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# Emissions from the Combustion Process in Vegetation

J.M. LOBERT<sup>1</sup> and J. WARNATZ<sup>2</sup>

<sup>1</sup>National Oceanic and Atmospheric Administration, Climate Monitoring and Diagnostics Laboratory, Mail Stop R/E/CG1, 325 Broadway, Boulder, CO 80303, U.S.A.

<sup>2</sup>Universität Stuttgart, Institut für Technische Verbrennung, Pfaffenwaldring 12, W-7000 Stuttgart 80, F.R. Germany

### ABSTRACT

In this chapter we present a detailed description of the processes involved in vegetation fires, emphasizing the flaming and smoldering stages of biomass burning. The major factors influencing the appearance of the single stages are discussed as well as their impact on emissions from fires. General production patterns, especially the importance of the ratio of flaming to smoldering combustion, are outlined for several classes of compounds, and some specific reaction paths that are likely to dominate certain emission formations are discussed. Finally, we summarize the global estimates of the most important emissions and propose that the complex nature of vegetation fires be simplified to enable reliable predictions of the emissions from biomass burning in a global scientific effort.

### INTRODUCTION

To describe the impact of global biomass burning on the environment, especially on the atmosphere, and to model the properties, behavior, and emissions of biomass burning, it is necessary to understand the processes involved in the combustion of natural biomass. Current estimates of both emissions from biomass burning and its global impact are based on empirical data and observations from natural and experimental fires as well as on highly uncertain global estimates of worldwide amounts of burned fuel and area (Crutzen and Andreae 1990). At this point, not many models are available to describe biomass burning or its elementary processes. Useful attempts have been made by the U.S. Forest Service (Albini 1976, 1981, 1984; Rothermel 1972; Wilson 1990); they predict fire behavior for different vegetation fuels and weather

conditions. However, these models do not consider the smoldering stage which is of special importance to the emission of atmospheric pollutants, and are not yet set up for the prediction of fire emissions per se. Current problems preventing a complete, easy, and reliable numerical estimate of biomass burning emissions are:

- a lack of quantitative knowledge about the heterogeneous process involved in vegetation fires, especially the quantitative description of the smoldering stage of a fire;
- the complexity of the whole process, which involves dynamic properties and a vast variety of fuel and environmental characteristics;
- a still limited data base on emission measurements, pointing out the relationships between fire properties and fire emissions.

In contrast to comparatively straightforward laboratory combustion processes of gaseous and liquid fuels—which have been well examined, not only because of their economic importance in energy production—the overall processes of vegetation fires have still not been satisfactorily delineated.

This chapter summarizes the general information about vegetation fires and provides a detailed outline of the burning processes. The process of biomass burning is subdivided into several single yet interconnected events. The emissions from vegetation fires are given special emphasis.

## BURNING PROCESSES IN VEGETATION FIRES

In this chapter, the different *stages* of fire—ignition, flaming, glowing, smoldering, and extinction—are described. These stages can occur in different physical *phases*, i.e., the solid, liquid, and gas phases.

### Ignition

The ignition of biomass is dependent on both fuel and environmental factors (fuel moisture and type, temperature, relative humidity, and wind). A spatially limited glowing area, very similar to that in the smoldering stage described below (see section on **Smoldering Stage and Extinction**) produces small flames with a limited rate of heat production. Although this initiation process is essential for the fire, it can hardly be separated as an independent process. Initial ignition is a kinetically controlled process that can terminate, under certain circumstances, before a sufficient, self-sustaining smoldering combustion or an open fire starts (Williams 1977). For a discussion of ignition probability for different types of fires and fuel beds, see Albin (this volume).

## Flaming Stage

In this section, we separate the flaming combustion for easier treatment into two independent phases: the fuel phase (referred to as the solid phase, also known as the condensed phase) and the flame (gas) phase.

### *Solid Phase Decomposition: Pyrolysis, Smoldering, and Glowing Combustion*

Vegetation material is basically made up of cellulose, hemicelluloses (together 50% to 75% of most dry plant material), lignin (15% to 35%), proteins, nucleic acids, amino acids, and volatile extractables. Additionally, there are minerals (up to 10%) that have to be considered for the process of fire spread and fire extinction and that may be important in the production of some emissions. Finally, the water content of the biomass, which can account for up to 60% of the plant's fresh weight, probably dominates fire propagation and the extent of flaming combustion, hence, the production pattern of emissions.

Thermal degradation of plants is a heterogeneous process of primary fuel decomposition. The initial effect of high temperature on the fuel is a *drying/distilling* process in which the water and volatile contents of the fuel (such as alcohols, aldehydes, and terpenes, i.e., volatile extractables) are removed from the bulk material or diffused into the inner layers of it. The initial distillation process is followed by a *pyrolytic step*, during which a temperature-caused cracking of the fuel molecules occurs. High-molecular weight components are decomposed to compounds of lower-molecular weight, first to char and tar products (intermediate molecular weight), which are the primary energy source for the flame process, and finally to compounds of gaseous nature. The spectrum of compounds produced in this phase is wide and contains theoretically every possible molecule with a chain length varying from one atom to the length of the original fuel molecules. This explains the high variety in emissions during the smoldering stage (see section on EMISSIONS FROM VEGETATION FIRES). Included in these products are particles, oxides, and carbonaceous material (char, elemental carbon) that remain on the ground rather than being emitted.

Peak temperatures within a fuel bed can be as high as 1800 K, but usually temperatures are lower. The pyrolytic process starts at about 400 K, below 450 K the process is endothermic (i.e., it requires an external heat source for sustaining), changing to an exothermic (heat-producing, thus, self-sustaining) decomposition above 450 K. During this process, the decomposition of dehydrocellulose takes place, forming the char ("charcoal") and delivering mostly water vapor (H<sub>2</sub>O), carbon monoxide (CO), and carbon dioxide (CO<sub>2</sub>). Along with this process, a number of high-molecular compounds are formed, called tar, which are emitted along with the gases and represent about two-thirds of the caloric value of the volatiles (Chandler et al. 1983). The ratio of char to tar is important to the overall process, since a high amount of char relative to tar prevents flaming combustion due to the large emissions of H<sub>2</sub>O and CO<sub>2</sub>. At this point, the pure pyrolytic stage would transform into *glowing*

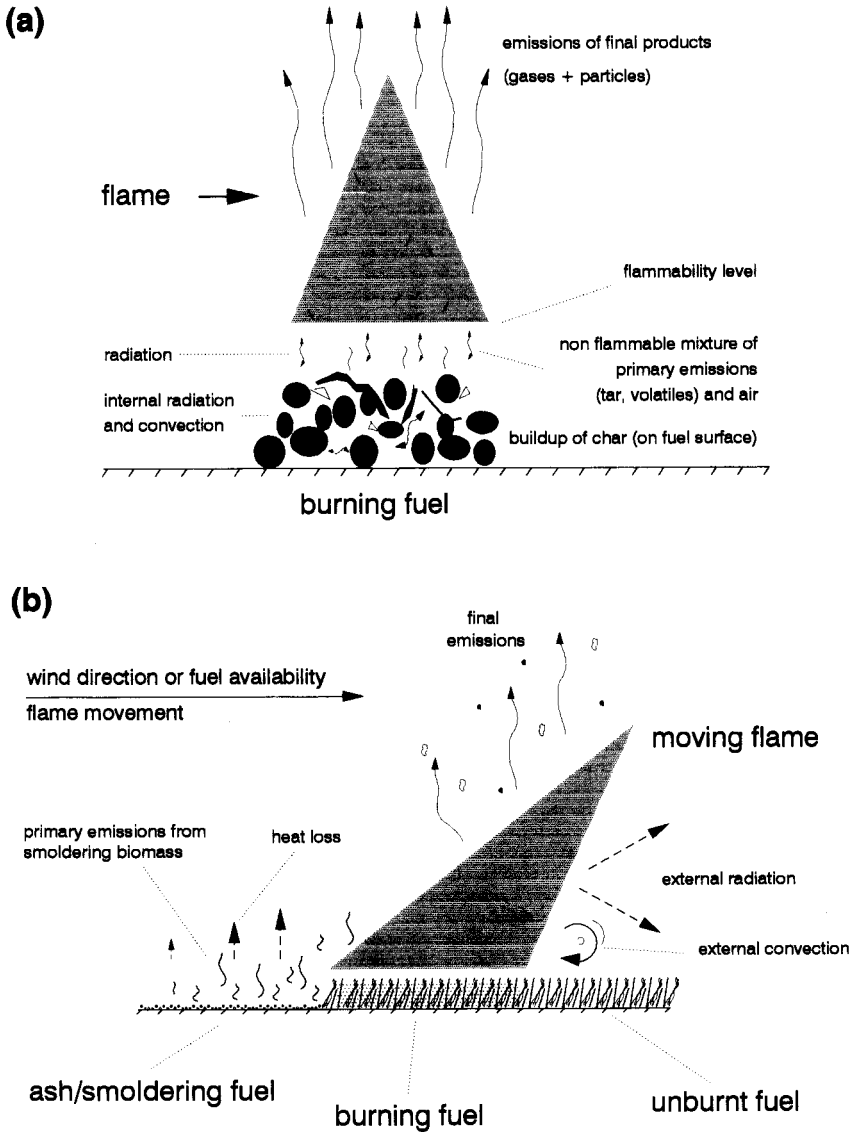
*combustion* at about 800 K if oxygen is present, resulting in char being oxidized directly in CO, which is further oxidized into CO<sub>2</sub>. Assuming that enough tar is present, the primary emissions of the fuel bed are diluted with air to a flammable mixture that (some distance from the solid fuel) forms the flame, converting the primary products to secondary emissions of lower-molecular weight. To summarize, pyrolytic decomposition of the fuel produces gaseous material of intermediate molecular weight, which feeds the flame and can, simplified, be seen as the highly turbulent outlet of a burner delivering gaseous fuel (see also Fig. 2.1a). The amount of flammable gases, hence the rate of pyrolysis, determines the geometry and intensity of the flame. The heat feedback to and heat transfer within the fuel particles is closely coupled to the dimensional characteristics of the flame itself (see also Fig. 2.1b and the description of moving fires below).

### *Gas-phase Processes: The Flame*

Although particles emitted by the condensed phase have to be taken into account, we consider here the flame process in the gas phase as homogenous. As pointed out, the flame basically converts the emitted intermediate volatiles to (secondary) combustion products of low-molecular weight: mostly oxides of the elements carbon, hydrogen, nitrogen, sulfur, and phosphorus. Low-molecular weight substances are either emitted as a final product of the burning process or form new molecules in one of the numerous flame reaction paths. These highly exothermic processes are well studied as long as simple, one-dimensional geometries (flat geometry or radial symmetry) are involved. Basic flame types are the laminar, premixed flame (Fig. 2.2a) and the laminar diffusion (or non-premixed) flame (Fig. 2.2b). The latter can be taken as a simplified model of a burning droplet or outgassing solid particle.

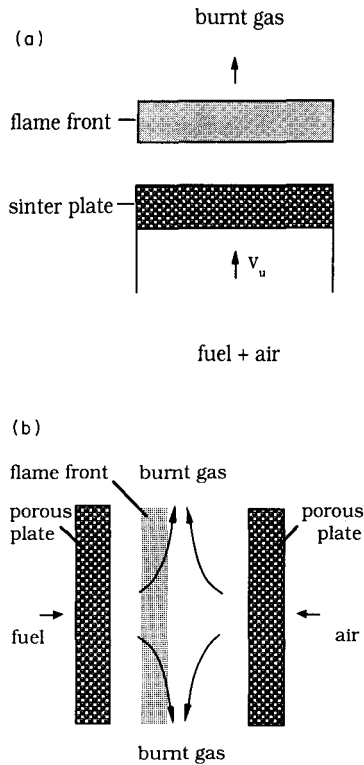
In both cases, flame propagation is caused by diffusive processes that equalize concentration and temperature gradients, while chemical reactions produce heat and reactive particles resulting in the buildup of concentration and temperature gradients. The influence of turbulence (generated by either wind or shearing effects due to velocity differences of outgassing material within the fuel bed) basically enhances the mixing process of fuel and air, which can be described by increased eddy diffusivity. Thus, increased turbulence changes the character of the flame from a laminar diffusion flame to a more premixed turbulent flame, resulting in, e.g., decreased CO production. However, if turbulences are not too large, the flame will still burn in overlapping laminar substructures, which can be treated more easily.

The gas phase of vegetation fires can be described as an intermediate of the two basic flame types; it is partially premixed, necessitating a two- or even three-dimensional description and consideration of complex nonstationary flow features (instabilities such as flickering or turbulence). A quantitative understanding of these processes through direct simulation (i.e., solution of the compressible Navier-Stokes equations, including a heat balance and detailed chemistry in species conservation balances) is not yet possible and will not be soon, as far as computer development can be estimated.



**Figure 2.1** Nonmoving (a) and moving (b) fires and their exchange processes.

The chemistry of the gas-phase combustion of simple hydrocarbons is well studied; the elementary processes should not be very different for more complex fuels (Warnatz 1981). Following this, the initial hydrocarbon is attacked by reactive species (atoms and radicals, such as OH) formed in the hot part of the flame. The radicals are rather

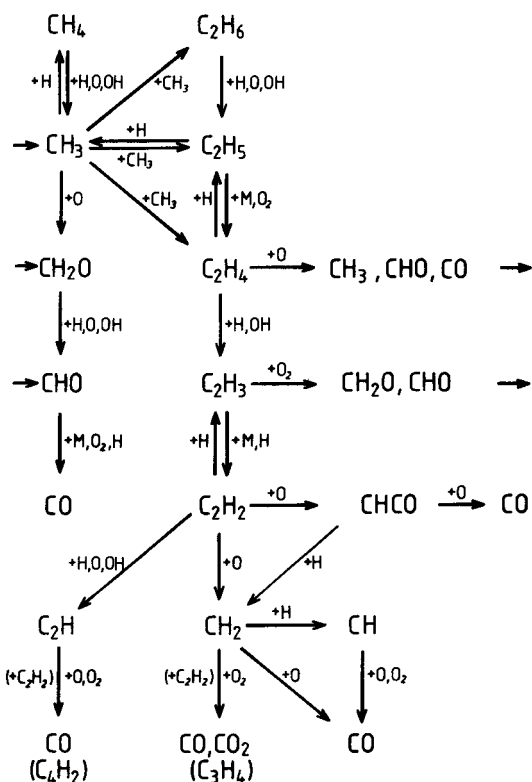


**Figure 2.2** (a) Premixed flat flame and (b) non-premixed flat flame.

unstable and decompose quickly to form comparatively stable, small hydrocarbon radicals (e.g.,  $\text{CH}_3$  or  $\text{C}_2\text{H}_5$ ), which are then oxidized in slow (hence, rate-limiting) reactions to  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  (see Fig. 2.3). This slow oxidation part is common to and is the reason for similarity of all combustion processes.

This outlined mechanism explains flame propagation in premixed systems, flame structure in premixed and non-premixed systems, and ignition processes at temperatures above  $\sim 1000$  K only; at lower temperatures, more complex, fuel-specific reaction mechanisms have to be taken into account (see Pollard 1977). Furthermore, pollution formation (e.g.,  $\text{CO}$ ,  $\text{NO}_x$ , unburned hydrocarbon, polyaromatic hydrocarbons [PAH], soot) can be explained by this mechanism (see also section on EMISSIONS FROM VEGETATION FIRES).

The heat released by the flame can lead to maximum temperatures of  $\sim 2200$  K for stoichiometric mixtures of pure hydrocarbons; thus, flames of vegetation fires are expected to have maximum temperatures several hundred Kelvin below this limiting value. The heat release is strongly coupled to the  $\text{CO}$  and  $\text{CO}_2$  formation within the flame. For stoichiometric and fuel-lean conditions, the final products of combustion



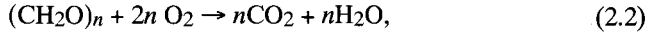
**Figure 2.3** Oxidation pathways of C<sub>1</sub> and C<sub>2</sub> hydrocarbons in flames

should be CO<sub>2</sub>, H<sub>2</sub>O, NO, and SO<sub>2</sub> at sufficiently high temperatures and long residence times, as suggested by the thermodynamic considerations already mentioned. CO formation can occur in locally fuel-rich parts of the flame (even under good mixing conditions) or at temperatures not large enough to form OH, which feeds the conversion reaction:



Because of the comparatively well-known chemistry, flame front structure and product spectrum can be easily simulated for one-dimensional cases (including the formation of pollutants such as NO<sub>x</sub>, CO, and in the near future PAH and soot). For two-dimensional geometries and detailed chemistry, much computational CPU time is required (~100 hours on a computer like the CRAY YMP; see Smooke et al. [1989] for stationary diffusion flames and Maas and Warnatz [1989] for nonstationary premixed flames). Three-dimensional codes for combustion simulation (commercially

available for fire simulation) solve averaged Navier–Stokes equations, including simple turbulence models, thus avoiding the resolution problem of direct simulation. Chemistry can be included into these simulations only in the form of global one-step approaches, such as



which, of course, do not explain pollutant formation or the two-step heat release via CO mentioned above.

### **Smoldering Stage and Extinction**

After most volatile extractables have been emitted from the surface of the bulk fuel and the rate of pyrolysis slows down, less flammable compounds are produced. The open flame ceases due to (a) low amounts of volatile gases and thus inflammable gas mixtures, (b) a buildup of charcoal layers on wet material or (c) simply the lack of unburned material (grass fires), all of these factors probably supported by an increasing content of ash, which contains mostly oxides and flame-inhibiting substances such as potassium, phosphates, and silicates.

The slower rate of pyrolysis results in lower heat production and therefore a lower decomposition rate, until the process terminates kinetically controlled. Extinction can also be influenced by (a) convective cooling due to entraining air and radiative heat losses to the sides and top of the fuel, (b) a low oxygen supply, if the fuel density is too high or the fuel elements too large (stemwood), and (c) changing fuel properties if, for example, the vegetation type changes to higher contents of water or flame-retarding minerals (Chandler et al. 1983).

On the other hand, smoldering combustion can proceed over days under conditions of high moisture (where flaming combustion would be impossible) if heat release and spread rate are balanced, which, again, depends on the fuel characteristics.

The major surface reaction below 850 K is one of oxygen with carbon to form carbon monoxide; if the temperature is higher than 900 to 950 K, carbon dioxide will also be formed. This explains the low amounts of CO<sub>2</sub> that are detectable during smoldering combustion. Although the flaming process requires oxygen concentrations of 15% or higher, smoldering combustion takes place at concentrations of oxygen as low as 5%, e.g., in densely packed fuel. As a result of the low amount of heat produced from the reaction of O<sub>2</sub> with C to form CO, smoldering combustion is a low-temperature process emitting large amounts of incompletely oxidized compounds which are similar to the outgassing material of the solid phase decomposition during the flaming stage. However, since there is no flame present during this smoldering process, all of these compounds are no longer oxidized and are emitted as final products. This is the reason for a broad spectrum of different “low- or nonoxidized” emissions as well as low amounts of oxidized compounds such as CO<sub>2</sub> or NO.



## Dynamic Fires

The major difference in a simplified model of static and dynamic fires is, as already mentioned, the movement of the latter in any given direction; thus, an external component of fire spread is added to the system described above. The effects of combustion are basically equal; in addition, however, macroscopic fuel properties such as aboveground biomass density as well as meteorological properties have to be considered for dynamic fires. For more information on fire spread, see Albini (this volume).

Although the macroscopic propagation of fire is not thought to change the principal burning processes described above, its spread *rate* greatly affects the emissions of a fire. Wind-driven fires usually propagate in two different directions, either *with* the wind (heading fires) or *into* the wind (backing fires). Heading fires typically move faster, produce larger flames, but oxidize the fuel less completely than backing fires. Backing fires move with smaller flames and a lower spread rate through the material; thus, they often leave less smoldering material behind than heading fires. Since the contact of combustibles is more thorough in backing fires, the spectrum of emissions is shifted toward higher-oxidized products, whereas in heading fires the production rate of emissions of incomplete combustion is higher, thus, the burning efficiency is lower. Experimental fires carried out by Lobert et al. (1991), for example, showed an enhancement in the total relative emission ratio of CO/CO<sub>2</sub> (which reflects the burning efficiency) from comparable savanna grass burns of 40%, if the burn was changed from a backing to a heading fire. Since many emissions are coupled to the emissions of CO and CO<sub>2</sub>, a similar change in their emission behavior can be expected.

## INFLUENCES ON VEGETATION FIRES AND THEIR EMISSIONS

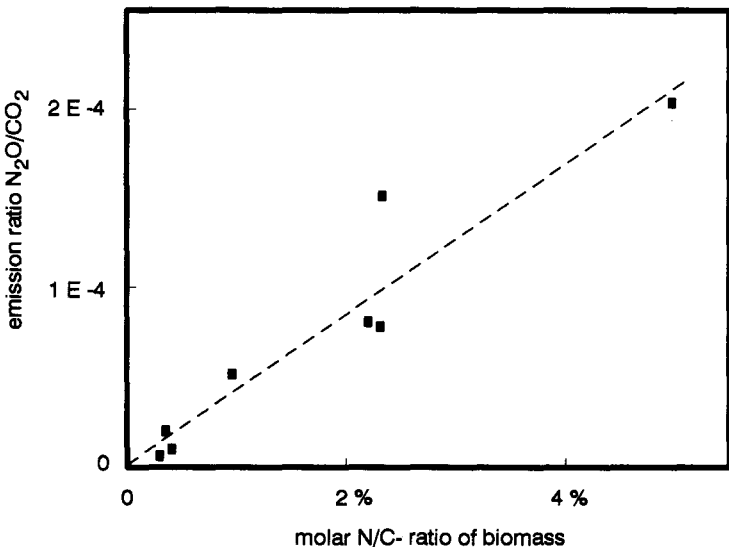
### Vegetation Characteristics

The most obvious fuel attribute influencing both fire behavior and emissions is the *water content* of plants. Moisture determines whether a plant is set on fire and, if so, how well it will burn, i.e., how high the burning efficiency will be. When liquid water is vaporized, it takes up a considerable amount of energy produced during a fire. The water in plants, usually between 5% (dead savanna grasses during the dry season) and 200% (in fresh needles or leaves) of the vegetation's dry weight, has the capability to either stop a fire completely or to slow down the burning process significantly to just a low intense smoldering process. Thus, the main effect of fuel moisture on emissions is through a change in fire behavior, namely the enhancement of smoldering or reduction of flaming combustion, hence, a reduction in overall burning efficiency (for a valuable definition of combustion efficiency, see Ward and Radke, this volume). An example of this was given in the experiments by Lobert et al. (1991): the ratio of CO/CO<sub>2</sub> increased by a factor of more than two in hay burns, when the fuel moisture was increased from 5% to 16%.

Another fuel characteristic of vegetation is its *density* and *structure*. High-density fuels like stemwood are much harder to ignite than low-density, loosely structured grasses, since higher density ensures that produced heat will dissipate into the fuel rather than stay on the surface. Fire propagation is much slower on a piece of wood because more material is available and has to be converted per volume unit; therefore, oxygen supply is a more important feature on the wood surface than it is on grassy leaves.

Closely related to this is the *fuel size*. Small fuel particles are easily ignited because of their low mass, which has to be heated to ignition temperature, and because, once burning, the rate of heat production is greater than on larger particles. For this reason, smaller particles are also capable of sustaining flaming combustion and supporting the burning of larger particles.

Finally mentioned are the amounts of elements other than carbon, hydrogen, and oxygen within the fuel. The elements nitrogen, sulfur, phosphorus, chlorine, and others as such usually do not influence burning behavior very much, but their abundance within the plants has a high impact on the amount of many emissions from biomass burning. For most of the nitrogen-containing compounds, a dominating, mostly linear relationship between fuel-nitrogen content and fire emissions of nitrogenous compounds can be shown (Lobert et al. 1991, 1990). An example of this is given for the relative emission ratio of nitrous oxide to carbon dioxide in Fig. 2.4. The same observation can be made for sulfur compounds (Bingemer et al. 1991) and most probably for other elements as well.



**Figure 2.4** Relative emission ratio of nitrous oxide in terms of  $\text{N}_2\text{O}/\text{CO}_2$  as a function of the fuel-nitrogen content (expressed as the molar N/C ratio).

## Environmental Factors

The *topography* in the vicinity of a fire can also change burning behavior. Large fires in valleys or canyons show a significantly different spread rate due to wind-channel effects (Chandler et al. 1983). Smaller-scale fires are heavily altered by sloping terrain. A burn behaves like a backing fire if it proceeds downslope, and thus burns more efficiently, while an upslope fire moves faster, converting the fuel more like a wind-driven heading fire (even more so, if enhanced by winds). This effect can be easily observed in experimental systems and can be used to simulate wind-driven fires by raising the burning platforms to a certain angle relative to the ground (Lobert et al. 1991; Patterson and McMahon 1984; Rothermel 1967).

## Weather and Climate

Vegetation exists and grows within the Earth's atmosphere and is greatly influenced by the changes (i.e., weather and climate) within this atmosphere. Climate, in the long term, determines the existence, settlement, and ecological support for plants, and thus determines the availability of fire fuel. Fire frequency and the fire season are also determined by climatic factors.

Weather, on the other hand, has a more short-term impact on fire. Temperature, precipitation, hence moisture, and wind are factors that determine the occurrence of fires as well as large parts of their behavior, especially the ratio of flaming to smoldering combustion and thus the types and amounts of emissions to the atmosphere. Temperature affects fire probability and ignition owing to its effect on fuel moisture (especially of dead plant material). *Precipitation* is capable of inhibiting, completely stopping or preventing a fire. The effects of *wind* have already been described. Finally *lightning* is one of the most important causes of *natural* fires, which contribute up to 10% to global biomass burning (Crutzen and Andreae 1990).

## EMISSIONS FROM VEGETATION FIRES

### General Production Processes

Based on the production pattern during the smoldering stage, emissions of low-oxidized compounds, such as (for carbon) CO, CH<sub>4</sub>, and other hydrocarbons, occur along with oxidized products of the flaming stage and depend on the parameters outlined in the preceding sections. The superior *number* of compounds from vegetation fires are produced during this stage of combustion, although the largest *amounts* of the fuel elements carbon (CO<sub>2</sub>), hydrogen (H<sub>2</sub>O), nitrogen (NO<sub>x</sub>, N<sub>2</sub>), and sulfur (SO<sub>2</sub>) are emitted during the flaming stage of a fire (Lobert et al. 1991; Crutzen and Andreae 1990).

As outlined above, most compounds can be attributed to one of the two burning stages (flaming or smoldering) and thus their emissions are coupled either to the

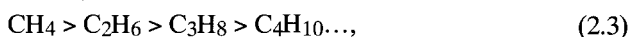
**Table 2.1** Emissions from biomass fires are emitted during different burning stages. Only few compounds cannot clearly be attributed to either flaming or smoldering combustion.

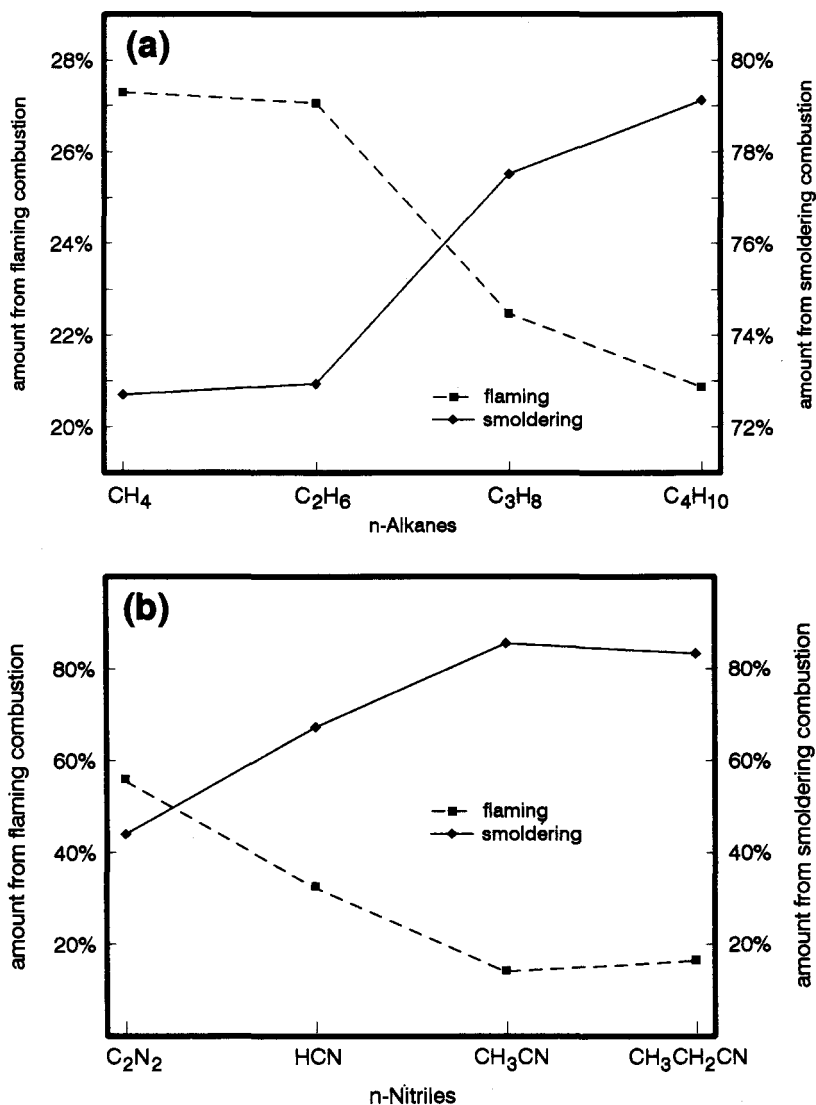
Flaming Stage Compounds	Ambiguous Compounds	Smoldering Stage Compounds
Carbon Dioxide (CO <sub>2</sub> )	Ethine (C <sub>2</sub> H <sub>2</sub> )	Carbon Monoxide (CO)
Nitric Oxide (NO)	Cyanogen (NCCN)	Methane (CH <sub>4</sub> )
Sulfur Dioxide (SO <sub>2</sub> )		Most Hydrocarbons (NMHC, PAH)
Nitrous Oxide (N <sub>2</sub> O)		Ammonia (NH <sub>3</sub> )
Nitrogen (N <sub>2</sub> )		Hydrogen Cyanide (HCN)
Particles (high elemental carbon content)		Acetonitrile (CH <sub>3</sub> CN)
		Amines, Heterocycles, Amino acids
		Methyl Chloride (CH <sub>3</sub> Cl)
		Most Sulfur Compounds (H <sub>2</sub> S, COS, DMS, DMDS)
		Particles (low elemental carbon content)

formation of CO<sub>2</sub>—if produced mainly during the flaming stage—or to CO—if emitted mostly during the smoldering stage of a fire (Table 2.1). There are very few exceptions to this general behavior, e.g., ethine and cyanogen, both of which are produced, on average, in about equal amounts during both stages.

Yet the relation to either one of these fire stages does not mean an absence during the other. First, the decomposition process of solid fuel and the compounds consequently produced are similar in both stages. Small amounts of less-oxidized emissions can “escape” the oxidation process at the edges of (fuel-rich) flames since the conversion of those products in the flame is not 100% efficient or because some of the compounds are thermally more stable than others and withstand a short period of time within the flame (since the final steps of oxidation are slow, as outlined in the section on *Gas-phase Processes*).

Second, the concentrations of the products of incomplete combustion generally decrease with increasing molecular chain length and increasing flame intensity; thus, small, thermally stable molecules are dominant over larger (mostly less-oxidized) molecules. The amount of emissions of straight hydrocarbons,





**Figure 2.5** Relative amounts of some hydrocarbons (a) and nitriles (b) in the two burning stages as a function of chain length (or oxidation state).

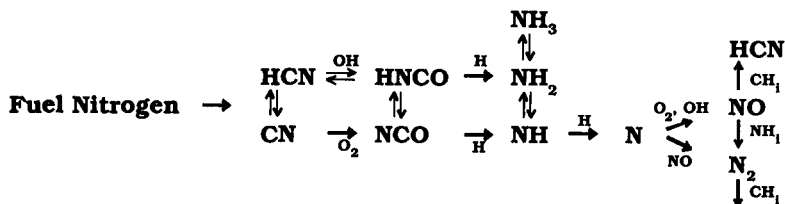
might serve as an example of this behavior, where along with the decreasing total amount, a decreasing abundance during the flaming stage can be observed (Fig. 2.5a). This is even more exposed in the series of homologous nitriles,



where the lower-molecular weight nitriles are formed from higher-molecular weight nitrogen compounds, usually amines or aminoacids (Lobert et al. 1991; see also Fig. 2.6, where HCN [and subsequent NO] is formed from  $\text{CH}_3\text{NH}_2$  with increasing oxygen [decreasing  $\Phi$ ]). The amount of cyanogen (NCCN), whose formation is not favored during these processes, is an exception. Nevertheless, due to its electronic structure and thermal stability, its *relative emission* is higher during the flaming stage (58%) than during the smoldering stage (42%; see Fig. 2.5b). Hydrogen cyanide is primarily a smoldering stage compound, yet 34% is emitted during the flaming stage; acetonitrile, a typical smoldering stage compound, expels only a 15% in the flaming stage. The larger the molecules are, the more likely a breakdown is to occur due to an attack by a reactive species in the flame.

The change in the product spectrum from (oxygen-free) pyrolysis to combustion can also be shown here. Nitriles are usually the dominant nitrogen-containing products of (oxygen-free) biomass pyrolysis (up to 95% of the fuel nitrogen) and are, therefore, the major products of solid phase decomposition, being mostly formed from amino acids and related compounds. In an oxygen-containing environment, these substances are further converted to ammonia, hydrocarbons, and nitrogen oxides, except for a small amount, which can be detected as gaseous emissions (around 4% of the total plant nitrogen; see also Fig. 2.6). Similar processes are most likely to occur for other compounds as well.

Finally, the absolute amounts of emissions produced during biomass burning are strongly dependent on the relative ratio of flaming to smoldering combustion. Most of the previously described influences on fire behavior cause an enhancement of one or both fire stages and hence alter the emission pattern during the burn. Again, the most important factors affecting the emissions are the moisture of the fuel and its elemental composition. A major task in estimating global biomass burning emissions is to determine the ratio of flaming to smoldering combustion during different fire types.



**Figure 2.6** Formation of NO, HCN, and  $\text{NH}_3$  from fuel nitrogen as a function of the equivalence ratio,  $\Phi$ , in premixed propane-air flames doped with 2400 ppm fuel nitrogen in the form of  $\text{CH}_3\text{NH}_2$  ( $\text{CH}_3\text{CN}$  would yield similar results). (a) shows measurements with decreasing oxygen concentration on the abscissa; (b) shows the simulation with the mechanisms outlined in Fig. 2.7 (Warnatz 1987). The difference between the sum of  $\text{NO} + \text{HCN} + \text{NH}_3$  and the initial 2400 ppm fuel nitrogen is  $\text{N}_2$  which represents a portion of 33% at  $\Phi = 1$ .

In addition to these general patterns, quantitative descriptions can already be given for several distinct production processes; these are outlined in the following sections.

### NO<sub>x</sub> Formation

The usual *Zeldovich* (or *thermal*) pathway of NO formation in a high-temperature environment, initiated by the attack of oxygen atoms on the molecular nitrogen of air,



will usually be unimportant owing to the comparatively low maximum temperatures in vegetation fires. Furthermore, the formation of *Fenimore* (or *prompt*) NO, stated by



will also be unimportant compared with the formation of NO due to fuel-nitrogen conversion, because of the large nitrogen content of the fuels considered. This fuel-nitrogen conversion is well studied for its importance in coal combustion (Wendt 1980), where (due to the same origin) similar nitrogen contents of fuels are given.

The principal pathways of fuel-nitrogen conversion are shown in Fig. 2.7. The rate-limiting steps are fortunately the simple competing steps taking care of NO formation and NO consumption:



(Warnatz 1987; Miller and Bowman 1989). Thus, the chemical nature of the nitrogen compounds in the hydrocarbon environment and the (fast) conversion to compounds like HCN and NH<sub>3</sub> are relatively unimportant for the understanding of the conversion process.

Reduction of nitrogen atoms and, at lower temperatures other species, is responsible for the fact that only 15% to 30% of the fuel nitrogen is converted to NO, whereas the remaining amount forms molecular nitrogen (N<sub>2</sub>) (Wendt 1980; see also Fig. 2.6). Although already known for high-temperature combustion processes, the high amount of N<sub>2</sub> emitted during vegetation fires was one surprising outcome of experimental fires (Kuhlbusch et al. 1991). During these experiments, more than 30% of the fuel-nitrogen was emitted as N<sub>2</sub> during the burning of vegetation material.

### CO Formation

CO has already been mentioned to be formed in locally fuel-rich parts of a flame or at temperatures below 1000 K (see section on *Gas-phase Processes*). It can only be a final product if it does not undergo mixing with air at temperatures above 1000 K

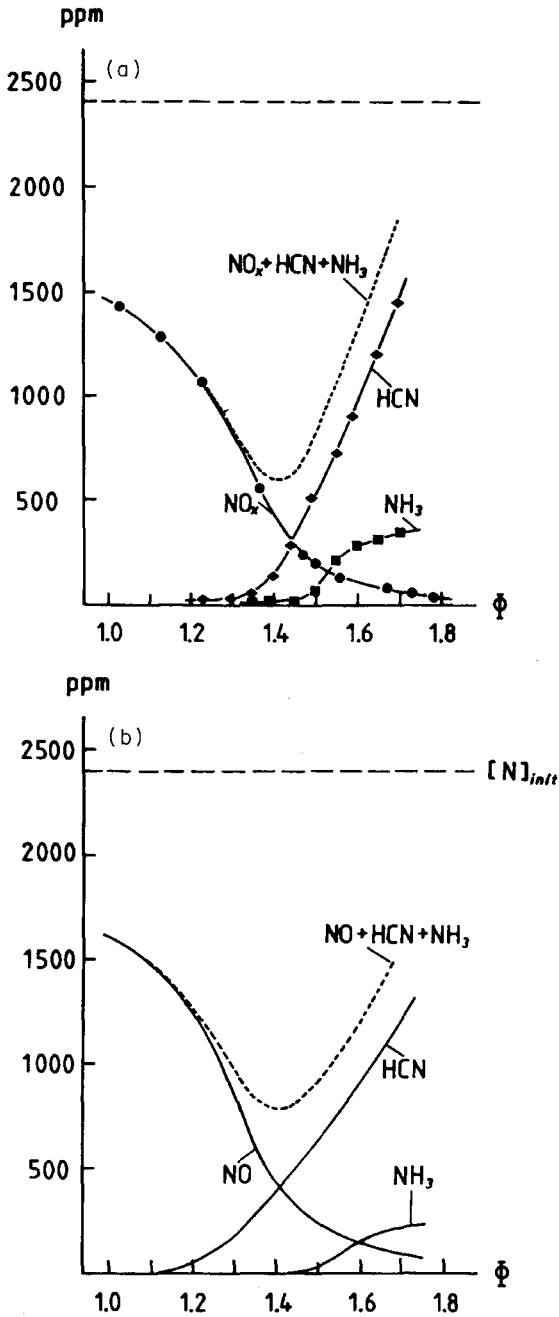


Figure 2.7 Reaction pathways in fuel-nitrogen conversion.



Therefore, its formation is kinetically controlled only in globally fuel-rich combustion, but it is dependent on certain flow conditions in globally stoichiometric or lean flames. Thus, CO is expected to be a major product of the smoldering combustion if no subsequent flaming combustion is taking place, whereas CO<sub>2</sub> as a final product is mainly connected to flaming combustion.

### PAH and Soot Formation

The understanding of soot formation has made substantial progress during the last few years (Proc. 202nd Am. Chem. Soc. Natl. Meeting 1991). Recent findings show that the first aromatic ring of a PAH or soot compound is formed by C<sub>3</sub>H<sub>3</sub> recombination and subsequent isomerization, where C<sub>3</sub>H<sub>3</sub> is formed from attacks of CH and CH<sub>2</sub> on C<sub>2</sub>H<sub>2</sub>. However, the further growth to form PAH and soot particles (also forming C<sub>60</sub> as a side-product if progressing to the third dimension) by simultaneous surface growth and coagulation is still rather speculative.

### Estimates of Biomass Burning Emissions

Here we present some estimates of fire emissions taken from various data sets. Global amounts of emissions are calculated based on global biomass consumption estimates by Crutzen and Andreae (1990).

#### *Carbon Compounds*

The major carbon emission is CO<sub>2</sub>, the only compound predicted by 100% complete stoichiometric combustion. As pointed out, vegetation fires are incomplete to a certain extent; thus, CO<sub>2</sub> emissions average at about 80% to 85% of the mass of fuel carbon, where the emissions can be as low as 50% in very low-intensity smoldering fires and as high as 99% in very efficient burns. The next most important product is CO, with around 7% of the fuel carbon in a range of 2% to 15%, which is anticorrelated to the range of CO<sub>2</sub>.

Hydrocarbons add up to about 2% to 3% of the fuel carbon, with methane as its major component at 0.5%, nonmethane hydrocarbons (NMHC) up to C<sub>10</sub> representing about 1%, and a contribution of another 0.5% in the form of higher, pure hydrocarbons and PAH. In addition, there is probably a significant portion of nitrogen and other hetero-atom-containing hydrocarbons (such as heterocycles, aminoacids, and amines), which amounts have not yet been determined in fire emissions.

The major fraction of NMHC is represented by the emissions of mono-unsaturated molecules, such as ethene, propene, butene, benzene, and toluene. Saturated hydrocarbons and triple-bond molecules of similar chain-length (e.g., C<sub>2</sub>H<sub>2</sub>) are usually emitted in smaller quantities.

Total emissions of methane range between 10 and 50 teragrams (Tg or 10<sup>12</sup> g) of carbon (C) per year, contributing 2% to 10% to its global source. Some estimates,

however, conclude that the global pyrogenic methane emission might be as large as 50 to 90 Tg C yr<sup>-1</sup>. NMHC emissions total 20 to 100 Tg C yr<sup>-1</sup>, contributing significant amounts to most of their individual budgets.

### *Nitrogen Compounds*

The most significant emission of reactive nitrogen is represented by nitrogen oxides, NO and NO<sub>2</sub>, usually referred to as NO<sub>x</sub>. The overall ratio of NO:NO<sub>2</sub> during a fire equals 85:15, since NO is a thermally stable product of the flaming stage of a fire and, in theory, the final product of nitrogen oxidation within the flame (see Figs. 2.6 and 2.7). NO<sub>2</sub>, which is thermally much less stable, is emitted about six times less than NO during the flaming stage. In the smoldering stage, however, its emission can increase to 40% of the NO<sub>x</sub>. In the fire plume, further away from the source region, most of the NO is converted to NO<sub>2</sub>, which eventually combines with water to form nitric acid or participates in other atmospheric reactions. Estimates show that biomass fires could contribute around 12% to the global nitrogen oxide source.

The only other flaming stage emission of interest to atmospheric chemistry is nitrous oxide. All of the latest measurements of N<sub>2</sub>O from vegetation fires (Hao et al. 1991; Griffith et al. 1991; Cofer et al. 1990) estimate only a minor contribution to the atmospheric budget in the order of 3% to 6% or 0.4 Tg N yr<sup>-1</sup>. However, soil emissions of nitrous oxide, enhanced by post-fire effects, could probably contribute a further significant portion to its global budget (Levine et al. 1988). At this point, sufficient long-term observations are still required to estimate these emissions.

Regarding high-temperature emissions, there is one more nitrogen compound that was determined to represent around one-third of the plant's nitrogen content. The emission of molecular nitrogen (N<sub>2</sub>) from biomass burning (Kuhlbusch et al. 1991) was detected to be a flaming stage emission. Although it is not an atmospheric pollutant, it is likely to affect the biogeochemical cycle of fire ecosystems, especially the post-fire rate of its net primary productivity (Vitousek 1991; Menaut, this volume). A conversion of plant nitrogen to N<sub>2</sub> reduces the net amount of totally fixed or deposited nitrogen available to plants. At this point, the importance of the loss of this essential nutrient to the soils is still in discussion. It is not yet known whether a possible enhancement in post-fire nitrogen fixation (Eisele et al. 1989) is likely to replace the loss, or to what extent post-fire soil emissions of N<sub>2</sub>O and NH<sub>3</sub> increase the nitrogen loss of fire ecosystems.

Most other nitrogen-containing compounds are emitted during the smoldering stage of fires. Significant amounts of nitrogen are contained in the emissions of:

- Ammonia with 4% to 15% of the available nitrogen, contributing between 5% and 25% to the global budget of ammonia (Lobert et al. 1991; Griffith et al. 1991; Lebel et al. 1991). As for nitrous oxide, post-fire soil emissions could also contribute to the overall ammonia emissions related to fires (R. Delmas, unpublished).

- Low-molecular nitriles, mostly hydrogen cyanide (HCN) and acetonitrile ( $\text{CH}_3\text{CN}$ ). Together they represent about 4% of the nitrogen balance of fires and are estimated to contribute a major amount to their global atmospheric source.
- Nitric acid ( $\text{HNO}_3$ ), which is emitted in amounts between 0.5 and 2 Tg N yr<sup>-1</sup> (Lobert et al. 1991; Lebel et al. 1991; Andreae et al. 1988).
- A large amount, on the order of one-third of the fuel nitrogen, is likely to be emitted in particles and a very large variety of compounds of intermediate molecular weight (chain length of C<sub>5</sub> and higher), such as amines, amino acids, and heterocycles, which are mostly products of incomplete biomass decomposition and each of which are only emitted in low quantities. Further investigation on this type of emission is necessary in order to budget the nitrogen balance of fire fuels.

### *Sulfur and Chlorine Compounds*

The most abundant sulfur emission is sulfur dioxide,  $\text{SO}_2$ . In contrast to nitrogen, only low amounts of the total sulfur contained in the plant are emitted; about 40% to 60% remain in the ash after the fire. Albeit its amount relative to the plant's sulfur, the biomass burning emission does not contribute much to the global  $\text{SO}_2$  budget. According to Crutzen and Andreae (1990), only 1 to 4 Tg S yr<sup>-1</sup> compared to 70 to 170 Tg of atmospheric  $\text{SO}_2$  are contributed from vegetation fires. More impact on their individual budgets is expected from the emissions of carbonyl sulfide (OCS), with a global pyrogenic source of 0.1 to 0.2 Tg S yr<sup>-1</sup>, and probably also from hydrogen sulfide ( $\text{H}_2\text{S}$ ), and dimethyl sulfide ( $\text{CH}_3\text{SCH}_3$ ) (Bingemer et al. 1991). Their absolute emissions add up to a total of about 1 Tg S yr<sup>-1</sup>.

Plants only contain chlorine in the form of electrolytes, i.e., dissolved salts. There are no significant portions of chlorine-containing organic compounds in a plant except for possible residues of pesticides. The most important chlorine product of biomass burning is chloro-methane or methyl chloride,  $\text{CH}_3\text{Cl}$ . According to measurements by Lobert et al. (1991), about 1 Tg of chlorine is emitted annually from biomass burning. This represents between 20% and 70% of the total source of methyl chloride to the atmosphere and may therefore be the single most important source of  $\text{CH}_3\text{Cl}$ .

### *Particulate and Mineral Emissions*

The last important class of products to be discussed is particulate emissions. Despite their incompletely oxidized nature (except inorganic ash), particles are, due to the same effects outlined above, emitted during both fire stages. From their elemental composition and size distribution, it can often be well distinguished whether they were emitted from the flaming or smoldering stage of a fire. Particles emitted by vegetation fires consist mainly of condensed hydrocarbons (tar, PAH), charcoal, soot, and ash (inorganic minerals). More than half of the particle content is carbon, a fraction of

which is black (or elemental) carbon, often referred to as soot. Black carbon contents vary between 4% of the total particulate weight, if emitted from low-intensity smoldering fires, and 40% in solid matter emitted from flaming combustion. Thus, the formation of black carbon, which also includes the (probably larger) fraction remaining on the ground, is likely to be formed during the hot combustion stage. The noncarbonaceous matter of particles is mainly composed of potassium, calcium, sulfur (as sulfate), and nitrogen (as nitrate); hence it contributes significantly to the atmospheric budgets of these elements. The emission rates of particles depend largely on the fire characteristics outlined above in the same way as other compounds of incomplete combustion are affected. Chandler et al. (1983), for example, show that the total particulate mass increases drastically with the fuel load of forest fires, which burn with the wind (heading fires), very much like the emission of reduced gases, while the particulate emission is significantly reduced during backing fires.

The total particulate matter (TPM) emissions are estimated to be around  $30 \pm 15$  grams per kilogram of fuel carbon equal to 40 to 150 Tg yr<sup>-1</sup> (Crutzen and Andreae 1990). This corresponds to a particulate carbon emission of 30 to 100 Tg C yr<sup>-1</sup>, containing 6 to 30 Tg yr<sup>-1</sup> of black carbon. For more information on particles, see Lacaux et al. (this volume).

## CONCLUSIONS AND FUTURE NEEDS

The gas-phase process of combustion is relatively well-known if realistic initial conditions of composition and flux of material outgassing from the solid fuel can be specified. A theoretical treatment of outgassing and heterogeneous combustion will probably not be available in the near future. Thus, empirical rate expressions have to be developed on the basis of evaporation measurements at well-defined and realistic conditions (especially with respect to the heating rate). This problem is similar to the problems in coal combustion, where an analogous strategy is used. Nevertheless, there are many other problems, since realistic conditions are not yet well defined and the reproducibility of these measurements is not satisfactory because of an insufficient characterization of the burning fuel and catalytic effects of minerals.

Given the complex nature of biomass fires, observations of experimental fires made by Lobert et al. (1991) have shown many similar emission patterns under totally different fire setups, i.e., fuels, loadings, and burning directions. Their results show that the average overall emission ratios (of all different experiments) are often sufficient to describe *global* biomass burning emissions, since other factors (like the estimate of globally burned biomass and areas) are currently far more uncertain than the differences between, e.g., heading and backing fires. However, examining different ecosystems, or even local events, requires a distinction between fuel types and fire properties. Assuming that global estimates of area and fuel amounts eventually improve, the weakest point will be the currently available fire models. Thus, in order to predict (or calculate) fire emissions, a simple schematic has to be found, which can be used to define predictive emission models.

As a first step, it should be assumed that fire can basically be divided into only two burning stages: flaming combustion and smoldering combustion. This assumption is not too far away from reality, since ignition and termination actually do not contribute much to the overall burning process. The biggest simplification here is to treat the flaming stage, which is a two-phase process, as only one phenomenon (i.e., "the flame").

Second, we must presume that all of the described factors affect the occurrence, enhancement, or reduction (hence, the intensity and extent) of these two burning stages. The final step is then to state that the occurrence and intensity of these two stages can explain most of the fire emissions, such as outlined in the previous two sections. Thus, modeling emissions of vegetation fires can (as a first attempt) be reduced to modeling these two stages as they were outlined. This simplified attempt could finally be included into a predictive global fire model containing information about vegetation, fuel properties, weather, burned area, and biomass. Available fire behavior models can and should be adapted and further developed to include smoldering combustion and the prediction of emissions. Further information is required for such a global model about:

- the types and amounts of different fuels in different ecosystems,
- the fuel properties, especially elemental composition, and
- the ratio of flaming to smoldering combustion in vegetation fires.

Undoubtedly, the most difficult task is to ascertain the amount of flaming combustion that occurs in different fires compared with smoldering combustion. Not much of this information is available yet, it can only be retrieved from extensive observations of natural fires or through medium-sized laboratory experiments. For the information about fuels and ecosystems, a coarse classification is proposed. The accuracy of determining burnt areas, finally, will hopefully be enhanced in the future by improved satellite observations.

What is currently missing, is a major attempt to put all the single bits of information into one large data base. Projects such as the International Global Atmospheric Chemistry (IGAC) program, for example, present a very good platform for such an attempt.

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