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Doroshenko, Alisa, Budarin, Vitaliy, McElroy, Robert et al. (5 more authors) (2019) Using in vivo nickel to direct the pyrolysis of hyperaccumulator plant biomass:In vivo nickel to direct the pyrolysis of hyperaccumulator plant biomass. *Green Chemistry*. pp. 1236-1240. ISSN: 1463-9262

<https://doi.org/10.1039/c8gc03015d>

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Journal Name

COMMUNICATION

Using *in vivo* nickel to direct the pyrolysis of hyperaccumulator plant biomass

Received 00th January 20xx,
Accepted 00th January 20xx

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DOI: 10.1039/x0xx00000x

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The effects of naturally occurring nickel in hyperaccumulator plants used for phytoremediation of contaminated soils on the biomass pyrolysis is described for the first time. Perhaps surprisingly, nickel taken up naturally by the plant behaves very differently to nickel introduced by conventional adsorption when microwaves are used for biomass pyrolysis. The presence of naturally accumulated nickel appears to protect the hemicellulose component of the plant leading to 3 times lower yields of bio-gas and increased quantities of bio-char. The composition of the bio-oil is also affected.

Large areas of land in many parts of the world are unavailable for agriculture due to the presence of high levels of metals within the soils. Although these areas are unsuitable for growing food crops, they are rarely considered for non-food applications, and this represents a missed opportunity for biorefineries which require increasing land area to be dedicated to non-food energy or chemical crops.^{1–3} While some soils naturally contain high levels of potentially toxic elements, including heavy metals, significant contamination has occurred from anthropogenic activities, such as industrial land use, mine tailings, wastes disposal, pesticides, irrigation of wastewater, spillage of petrochemicals, and others.^{2,4} Heavy metals represent an ill-defined group of hazardous inorganic chemicals, and those most commonly found include lead, chromium, arsenic, nickel. Land pollution with heavy metals is a long-term problem because the majority of these elements do not undergo microbial or chemical degradation unlike organics.^{5,6}

One of a number of ways to clean-up contaminated land is phytoremediation, the use of plants to detoxify the

environment. This method is relatively simple, can be cost-effective, and presents the opportunity to restore the local ecology.⁷ Moreover, the use of plants to remediate polluted land presents an aesthetically pleasing approach with high public acceptance.^{7,8} One facet of this technique is the use of hyperaccumulator plants to take up heavy metals. These species naturally accumulate specific metals to concentrations in their tissues that can be many thousand-fold higher than in the surrounding soil.^{8,9} When the biomass of these plants is harvested to recover the metals, this process is called phytomining.⁷

Phytomining by hyperaccumulators has the potential to allow economic exploitation of low-grade surface ores or metal-contaminated soils. The final product could be both recovered metal and remediated land suitable for agriculture. A number of publications have highlighted the economic potential of phytomining,^{10–13} with this technology mainly developed for nickel-contaminated soils.¹⁴ Nickel has a relatively high market price compared to many other metals. Moreover, there are many countries such as Australia, Canada, Italy, Russia, Brazil, and Turkey that contain large areas of low-grade, surface Ni ore. Currently, these nickel-contaminated lands are mostly left unused.¹⁴

An essential step in phytomining is the use of Ni – hyperaccumulators for metal recovery but this metal containing biomass can itself be converted to valuable products as part of a holistic biorefinery.¹⁵ One pathway to recover the metal from such plants involves their thermal treatment to produce catalysts for use in organic chemistry,^{16,17} or metal salts.^{18,19}

Several studies have focused on the catalytic effect of different transition metals on the thermal conversion of plant biomass to platform chemicals.^{20–22} Nickel is considered to be one of the more promising metals for this because of its complex oxidation chemistry that involves the accessibility of different oxidation states and its ability to activate unsaturated organic molecules.^{23,24} Impregnated nickel has been reported to reduce the coke deposition on the surface of some catalysts and increase the yields of syngas and aromatic hydrocarbons in

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

some reductive conversions of biomass.^{25–27} The Ni-impregnated catalysts demonstrated good thermal stability and reduced oxygenate breakthrough.²⁷ Extrapolating from this result, it is likely that the catalytic activity of naturally accrued nickel in plant hyperaccumulators could

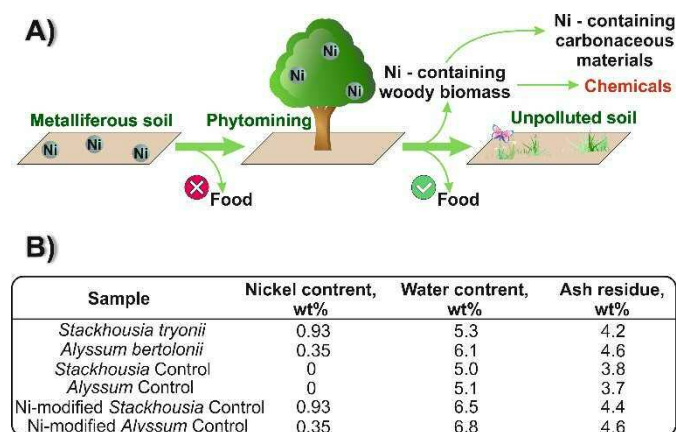


Fig. 1. The concept of the work and characterisation of the ground leaf materials used in this study.

improve biomass valorisation processes (see Figure 1A). To our knowledge, the production of value-added products in the further processing of Ni-hyperaccumulators has not yet been studied.

Use of microwave-assisted pyrolysis as an energy-efficient, and more controlled, way of converting biomass to chemicals has recently been reported^{28,29}. Microwave (MW) heating has a number of advantages over conventional types of heating including the selective activation of the principal components of the biomass.^{30,31} Herein, the initial results studying the effect of hyperaccumulated nickel on biomass pyrolysis using microwave activation are reported.

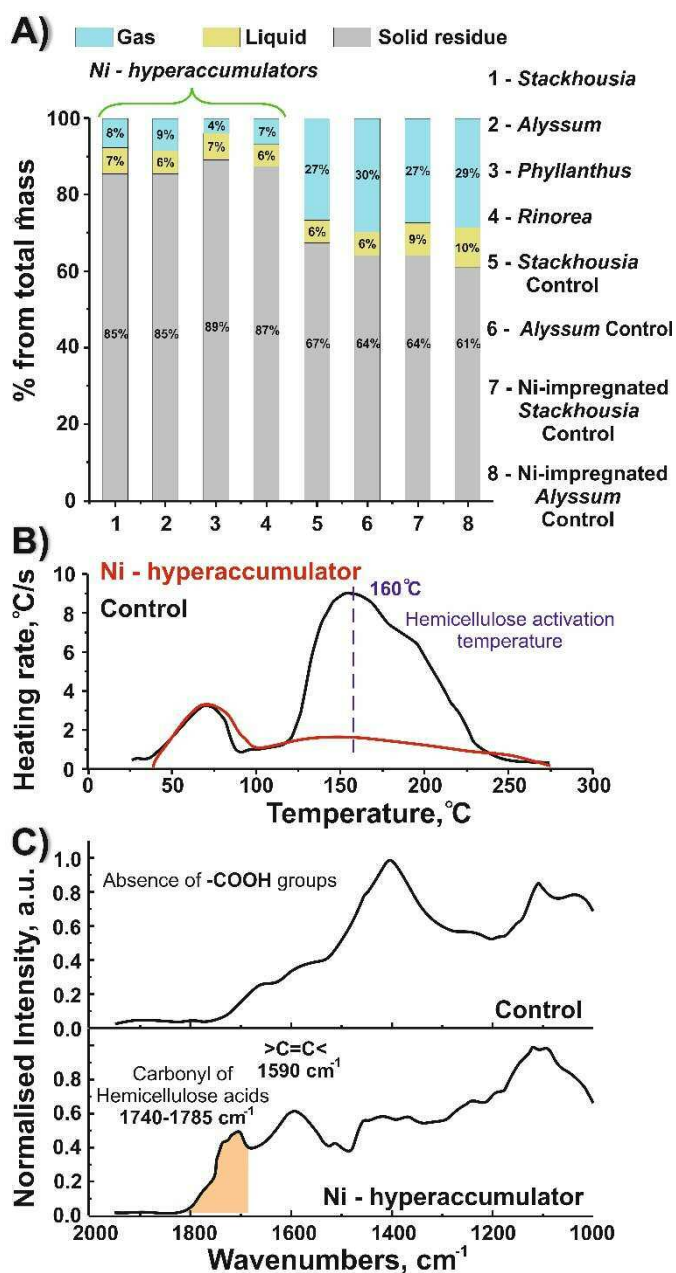
The role of nickel in the MW-assisted pyrolysis of biomass, including its structural components, both using classically impregnated and naturally accrued metal has been investigated. Samples of the temperate growing, Ni-hyperaccumulator plant species, *Stackhousia tryonii* were field collected from natural populations growing on nickel-rich soils in Queensland, Australia, while samples of the hyperaccumulator *Alyssum bertolonii*, were provided from plants growing on nickel-rich soil under controlled growth conditions by the University of Queensland in Brisbane, Australia. These hyperaccumulator species have evolved to grow on nickel-rich soils, and are difficult to cultivate in nickel-poor soils. All land plants require trace quantities of nickel as an essential element for growth, so providing nickel-free plant biomass is not possible, therefore, as controls, the non-hyperaccumulator species sweet alyssum (*Alyssum maritimum*) and *Lobelia sp.* purchased from a commercial garden centre in New Zealand were chosen for this study. In the current work, *Alyssum maritimum* and *Lobelia sp.* are coded as *Alyssum* Control and *Stackhousia* Control respectively.

Firstly, the MW pyrolysis on ground leaf tissues from the hyperaccumulator species was compared with the control plants. Ground leaf material from these control samples were then impregnated with Ni using 0.1 M $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ aqueous solution to achieve final nickel concentrations equivalent to those in the hyperaccumulator species - 0.93 and 0.35 wt% for *Stackhousia* and *Alyssum* respectively. Water and ash residue contents were measured using STA-625 under nitrogen and oxygen atmospheres respectively (10 K min^{-1}). Nickel content was determined using

Microwave Plasma Atomic Emission Spectroscopy (see Figure 1B). The nickel content between the two hyperaccumulators was significantly different. The higher ash contents of the two Ni-hyperaccumulators could be due to the presence of nickel oxide and increased level of the charring reactions. It is possible that nickel catalyses the condensation of organic products of biomass depolymerisation to produce graphitic species that survive the STA-heating (to 625°C).

Microwave assisted pyrolysis was conducted at dynamic power mode, on a CEM Discover, equipped with 10 ml closed vial. The target temperature was 280°C . The extraction of bio-oil was carried out using acetone; centrifuged, decanted, filtrated. GC-MS and GC-FID analysis was performed (see ESI).

The mass balances from the microwave-assisted pyrolysis



experiments are shown in Figure 2A. To better understand the **Fig. 2.** A) Mass balance for all the samples; B) MW traces; C) ATR-FTIR spectra of the Ni-hyperaccumulator and its control

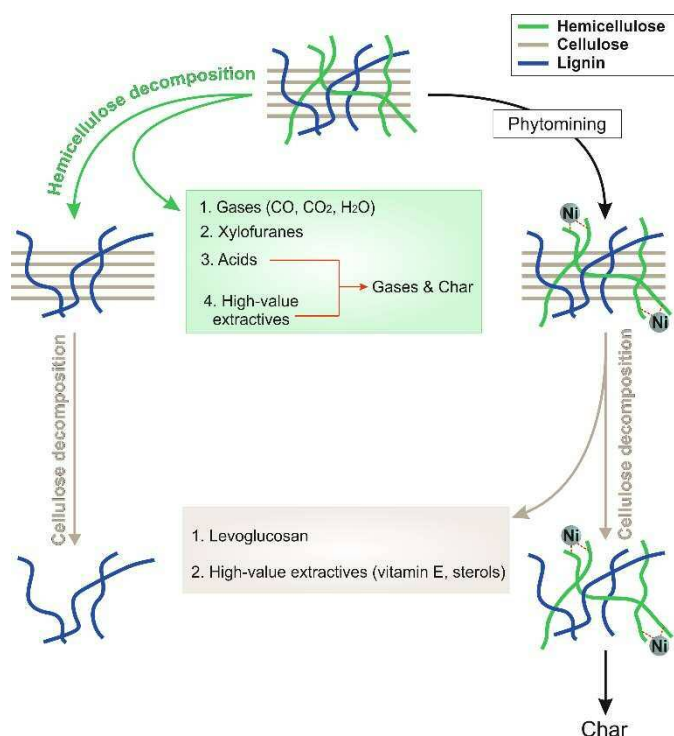


Fig. 3. Proposed role of naturally accrued nickel found in hyperaccumulator species during microwave-assisted pyrolysis.

nickel role in the MW pyrolysis, we extended the range of the natural Ni-containing plants to include two tropical hyperaccumulator tree species, *Phyllanthus balgooyi* collected from field populations growing on nickel laterite soils in Sulawesi, Indonesia, and *Rinorea bengalensis* collected from field populations growing on nickel laterite soils in Malaysia (leaf tissues contained 3.19 and 0.81 wt% of nickel respectively). The MW-assisted pyrolysis of ground leaf material from these hyperaccumulator species resulted in substantially lower yields of biogas than control samples (including artificially impregnated). Furthermore, samples from all four of the hyperaccumulator species showed the same product distribution pattern (different from control) clearly demonstrating that naturally accumulated nickel has a fundamentally different effect on biomass pyrolysis to artificially impregnated. It is also interesting to note that artificially impregnated samples gave significantly increased yields of bio-oils, which was not observed with samples from the hyperaccumulators.

The influence of nickel on MW-pyrolysis of the plant materials can also be observed in the different temperature profiles of the microwave experiments (Figure 2B). For the samples from the hyperaccumulator plants, the heating rate at

around 160 °C was significantly reduced in comparison with the control plants. It has been recently shown that this temperature corresponds to the activation of hemicellulose [Ref]. The amount of hemicellulose for the Ni-hyperaccumulators and their controls before the MW-assisted pyrolysis were similar (see ESI) and the heating rate intensities at 160 °C were expected to be similar as well (figure 2B). It is likely that the presence of nickel inhibits the decomposition of hemicellulose. The presence of substantial amounts of hemicellulose remaining in the leaf material from the hyperaccumulator species after microwave-assisted pyrolysis was confirmed by ATR-FTIR (evident from the strong carboxyl stretching bands). This inhibition could also explain the reduction of gas production (Figure 2A) since it is well-known that the main gas production in biomass pyrolysis is as a result of decomposition of glucuronic/galactonic acid present in hemicellulose.³² Nickel has a high affinity for oxygen and nitrogen centres as ligands.^{33,34} Moreover, Ni and chemically similar metals tends to accumulate in the hemicellulose part of the plant.³⁵ Thus nickel could be acting as a stabiliser of hemicellulose, preventing its decomposition. This stabilisation effect was not seen with the artificially impregnated control plants, and could be due to the accumulation of the metal on the biomass surface, rather than its incorporation within the plant biomass. Thus the artificial addition of nickel to plant biomass does not affect the temperature profiles on microwave heating and gives the yields of biogas same to the control samples. There was no evidence of any significant amounts of residual hemicellulose in the artificially modified Ni materials (Figure 2C). Interestingly, the presence of nickel in the hyperaccumulator species does not influence the pyrolysis of plants using conventional heating. The deconvolution of the DTGs show no changes in the decomposition order, giving a natural one³⁶: hemicellulose → cellulose → lignin (see ESI). This suggests that the inhibition effect of the metal on hemicellulose decomposition is related to the dielectric properties of materials. It is recognised that the efficiency of the interaction of microwaves with matter depends on both the polarity of the molecule or functional groups and their ability to rotate. Typically, molecules involved in intense physical and chemical interactions do not interact with microwave as they are not free to rotate. The unique selective interaction of nickel with hemicellulose makes it stable in the presence of MW and can be used to activate the cellulose before the hemicellulose – the opposite of what is normal (see Figure 3).

The nickel in hyperaccumulator plants also affected the bio-oils composition, significantly, increasing production of nitrogen-containing compounds such as triacetoamine (see Figure 4) which a known product of biomass pyrolysis.³⁷ The

CHN analysis of the bio-oil also demonstrated that nitrogen was present showing an overall composition profile of 49.3 % of carbon, 8.8 % of hydrogen and 8.3 % of nitrogen. The bio-oil from the microwave-assisted pyrolysis of the Ni-hyperaccumulator-derived samples showed significant quantities of levoglucosan resulting from the cellulose in the plants. Alternatively, the quantities of extractives such as sterols and vitamins were significantly reduced in the samples from the Ni-hyperaccumulators, possibly as a result of the catalytic effect of acids produced from hemicellulose on the pyrolysis chemistry.

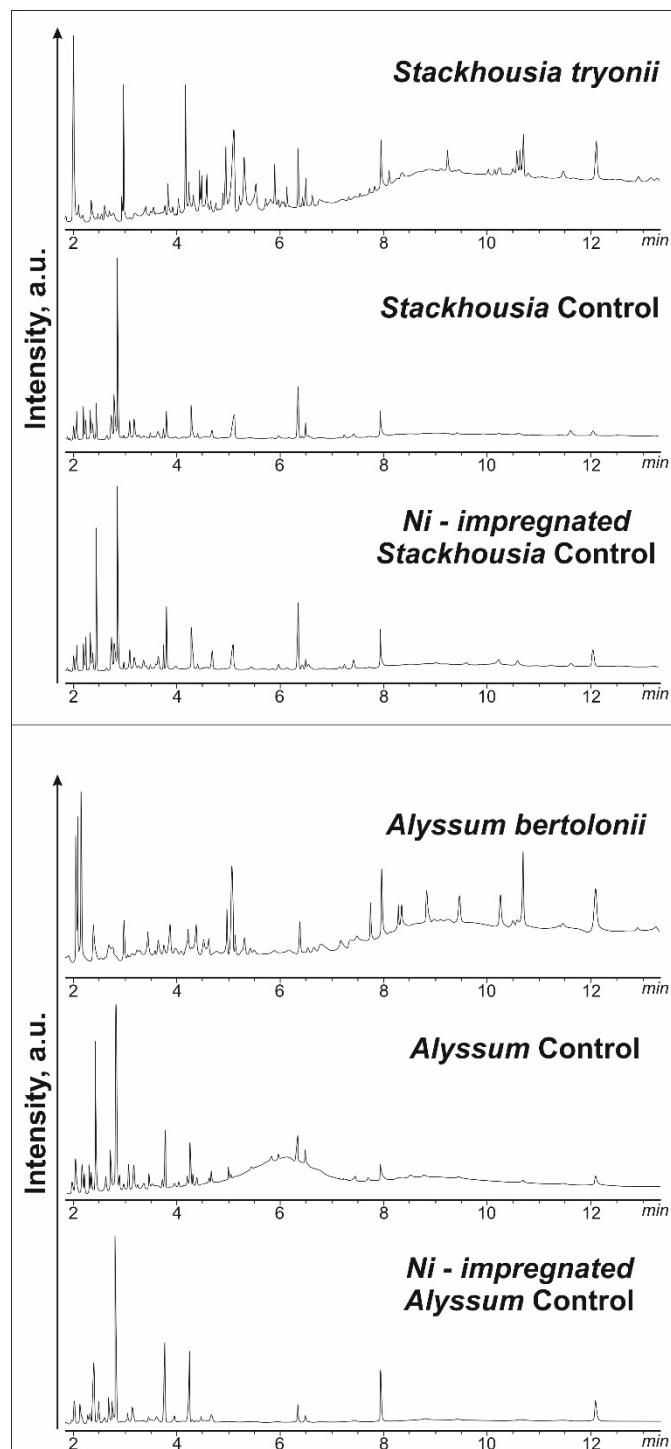


Fig. 4. GC-FID spectra of all the investigated samples

Conclusions

By studying the effects of naturally accumulated nickel on the pyrolysis behaviour of the host plants, we have demonstrated both an interesting inhibitory effect of the metal on parts of the plant biomass decomposition and a surprising microwave-specific effect. Compared to leaf material from low nickel, non-hyperaccumulator species and artificially impregnated plant biomass, the naturally accumulated Ni-rich biomass from hyperaccumulator species offer very different product distributions with unusually high bio-char yields and different, more cellulose-derived chemical products. Thus the phenomenon may be exploitable in both maximising the energy value of biomass (by co-firing with coal) and the more selective production of cellulose-derived important platform chemical products. The use of hyperaccumulator plants to make chemicals and energy can significantly add to the economic attractiveness of using these species to remediate nickel contaminated land, or in the alternative land use of metalliferous soil that is poorly suited to food crop production. We believe our research also opens the door to further studies using metals introduced during plant growth to catalytically influence subsequent biomass valorisation thermal chemistry.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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