Te Tari Pūhanga Tukanga Matū | Chemical and Process Engineering

Te Kaupeka Pūhanga | Faculty of Engineering

https://profiles.canterbury.ac.nz/Shusheng-Pang
Tel: +64 3 3694 094 Mobile: +64 27 2747 091
Enquiries: shusheng.pang@canterbury.ac.nz

Report to Gisborne District Council

Impacts of The Combustion of Forestry Harvest Residues and Large Woody Debris (LWD) Immersed in Seawater

Shusheng Pang

Department of Chemical and Process Engineering

University of Canterbury

June 2024

Executive Summary

It is reported that in the Gisborne/Hawkes Bay region, a significant portion of forest slash wood was washed into sea and then immersed in the seawater over various periods of time before it was pushed back to beaches by waves. This report assessed the processes and the potential impacts of open-firing of the seawater-immersed wood on human health and environment based on available literature.

The impacts are related to released compounds from combustion of wood and absorbed salts from seawater. Seawater in most locations has a salinity between 31 and 38 g/kg, that is 31–38 $^{0}/_{00}$ salts by weight. The major salts in the seawater are NaCl, MgCl, NaSO and CaCl, however, these salts exist in water in cations (Na^{+}, Mg^{2-}, Ca^{2+}) and anions (Cl^{-}, SO$_4^{2-}$) which diffuse into wood during the immersion.

Wood itself contains cellulose, hemicellulose and lignin which decompose to form gases and organic compounds (volatiles), and char during the combustion through various stages (water vaporisation, devolatilisation or pyrolysis, volatile combustion and char combustion). In the open firing, some released volatiles and particulates (unburnt char and ash) may be blown away by wind. These form the smoke and soots. Inhaling of these matters would have negative impact on human health.

Combustion of the seawater immerged wood would increase the negative impacts as the wood would be wetter thus the combustion temperature is lower and requires longer time to burn completely than normal slash wood. Release of Cl and SO related compounds would be undesirable. Majority of the minerals in the absorbed seawater and wood ash will remain in the residues from combustion of the seawater immersed wood. However, the residues will also contain char as the minerals have been found to melt during the combustion, coating the char particles.

Studies on combustion of the seawater immersed wood is limited in the open literature and further studies are recommended to analyse chemical composition of the released gaseous compounds and residues from combustion of the seawater immersed wood.

1.0 Introduction

1.1 Objectives

The objective of this project is to provide a review on potential consequences of combustion of slash wood which was immersed in seawater for variable periods of time. The focus is on potential impacts of smoke from firing of the seawater-immersed wood on health and environment. Ashes from the combustion are also included for potential treatment or use.

1.2 Background

The 2021 Gabrielle Cyclone had huge impacts on the Gisborne/Hawkes Bay region and one of the major hazards is the generation of large quantity of forest slash wood. Direct processing of the slash wood was assessed in previous report (Pang et al., 2022). However, a significant portion of the forest slash wood was washed into sea and then immersed over various periods of time before it was pushed back to beaches by waves. This has converted many of previously beautiful and tourism beaches into waste wood landing sites.

Open-firing of the seawater-immersed wood was proposed, however, concerns were raised for potential impacts of smoke from the wood firing on human health and environment. There are many unknowns regarding chemical changes of the slash wood during the seawater immerging, and chemical composition of the smoke and the ashes from the open-firing of the seawater-immersed wood.

This report will provide a review to better understand the processes of the open-firing of raw wood and seawater-immersed wood on the following topics:

- Seawater composition;
- Wood composition changes with seawater immersion;
- Processes of combustion of wood and seawater-immersed wood, and chemical analysis on smoke and ashes from the combustion;
- Preliminary assessments of the smoke on health and environment.

2.0 Seawater Composition

The chemical composition of seawater was first investigated by Robert Boyle (1627–1691) who published a tract in 1673 entitled ‘Observations and Experiments about the Saltness of the Sea’, in which he reported experiments on the chemistry of seawater. Boyle was the first perceptive analyst of seawater, but he could not get reliable estimates of the salt in seawater by drying it and weighing the residue. Nevertheless, he did report an approximate value of 30 g salts in a kilogram of seawater, very close to the values later found with better analytical technologies. Boyle also introduced the silver nitrate test and specific gravity for the saltness of water, the total salt content in the seawater. It was found that the total salt content and specific gravity varied regionally, but only to a small extent. Forchhammer (1794-1865) introduced the ratio of the concentration of each of the major elements to that of chloride, and demonstrated the remarkable constancy of these ratios of seawaters from different regions. It was Forchhammer who introduced the term “salinity” to characterize the total salts.

The term 'salinity' is the specific term for seawater indicating the saltiness or total amount of salts dissolved in a body of water (saline water). It is usually measured in g/L or g/kg (grams of salts per litre or kilogram of water); the latter is dimensionless and equal to ‰. The vast majority of seawater has a salinity between 31 and 38 g/kg, that is 31–38 $^{0}/_{00}$ with average value of 35 $^{0}/_{00}$.

As many as 54 salts, double salts and hydrated salts can be obtained by evaporating seawater to dryness. The salts present in seawater are in the form of ions (cations for positive ions and anions for negative ions). The major cations and anions are given in Table 1 in a seawater example with salinity of 35$^{0}/_{00}$ (Lower, 2024).

Table 1. Major ions (cations and anions) of seawater of 35 $^{0}/_{00}$ salinity (Lower, 2024).

Cations	g/kg seawater	Anions	g/kg seawater
Na^+	10.770	Cl^-	19.354
Mg^{2+}	1.290	SO_4^{2-}	2.712
Ca^{2+}	0.412	Br^-	0.087
K^+	0.399		
Sr^{2+}	0.008		
Al^{3+}	0.005		

As salts in seawater exist in the form of ions, individual salts may be identified through elemental balance analysis. Standard Practice for the Preparation of Substitute Ocean Water was proposed as ASTM D 1141 – 98, quantifying the compositions of individual salts as shown in Table 2 which can be used for mixing of artificial seawater (Uy et al., 2019).

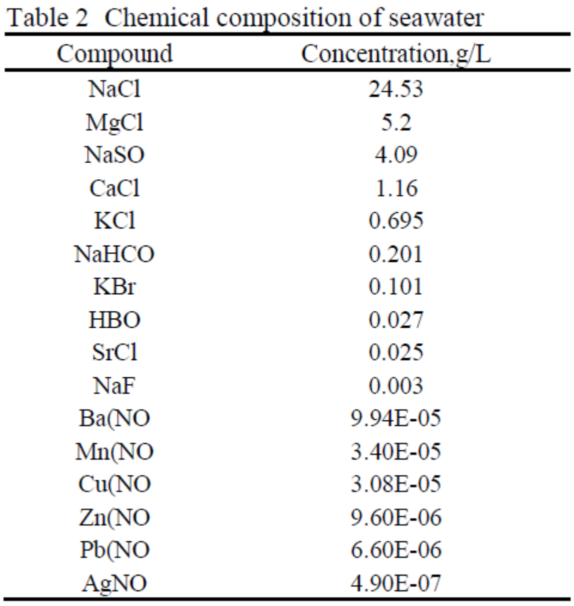


Table 2 Chemical composition of seawater

Compound	Concentration,g/L
NaCl	24.53
MgCl	5.2
NaSO	4.09
CaCl	1.16
KCl	0.695
NaHCO	0.201
KBr	0.101
HBO	0.027
SrCl	0.025
NaF	0.003
Ba(NO	9.94E-05
Mn(NO	3.40E-05
Cu(NO	3.08E-05
Zn(NO	9.60E-06
Pb(NO	6.60E-06
AgNO	4.90E-07

3.0 Wood Composition Changes with Seawater Immersion

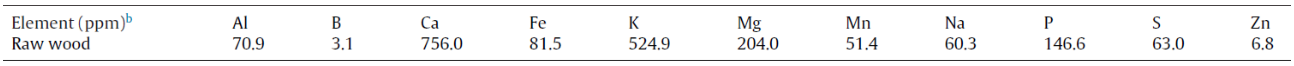
Wood consists of three main components of cellulose, hemicellulose and lignin plus minor extractive. At elemental level, C, O and H form more than 97% of the wood mass with remaining being minerals which form ashes in combustions. In our previous studies (Wigley et al., 2017), chemical and proximate analyses were performed for radiata pine chips and the results are listed in Table 3. In a separate study, mineral elements were also quantified for the radiata pine chips and the results are given in Table 4 (Wigley et al., 2015).

In freshly fell stem, more water is contained than the wood mass with moisture content of radiata pine, varying from 40% (oven-dry based) in heartwood to 200% in sapwood. The stem dries in natural environment once being felled. During the seawater immersion, the water originally present in wood can be extracted and replaced with seawater through ion diffusion.

Table 3. Chemical composition and elemental analysis results for radiata pine chips (Wigley et al., 2017).

Chemical Composition	
Cellulose	43.3 wt.%
Hemicellulose	26.0 wt.%
Lignin	28.2 wt.%
Elemental Composition	
C	50.3 wt.%
O	43.5 wt.%
H	6.1 wt.%

Table 4. Mineral elements in wood (Wigley et al., 2015).



Element (ppm)[b]	Al	B	Ca	Fe	K	Mg	Mn	Na	P	S	Zn
Raw wood	70.9	3.1	756.0	81.5	524.9	204.0	51.4	60.3	146.6	63.0	6.8

When being exposed to seawater, wood undergoes a complex process known as marine biodeterioration and ions penetration. Previous research has reported the detailed process of biodeterioration of wood immersed in the seawater which can be classified into four stages.

Biofilm Development: When wood comes into contact with seawater, microorganisms like bacteria and protists colonize its surface, forming a thin layer called a biofilm. This biofilm plays a crucial role in subsequent deterioration processes.

Biocorrosion: Biocorrosion occurs as a result of the biofilm's activity. It affects various materials exposed to seawater, including metals and alloys. In the case of wood, biocorrosion leads to decay and disintegration due to its biological origin and recyclable nature.

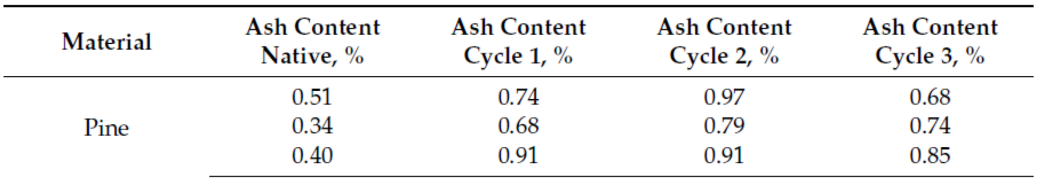
Biofouling: Wood submerged in seawater face biofouling, which involves the settlement of organisms like barnacles, algae, and other marine life. These organisms attach to the wood surface, affecting its integrity.

Bioboring: Marine wood borers, such as shipworms and gribbles, pose a significant threat to wood submerged in seawater. They bore into the wood, causing structural damage.

The above process takes long time. Therefore the ion exchange and diffusion into wood are more dominant in the wood immersion in seawater, however, this process is not well studied and only limited data has been found in the literature .These studies show mineral content increase in the wood through seawater immersion (Roman et al., 2023). Therefore, estimation is performed from theoretical analysis based on the limited available data. In the study of Roman et al. (2023), simulated NaCl salty water with salinity of 7 $^{0}/_{00}$ was used for the wood immersion for different period of times of 2 weeks (Cycle 1), 4 weeks (Cycle 2) and 6 weeks (Cycle 3). Afterwards, the immersed wood was combusted at 805°C, and ashes were collected and weighed. The results for pine wood are shown in Table 5 which also includes the results of untreated wood (raw wood) for comparison.

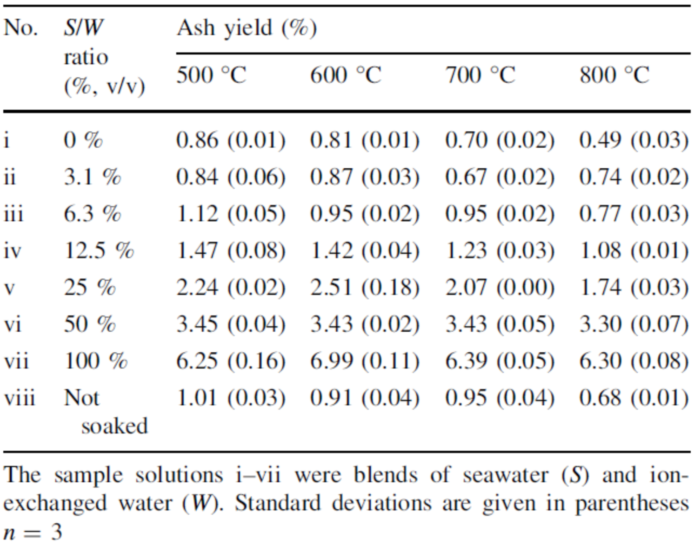
The results in Table 5 show that significant amount of salt ions diffused into wood during seawater immersion and the maximum increase gain is when the wood was immersed for 2 to 4 weeks. However, biodeterioration of wood will be more significant when being immersed for longer time.

Table 5. Ash yields from combustion of both untreated and seawater immersed pine wood (Roman et al., 2023).



Material	Ash Content Native, %	Ash Content Cycle 1, %	Ash Content Cycle 2, %	Ash Content Cycle 3, %
Pine	0.51	0.74	0.97	0.68
	0.34	0.68	0.79	0.74
	0.40	0.91	0.91	0.85

Table 6. Ash yields from combustion of sweater-immersed wood with different ratios of sea-water to fresh water. The seawater has salinity of 36 $^{0}/_{00}$ (Yamada et al., 2014).



No.	*S/W* ratio (%, v/v)	Ash yield (%)			
		500 °C	600 °C	700 °C	800 °C
i	0 %	0.86 (0.01)	0.81 (0.01)	0.70 (0.02)	0.49 (0.03)
ii	3.1 %	0.84 (0.06)	0.87 (0.03)	0.67 (0.02)	0.74 (0.02)
iii	6.3 %	1.12 (0.05)	0.95 (0.02)	0.95 (0.02)	0.77 (0.03)
iv	12.5 %	1.47 (0.08)	1.42 (0.04)	1.23 (0.03)	1.08 (0.01)
v	25 %	2.24 (0.02)	2.51 (0.18)	2.07 (0.00)	1.74 (0.03)
vi	50 %	3.45 (0.04)	3.43 (0.02)	3.43 (0.05)	3.30 (0.07)
vii	100 %	6.25 (0.16)	6.99 (0.11)	6.39 (0.05)	6.30 (0.08)
viii	Not soaked	1.01 (0.03)	0.91 (0.04)	0.95 (0.04)	0.68 (0.01)

The sample solutions i–vii were blends of seawater (*S*) and ion-exchanged water (*W*). Standard deviations are given in parentheses $n = 3$

In a separate study by Yamada et al. (2014), actual seawater with salinity of 36$^{0}/_{00}$ was used to soak cedar wood which was then dried and combusted at different temperatures from 500 to 800°C. Ash yields and ash colour were examined. The ash yields are presented in Table 6 from which it is found that the ash yields from seawater-immersed wood were increased by 6 to 7 times than the raw wood.

4.0 Processes of Combustion of Seawater-immersed Wood

4.1 *Combustion of raw wood*

The combustion of wood may be divided into four stages:

Initial water evaporation (drying). This stage starts when the wood temperature increases to about 100°C at which temperature the water in wood evaporates, generating steam. The steam is colourless, however, looks like cloud in blue sky where temperature is reduced. The water evaporation is enhanced with increase in the temperature.

Devolatilisation (pyrolysis). When the wood temperature reaches to about 250°C, the wood starts to decompose when chemical structure of the wood breaks down, starting with hemicellulose followed by cellulose and lignin. Lignin decomposition occurs in a wide range of temperatures due to its complex chemical structure. This process creates a mixture of hydrocarbon vapours, acetic acid vapour, methanol vapour and combustible gases, and these are termed as volatiles. Heavier hydrocarbon vapours may condense with temperature reduction when moving away from the flame region, forming tars. This is indicated by dark coloured smoke. At this point, we have hydrocarbon vapours and fine droplets, carbon monoxide, methane, water vapor, carbon dioxide, and a mix of other vapours. In the meantime, the remaining solid wood structure turns to char.

Gasification. With further increase in temperature, the combustible gases such as CH_4, CO and other light hydrocarbons start to ignite and react with oxygen in the surrounding air which generates heat. The minimum threshold temperature for combustion to occur at around 550, depending on wood species and moisture content in the wood. In the meantime, heavier hydrocarbon compounds such as tar vapours are cracked to form hydrogen and lighter ones, which process is more significant at higher temperatures. Part of char also reacts with oxygen, if available, through combustion to form CO_2. This process continues to about 900 - 950°C. It is worthwhile to note that water vapour is also produced from combustion of hydrocarbons as well as evaporation of bound water which stays within wood cell wall thus is difficult to remove. Consequently, significant amount of water vapour is found in the flue gases.

Char burning. The carbon left in the previous devolatilization (pyrolysis) and gasification stages burns at temperatures above 950°C, which is indicated by sound and heat at the tail end of a fire. This process generates CO_2. After the charcoal burning, only minerals and mineral oxides are left which are the ashes. The ashes may also contain some unburnt char when it is covered by molten minerals.

In uncontrolled burning of wood, the intermediate products and fines can be entrained and carried away by gases generated from each stage of the combustion or by wind. Therefore, when wood is burned, various chemical compounds are emitted that can cause symptoms such as irritation in eyes, nose and throat; headaches, nausea and dizziness. Some of these compounds are given as follows (Zelikoff., 2002; http://www.cec.org/files/documents/publications/11474-wood-burning-en.pdf):

- **Particulate Matter (PM)** These are fine particles composed of pollutants adhered to very tiny pieces of ash and carbon. These particles can be so small that they penetrate deep into the lungs, and cause lung and heart problems. PM is associated with health problems such as respiratory tract irritation, diminished pulmonary function, asthma aggravation, chronic bronchitis and premature death of persons with heart ailments.

- **Carbon Monoxide** (CO) This is an odourless, colourless gas that inhibits the blood's ability to carry oxygen. It is toxic and may cause serious concerns for high concentrations.

- **Irritant Compounds**, such as acrolein, which cause inflammation and allergic reactions.

- **Polycyclic Aromatic Hydrocarbons** (PAHS), which cause cancer if being exposed for sustained period of time and are also found in cigarette smoke and chimney soot.

- **Volatile Organic Compounds (VOCs)**, such as benzene, which also cause concerns.

- **Dioxins**, which are highly carcinogenic.

Particular attention should be paid to the dioxins, a general term for a group of chemical compounds consisting of 75 polychlorinated dibenzofurans (PCDFs) and 135 polychlorinated dibenzofurans (PCDFs) (Lavric et al., 2004). These compounds are structurally similar, only differing in the number and spatial arrangement of chlorine atoms in the molecule.

4.2 *Combustion of seawater immersed wood*

The combustion of seawater immersed wood follows similar stages to combustion of raw wood as described above. However, the turning temperatures from one stage to another may be different due to the high moisture content and increased salts content in the seawater-immersed wood. The gas emission and ashes are consequently altered to a different extent.

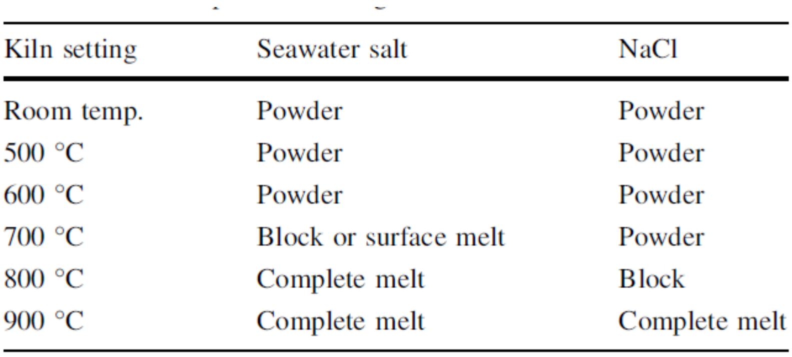
The page of '*Times Colonist*' June 7, 2015, reported that gases from combustion of seawater-immersed wood contains highly persistent and carcinogenic dioxins and furans as chlorine is in the salt-laden driftwood (https://www.timescolonist.com/opinion/letters/burning-driftwood-makes-dangerous-smoke-4623254). This is also due to the incomplete combustion of wood with high moisture content.

Although there is no direct study found in the literature on dioxin emissions from seawater immersed wood, Lavric et al (2004) found that higher dioxin emissions were generated from combustion of salt laden fuels.

Nevertheless, various sources advise to avoid burning wood that has been in contact with seawater to prevent the release of the harmful substances. Chlorine combines with the smoke to produce dioxins and furans, which are dangerous carcinogens (https://valemount.ca/uploads/Wood-Burning-Tips_Mailout.pdf)

Normally, wood ash appears white after combustion. However, when seawater-soaked wood is burned, the resulting ash takes on a black colour. This phenomenon occurs due to the high concentration of seawater salts present in the wood. The colour of ashes was darker with increase in salt content in wood with combustion temperatures examined from 500 to 800°C. SEM examination of the ash samples revealed that the ash material consisted of Na, Mg, and Cl (sodium, magnesium, and chloride) and appeared to be crystallized seawater salt. When the black ash was washed and the translucent seawater salt was removed, the underlying wood tissue became visible. The black ash was identified as carbonized wood tissue residue, generated when seawater salt interacts with woody biomass. This was due to the melting of seawater salts at temperatures lower than those of the raw wood. The melting of seawater salts is even lower than pure NaCl as shown in Table 7 (Yamada et al., 2014).

Table 7. Melting temperatures for seawater salts and pure salt (NaCl) (Yamada et al., 2014).



Kiln setting	Seawater salt	NaCl
Room temp.	Powder	Powder
500 °C	Powder	Powder
600 °C	Powder	Powder
700 °C	Block or surface melt	Powder
800 °C	Complete melt	Block
900 °C	Complete melt	Complete melt

5.0 Conclusion and Recommendations

Salinity of seawater is relative constant varying from 31 to 38 $^{0}/_{00}$, that is 31 to 38g salts per kg water with average value of 35 g/kg. The major salts in the seawater are NaCl, MgCl, NaSO and CaCl which exist in the form of ions (cations and anions). Wood immersed in the seawater absorbs these salts through ion diffusion, which is proven by ash increase from combustion.

Combustion of wood can be divided into four stages including water evaporation (drying), devolatilization, gasification and char burning. The wood combustion releases Particulate Matter (PM), Carbon Monoxide (CO), Polycyclic Aromatic Hydrocarbons (PAHS), Volatile Organic Compounds (VOCs), and dioxins. All of these compounds have negative impacts on health with dioxins needing more attention.

Combustion of the seawater immersed wood follows the same pattern as the combustion of raw wood, however, the gas emission and ashes are altered to a different extent due to the salts absorption and high moisture content. Gases from combustion of seawater immersed wood contain highly persistent and carcinogenic dioxins and furans as chlorine is in the salt-laden driftwood. This is also attributed by incomplete combustion.

The ash yields from combustion of the seawater immersed wood are much higher than the raw wood, and the ashes become darker whereas the ashes from raw wood are light in colour. The dark colour is due to the melting of salts on the char particles and the chemical compositions are more complex.

In summary, the combustion of seawater immersed wood is most likely to have negative impacts on human health than burning of raw wood due to the emissions of many harmful compounds, particularly the emission of dioxins. Various sources advise to avoid burning wood that has been in contact with seawater to prevent the release of the harmful substances.

Ashes from the combustion of seawater immersed wood are complex and thus its treatment or reuse requires caution.

Studies on combustion of the seawater immersed wood is limited in the open literature and further studies are recommended to analyse chemical composition of the released gaseous compounds and residues from combustion of the seawater immersed wood.

References

Lavric, E.D.; Konnov, A.A.; de Ruyck, J. 2004. Dioxin levels in wood combustion—a review. *Biomass and Bioenergy* 26, 115 – 145.

Lower, S. 2024. Geochemistry. LibreTests^{TM} (https://LibreTexts.org).

Pang, S.; Yip, A.; Zhao, P. 2022. Waste Wood Processing Technologies Review. A report to Report to Gisbourn District Council, New Zealand.

Roman, K.; Leszczynski, M.; Pycka, S.; Wardal, W.J. 2023. The effects of seawater treatment on selected coniferous wood types. *Materials* 2023, 16, 5831. https://doi.org/10.3390/ma16175831.

Uy, E.E.S.; Mary Ann Q. Adajar, M.A.Q.; Dungca, J.R. 2019. Volume change behavior of sea water exposed coal ash using hyperbolic model. Int. J. GEOMATE, 16(58), 97 – 103.

Wigley, T., Yip, A.C.K.; Pang, S. 2015. The use of demineralisation and torrefaction to improve the properties of biomass intended as a feedstock for fast pyrolysis. *J Analytical and Applied Pyrolysis*, 113, 296-306.

Wigley, T., Yip, A.C.K.; Pang, S. 2017. A detailed product analysis of bio-oil from fast pyrolysis of demineralised and torrefied biomass. *J Analytical and Applied Pyrolysis*, 123, 194-203.

Yamada, H. Yamauchi ,H, and Kurimoto, Y. 2014. Color analysis of combustion ashes of seawater-soaked wood: estimation of salt concentration. *J Mater Cycles Waste Manag* (2014) 16:576–582.

Zelikoff, J.T. et al. 2002. The toxicology of inhaled woodsmoke. *J. Toxicology and Environmental Health*, Part B, 5, 269–282.