Fire Emissions and Smoke Impact on Industrial Environments

Entegris

INTRODUCTION

Man-made or wild vegetation fires produce a very large amount of pollutants that can have significant impact on any industrial operation and process. This paper reviews the impact that fire emissions and smoke can have on industrial environments and the filtration technology available to mitigate the impacts to product yield and personnel wellbeing.

VEGETATION FIRES ARE VERY COMMON

Vegetation fires, known as biomass burning, include wildfires, which occur almost each year in the western United States and elsewhere in temperate and boreal forests, but also prescribed fires purposely carried out by forestry services mostly in the U.S. and Australia. Wood and dung are burned worldwide for heating and cooking purposes, and intentional savannah and forest fires are started to create agricultural land, hunt, or keep pests from approaching villages. The latter types occur mostly in southern America, Africa, India, and Indonesia.[1, 2]

Whereas most of these fire types are more or less controlled, wildfires are not, and they typically create more unforeseen problems and unpredictable reactive measures to deal with the emissions.

WHAT HAPPENS IN A FIRE?

Once a fire starts, either through intentional ignition or through an accidental spark, a distillation process vaporizes the more volatile compounds inside the wood or plant.[3] Some of that might escape without being altered, which explains several volatile gases such as IPA (isopropyl alcohol), formaldehyde, etc. As the material gets hotter, less volatile compounds evaporate and might get burned up by open flames.

When the fuel starts glowing, the core structural components like lignin and cellulose degrade, which is the most efficient stage of material decomposition. However, pyrolysis is the underlying process, where parts of the material are decomposed without oxygen, and those emissions may later be oxidized by the flame or escape unchanged.

Fires, accidental or intentional, emit heavy smoke and gases into the environment

Depending on the air supply, the presence or lack of wind, the direction the fire is moving, and the temperature of the fire, a burn is either efficient and burning into the wind (backing fire) or is less efficient and being driven by the wind (heading fire). The heat of the fire can create upward drafts, which then draw in more air. In situations without wind, or if the fuel is wet, the burn smolders more with few large flames, much heavier smoke, and less efficient combustion.

The presence of large flames, the heat inside the fuel, and the supply of oxygen all drive the efficiency of a fire and whether the emissions are more oxygenated or create more smoke and heavier gases. The more intense a fire is, the further emissions can get transported up into the atmosphere.

Emissions from intense wildfires from the North American west coast have been shown to get transported through the Jetstream to the east coast and even Europe.[4] Smoke impact is then no longer just local but can be international.

BIOMASS BURNING EMISSIONS CHARACTERIZED

Emissions from fires are a very complex mix of gases and particles. The particulate matter is what we see as smoke, but it is mixed with thousands of gas-phase contaminants, products from the combustion of the material.

High temperature combustion of biomass with sufficient air supply should yield only the oxides of elements in the fuel:

- CO_2, carbon dioxide from the organic carbon
- H_2O, water vapor from the organic hydrogen
- NO_X, SO_X, oxides from plant nutrients
- The remains are ash and salts, the non-volatile oxides of heavier elements, particularly metals

Particulate matter emitted from fires is mixed with thousands of gas-phase contaminants and is visible as smoke.

However, as outlined above, air supply and temperatures in biomass burning are much lower than in high efficiency furnaces, causing incomplete combustion, which, in addition to the above oxygenated gases, produces a variety of partially combusted organic matter of lesser oxidation, which are referred to as reduced species:

- Thousands of organic gases across the entire spectrum
- Organic gases of plant nutrients, such as hydrocarbons with nitrogen, sulfur, phosphorus, halogens, and other elements
- Very large amounts of particles, from submicron to visible
- Glowing, burning, or burnt pieces of vegetation (visible ash)

Figure 1 from right to left:

- Visible ash and partially burnt vegetation will settle out by gravity, or coagulate to larger pieces
- The main content of smoke that travels for miles contains micron sized and smaller particles plus gases
- Gas-phase emissions that we classify as condensable, volatile and very volatile, based on their boiling points
- During transport, both small particles and gases can significantly change through chemical reactions with the surrounding air or with each other

There are a number of filtration solutions that are often used in industrial settings:

- Particles can be successfully removed with Minimum Efficiency Reporting Value (MERV), High Efficiency Particular Air (HEPA) or Ultra Low Particular Air (ULPA) filters, but the high particle mass will load them quickly
- The gas mixture contains just about every possible combination
  - Inorganic gases: oxides of C, N, S, P: CO, CO_2, NO, NO_2, SO_2, SO_3, many of which react to acids with water vapor. Also, ammonia and amines, basic compounds
  - Organic gases: everything from methane (C_1) to visible organic matter (C_{many})

Note that there is a small gap between submicron particles and gases, those particles that are less than 0.1 µm large and pass through even ULPA filters. There is currently no solution to completely remove these.

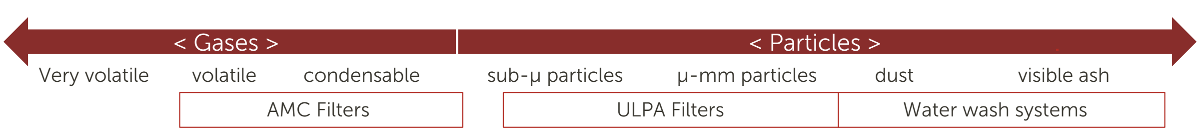

Figure 1. Emissions range from very volatile organic and inorganic gases to visible, large pieces of partially burnt plants.

Likewise, what we call *very volatile organic* matter (VVOC) is not retained by any chemical filter. However, that is the case with or without fire emissions. We do not have solutions to filter these contaminants, nor does there appear to be a concern about them. We are talking about organic compounds in the C_1 to C_3 range, but also a lot of inorganic gases, such as NO, NO_2, many halogenated gases, etc. For all other ranges, there are filtration solutions, which are discussed in more detail below.

SMOKE AND EMISSIONS IMPACT

The impact of smoke can be quite severe, depending on which environment is investigated. There are health concerns, mostly from particles smaller than 10 μm (PM 10), but also from the variety of toxic and many carcinogenic gases. Think of biomass burning as a very large-scale version of tobacco smoke, for which health impacts are well documented.

Semiconductor processes are all impacted by particles. Whereas ULPA filters will remove most of the concern, particles smaller than 0.3 μm are not fully or not at all filtered out and can negatively impact yield. With state-of-the-art technology producing critical feature dimensions around 3 nm (0.003 μm), particles of that size and larger cause fatal defects. The sheer amount of those particles in fire smoke can shut down a process if outside air is drawn into a fab.

Any process that involves thin coatings or laminations can be impacted by the large amounts of organic matter, which can cover a surface and either prevent industrial coatings or delaminate them after application.

Likewise, coatings of partially conductive organic and inorganic matter can build up over time, causing electrostatic discharge and short circuits in electronics of data centers and control rooms.

Chemically reactive organics and the large amounts of acids can degrade artwork and archival materials and corrode mechanical systems such as turbines, compressors, and fan motors.

And of course, there is a nuisance factor from the burnt ash smell. That is mostly created by creosote, a category of very non-volatile organics, but these can adsorb on particles that are small enough to migrate through chemical and even ULPA filters.

That is the reason why smoke can be smelled downstream of even the most efficient, multi-step air filtration systems.

AIRBORNE MOLECULAR CONTAMINATION (AMC) FILTERS AND FIRE SMOKE

Chemical filters for the removal of AMC have two functions, filtration and purification. The filtration function, which is not usually exploited, removes particles through impact, coagulation, and surface interactions. This function could potentially remove significant amounts of larger fire smoke particles, if directly exposed to that air. Smaller, submicron-size particles, however, will move through AMC filters rather quickly, and these can carry the typical "burnt ash" smell.

VaporSorb™ filters help control AMC by removing particles and gas-phase contaminants.

The purification function of AMC filters, which is their primary purpose, removes gas-phase contaminants in air through chemical or physical adsorption on the filter adsorbents:

- Acids are adsorbed on coated carbons
- Bases are adsorbed on ion exchanger
- Organics are adsorbed on activated carbons

The high load of gases and particles in fire smoke will be well removed but will cause AMC filters to load up more quickly and reduce their usable lifetime.

Note that the presence of burnt ash smell downstream of AMC filters is caused mostly by very fine particles and does not necessarily mean that the removal of gases has stopped or is inefficient. Smell is not a good metric to gauge AMC filter performance.

HEPA or ULPA filters upstream of AMC filters will reduce the impact on AMC filters to some extent by reducing large and smaller chemically active particles.

SMOKE CLEANING SOLUTIONS

Fire smoke can have wide-ranging effects. The highest impact of smoke is to be expected at the makeup air handler stage, where outside air is drawn into the facility.

- Dust and visible particles will be removed by water wash systems or MERV filters
- Particles in the range of 0.1 µm to mm size will be well removed by HEPA/ULPA filters
  - The higher than normal amounts may clog those filters more quickly
- Very small, sub-0.1 µm particles will not be removed well and may have a significant impact
- Condensable gases (C_6-C_{many}) will be well removed by AMC filters
  - Lifetime of those filters will be reduced due to the high AMC load (which can be in the ppm range); The same applies to acidic and basic AMC
- Volatile AMC (C_3-C_6) will be partially removed by AMC filters
  - Lifetime may be short, but removal efficiency and capacity increase with concentration
  - This behavior is no different from normal operation, but the higher AMC load in smoke plumes will make the partial break-through more noticeable
- Very volatile gases (C_1-C_3) may be reactive and may be removed in the plume during transport, or they may not be a concern (mostly organic nature), as they are not a concern without smoke. However, the higher concentration may now have an impact, even though there is none during normal operation.

A combination of multiple stages of filtration and air cleaning is advised when fire emissions may be encountered. Crude dust filters followed by high efficiency water wash systems, then AMC filters, then ULPA filters are a good first step in makeup air handlers. These should be followed by more layers of protection in recirculation air handlers, ceiling fan filter units, and specific tool-level or individual space filter combinations.

ENTEGRIS AMC FILTER PERFORMANCE TESTING AND BEST PRACTICES

Monitoring AMC filter performance during fire smoke impact is recommended. This can be done by AMC measurement upstream and downstream of the filters at least at makeup air handlers/outside air intake, where smoke enters a facility.

The filter removal efficiency (RE) is defined as the ratio of downstream to upstream contaminant concentration:

$$RE = 1 - \frac{[downstream]}{[upstream]} \times 100(\%)$$

and can be calculated from the measurement of those concentrations. It is recommended to test RE for acids, bases, and organics. Organics might be the best indicator of smoke impact, but for corrosion and degradation concerns, acidic AMC may have a higher impact or trigger AMC alarms earlier than organic AMC.

If downstream concentrations are much higher than usual, the filters may be exhausted, or the smoke level may be very high, even if the filter still performs normally. However, if outlet concentration is consistently higher than the inlet concentration, the filter is exhausted or may even be outgassing excess AMC.

It is also recommended to consider filter installation date. If filters are close to their targeted end of life, an early or impending filter change should be considered, perhaps triggering an early order placement or increased stock inventory to accommodate lead times.

Entegris provides onsite AMC measurement services to measure concentrations of molecular acidic, basic, refractory, and organic contamination, if needed. Those can be done with onsite operators or with our customer-operated gas sampling service.

Postmortem filter testing is also available to test removal efficiency and remaining lifetime for organic AMC. One filter out of a larger installation can be tested to gauge performance of the whole filter bank.

- Removal efficiency tests the current performance
- Remaining lifetime can be compared to the performance curve of a new filter to show deviations from a normal life cycle

CONCLUSION

Smoke emissions from vegetation fires can have a significant impact on sensitive industrial processes and personnel health or wellbeing, both through particulate but also gas-phase components. Implementing AMC filters in air handlers and industrial environments can reduce the impact, protect processes and personnel, and increase production yield.

Please contact Entegris if you need AMC measurement services, filters, or best practices advice.

ABOUT ENTEGRIS

Entegris is a world-class supplier of advanced materials and process solutions for the semiconductor and other high-tech industries. Entegris is ISO 9001 certified and has manufacturing, customer service, and/or research facilities in the United States, Canada, China, France, Germany, Israel, Japan, Malaysia, Singapore, South Korea, and Taiwan. Additional information can be found at entegris.com.

References

[1] Paul J. Crutzen, Meinrat O. Andreae, *Biomass Burning in the Tropics: Impact on Atmospheric Chemistry and Biogeochemical Cycles*, Science 250, 1669, 1990.

[2] Jürgen M. Lobert, William C. Keene, Jennifer A. Logan and Rosemarie Yevich, *Global Chlorine Emissions from Biomass Burning: Reactive Chlorine Emissions Inventory*, J. Geophys. Res. 104, 8373-8390, 1999.

[3] Jürgen M. Lobert and Jürgen Warnatz, *Emissions From the Combustion Process in Vegetation*, in: P.J. Crutzen and J.G. Goldammer (eds) *Fire in the Environment: The Ecological, Climatic, and Atmospheric Chemical Importance of Vegetation Fires*, John Wiley & Sons Ltd. Chichester, 15-37, 1993.

[4] Dimitris Akritidis et al., *A complex aerosol transport event over Europe during the 2017 Storm Ophelia in CAMS forecast systems: analysis and evaluation*, Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-467, in review, 2020.

FOR MORE INFORMATION

Please call your Regional Customer Service Center today to learn what Entegris can do for you.
Visit entegris.com and select the Contact Us link to find the customer service center nearest you.

Entegris

Corporate Headquarters
129 Concord Road
Billerica, MA 01821
USA

Customer Service
Tel +1 952 556 4181
Fax +1 952 556 8022
Toll Free 800 394 4083