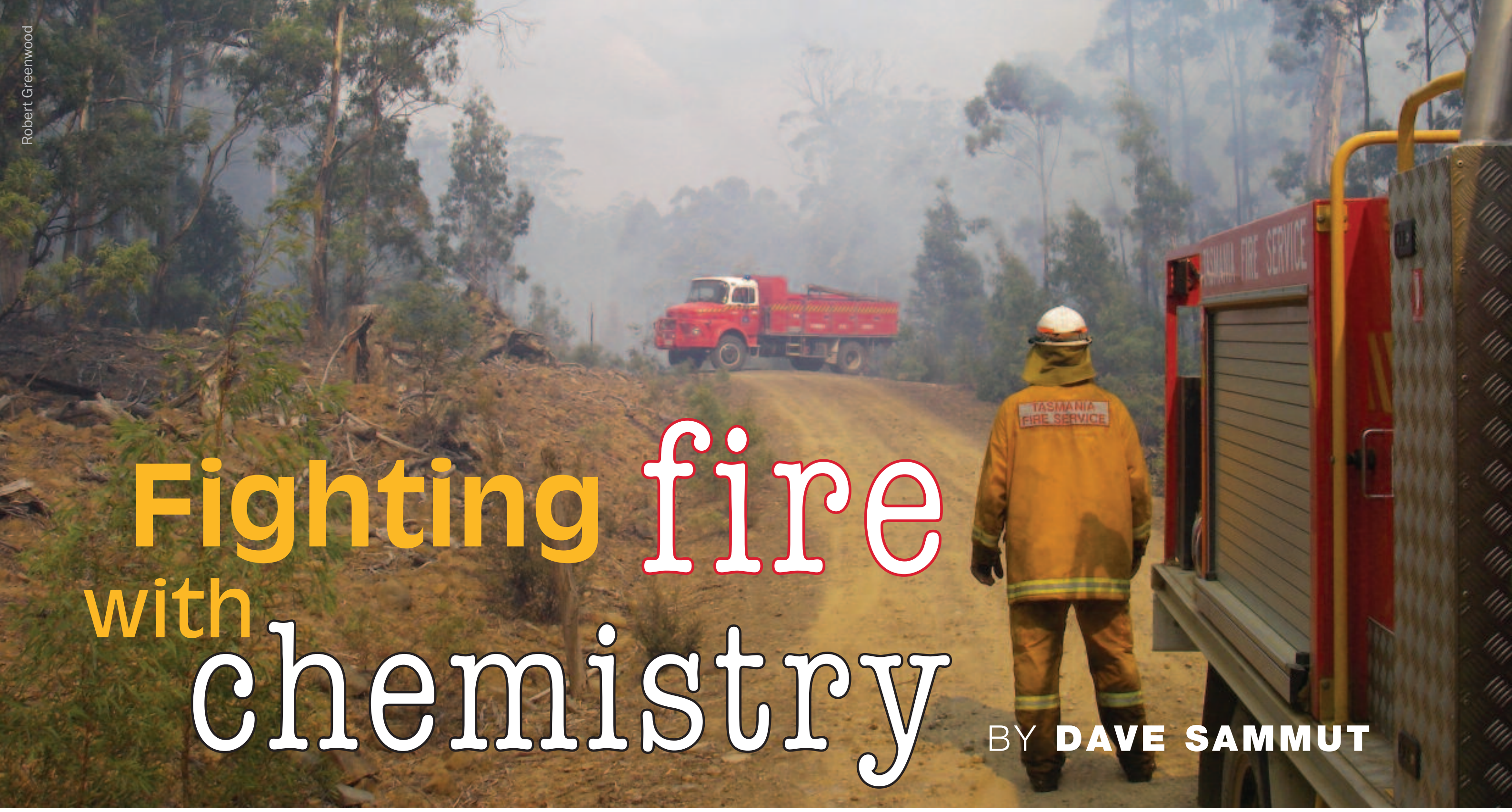
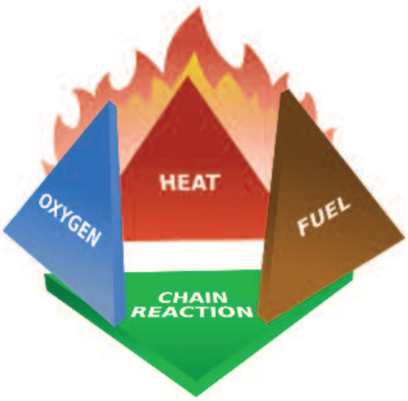
Fighting fire with chemistry

BY **DAVE SAMMUT**



Robert Greenwood

After a dry winter, much of Australia's east coast is likely to be on high alert this bushfire season. An understanding of the science of fire informs both fire alert and firefighting systems.



The fire triangle has been expanded to include chain reactions. Gustavb

Although the chemistry of exothermic reactions is pretty straightforward, the science of fire can be surprisingly complex. A great deal of study has gone into understanding fire, its propagation, prevention and mitigation.

Fire 101

Standard textbooks on fire refer to the 'fire triangle' of heat, fuel and oxygen. More recent texts update this to the 'fire tetrahedron', in which oxygen is replaced with an oxidising agent (typically air) and uninhibited chain reactions.

The basic reactions are simple: an organic molecule reacts with oxygen to form carbon dioxide and water. Where oxygen is limited, a portion of the combustion products will be intermediates, such as carbon monoxide or soot. Heat energy overcomes the initial activation energy, and the overall combustion is exothermic. In simple terms, the reaction is self-propagating until either the fuel or the oxygen runs out, or the heat is removed.

However, there are interesting nuances. The reactions primarily occur in the vapour phase, so other physical and chemical reactions must occur prior to combustion where the fuel is liquid or solid.

Liquid organics first volatilise to form a combustible gas-phase mixture. The classic example is kerosene in a lamp. The liquid fuel is volatilised via a wick (to increase the surface area), and combustion occurs in the gas phase immediately adjacent to the wick. Due to limitations in oxygen mass transfer, the zone closest to the wick is oxygen deficient, and the blue flame observed is due to the secondary oxidation of carbon monoxide from initially incomplete reaction.

For solids to burn, they must first undergo pyrolysis – thermochemical decomposition of solid-phase large molecules into vapour-phase smaller molecules and free radicals, typically leaving solid-phase carbon residues. In established fires, the residual char may then combust directly from the solid phase via flameless 'glowing' or 'smouldering'.

It is also noteworthy that the rate of reaction is temperature related, so the hotter the fire is, the faster it burns. This is an important issue in firefighting.

Fuel load, terrain and atmosphere

In the science of bushfire prediction and control, the rate and mode of spread of fires is determined by a complex interplay of factors – the type and density of biota, including the 'fuel load' of readily combustible (dehydrated) dead material, terrain, fire intensity and atmospheric conditions.

Growing up, I used to dread the summer days with the hottest, driest westerly winds. They swept across our area with the dead hand of foreboding. On bad fire days, they carried embers far ahead of the fire front to start new spot fires.

From a more scientific perspective, most of the effect of bushfires is associated with the convection (such as into the soil) and radiation of heat from flames. Substantive heat is also lost with the combustion gases in the convection column.

Plant cells die at around 60°C, while the charring of plant tissues starts at around 300°C and ash forms above about 500°C. With high surface area and being poorly insulated, leaves are easily subject to hot, dry conditions. They burn quickly, and generate a lot of flaming embers.

Bark tends to protect active tree tissues through reduced thermal diffusivity. The period that the plant surface remains at 100°C is critical to predicting the extent of tissue death. Once the water in the tissues has been exposed long enough to boil away, then the temperatures can rise rapidly and sensitive inner tissues can be irreparably damaged.

The overall fire hazard from fuel is measured by assessing the type of bark on the trees ('Bark Hazard'), the amount of elevated fuel such as grasses and ferns ('Elevated Fuel Hazard') and the ground detritus ('Surface Fine Fuel Hazard'). The accumulation of fine fuel depends on how much the local vegetation sheds dead litter, how quickly it rots, and the frequency of fires.

While many plant species in Australia have evolved in the presence of fire, developing adaptations to improve their survival, our country has many varied ecosystems. Not all of our ecosystems have evolved for frequent or intensive fire regimes (see box p. 25). For example, New South Wales contains large areas of wet sclerophyll rainforest and wetlands, which in some cases could take hundreds of years to recover from a substantive fire. Prescribed burning protocols for hazard reduction therefore need to consider the ecosystems affected, and the influence that they may have on the diversity of species in a given area (such as through replacement with more fire-resistant species).

More than just the fact that fires burn more easily uphill, topography can have a significant influence on fire behaviour. The NSW Department of Environment and Heritage notes 'Aspect will influence the type of vegetation and fuel moisture. In NSW west facing slopes are usually hotter and dryer and support more fire tolerant (therefore more flammable) vegetation. South facing slopes however, are usually cooler and wetter and support more fire intolerant (less flammable) vegetation.' (bit.ly/2yEoMzF)

For the survival of the plants, fire intensity is important. Described as the heat released per metre of fire front, fire intensity is a multiple of the heat yield of the fuel (J/g), fuel load (kg/m^2) and velocity of the fire front (m/s). Low-intensity fires generate up to around 500 kW/m (the limit recommended for fuel-reduction burning), producing flames up to 1.5 metres high. High-intensity fires can generate more than 3000 kW/m, with flames up to 15 metres high and spotting up to two kilometres away.

At the extreme, 'fire storm' or 'crown fire' bushfires can generate up to 100 000 kW/m. Over a fire front of just one kilometre, that's substantially greater than all of the power station capacity in NSW.

Just as importantly, even a fire of moderate intensity (2500 kW/m) can heat the soil to a depth of six centimetres and increase surface temperatures to more than 250°C. This can kill microorganisms, seeds and plant tissues, and can cause changes in soil chemistry. In turn, this can result in long-term changes that affect the recovery of particular ecosystems.

Excluding, absorbing and retarding

The science of firefighting comes back to the fire triangle – the removal of fuel, oxygen and/or heat. The use of water remains the bedrock of firefighting through the simple thermal capacity of water (with its heat of vaporisation of 2257 kJ/kg). However, this is not nearly as effective in bushfire fighting, where the transport of water to the fire is a major challenge. In intense fires, even water-bombing can prove ineffective, because the water simply evaporates in the radiant heat above the fire.

Similarly, the removal of oxygen is much more difficult in bushfire fighting. Smaller, contained spaces (such as high-value IT hardware centres) can use gas-based systems

Fire activity looking south-west towards Dargo from Swifts Creek, Victoria, 11 January 2007.

Fir0002/Flagstaffotos

Single-engine airtanker dropping retardant at Mudgee, NSW. Phos-Chek Australia

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that both starve the fire of oxygen and minimise water damage. And most household and industrial fire extinguishers are either carbon dioxide, foams or suppressant powders.

Bushfire fighting may use chemical foams or gels. The foams are made of a combination of wetting and foaming agents mixed with water, while gels use polymers such as potassium polyacrylate that can absorb a multiple of their mass of water. As long as they remain wet, the foams can help exclude air directly at the fire site, while the gels can absorb heat. However, the CSIRO noted that these tend to dry out quickly and can be ineffective for higher intensity fires.

Fire retardants are designed to directly inhibit the fire. The NSW Rural Fire Service (RFS) declares the use of three variations – PHOS-CHeK, BlazeTamer and Thermo-Gel – the safety data sheets for which are spectacularly unhelpful in elucidating their chemistry. Other sources cite the use of ammonium and diammonium sulfate and ammonium phosphate, guar gum as a thickener, and corrosion inhibitors (to protect the aircraft used for delivery). The RFS states that the PFOS class of chemicals, now notorious for contamination at sites around Australia (see box), is not used in bush firefighting.

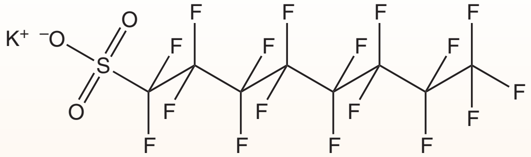
The fire retardants are mixed with water, and are commonly highly coloured with pigment (often iron oxides) to make it easier to see where they have been delivered. After the water has evaporated, the remaining residue continues to inhibit ignition of vegetation via heat adsorption and endothermic decomposition (for example, to sulfuric and phosphoric acid and ammonia). However, as noted by the CSIRO in 2010: 'The ability of retardant lines [0.5–1.0-kilometre long from a single air drop] to halt fire spread in eucalypt forests is limited to low fire intensity conditions (<2 MW/m) because of the spotting potential associated with higher-intensity fires. Retardant lines require

Investigating PFOS contamination

PFOS (perfluorooctane sulfonic acid, its salts and perfluorooctane sulfinyl fluoride) have gained a lot of attention of late. Part of a group of chemicals termed POPs (persistent organic pollutants) under the UNEP Stockholm Convention, they are used in a wide range of products. It is their use (or misuse) as surfactants in firefighting foams and the subsequent potential for contamination of areas surrounding particular facilities – airports, firefighting training facilities and some industrial sites – that has become contentious.

The Royal Australian Air Force has more than 20 sites under investigation for potential PFOS contamination. Its air base at Williamtown, near Newcastle, is a case in point. Nearby residents were alarmed to discover that the RAAF had in 2012 become aware and failed to report the presence of PFOS in groundwater leaving the site. The residents have now been advised not to shower, bathe or fill pools with groundwater, nor to consume products from livestock grown within the area.

While a government-initiated report found the contamination to have a 'low and acceptable' risk, it is being criticised as seeking to downplay the seriousness of the situation. By contrast, a 2006 UNEP report (bit.ly/2yXlFij) concluded 'that PFOS is likely, as a result of its long-range environmental transport, to lead to significant adverse human health and environmental effects, such that global action is warranted'.



Potassium salt of PFOS.

The Department of Defence is now providing water to more than 70 properties, as part of a $55 million nationwide project to address PFOS contamination concerns. At another affected site, residents of Oakey, Queensland (near the Army Aviation Centre), are preparing a class action for compensation on claimed health effects and loss of property values.

A UNEP study (bit.ly/2i2kP0q) into effective alternative foaming agents showed that fluorine-free alternatives, expected to not persist in the environment or bio-accumulate, would cost just 5–10% more, and that this would decrease as the non-PFOS market grew.

support from ground firefighting resources to be effective.' (http://bit.ly/2gtOOKW)

The last line of defence

The CSIRO's conclusion points to the fundamental aspect of fighting bushfires in Australia. For those at the front lines, the strategy most often centres on removing the fuel – creating fire breaks with dozers or graders, preparing controlled burns, and fighting the fires hand-to-hand with packs and shovels.

It comes down to the hardworking men and women, significantly including large numbers of volunteers, who give their time and risk their safety under the worst of conditions. This article can only conclude with a solemn salute to their effort, to the generosity of spirit, and the sacrifice made on behalf of us all. Let the weather this summer be kind, and let each of us do our part by preparing our homes, our properties and our fire plans.

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Improving bushfire behaviour models for Tasmanian wet forests

The 2016 Tasmanian bushfires have been described as the worst crisis in decades for world heritage forests. Seventy fires that started by a severe dry lightning storm on 13 January burnt more than 124 000 hectares over a month and a half – affecting about 2% of the Tasmanian Wilderness World Heritage area – and have been linked to human-induced climate change by recent research. As the maps on the news portrayed, fires burnt across western Tasmania affecting a range of vegetation types including tall wet forests such as those at the Terrestrial Ecosystem Research Network Warra Tall Eucalypt SuperSite.

Even while the fires were still burning in other parts of Tassie, University of Tasmania Biological Sciences PhD student James Furlaud was camped among the tall eucalypts at the Warra SuperSite collecting post-fire data on forest fuel loads.

'The goal of my project is to improve current and future bushfire behaviour models and calibrate them specifically for Tasmanian wet forests', says James. 'Current bushfire behaviour models used in Tasmania are calibrated for fuel loads in Victoria, so a field-based assessment of Tasmanian fuel loads is critical.'

James, who is partly supported by the Bushfire and Natural Hazard CRC, has done fuel load surveys at eight monitoring plots located at the Warra SuperSite – part of TERN's Australian SuperSite Network – using a methodology based off of the TERN AusPlots Forests methodology that's openly available via the TERN website.

'The sampling is designed primarily to estimate the surface, elevated, and bark fuel loads, but also makes a number of qualitative measures that are commonly used by fire managers. I can then model these fuel loads as a function of time since previous fire. This will create fuel accumulation curves that are compatible with current and future fire behaviour prediction models.'

'Behaviour models predict fuel load as a function of time since previous fire. This is why the TERN chronosequence plots at the Warra long-term ecological research site are so valuable: they allow me to simultaneously sample fuel loads across a range of differently aged forests and quantify how fuel loads increase as a forest ages.'

Four of the eight plots James surveyed overlap with AusPlots. By sampling at these sites James is able to use nationwide AusPlots data to compare how fuel loads vary across both chronological and ecological gradients. Such comparison will allow James to examine how fuel accumulation rates might change with climate change.

The ultimate goal of this project is to develop improved bushfire behaviour prediction models. This will allow for updated risk assessments, an improved ability to evaluate fuel management regimes, and better fire suppression decisions.

James' supervisor, Professor David Bowman, says 'Given that such destructive fires are likely to become more common in Tasmania under a warming and drying climate, James's research will form an important part of improving our fire risk assessments, fuel management regimes and increasing the capacity to attack fires quickly and efficiently. It is research like this that will help better manage future fire crises in Tasmania and in other forest environments around Australia.'

James collects data on fuel load at a monitoring plot located at the Warra SuperSite – part of TERN's Australian SuperSite Network – that will be used to estimate the surface, elevated, and bark fuel loads, and a number of qualitative measures that are commonly used by fire managers. Forestry Tasmania

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