



BIOMASS - Carbon monoxide generation from wood chip and wood pellet.

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March 2016



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Title	A summary paper - COSHH Hazards arising with the storage of wood fuel.
Status	Published via CEA, Element and other
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Date	February 2016

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Carbon monoxide generation from wood chip, aged wood chip and wood pellet

Introduction

It is appropriate to note that the comminution of aged timber will produce dust of all sizes including tiny particulate regardless of fuel specification. That dust will contain or have attached any of the residues of any chemical treatments etc and will because of its size remain airborne for long periods, post shredding and movement. Inhalation will present a COSHH risk (particularly with organo-chlorides) and will, very likely, with accumulation present an explosion risk. The risk of explosion will be most acute with enclosure e.g. above conveyors that are enclosed (reference the OSB investigation into the Imperial sugar explosion). Where wood is treated or where wood is wet and rotting wood is stored there is also the inherent risk of fungal growth and the attendant COSHH risk.

The use of Biomass has increased significantly over the last ten years. This increase is in large part due to a perception that biomass is green, clean and sustainable. These conceptions are in part driven by market pressure and in part underwritten with Government commercial interventions. The rapid development and deployment of biomass has alarmingly resulted in the un-informed design, review, installation and operation of allied storage and combustion technologies (with attendant fatality and injury)

Wood and the principal mechanisms for CO production

Wood has three principal fractions, namely; extractable compounds, cell wall (woody material) and ash. The extractable component is what is typically 4-20% of the total. The extractable content is notably higher for pine and spruce species (woods used as bio-fuels and for pellet production). The remainder of the wood is comprised of cellulosic, Hemi-cellulosic and lignin polymers (nom. Phenyl propane).

When wood decomposes naturally (microbiological decomposition) this process of decay occurs over a relatively long period of time and the initial products of decomposition are et al, CH₄, CO₂ and potentially CO. These emissions result from the decomposition of cellulose, hemi-cellulose and Lignin and could result in the production of phenol and furfural based intermediates. These processes can be artificially replicated and accelerated as in the case of Enzymatic Hydrolysis to eventually bio digest the wood biomass to produce alcohol. However, this is a natural process of organic decay and where there is rapid turnover of aged (recycled) wood chip it appears that the mechanism of slower decomposition of **cellulosic and lignin components** (the solid components) will not constitute any major hazard - at least from the perspective of rapid CO production. (Because the fuel is dry and aged).

Large scale storage of wet (and more particularly) untreated (Heat or fungicide) fresh wood will result in fungal contamination and the release of spores which will give rise to a COSHH risk. This may be particularly the case where the wood is stored with high moisture content (as opposed to simply surface water content) and where temperatures are elevated by natural or artificial means.



Of more concern is the derivation of Carbon Monoxide from the direct and indirect degradation (thermal, chemical oxidation or biological) of the extractable in wood. The extractable components of wood vary significantly but are likely to include:

Volatile oils (terpenes, sesquiterpene and oxygenated derivatives)

Resins and fatty acids

- Resin acids
- Fatty acids (linoleic,oleic)
- Glycerol esters
- Waxes
- Phytosterols

Pigments

- Multi ring naphthenic and aromatic compounds
- alcohols
- Ketones
- Polyhydroxylic Phenols

Starches and sugars

These extractable are most prevalent in soft woods used typically for biomass and widely for construction. The extractives such as terpenes, fats, or fatty acids, undergo oxidation during storage and the process of pelletisation allows migration of the VOC and fatty acids to the surface of the pelleted fuel - exacerbating oxygen exposure increasing the propensity for VOC emissions. Thermal degradation produces VOCs, such as aldehydes and carbon monoxide¹

The extractable materials in some species are actually recovered (by pulping) e.g. turpentine and it is these materials that give fresh cut wood distinctive smell. The extractable occur principally in the cytoplasm and in the intercellular resin canals.¹

The biological degradation of the varied, but accessible extractable compounds may result in processes of Hydrolysis with acetogenesis, acidogenesis, methanogenesis which, where partially completed, will give a range of intermediates including, potentially, CO. Again the biometabolised products require the establishment of a biological process. In some cases Furans are derived from the biological hemicellulose digestion, there is also the potential for chemical or thermal synthesis of the same materials.

In fresh cut spruce and pine species there is an immediate release of the volatile and terpene components - and these give rise et al, to a strong pungent smell - with attendant COSHH risks for those exposed. A significant % of the principally terpene derived volatile content will be lost by chipping and during drying. However, the fatty acids remain and may be oxidised

¹



(albeit at a lesser potential rate than the accelerated rate induced in pellets) to produce Carbon monoxide and or consume oxygen in that process contributing to a depleted oxygen level if not CO production.

There are various studies undertaken to determine the extractive content, CO production and CO₂ production from fresh wood chip. The fat and the terpenes content of wood (most prevalent in fresh pine and spruce species) dictates the CO₂ and CO emission. The higher fatty acid components the higher the CO production. Tests of fresh cut pine species show rapid evolution of CO over 24-120h when stored gas tight to levels approaching 300ppm* with severe health implication and greatly exceeding any nationally acceptable standard. The allied estimations of generation indicated that a maximum CO-emission factor of about 10.60 and 6.96 mg/kg (40°C) and about 1.4 and 1.81 mg/kg (20°C**) was recorded by wood pellets and wood chips, respectively. My concern in regard of these studies is the scalability. (Sebastian Paczkowski*, Redelf Kraft and Alireza Kharazipour 2013). ** Jaya Shankar Tumuluru ,C. Jim Lim, Xiaotao T. Bi, Xingya Kuang , Staffan Melin, Fahimeh Yazdanpanah Shahab Sokhansanj

There is a correlation between fat content and CO formation. The recognised , researched and principal mechanism for the production of CO is via the oxidation of fatty acids. The oxidation of terpenes may also contribute to CO production. Woods with the largest fat and terpene content are therefore problematic. Without ventilation the storage of pellets or fresh chips could produce VOC and CO levels that are harmful to health.

There is therefore no doubt that the unventilated storage of freshly chipped biomass (particularly pine or spruce) will generate dangerous CO levels and potentially levels of VOC that also present a COSHH risk.

Chips that are fresh cut and piled will (by virtue of combinations of chemical and biological oxidation processes) experience a temperature rise during which time, the oxidation of principally fatty acids will result in the production of CO and the release of hexanal (an aldehydhe with a fresh cut grass smell). A problem because of the risk of fatality in enclosed storage e.g. ships holds. More extensive research and empirical measurement, suggests that at storage temperatures >30 °C wood chips and wood pellets resulting in unventilated levels as high as CO (>10,000 ppmv), CO₂ (>30,000 ppmv), and CH₄ emission (>2000 ppmv). These levels will result in virtually immediate death on exposure. Thus unventilated or totally or even partially enclosed fuel storage with chips or pellets constitutes a severe hazard, and requires control methods to eliminate the hazard. (Sources Various)

The extent of off gassing for pellets and biomass is a function of temperature and cold ventilated storage as associated with most biomass chip stores probably reduces chemical and biological conversion, and affords dissipation of any generated offgas. However, contained storage which may even be intentionally preheated may greatly exacerbate the rates of off gassing. Entry to fuel stores must be considered as extremely dangerous and these spaces may have to be treated confined spaces. Carbon Dioxide production and Oxygen depletion are largely the result of biological activity. CO (initially at least) is primarily a function of auto -oxidation and does not rely on terpene content. .

The problem associated with fresh chipped or pelleted fuel is therefore serious and documented. For issues associated with aged wood there is much less clarity. The terpene



content of chipped wood will diminished very rapidly after chipping or pelletising. However, it is not the Terpene content that is the primary mechanism for CO formation. However, the concentration of Terpene may have an adverse effect on the lung gas exchange ability.

The extent of fatty acid content of older processed timber is very difficult to ascertain because there are likely many differing ages of wood. Initially timber for pallet construction, constructional timber etc will have been cut and kiln dried with an associated loss of terpenes. Secondary processing might include board manufacture, thermal treatment (for sterilisation/pasteurisation), and potentially the addition of the addition of fomaldahyde resins. Fomaldahyde may be produced by the shredding destruction of bonded timbers such as Plywood - the extent depends on the age and quantity of these materials in the mix. All plywood products bonded with phenol formaldehyde adhesive will produce fomaldahyde emissions, which will be at their highest levels immediately after manufacturing, progressively decreasing in a matter of weeks.

Aged, processed and recycled wood

The total extractable will diminish with time and processing. However, for large and relatively young timbers it might be safer to assume that, whilst a terpene emission will be reduced, the reduction in fatty acids will not be as rapid and certainly new wood will have the propensity to produce CO from fatty acids remaining despite processing.

That supposition might best be exemplified by the fact that timbers used for construction may exude resins waxes long after they are used in construction - creating difficulty for painting and other finishing. Furthermore tests conducted into the age related fire resistant properties of timbers conducted on behalf of the NFPA imply that carbon content reduces with age as extractable content oxidises. There are various papers published citing the age and durability of timbers as being related to their residual extractable content. There are various papers (some cited here) addressing the longer term VOC emissions from engineered wood.

Comminution of any kind will expose large surface to volume ratio. As it has not proven possible to obtain accurate quantitative information relating to age related fatty acid reduction and because it is impossible to model every age and dimension of timber input, it must be the safest solution to assume that CO will potentially be produced by chipping waste wood - and where that operation is significant - with significant allied storage then it would be remiss not to address this by test if necessary.

It appears likely that the extent will be much less than chipping fresh wood. The propensity to produce CO will be influenced by the temperature and moisture content (for these will raise oxidation rates). It might also be assumed that fomaldahyde will be released during the shredding of waste ply, OSB and composite boards.

It is not possible to determine (Without testing) the extent of fungicide and other treatments that have been used (CCA testing can be achieved but the reducing volume of CCA in the supply chain should reduce this to low levels).

Addressing the problem as part of a Hazid (Hazard Identification)



In the apparent absence of any definitive guidance, research, or data on the diminished fatty content of processed wood there is really no option but to assume that much wood (of unknown age and composition) will, when subject to comminution of some kind, have the potential to produce CO and to assume that in the worst case, will reach levels of CO as documented for shipping timber and accordingly apply ventilation rates (natural or mechanical) to achieve WHO standards for exposure.

A simpler empirical (and we believe acceptable) solution to this problem would be to undertake measurement of CO levels at existing large shredded wood storage facilities -

What are acceptable levels for prolonged exposure ?

The implications for long term exposure are not as well understood as short term acute exposure. However the WHO has published guidance, which might acceptably be adopted (given the status of the WHO). These limits are as follows:

The World Health Organisation issued the following guidelines for levels of CO in the air, to prevent blood COHb levels from rising above 2.5%.

- 100 mg/m³ (87.1 ppm) for 15 minutes
- 60 mg/m³ (52.3 ppm) for 30 minutes
- 30 mg/m³ (26.1 ppm) for 1 hour
- 10 mg/m³ (8.7 ppm) for 8 hours.

Summary

The production of CO from chipped wood and or wood pellets (Or indeed other biomass crops and fuels) results initially and principally (But not exclusively) from the auto-oxidation of fatty acids forming a component of the extractable element off wood.

The oxidation mechanism will be greatly accelerated in processed pellets because fatty acids are sweated out of the pellet to the pellet surface and thus the exposure is greater.

The production of CO₂ and depleted O₂ atmospheres results principally (but not exclusively) from biological degradation of wood chip and it appears more likely this will affect fresh lumber and fresh cut chip.

The transport of fresh cut timber, lumber and storage of wood chip or pellets will be associated with the production VOC emissions, CO emission CO₂ emission and oxygen depletion - The CO₂ production and O₂ depletion being principally but not exclusively associated with biological process as opposed to chemical oxidation. Appropriate ventilation and access, categorisation and restriction should be implemented during design.

There is apparently little research or published material which focuses on the age related fatty acid content in processed and recycled wood. There is material which suggests that carbon content will diminish with age but rates and residual potential is not (insofar as we are able to determine) documented. Equally there is material that illustrates that fatty content (Larnoy et al) will diminish slowly.



The fact that CO contaminated atmospheres appear not to exist at existing recycled wood storage facilities offers (in my opinion) no guarantee that there is not a potential problem.

Exposure to even very small long term levels of CO may have adverse health impacts and constitute a COSSH risk that should be addressed.

Carbon monoxide derived from combustion

In my opinion the significant risk associated with the back-draft of combustion gases (often containing CO levels in excess of 125,000ppm is widely overlooked. It is relatively easy for flue gases to leak from the combustion appliance to the fuel storage via the stoker and successive transfer augers when intentional sealing is damaged or defective and when some combustion and or atmospheric conditions exist. This has been causal in at least three significant smoke explosions that had sufficient severity to cause structural damage and where the smoke explosion occurred in the fuel supply system or components thereof. Whilst the volume of the fuel supply system is generally smaller than the flue system and the explosions are generally of lesser magnitude than flue/fireside explosion, the fuel side explosions underline the HAZARD of CO feedback which may be temporary or transient but with concentration that will cause immediate loss of consciousness and rapid death - and where the evidence may be dissipated just as quickly.

A review and guidance on internal storage and safe connection to the combustion appliance is urgently required and may be incorporated in the pending BG05.

CO Dilution by ventilation

If the tests conducted by Tumuluru et al, represent valid scalable findings (and these papers cite corroboration of other findings for pellets at least) then it might be expected that CO evolution of say 2mg/kg might occur in fresh cut wood and by virtue of other anecdotal reporting, a lesser rate in aged wood.

It is quite clear that in pellet or wood chip storage, the ratio of storage to unventilated head space is significant in the determination of the concentration build up of CO. If the ratio of head space is small then the concentration will be higher. The supposition that smaller stores are safer is far from true - all that could be said about smaller stores is that the ventilation may potentially be achieved more rapidly and effectively. Note in smaller facilities where the ratio of headspace to that of total storage were lower, the unventilated concentrations achieved could, it appears, reach levels that would be immediately debilitating and subsequently fatal. This actually is commensurate with various coroner findings, evaluations and theoretical analyses.

The evolution of CO (and probably the rate of BOD) will depend on the duration of storage, surface area, interstitial air (compaction) and temperature et al and it might be foreseen that summer temperatures in this building might be very high indeed with accelerated biological degradation - accordingly it will almost certainly be necessary to increase ventilation rates in summer.



The rate of evolution cannot also be considered as linear over the initial post chip storage period and therefore adequate margin should be allowed above averaged design ventilation rate.

One might speculate that the CO formation and indeed oxygen consumption will occur at the surface of chips or wood shred and initially within the interstitial air spaces of the shredded pile (I have not counted this as head space). CO formed here with a weight some 97% that of air and warmed by mild auto oxidative and Biological degradation will rise to the surface of the pile and despite the very marginal difference in weight I would expect that fuel pile will provide a degree of drag holding a blanket of CO closer to the fuel pile. Any design for ventilation must prevent layering and good air mixing in the headspace without dead zones.

Where entry has to be effected to unventilated fuel storage area for whatever reason then this activity should also be considered in the context of the Confined spaces regulations.

Summary

The research and information and in particular the formulation and execution of large scale trials for CO production from wood chip is very limited. There is sufficient evidence to show that large scale storage of any organic material but in particular soft wood lumber or chip will produce CO and generate an oxygen depleted high CO₂ atmosphere. Where headspace ratio is small that will result in unacceptable CO levels.

Entry to a space storing large quantities of organic materials requires special and sensible consideration and precaution.

My consideration is based on this very limited data and analysis available for fresh wood chip. In the context of auto oxidative CO formation at least this will provide some safety margin because there is research available which suggests that the fatty content of wood reduces with age and accordingly the propensity to generate CO reduces.

Keeping the wood very dry will hamper biological degradations with attendant, CO, Methane and CO₂ production, and for that reason a high fuel turnover and no dead spaces are preferable.

Ventilation must assure mixing or else stratification or binding may occur, creating pockets or layers of high CO concentration.

The detection systems must at least detect at the level where any human operator might be. Additional low and high level alarms might be used to provide a robust alarm system and warning of over pile CO build up and stratification.

Operational and maintenance activity that requires entry to a large store will merit special precaution. e.g. a risk assessed entry, COSHH test, extraction and evacuation procedures (written and **tested**) - and published emergency procedures to mitigate the effects of any Hazard being realised e.g. initial healthcare procedures for persons suspected of carbon monoxide poisoning or Oxygen deficiency.

Conclusions and recommendations

In the context of wood pellet storage there is a severe hazard arising and the risks associated are easily realised. The HSE , local authorities and other regulatory bodies e.g. HETAS, CEA and others should be promulgating firmer advice in respect of storage and the risk of CO from auto-oxidation and backdraft. Pellet storage which is constituted within a basement or similar in existing buildings merits some careful examination. There are several documented deaths

In the context of fresh wood chip storage - the hazard appear to be reduced but potentially significant if there is sealed storage or high wall storage within an existing building - e.g. a farm building with ladder up, ladder down access. No comfort should be drawn from the fact that documented deaths only relate to large shipboard storage. Operators of large enclosed or physically deep storage should be made aware of the Hazards and potential risks. The CO risk from backdraft through connected combustion appliances must be highlighted.

In the context of aged wood storage - Further testing should be conducted - Perhaps by HSEL or similar. The HAZARD appears to be diminished by age but generally the volumes involved are typically very large and designs which are for total enclosed dust containing storage may not represent competent or safe design under CDM2015. Natural ventilation may afford a solution if adequate and where layering is avoided.

These concepts are evidenced by reported deaths and subsequent inquests. These suppositions are not without precedent

Theoretical consideration cannot represent the vast array of fuel storage arrangements in the UK - particularly because there are so many factors involved and influencing the oxidation and biodegradation processes. Testing must be a design requirement and a significant part of the commission and provision of safe Biomass fuel storage.

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