The earliest written observation on the topic is a note on SC in hay, attributed to Columella in 1st century Rome (cf. Browne 1929). Much more recently, and

TABLE 1. Materials of biological origin susceptible to spontaneous combustion (adapted from Kayser & Boyars 1975)

Material	Remarks		
Animal fibers – wool, shoddy (reworked, short-fiber wool), silk	Animal fibers are solid, versus plant fibers that are hollow; the latter are more prone to spontaneous ignition and will smolder and sustain combustion, versus the former.		
Alfalfa meal	Subject to spontaneous combustion		
Bags, used – burlap, jute	Tendency to ignition dependent on previous use		
Beans – locust, etc.	Subject to spontaneous combustion		
Bone meal, bone black, bone charcoal	и		
Celluloid scrap	"		
Coal – bituminous, brown, fossil	Tendency to self-heating depends on origin, nature and degree of volatile ingredients		
Colophony (rosin) powder, gum rosin	Subject to spontaneous combustion		
Copra (coconut fiber)	n.		
Cork	"		
Cotton, cotton waste, wet cotton	"		
Distillers dried grains	Subject to spontaneous combustion; maintain moisture content between 7-10% and cool below 100F before storage		
Feeds, various	Subject to spontaneous combustion		
Fertilizers, manure	"		
Fibers – bast, cocoa, coir, esparto, flax, hemp, jute, oakum, palmetto, sisal, etc.	Subject to spontaneous combustion; safe moisture content <6>20%		
Fish meal, fish scraps	Subject to spontaneous combustion		
Grains – various	n e e e e e e e e e e e e e e e e e e e		
Hay	"		
Hides various	"		
Ixtle (fibers from Mexican agave leaves)	u .		
laggery and jaggery sugar (derived from East Indian palm sap)	n .		
Lycopodium and Selaginella spores	Can spontaneously ignite when scattered in air		
Oils, animal and vegetable*	Subject to spontaneous ignition		
Paper, waste paper – treated with unsaturated oils, ncompletely dried	"		
Rags, used	Spontaneous combustible tendency depends on previous use		
Sawdust	Subject to spontaneous combustion		
Scrap leather	"		
scrap rubber	и		
eeds, seed cakes, seed hulls – containing vegetable oils	и		
traw of flax, maize, oats, rice, rye, wheat, etc.	Subject to spontaneous heating and combustion		
l'ankage (dried animal residue, usually freed from fat and gelatin and used as fertilizer or feedstuff)	Subject to spontaneous combustion		
Textile waste, wet	"		
Wood – chips, excelsior, shredded wood, wood flour, havings, wood wool	n		

^{*}Some common animal and vegetable oils in decreasing tendency to spontaneously ignite: cod liver oil, fish oil, linseed oil, menhaden oil, perilla oil; > corn oil, cottonseed oil, olive oil, pine oil, red oil, soybean oil, tung oil, whale oil; > castor oil, lard oil, black mustard oil, oleic oil, palm oil, peanut oil — avoid contact with any fibrous combustible materials.

following a decade of research on the outside storage of wood chips (cf. Buggeln 1999), SC in woody materials was reviewed by Bergman (1974) and exhaustively treated by Kubler (1987, 1990). SC has received extensive study in coal. Some chemical constituents in "brown" coal, the type of coal having the greatest propensity toward SC, are chemically-related to some plant compounds, perhaps including those involved in abiotic heating reactions. In any case, the physical factors governing heat flux and conditions leading to SC are fundamentally the same in both materials types. References to studies with coal are noted for comparative reference throughout the text.

This paper begins with a simple model and overview of SC as a way to introduce the topic (Section 1). Then we proceed to a discussion of the processes that generate heat in yard trimmings (Section 2) and the factors that influence whether the heat will lead to SC (Section 3). The influence of water and particle size in heat accumulation and heat transfer within piles of plant materials is treated in Sections 4 and 5. Studies with coal are noted for comparative reference throughout the text but especially in Section 6. Finally, in Section 7 we attempt to summarize the development of conditions leading to SC in a pile of yard trimmings. Terms are defined throughout the paper.

Section 1.0 A Basic Model Of SC: To Self-Combust Or Not, That Is The Question

The model shown in Figure 1 identifies the key factor that may or may not lead to SC in a pile of ground yard trimmings: *heat*. The model develops from right to left, and upwards with increasing temperature. Starting in the lower right hand oval, we show

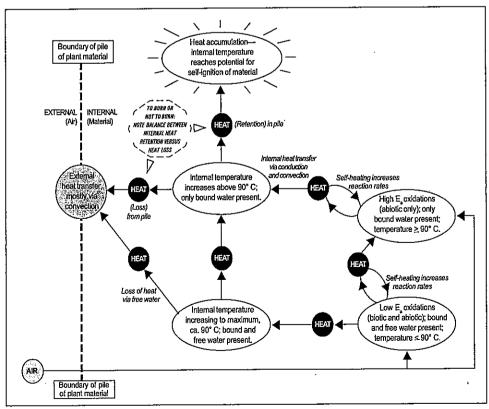


Figure 1. Self-heating in plant materials leading to spontaneous ignition.

that heat is generated in the pile by the aerobic respiration of still-living plant cells and microbes as they consume plant constituents (biotic). Shown within the same oval, heat is also liberated by direct oxidation of plant chemicals that easily react with oxygen in the air (abiotic). As the pile starts to heat up (oval to the left), some heat is redistributed (and retained) within the pile and some is carried out of the pile, in the form of water vapor, a commonly observed phenomenon at composting and mulching facilities. As the pile heats up to 70 - 90°C range, two important changes occur (see the next pair of ovals, one tier up in the model). First, the pile has lost nearly all of its free or unbound water (recall that water *boils* at 100°C), and second, heat has killed the microbes. However, air is still flowing into the pile, and oxygen is reacting with plant chemicals (abiotic only) to produce even more heat, with increasing pile temperature accelerating rates of chemical reactions. Now one starts to worry! If the rate of heat loss from the pile can keep up with the accelerating rate of heat production then SC will be avoided. If not, SC is a possibility. Much depends on the factors at work including air movement, oxygen concentrations and moisture.

Definition of Spontaneous Combustion

With the model above in mind, we may now define spontaneous combustion and acknowledge a prominent theoretician who developed the currently accepted theoretical model for thermal ignition. As previously stated, when physical conditions within a pile of yard trimmings are such that more heat is trapped internally than is released from the pile surface, the temperature of the pile increases. In time, the *critical temperature* is reached at some location in the pile where the oxidation of substrates is "highly exothermic and temperature sensitive", and heat production is "self-accelerating" resulting in thermal ignition. As stated by Frank-Kamenetskii (1969), "The phenomenon of spontaneous inflammation manifests the impossibility of thermal…equilibrium in the volume of a com-

bustible mixture with given conditions and properties." Spontaneous combustion may therefore be defined as combustion of a material that occurs in the absence of "forced ignition" (Frank-Kamenetskii 1969), that is, without a spark or flame. From a theoretical perspective, the author considered spontaneous ignition to be the simplest form of combustion.

Figure 2 shows the classic graphic representation by Semenov of the relationship between heat generation within a mass and three hypothetical rates of heat loss (cf. Frank-Kamenetskii 1969). The point of SC is at the tangent of the heat generation curve, q₁ and the "critical" heat loss rate, q₃. At a heat loss rate greater than the critical rate (e.g. q₂), combustion will not occur. Note that this model is conceptual in nature. It is not concerned with the source of heat or mechanism of heat loss, only in the relationship between heat loss and gain.

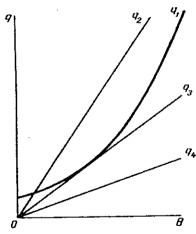


Figure 2. Semenov's diagram. q is the heat flux (heat gain or loss to the system), θ is the dimensionless temperature difference within the system. q_1 is the heat supply curve (i.e. heat generation within the system), q_2 , q_3 , and q_4 represent different possible positions of the heat-loss curve. q_4 is within the inflammation region (combustion in the system is already occurring). q_2 is outside the region of SC. q_3 is the boundary or "critical condition" of heat loss where the tangent with q_1 is the point of SC (From Frank-Kamenetskii 1969; reproduced by permission from Kluwer Academic/Plenum Publisher, New York).

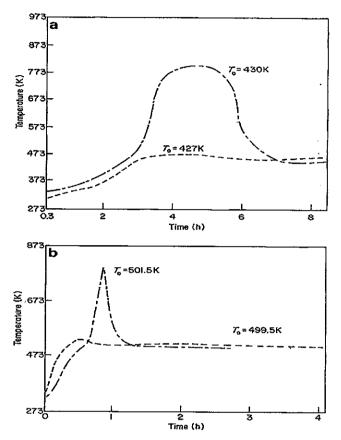


Figure 3. a) Sub- and supercritical trajectories for Eucaluptus saligna leaves when heated in a 10 cm cubic basket; b) sub- and supercritical trajectories for wood shavings heated in a 4 cm side cubic basket. [To is chamber temperature]. (Reprinted from Fuel, 67, J. C. Jones and C. Raj. The self-heating and ignition of vegetable debris, 1208-1210, 1988, with permission from Elsevier Science.)

Figure 3, from Jones and Raj (1988), illustrates a key feature of Frank-Kamenetskii's ignition theory. A small change in an external factor can trigger a dramatic temperature rise, or incipient ignition ("temperature jump," cf. Bowes 1984) within the material. In the example of Figure 3, the change was a 2 to 3°C rise in the temperature of the chamber containing a small basket of Eucalyptus leaves and wood.

Section 2. 0 Processes That Generate Heat in Yard Trimmings

Heat is produced from plant chemicals that are "oxidized" or broken down into simpler compounds, liberating some of the energy stored in the chemical bonds. There are two categories of chemical reactions that carry out these *exothermic*, or heat-producing, reactions: (1) biochemical (biotic) reactions involving living organisms (plant cells, bacteria and fungi), and (2) direct chemical reactions (abiotic). Some of the chemicals for either type of reaction are present in leaves and shredded/chipped woody residues. Others appear as the large complex compounds are broken down into smaller ones, in part by the action of heat itself (see Section 2.3.1). We will consider both categories of chemical reactions and position their respective roles in relation to heat build up in piles.

166 Compost Science & Utilization

2.1 Biotic Heat Generation (Plant and Microbial Respiration)

As noted by Kubler (1990), cutting off a blade of grass or a shrub branch from its base is not necessarily a quick death. The severed plant cells remain alive and continue to respire until they exhaust their food or moisture supply or until they are subject to lethal conditions (e.g. high temperatures). Even woody materials contain living respiring cells if they include the outer or cambial layer of the tree. Whole tree chips and sapwood branches fall into this category. As they respire, these plant cells generate heat. It is uncertain how much of the initial temperature rise in a pile of vegetation is due to the respiration of surviving plant cells versus microbial activity. However, casual observations, such as the rapid temperature rise of a pile of freshly cut grass, suggest that plant cell respiration can be an accelerating factor, if not the initiating step, in the temperature climb that can eventually lead to SC. With moisture, plant cell respiration contributes heat at least until temperatures rise to levels that are intolerable to plant cells, between 25 and 50°C (Kubler 1990).

Free sugars, amino acids, organic acids and a variety of other water soluble cellular metabolites are released from plant cells upon their death. These are the preferred food of epiphytic microflora, mostly bacteria, covering surfaces of vegetation. For wood, and other lignocellulosic materials, fungi are important agents of biodegradation and heat generation.

Early studies of SC in plant matter, most notably hay (cf. Rothbaum 1963), raised a question that has neither required nor received serious attention in respect to SC in coal or other "non-plant" materials. The question is based on the observation that a temperature rise in piles of hay (up to about 80°C) was attributed to heat generated from microbial respiration, i.e., biochemical oxidation of chemical constituents of hay — the same phenomenon observed in compost piles today. The question: Is SC in hay (and yard trimmings) *ultimately* dependent on heat generation from biological activity up to the point where temperature kills most of the microbes, about 80°C? The answer is, no. Rothbaum (1963) reported results of an experiment in which hay self-heated in the absence of low temperature microbial activity (following a pretreatment temperature at 90°C designed to kill most microbes, except resistant spores), a result reviewed by Koegel & Bruhn (1971) and Bowes (1984). Thus, biotic and abiotic heat generation at low temperatures (27 – 65°C) have been reported (cf. Kubler 1987).

What is the likelihood that abiotic heat-generating reactions *predominate* in piles of yard trimmings under natural conditions, at temperatures below 80°C? Some evidence suggests that abiotic heating is not a large factor. Springer and Hajny (1970) compared O_2 consumption and CO_2 evolution from sterilized and non-sterilized samples of Douglas fir and aspen wood chips. Finding relatively little O_2 consumption or CO_2 formation in the sterile chips, the authors concluded that direct oxidation of chemical components in the wood is of little significance in the initial stages of self-heating. While this question does not appear to have been experimentally examined for other materials, the answer seems to depend on four factors: (1) initial moisture content in the material; (2) temperature, (3) relative humidity of air to which the material is exposed, and (4) the chemical character of the material.

Setting aside these important factors for discussion below, let us focus on "activation energies," E_{α} , of plant constituents. Activation energy may be defined as the amount of energy, assumed to be in the form of heat, that must be applied to initiate a chemical reaction. An analogy is: heat must be applied to a pot of water to raise the water temperature to the point where the water starts to boil. In this case, the "boiling point", 100° C, is analogous to the temperature threshold that initiates a chemical reaction.

and the second state of the special state and the second state of the second state of the second second second

2.2 Activation Energy, E_a : A Key To Heat Generation

Take a hypothetical example of two piles of moist hay — one sterile, the other containing a natural microbial flora. Assuming equal access of chemical substrates and microbes to oxygen, it seems reasonable to expect that the pile with the microbes will heat up more rapidly. Why? A fundamental concept in chemical thermodynamics says that total heat released from oxidation of a simple substrate, like glucose, i.e., 2,818 kJ/mol (Miao et al. 1994), is not dependent on the type of process involved in generating the heat. Indeed, the idealized chemical equations for both biotic and abiotic oxidation are identical.

Carbohydrate, e.g., sucrose: $C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O + heat$

However, the reaction times do differ. E_a required for direct chemical oxidation of glucose in air is much higher than the E_a for glucose undergoing biochemical oxidation via a series of microbial enzymatic reactions. For example, the hydrolysis of sucrose has an E_a of 106.6 kJ/mol. The E_a for hydrolysis by invertase is about 48.1 kJ/mol (Moelyn-Hughes 1933, 1950 and Huennekens & Chance 1963). The hydrolysis of starch by amylase has an E_a of 12.2 kcal at 15°C and 4.4 at 45°C (or 51 and 18.4 kJ/mol, respectively) (Stearn 1949). Thus, it takes less energy to produce heat during decomposition of a substance when a series of microbial processes are involved, than if the substance were decomposed by direct chemical attack in air. This means that temperature rise in a sterile pile of yard trimmings will occur less rapidly than in a nonsterile pile.

In self-ignition heating experiments, Jones and others (cf. Table 2 in Jones and Rahmati 1990) have determined E_a for various types of plant matter: 71 – 125 kJ/mol (see Section 3.1 below). Therefore, following the death of plant cells in woody and leafy materials, microbes will readily metabolize low molecular weight substances, with concomitant release of heat. Biochemically-catalyzed decomposition of some complex carbohydrates and proteins will continue and biologically driven reaction rates will accelerate (at an average Q_{10} =2) as pile temperatures increase up to roughly 50 to 60°C, the temperature optimum for thermophilic microorganisms (Haug, 1993). With a further temperature rise, the biological reaction rates drop off as the temperature approaches the lethal limit of the microflora, about 80°C. At this point, and possibly sometime prior to reaching the 80°C level, decomposition of organic substances becomes abiotic, that is, via direct chemical oxidation or by the action of heat itself, and with some of the reactions themselves releasing heat.

2.3 Abiotic Heat Generation

While the above discussion argues for a dominant role of microbial oxidation at pile temperatures below 80°C, it does not preclude a significant influence of abiotic oxidation in the lower temperature stages of the process. Consider the following example. Linolenic acid is the major fatty acid contained in plant chloroplasts (Stumpf 1965). Linolenic acid (18:3) is straight-chained with three conjugated double bonds, i.e., the bonds are located close to each other, making them readily susceptible to oxidation — and heat generation — at room temperature (Abraham 1996). This chemical is also the ingredient in linseed oil making it prone to SC at room temperature! So-called "enoic" or double bonds earlier were hypothesized as candidates for oxidation reactions in plant material (e.g., Walker 1967). We hypothesize that linolenic acid may be strong candidate as a fuel in auto-oxidation reactions in leafy plant matter. Other plant oils, e.g., corn and cottonseed (Table 1), are not as reactive (Khattab et al. 1996), an effect cor-

related with fewer double bonds in fatty acids in those oils. Nevertheless, the presence of plant oils and resins generally can facilitate abiotic oxidation within the lower temperature regime while concurrently inhibiting biological processes. For example, coniferous materials, which contain more resins, are considerably slower to decompose than hardwood species.

In the common situation, yard trimmings does not contain a high proportion of reactive compounds. Therefore, abiotic oxidation seems not to play a large role in self-heating, that is until the biological agents raise the temperature to a very high level. Kubler (1987) states that heat generation by abiotic "auto-oxidation" begins to be detectable at about 80°C — lower in the presence of moisture, which is a catalyst (just as it catalyzes iron oxidation or rusting). The process potentially feeds itself as higher temperatures cause faster reactions rates that further raise temperatures and oxygen demand. The availability of oxygen can determine where the process eventually goes.

2.3.1 Pyrolysis And Its Role

So far, we have considered naturally occurring chemicals in plants and their decomposition with accompanying heat production. As the temperature of the pile slow-ly rises, another heat producing phenomenon, pyrolysis, is initiated. Pyrolysis may be defined as the decomposition of a substance by the action of heat under oxygenstarved conditions. Kubler (1987) exhaustively reviewed pyrolysis of wood, an interesting but complex process. Pyrolysis can either consume or liberate heat, depending on the circumstances. Pyrolysis products include CO₂, CO, and products that can still react with oxygen to produce heat. These reactive substances include gaseous compounds, a solid residue called char and finally, under some conditions, oil or tar.

Several key points drawn from Kubler's review fit into heat development leading to SC. First, the kinds of pyrolytic degradation products, which are accompanied by a release or consumption of heat, depend on the temperature and duration of heating. Decomposition of complex organic molecules at temperatures of 65-70°C (or even lower, e.g., 35°C), maintained for prolonged periods (weeks to months), involves water and oxygen (processes of hydrolysis and oxidation, respectively) and result in the production of water, carbon dioxide, and heat. The resulting carbon dioxide dissolves in water forming a weak acid, further accelerating the decomposition of complex molecules and formation of additional acidic (organic) compounds. Taken as a whole, the multistep process is termed *slow pyrolysis* with individual reactions releasing heat in piles of compost and mulch. Accumulation of acidic products is well documented in piles of wood chips stored for several months (cf. Buggeln 1999).

There is much more information on pyrolysis of woody materials at temperatures above 100°C, e.g., 150 - >400°C. Wood is heated for various periods (days to months) to determine: the temperature at which plant chemicals come under attack from heating, the kinds of reaction products produced, and whether the decomposition process releases or consumes heat. Reactions at higher temperatures are termed *fast pyrolysis*. Vigorous reactions at high temperatures generally consume energy (heat) and reaction products have higher energy contents than the reactants (unlike the largely water and carbon dioxide, products of slow pyrolysis). These reactants may include volatile gases, liquid tars and solid chars. However, contrary to the above discussion, Davis *et al.* (1983) reported decomposition of cellulose in three stages. First, at 80°C, a heat-requiring reaction occurred where water was absorbed; then, two heat producing reactions occurred at 370°C and about 450°C, corresponding to characteristic cotton de-

mo

id r

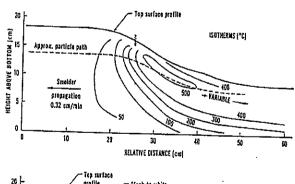
101

Richard Buggeln and Robert Rynk

composition and char oxidation, respectively. The latter temperatures are considerably higher than the 300°C maximum for cellulose decomposition reported by Kubler (1987). One may suggest that pyrolytic reactions relating to SC occur up to the point of the critical ignition temperature, i.e., 120 - 145°C. However, under some situations, pile temperatures can reach 500°C, when the $\rm O_2$ concentration is approaching zero. In this case, vigorous decomposition of wood into highly reactive solid and gaseous constituents can occur (see Section 2.4). Charring is evidence of the incomplete oxidation resulting from high-temperature and oxygen-limited pyrolysis.

2.4 Smoldering

On occasion, meandering pathways of charred remains are uncovered after an SC event in a pile of ground yard trimmings. Telltale trails are remnants of smoldering, a complicated process that includes combustion (requiring oxygen) and pyrolysis processes. Ohlemiller (1985) showed a diagram of a horizontal profile of a smoldering pathway in layer wood fibers 20 cm thick (see Figure 4). He describes the processes in Figure 4 as a "coupled-forward and — reveres smolder zones since oxygen enters the reaction zone ahead of the wave permitting an exothermic oxidative pyrolysis process (reverse smolder zone); oxygen also enters from above and behind permitting exothermic char oxidation (forward smolder zone)." There was a sharp temperature gradient from 50 to 500°C, within a very short distance about 10 cm, from head to core. The 400-500°C core temperature had an oxygen level of nearly zero. Frequently, at the head of a smoldering pathway, a cavity (enlarging centrifugally) develops just under the surface of the pile, and is often followed by collapse of surface material. When collapse occurs, the air



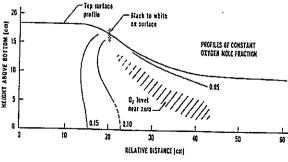


Figure 4. Example of smolder wave structure in a permeable horizontal fuel layer; wood fibers with bulk density of 0.04 g/cm³. (Reprinted from Proc. Energy & Combustion Science, 11, T. J. Ohlemiller, Modeling of smoldering combustion propagation, 277-310, 1985, with permission from Elsevier Science).

supply is increased and smoldering can become flaming combustion (Jones 1993). The propagation rate of smoldering in sawdust, vegetable fiberboard, and tobacco shreds (under natural convection/diffusion) is on the order of $4.0-4.5 \times 10^{-3}$ cm/s. According to Ohlemiller oxidative pyrolysis is a likely source of heat in smoldering, though the chemistry of the reactions is obscure. It is possible that more than one site in a large pile, whose temperature is elevated throughout, could be receiving sufficient oxygen to initiate smoldering and create multiple pathways, i.e., flues, to the pile surface (Bowes 1984). Kubler (1990) reported an interesting story of smoldering and pyrolysis of buried woody materials in a demolition landfill.

Section 3. 0 Factors Influencing the Mode of Heat Generation in Yard Trimmings

Using the cellulose part of wood as an example, what may be likely roles of biotic and abiotic decomposition/heat generation in piles of compost and mulch? In the interior part of piles, cellulose decomposition may be initiated by microbes, predominantly fungi with temperature optima of 25-45°C (cf. Buggeln 1999) and a moisture requirement of at least 20-24% (Springer 1980). Slow pyrolysis may start as interior pile temperature rises above 35°C. At temperatures above 90°C, microbial activity ceases and, depending on the oxygen levels, initial stages of abiotic oxidation or fast pyrolysis may start, accelerating the rate of thermal degradation of cellulose and hemicellulose (see Miao *et al.* 1994). Toward the cooler, outer surface of piles microbial decomposition of cellulose probably predominates. So, for cellulose, and for many other plant chemicals, there may be multiple pathways for chemical decomposition with heat release. The dominant mechanism — direct chemical oxidation versus pyrolysis versus biochemical enzymatic reactions — will depend on temperature and oxygen levels, each a consequence of the substrate's character, moisture and location within a pile.

3.1 Chemical Constituents — Activation Energy, Critical Temperature, And Critical Mass for Thermal Ignition

Let us assume that we have progressed in the heating process where the interior pile temperature is now well above 90°C, and woody materials have been undergoing pyrolysis with the formation of numerous compounds capable of auto-oxidation and heat generation. As plant chemicals differ in their susceptibility to pyrolitic and oxidative decomposition, so too botanical residues (and their constituent chemicals) have different propensities for self-ignition. This was clearly shown by Jones and Raj (1988) in experiments in which small quantities of plant matter, pressed into spherical baskets (e.g., 5 cm diameter), were slowly heated in an oven to determine critical ignition temperatures, i.e., determining two oven temperatures that straddle the ignition temperature of the sample. From such temperature data, Jones and Raj calculated the activation energy, E_a , for leaves and wood shavings of *Eucalyptus saligna* to be 71 kJ/mol and 95 kJ/mol, respectively. Importantly, these data were also used to predict maximum-safe-pile height of these materials (see Section 5.0).

Jones et al (1991) further studied the contribution of two components (oil and solid matter) to the overall ignition behavior of green leaves of 7 species of Eucalyptus. The overall E_a for the leaves ranged from 67 to 118 kJ/mol. The E_a for leaf oils varied (100 – 200 kJ/mol) while the solid matter was assumed to be similar in all species (70 kJ/mol). Other vessel shapes, e.g., simulating an "infinite slab", yielded similar activation energies for E. haemastoma shavings in both basket- and slab-type experiments (Jones et al. 1992). Leaves from a highly reactive species (E. paniculata) gave a critical oven temperature of 215°C. Leaves from a less reactive species, E. microcorys, ignited at a higher critical temperature of 235°C. Other reported activation energies for plant materials include: 125 (\pm 6) kJ/mol for sugar cane bagasse (Gray et al. 1984); 106 (\pm -4) kJ/mol for P. radiata sawdust (Chong et al. 1995); ca. 109 kJ/mol for "sawdust;" and 101 kJ/mol for solvent-extracted wood fiber (Walker & Harrison 1978).

Earlier, Walker & Harrison (1978), comparing acetone-extracted samples of milled *Pinus radiata* wood fiber insulating board versus controls, concluded that resins may participate in early stages of heat generation. Pine resin added to a sawdust sample reportedly reduced the critical ambient temperature required to induce sample ignition

Compost Science & Utilization Spring 2002 171

b:

CI

m

w

w.

Richard Buggeln and Robert Rynk

by about 40°C (cf. Bergman 1974, and other examples in both Bergman, and Kubler (1987)). Lower ignition temperatures were reported in wood high in lignin, a complex organic molecule in the cell walls of woody plants (cf. Bowes 1984 and Kubler 1987). Pure cotton is 100% cellulose and when devoid of other constituents, e.g., oils (Horrocks *et al.* 1991). It does not self-ignite (Bowes 1984). On the other hand, mixed residue of leaves, stems, seeds, and bits of cotton produced when cotton is ginned, are very susceptible to SC, even while piles are small, e.g., < 10′ high.

In the self-heating experiments, oven temperatures required to reach the ignition temperature of a sample, the so-called "critical temperatures", are a function of sample dimensions with critical oven temperature decreasing with increasing sample size (see Table 2, adapted from Bowes 1984). By extrapolation, one can imagine — and operators of yard trimmings sites can assert — a critical ignition temperature being reached in a large pile of yard trimmings at ambient air temperatures! See also Table 3 and Section 3.2.

Other methods used to investigate the propensity for self-heating in materials, especially coal, were listed by Vance *et al.* (1996) and include: the adiabatic method (cf. Ren *et al.* 1999), crossing point method (Ogunsola & Mikula 1991); and isothermal method (Banerjee *et al.* (1970).

TABLE 2.

Critical chamber temperatures for sawdust and wood fiber insulating board in relation to the mass of heated material (adapted from Bowes 1984, Tables: 5.4, 6.1, and 6.2)

Cube size Side dimension (mm)	Sawdust ¹ Chamber Temp. (°C)	Sawdust ² Chamber Temp. (°C)	Wood fiber insulation ³ Chamber Temp. (°C)	
1.6	-	•	317	
3.2	-	-	250	
6.4	-	•	212	
12.7	-	-	202	
25.4	212	232	177	
51	185	203		
76	173	188	-	
152	152a	· -		
303	135	•	_	
910	109a	-	_	

 $^{^{1}}$ From Table 6.2; sawdust density 250 (kg/m 3); a calculated values. 2 from Table 6.1; sawdust density 200 (kg/m 3). 3 from Table 5.4.

TABLE 3.

Critical size and critical ambient temperatures for selected materials: extrapolation from laboratory data to practical application

Reference	Plant Material	Idealized Shape		Critical Ambient Temperature (C)
Gross & Robertson (1958)	Wood-fiber board	Sphere .	13.6 (diameter)	48.9
н	Cotton linters	"	66 "	"
"	Sugar Pine	"	10 "	"
"	Cotton gauze with linseed oil (6:1) "	0.14 "	"
Jones & Raj (1982)	Eucalyptus saligna leaves	Cube	3.9 (side)	40
	E. saligna wood	"	48.5 "	,,
Bowes (1984)	Dry hay	u	51 "	15
Gray et al. (1984)	Bagasse processing residue	Rectangular rod	66 m (base) x 18m (heigh	

It is important to remember that chemical changes are continuously occurring in piles of yard trimmings, with different reactions occurring in different parts of piles, depending on moisture content, pile temperature, and composition of the microflora (cf. Bergman 1974 and Buggeln 1999). Are there any organic moieties in the dynamic "stew" of original reactants, and those generated during pyrolysis, that may be positively excluded from biotic or abiotic heat generating processes? Probably there are few, if any.

3.2 A Extrapolation of Laboratory Data to Field Situations (Critical Size)

Bowes (1984) summarized the relationship between critical mass and critical ambient temperature in ignition experiments with sawdust and wood-fiber board. Some of the data are shown in Table 2. Critical ambient temperature decreased with increasing size of the mass being heated. Cubical baskets of sawdust at diameters of 25 to 910 mm gave ambient critical temperatures of 212 to 109°C, respectively.

Gross & Robertson (1958) may be amongst the first to extrapolate small-scale heating experiments to potential field applications, that is, the critical pile size and corresponding critical ambient temperature. The critical pile size refers to the minimum dimensions of a pile of material that may theoretical undergo SC under ambient conditions. The data for several kinds of plant matter are given in Table 3. Notice the critical diameter of a pile of cotton/linseed oil is 0.14 m, or just under 0.5 ft! Compare this with a pile of cotton linters (by-product in cotton fiber preparation) where the critical pile diameter could be as great as 66 m, or just over 200 ft. Large differences are also seen in critical cubic dimensions of Eucalyptus leaves and wood — 4 versus 49 m, respectively (Jones and Raj 1988). A recent guideline for storage of wood chips recommended a pile height of 7.5 m for a storage period of up to three months. For long-term storage, the guideline recommended a height of 4m (8m width, or less, at base) and length of ca. 67m, at a maximum bulk volume of 1,000 m³ (OFM 1998). Two estimates of critical pile size for "dry" hay, i.e., 44 m and 51 m cubes (both at 15°C), are enormous relative to piles commonly encountered (Bowes 1984). For "wet" hay, the interaction between wet oxidation processes and biological heating is complicated and unresolved, Bowes (1984) calculated that critical dimensions of a wet but sterile pile could be, as a minimum, 3.2 x greater than the size of a wet pile with microbial activity.

Regarding heat retention and loss within a pile, maximum air convection from a pile can be achieved by accentuating the "chimney effect." That is, a tall and narrowbased pile will provide greater opportunity for heat loss than short pile with a flattop and broad base (Kubler 1982). Gray et al. (1984) noted that SC has been recorded in bagasse piles substantially smaller, e.g., 18m (base) x 4m (height) than the dimensions given in Table 3. They concluded that additional factors came into play that intensified the rate of heating, such as creating the initial pile when the bagasse-processing residue

was above ambient temperatures.

Time to ignition for a 5.8 m cube of sawdust at an ambient temperature of 20°C was calculated to be 2,000 h (Bowes 1984). Rarely do authors venture this kind of estimate. Indeed, in respect to hay, Bowes was more cautious, stating, "The most intractable problem likely to remain will be prediction of time to ignition." (Note: experts in the engineering of composting cannot tell you exactly how long it will take to make fully cured compost!) Initial material composition and moisture conditions of piled yard trimmings, coupled with variable weather patterns under field conditions, interact to control the rate of pile heating and thus the length of time to potential ignition. For example, SC events occurred several times at a local mulch-making facility

Spring 2002 173 Compost Science & Utilization

following extended periods of strong winds impacting 20 ft high piles at right angles to the long axis of the piles. In these instances, the *propensity* for SC was at hand in respect to necessary physical and chemical factors save one: oxygen supply. Windy conditions met the oxygen requirement and shortly thereafter, municipal fire trucks arrived!

3.3 Oxygen

Oxygen is a key reactant in heat generation in both microbial and abiotic processes. See Haug (1993) for a discussion of oxygen in microbial systems related to composting. The effect of oxygen on abiotic self-heating in sawdust was reviewed by Bowes (1984). In self-heating experiments with sawdust, the minimum ambient temperature for sample ignition (5.1 cm cube) was 35°C lower in 30% oxygen than in 4%. In addition, the time to ignition approximately doubled at the lower concentration. Berman (1974) showed of photograph of a shovel-full of wood chips that burst into flame as soon as the chips were moved from a heated pile in the vicinity of the combustion zone. Clearly the chips had already reached a temperature for ignition, but didn't ignite *in situ* for lack of oxygen. Ground plant material undergoing fast pyrolysis at 300 – 500°C, where oxygen levels are very low, could be expected to exhibit this conflagration when exposed to air.

3.4 Moisture

Apart from its vital role in microbial functions and temperature regulation (see Section 4.0), moisture influences self-heating in several ways. There is some experimental evidence suggesting that moisture enhances oxidation of chemicals by oxygen. Vance *et al* (1996) reported a maximum oxidation rate in sub bituminous coal at a moisture content of about 7% (wt) and temperatures < 80°C. According to Kawatra & Hess (1999), 10-15% moisture induced rapid heating, via atmospheric oxygen, of iron grinding swarf. At higher moisture levels, heating was much reduced, possibly rate-limited by oxygen diffusion though a thick boundary layer of water surrounding iron particles. Diffusion of oxygen is >10,000 times slower in water than in air (Armstrong 1979). However, it may be just as likely that the temperature was suppressed by higher thermal conductivity in the moist swarf and/or evaporation.

In experiments with hay initially dried at 70°C to 1-2% moisture, air-flow at 95% relative humidity (RH) showed progressively higher heating rates, with decreasing lag times, at temperatures of 70, 90 and 110°C. No heating occurred at 50°C or at 5% RH (Miao and Yoshizaki (1994). Results at 95% RH extended the earlier work of Rothbaum (1963) who showed the effect of moisture (as RH) on microbial heat generation as well as abiotic heat generation above 90°C. The interaction of moist air and dry substrates can also cause a temperature rise due to the heat of absorption, an abiotic mechanism. Latent heat of condensation or "wetting" is released as the moisture from the air is absorbed by a dry substrate. This is the reverse of what occurs when water evaporates from materials and removes latent heat.

3.5 A Catalytic Role for Pieces of Metal?

Operators of composting and mulching sites have reportedly identified "tramp metal," particularly iron, ranging in size from shards from grinding equipment to a threaded nut, in charred cavities following SC events in piles of ground yard trim-

is ca fro

> hi Zl

m

id

di & vc m ba

or be

ar. et

(19

in ch an me me

Ιtϵ

w:

mings. It has been hypothesized, but not yet experimentally demonstrated, that oxidized tramp metal may catalyze SC in piles of wood chips (cf. Bergman 1974).

According to Walker (1967) the effect of iron salts on the degradation of cellulose is well known. Similarly, Christie & Mainwaring (1992) cite research demonstrating a catalytic role for metals and their oxides on coal oxidation. When cations are removed from coal, higher temperatures for oxidation and combustion are required. A range of inorganic compounds added to samples of coal showed pyrite (FeS₂) contributed to highest reactivity and lowest critical temperature in heating experiments (Sujanti & Zhang 1999). As noted below, low-ranked coals with pyrite-containing igneous extrusions have a high propensity for SC due to heat from pyrite oxidation.

Section 4.0 Role of Water in Heat Accumulation and Transfer

There are two main "forms" of water that participate in the development of conditions potentially leading to thermal ignition: bound water and free water (see Badr & Karim 1992). Bound water (possibly 10% by wt., Walker (1967)) presumably is involved in facilitation (by unknown mechanisms) of the rate of abiotic oxidation by atmospheric oxygen (Miao et al. 1994; Vance et al. 1996). Free water participates in heat balance (gain and loss) within a pile of material, i.e., due to heat of wetting and evaporation, and diffusion and convection via water movement. Attention has frequently been called to the complexity of elements within the latter category e.g., Kubler 1987, and resultant difficulty in developing mathematical models of SC in coal (e.g., Vance et al. 1996). See Walker (1967) for an historical review of the role of water in SC, Kubler (1987) for data pertaining to woody materials, and Bowes (1984) for a concise overview, including this statement: "In general, the effects of the presence of water, and of moisture exchange with the environment, on self-heating material will depend on the initial temperature and moisture content of the material relative to the temperature and humidity of the environment and on diffusional resistances...applied to the mass transfer of water vapour. There are many possible combinations of these factors..."

Gray *et al.* (1984) itemized broad effects of water and their list is quoted below. Items *i-iv* pertain to free water; item *v*, to proposed reactions that occur in the bound water fraction.

- (i) "Evaporation and loss of water can confer an endothermicity [i.e., process requiring heat] which tends to stabilise the system. Completely dry cellulosic materials are hygroscopic. The rate of heat release which is due to condensation of water vapour and evolution of its latent heat can be sufficient to cause self-heating and thermal ignition. [Bowes (1984) emphasized the effect of moisture on "over dried" materials. Hot spots have been noted in coal piles after rain (see Ren et al. 1999). Somewhat similar observations have been observed at composting and mulching operations where substantially higher temperatures in windrows were recorded the day after rain. Heat of wetting may be the cause in the former example and resurgence of microbial activity in what might have been slightly dry conditions, in the latter case (or both effects, if the pile was excessively dry). The transfer of heat within piles may occur via this mechanism until only tightly bound water remains at pile temperatures above 90°C.]
- (ii) When movement of water through a mass takes place by evaporation and condensation, no net thermal effect will result when the two rates balance. The overall heat release from the system will then approximate to that of dry mate-

- (iii) Balanced internal rates of evaporation and condensation do not lead to identical conditions for criticality [propensity for SC] of wet and dry masses. The thermal diffusivity [i.e., movement of heat] within wet material is greater than that within dry material and the stability of the wet mass is enhanced because of it.
- (iv) When a net loss of water occurs from the system, there is a gradual decrease in thermal diffusivity. [Thermal stability in the 60-90°C range has been reported in heating experiments, e.g., Gray et al (1984) and temperature plateaus (60-70°C) have been observed in piles of compost and mulch. Both observations are attributed to heat required for evaporation of moisture (presumably free water) that must occur prior to a significant rise in temperature. When only the bound fraction remains, heat produced by abiotic oxidations will be retained in the "dry" matter that now possesses a low thermal conductivity, and a rapid temperature rise can occur. Practically speaking, keeping "free water" content in piles at elevated levels, say above 30%, is clearly a way to keep pile temperatures below 100°C, thereby lowering the risk of SC. In addition, as bulk materials, like yard trimmings, dry, their thermal conductivity decreases. In other words, a drying pile of compost becomes a better insulator and thus retains more heat.]
- (v) As long as water remains in the system, liquid-phase oxidations and acid hydrolysis of hemicellulose may take place, making additional contributions to the heat release rate." [Some of these could involve pyrolytic mechanisms.]

In the discussion above, the initial water content of piles of compost or mulch have been assumed to be about 50%, decreasing with time as pile temperature increases. Suppose the water content was much higher...the material was soggy? The answer is simple: access of plant materials to oxygen will be severely restricted and those processes requiring oxygen, whether biotic or abiotic, will proceed slowly or not at all. Microbes that flourish in the absence of oxygen will become dominant and heat generation will be undetectable. Bowes (1984) did not include coal as a microbial substrate. Some types of coal have moisture contents of 20 to 37% (Jones 1993), theoretically sufficient to support fungal activity, but not high enough for bacterial growth. It is also unlikely that fungi could use coal as a food source. A suitable source of nitrogen for microbial growth may be present in coal but at a rather low a C:N ratio, e.g., 70:1 (Ogunsola & Mikula 1991).

Section 5.0 Role of Particle Size in Heat Generation and Transfer

In a general sense, particle surfaces, including pores and invasive channels, are sites of heat management, i.e., competition between heat production and loss by conduction, convection, and radiation. Water vapor adsorption and evaporation, and chemical oxidations (biotic and abiotic) occur at particle surfaces. Exclusive of pores and channels, a large particle has a smaller surface-to-volume ratio than a small particle, with particle mass affecting heat flux dynamics. At the particle level, as parti-

I

cle size decreases, potential heat loss by convection increases, because of the greater surface/volume ratio of smaller particles. Aggregations of small particles can become compacted, reducing overall porosity and convective heat dissipation On the other hand, the pathway for the air that feeds oxygen to heat releasing reactions is similarly restricted. There doesn't seem to be a specific particle size representing a "boundary" condition in studies with coal. There is more of a continuum effect of particle size on various processes discussed below.

It has long been known that the propensity for SC in coal is related to particle size with oxidation rates increasing with decreasing particle size down to some lower limit (cf. Ren et al. 1999). Experimental evidence in coal piles of different particle sizes showed piles with greater density, i.e., smaller particle size, greater compaction, and lower porosity, heated more quickly, e.g., De Faveri et al. (1989). Greater apparent reactivity with oxygen at small particle sizes was shown experimentally, but an overall explanation was complicated by particle porosity, diffusion, and temperature (Akgun & Arisoy 1994; Wang et al. 1999). According to the mathematical model of Monazam et al. (1998), hydration rate was predicted to be inversely correlated with particle size. Commenting on the role of small particles of coal, Bowes (1984) suggested that as oxidation is related to surface area, large lumps of coal were unlikely to contribute significantly to heat generation in piles composed of a wide range of particle/lump sizes.

Is it reasonable to take the experimental data and conclusions on particle size for coal and apply them to yard trimmings in the absence of similar data? To an extent, yes. Given moisture levels similar to those found in coal, and sufficient time for abiotic heating to take hold, yard trimmings piles may behave like coal in regard to particle size.

However, unlike coal, self-heating of yard trimmings primarily begins via biological processes that depend on sufficient and continuing supplies of both moisture and oxygen. Lacking sufficient oxygen, piles of yard trimmings fail to heat. In composting systems, the availability of oxygen is associated with the free air space (FAS) of the composting substrates. The FAS is in turn dependent on the size and size distribution of particles as well as the moisture content. At a given moisture level, FAS decreases with particle size. Thus, there is, theoretically, a pivotal size at which smaller particles, i.e. a more dense pile, decrease the chance that self-heating even begins. The balance of particle size with moisture, reaction rates, heat loss and oxygen transfer is a complex situation that composting scientist and practitioners continue to struggle with. See Haug (1993) for a discussion of the relationship of FAS to particle size and temperature.

Further complicating the matter, yard trimmings are physically and chemically heterogeneous — much more so than coal. Particles are rarely consistent in size nor uniformly distributed, even after grinding. For example, in piles of yard trimmings it is common to find a layer of wood chips sandwich between layers of dense ground vegetation. A lens of wood chips can provide a vent that channels oxygen (and moisture) to the small particles of vegetation at the boundary of that lens. In effect, the vent supports decomposition and heat generation deep within the pile. Charring has been observed along layers of coarse materials, like leaves and chipped wood, deep within storage piles.

Finer particles may lead to SC in yard trimmings if the initial rise in temperature is not dependent of biological decomposition. For example, it has been reported that SC in a wood chip pile started in pockets of "fines" (Berman 1974). At yard trimmings grinding operations, fine particles frequently accumulate on the ground in conical piles (to about 3-4' high) around metal struts of conveying machinery. These piles have ignited (personal communication, A. Ashford). It is possible that the struts became

heated by sunlight or by heat transferred from motors powering the equipment, providing an external source of heat to dry the fines, inducing an influx of air into the pile, and resulting in self-ignition of the fines. Ensuring piles of ground residues are frequently cleared from steel supports can prevent this potential SC problem. Bergman (1974) and Bowes (1984) discuss reports of charring and SC in wood timbers and sawdust, initiated by radiation heat from steam pipes and heating ducts. SC in stacked fiberboard, emerging from manufacturing processes at higher than ambient temperatures, has been reviewed by Bowes (1984) and Kubler (1987).

5.1 Compaction

Under the assumption that dense piles fail to heat, some compost operators drive equipment on large storage piles of yard trimmings in attempt to prevent the initial heating. However, this strategy not fool proof. In fact, it can even back fire. As noted by Kubler (1987), events that lead to pile compaction, e.g., pile settling, infiltration of fines filling spaces between larger particles, and physical compaction from heavy equipment driven on piles, lead to greater heat retention within the mass. Although compaction of fines might reduce oxygen penetration, it may lead to heat generation via fast pyrolysis. In addition, fines becoming stratified and compacted in piles would tend to block vertical airflows and reduce convective heat transfer and loss, thereby increasing pile temperature.

Section 6.0 Research Results with Coal: Food for Thought

Coal is "ranked" on the basis of relative transformation from initial plant matter, i.e., degree of coalification due to compression (e.g., Jones 1993). Subtypes of lowranked coal, those closest to peat, e.g., lignites, have the greatest propensity for SC. Physical and chemical characteristics correlated with a tendency toward SC include: (1) high moisture and oxygen content (Misra et al. 1994); (2) extensive porosity and great internal surface area (Ibid); (3) involvement of external factors: igneous intrusions into coal seams and prevailing climactic conditions, especially high relative humidity (Ibid.); (4) possible catalytic role of water in oxidation reactions (Guin et al. 1986); (5) high surface polarity leading to high heats of wetting (Christie & Mainwaring 1992; Vance et al. 1996); (6) putative role of carboxylic acid and phenolic functional groups (Ibid) and terpenoids (Shu et al. 1996); (7) exploration, via fractal geometry, of micro-structure and porosity in relation to oxidation potential (McMahon et al. 1999); (8) potential reactions with oxygen, chemical pathways and process controls by diffusion in micropores (Lopez et al. 1998; Clements et al. 1991; & Wang et al. 1999); (9) four stages of reactions involving oxygen and oxygenated compounds proposed, each with its own range of activation energies (cf. Medek & Weishauptova 1999).

Due to concern about the origins, i.e., chemical characteristics, of coal shipments, and hence, uncertainty about their propensity for spontaneous ignition, researchers have used an adiabatic oxidation apparatus to evaluate the safety of the coal during storage (Ren et al. 1999). See Krishnaswamy et al. 1996 and Gong et al. 1999 for recent SC models for coal.

Section 7.0 Summary

Armed with information from Sections 2.0 through 5.0, the reader should return to Figure 1 (lower right hand oval) and retrace the steps that may lead to SC, filling in

this general framework and developing a sense of the numerous interactions between factors and processes. Let's begin this reprise with a newly created pile of shredded yard trimmings. Some of the heat naturally produced by bacterial and fungi living and multiplying on the surfaces of plant particles becomes trapped and the temperature inside the pile starts to rise. Plant chemicals, possibly linolenic acid, can directly react with air at ambient temperature, generating more heat. While the relative contributions of the biotic and abiotic heat production (up to the lethal temperature of microbes, about 80°C) have not been quantified, microbes generate most of the heat in early stages of the temperature climb.

One may visualize each bit of plant matter lightly bathed in a thin layer of water. This is the place where both biotic and abiotic chemical reactions occur. Water temporarily stores heat produced by reactions, but water also evaporates, carrying heat (via convention) toward the cooler, outside layers of the pile and subsequently to the atmosphere. Picture heating water over a campfire in winter. As the fire heats the pot and contents, warm water evaporates from the water surface and condenses as water vapor in the cool air above the pot. Is the water vapor carrying heat? Put your hand into the vapor and find out! Water vapor is commonly seen emerging from the top of piles of ground plant matter on a cool day.

The great range of particle sizes in the pile affect the rate of heat generation and redistribution — with sufficient moisture and oxygen, smaller particles with large surface-to volume ratio will generate more heat than larger particles, and clusters of smaller particles with tortuous channels that restrict air flow will retain more heat than similar aggregates of larger particles with larger channels and greater air flow. At any given location within a pile the mixture of particle sizes is going to affect heat dynamics: production and retention/loss — (oh, a painful thought given the possible combination and variations of particle sizes and reaction rates!).

Rather than become mired in these possibilities, let's concentrate on a more critical factor, the ubiquitous water. Why care about water? Water happens to be the "governor" of temperature increase — up to a point, that is: a governor with a restricted sphere of influence. On revisiting the campfire, we see that a camper has tossed a handful of potatoes into the pot of water. The temperature of the potatoes has reached the boiling temperature of water (100°C) but never climbs higher…as long as there it still water in the pot! Once the water boils off, heat from the fire is now transferred through the metal pot to the potatoes, potato temperatures rise rapidly, and they start to burn. In a pile of yard trimmings, you can imagine many isolated local pots simultaneously boiling. If just one empties, SC is a possibility. So, water is the governor of temperature as long as it is around! In the pile of plant matter, the governing role of water is the same. While microbial life was largely killed as pile temperatures reached 80 - 90°C, pyrolysis (the destruction of chemicals by heat alone) and oxidation of byproducts continued to generate even more heat. Now at more than 100°C, the pile has essentially lost all easily removable water, heat production via pyrolysis continues, and heat accumulates in solid particles. Air carrying oxygen flows into pile and continues to fuel heat production processes. Removal of heat from particles by airflow alone is less efficient than heat transfer and removal, via water vapor, from particles, so particle temperatures may start to approach the critical temperature for SC.

As the pile continues to heat up, the "dimension" of the heating problem comes into play. That is, the role of pile surface area to pile volume becomes important. We know that large piles of plant residues are more prone to SC than smaller ones. We also know that increasing the number of layers of clothing will trap body heat, keep-

Compost Science & Utilization Spring 2002 179

ing us warm, when the external air temperature is cold. In the same way, increasing the distance from the center of a pile to the outer edge acts as a thermal blanket that contains heat. When the outside temperature increases, we shed layers of clothing in order to get rid of excess heat. In conclusion, one can prevent spontaneous combustion in piles of yard trimmings by keeping two general rules mind: small is beautiful and wetter is better.

Acknowledgements

The authors gratefully acknowledge assistance from Professor J. Clifford Jones, Messers. Adam Buggeln and Steve Street, and Ms. Kathy Ellis, and Ms. Anne Jordan, and the helpful comments of two reviewers. The Tennessee Department of Environment and Conservation Division of Community Assistance provided financial support.

References

- Abraham, C. J. 1996. A solution to spontaneous combustion in linseed oil formulations. *Polymer Degradation and Stability*, 54:157-166.
- Akgun, F. & A. Arisoy. 1994. Effect of particle size on the spontaneous heating of a coal stockpile. *Combustion & Flame*, 99:137-146.
- Armstrong, W. 1979. Aeration in plants. Advances in Botanical Research, 14:225-332.
- Badr, O. & G. A. Karim. 1992. Experimental study of self-ignition and smoldering of moist cellulosic materials. *Transactions American Society of Mechanical Engineers*, 114:146-151.
- Banerjee, S. C., B. D. Banerjee and R. N. Chakravorty. 1970. Rate studies of aerial oxidation of coal at low temperatures (30-170 C). *Fuel*, 49:324-331.
- Bergman, O. 1974. Thermal degradation and spontaneous ignition in outdoor chip storage. Department of Forest Products, *Royal College of Forestry*, Nr R 91, 18 pp + appendices.
- Bowes, P. C. 1984. Self-heating: evaluating and controlling the hazards. vi + 500 pp. Elsevier Science Publishers. Amsterdam.
- Browne, C. A. 1929. The spontaneous combustion of hay. USDA Tech. Bull., 141, 38 pages.
- Buggeln, R. G. 1999. Outside storage of wood chips. BioCycle, 40(6): 32-34.
- Chong, L. V., I. R. Shaw, & X. D. Chen. 1995. Thermal ignition kinetics of wood sawdust measured by a newly devised experimental technique. *Process Safety Progress*, 14:266-270.
- Christie, G. B. Y. & D. E. Mainwaring. 1992. Oxidative and immersional heating on low rank coal surfaces. *Fuel*, 71:443-447.
- Clemens, A. H., T. W. Matheson & D. E. Rodgers. 1991. Low temperature oxidation studies of dried New Zealand coals. *Fuel*, 70: 215-221.
- Davis, D., A. R. Horrock and M. Greenhalgh. 1983. Ignition studies on cotton cellulose by DTA. *Thermochim. Acta*, 63: 351-362.
- De Faveri, D. M., C. Zonato, A. Vidili & G. Ferraiolo. 1989. Theoretical and experimental study on the propagation of heat inside deposits of coal. *Jour. Haz. Mat.*, 21:135-142.
- Frank-Kamenetskii, D. A. 1969. Diffusion and heat transfer in chemical kinetics. Plenum Press. New York-London. xxvi + 574 pp.
- Gong, R., J. G. Burnell & G. C. Wake. 1999. Modelling spontaneous combustion in wet lignite. Combust. *Theory Modelling*, 3:215-232.
- Gray, B. F., J. F. Griffiths & S. M. Hasko. 1984. Spontaneous ignition hazards in stockpiles of cellulosic materials: criteria for safe storage. *J. Chem. Tech. Biotechnol.*, 34A:453-463.
- Gross, D. & A. F. Robertson. 1958. Self-ignition temperatures of materials from kinetic-reaction data. *Jour. Res. Nat. Bureau Stds.*, 61:413-417.
- Guin, J. A., C. W. Curtis, & B. M. Sahawneh. 1986. Laboratory study of the self-heating tendency of coals and their pyrolysis chars. *Ind. Eng. Chem. Process Des. Dev.*, 25:543-546.
- Haug, R. T. 1993. The practical handbook of compost engineering. Lewis Publishers, Boca Raton, FL. 717 pgs.

Η

H

Jo

Ĭο

Jo

Ιo

Jο

K:

K:

K.

K

K.

K.

K.

K.

M

М

M

Μ

 \circ

- Horrocks, A. R., W. A. Moss, N. C. Edwards & D. Price. 1991. The spontaneous igniting behaviour of oil-contaminated cotton. *Polymer Degradation and Stability*, 33:295-305.
- Huennekens, F. M. & B. Chance. 1963. Enzymic reactions. *In*: (A. Weissberger, ed). Technique of organic chemistry. Vol. VIII-Part II Investigations of rates and mechanisms of reactions. p. 1231-1360.
- Jones, J. C. 1993. Combustion science. xi + 306 pp. Millennium Books. Newtown, NSW, Australia.
- Jones, J. C. & H. Rahmati. 1990. The self-heating and ignition of vegetation debris. 2. Authentic litter samples. *Fuel*, 69: 253-255.
- Jones, J. C., H. Rahmati & G. C. Wake. 1991. The unpiloted ignition of Eucalyptus leaves treated as parallel reaction system. *Jour. Fire Sci.*, 9:311-329.
- Jones, J. C. & S. C. Raj. 1988. The self-heating and ignition of vegetation debris. Fuel 67:1208-1210.
- Jones, J. C., B. F. Gray, & H. Rahmati. 1992. Experimental simulation of the infinite slab in thermal ignition. *J. Chem. Tech. Biotechnol.*, 53: 383-387.
- Kawatra, K. S. & M. J. Hess. 1999. Environmental beneficiation of machining wastes Part II: Measurement of the effects of moisture on the spontaneous heating of machining swarf. *Jour. Air & Waste Mgmt. Assoc.*, 49: 477-481.
- Kayser, E. G. & C. Boyers. 1975. Spontaneous combustible solids A literature survey. National Technical Information Service, U.S. Dept. Commerce. PB-244 046. 35 pgs.
- Khattab, M. A., M. E. ElRafey, A. A. Darwish & S. H. Kandil. 1996. Spontaneous ignition of oil-contaminated cotton fabric. Fire & Materials, 20:167-172.
- Koegel, R. G. & H. D. Bruhn. 1971. Inherent causes of spontaneous ignition in silos. Transactions of the American Society of Agricultural Engineers, 14:273-276;281.
- Krishnaswamy, S., P. K. Agarwal & R. D. Gunn. Low-temperature oxidation of coal. 3. Modelling spontaneous combustion in coal stockpiles. *Fuel*, 75:353-362.
- Kubler, H. 1982. Air convection in self-heating piles of wood chips. *Tappi*, 65:79-83.
- Kubler, H. 1987. Heat generating processes as cause of spontaneous ignition in forest products. *Forest Products Abstracts*, 10: 299-327.
- Kubler, H. 1990. Self-heating of lignocellulosic materials. In: (G. L. Nelson, ed). Fire and polymers hazards identification and prevention. ACS Symposium Ser. 425. American Chemical Society, Washington, DC. p. 429-449.
- Lopez, D., Y. Sanada & F. Mondragon. 1998. Effect of low-temperature oxidation of coal on hydrogen-transfer capability. *Fuel*, 77:1623-28.
- McMahon, P. J., I. K. Snook, S. D. Moss and P. R. Johnston. 1999. Influence of fractal pores on the oxidation behavior of brown coal. *Energy & fuels*, 13: 965-968.
- Monazam, E. R, L. J. Shadle, R. Evans & K. Schroeder. 1998. Water adsorption and desorption by coals and chars. *Energy & Fuels*, 12:1299-1304.
- Medek, J. & Z. Weishauptova. 1999. Effect of coal interaction with oxygen on its ignition temperature. *Energy & Fuels*, 13: 77-81.
- Miao, Y., M. Amari & S. Yoshizaki. 1994. Mechanism of spontaneous heating of hay. Part 2—chemical changes in spontaneously heated hay. Transaction of the American Society of Agricultural Engineers, 37:1567-1570.
- Miao, Y. & S. Yoshizaki. 1994. Mechanism of spontaneous heating of hay. Part 1 Necessary conditions and heat generation from chemical reactions. *Trans. Amer. Soc. Agric. Eng.*, 37:1561-1566.
- Misra, B. K. & B. D. Singh. 1994. Susceptibility to spontaneous combustion of Indian coals and lignites: an organic petrographic autopsy. *Internat. Jour. Coal Geol.*, 25: 256-286.
- Moelwyn-Hughes, E. A. 1933. The kinetics of reactions in solution. Oxford. Clarendon Press. vii + 313 pp.
- Moelwyn-Hughes, E. A. 1950. Physical chemistry and chemical kinetics of enzymes. In: (J. b. Sumner & K. Myrback, eds). The Enzymes. Chemistry and mechanism of action. Vol. 1, Part 1:28-78.
- OFM. 1998. Storage of wood chips. Office of Fire Marshall (Ontario, Canada), *OFM-TG-03-98*, 4 pgs.
- Ogunsola, O. I. & R. J. Mikula. 1991. A study of spontaneous combustion characteristics of Nigerian coals. Fuel, 70:258-261.

- Ohlemiller, T. J. 1985. Modeling of smoldering combustion propagation. *Proc. Energ. Combust. Sci.*, 11:277-310.
- Ren, T. X., J. S. Edwards & D. Clarke. 1999. Adiabatic oxidation study on the propensity of pulverised coals to spontaneous combustion. *Fuel*, 78:1611.1620.
- Rothbaum, H. P. 1963. Spontaneous combustion of hay. J. Appl. Chem., 13: 291-302.
- Shu, X., Jingcai Xu, Jingqui Xu, L. Ge, & D. Chen. 1996. Study of spontaneous combustion coals by GC and GC-MS. Fresenius J. Anal. Chem., 355: 390-392.
- Springer, E. L. 1980. Should whole-tree chips for fuel be dried before storage? USDA Forest Service, Forest Products Laboratory Research Note (FPL-0241), 5 pgs.
- Springer, E. L. and G.J. Hajny. 1970. Spontaneous heating in piled whole wood chips. I. Initial mechanism. *Tappi*, 53(1):85-86.
- Stearn, A. E. 1949. Kinetics of biological reactions with special reference to enzymic processes. In: (F. F. Nord, ed). *Advances in enzymology*, Vol. 9: 25-74.
- Stumpf, P. K. 1965. Lipid metabolism. In: (J. Bonner & J. E. Varner, eds). Plant Biochemistry. p. 332-345. Academic Press. New York and London.
- Sujanti, W. & D. Zhang. 1999. A laboratory study of spontaneous combustion of coal: the influence of inorganic matter and reactor size, Fuel, 78:549-556.
- Vance, W. E., X. D. Chen & S. C. Scott. 1996. The rate of temperature rise of a sub-bituminous coal during spontaneous combustion in an adiabatic device: the effect of moisture content and drying methods *Combustion & Flame*, 106:261-270.
- Walker, I. K. 1967. The role of water in spontaneous combustion of solids. Fire Research Abstracts & Review, 9:5-22.
- Walker, I. K. & W. J. Harrison. 1978. Exothermic aerial oxidation of wood-fibre insulating board. New Zealand Jour. Sci., 21:527-36
- Wang, H., B. Z. Dlugogorski & E. M. Kennedy. 1999. Experimental study on low-temperature oxidation of an Australian coal. *Energy & Fuels*, 13: 1173-1179.