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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

Alisa Doroshenko,^a Vitaliy Budarin,^a Robert McElroy,^a Andrew J. Hunt,^b Elizabeth Rylott,^c
Christopher Anderson,^d Mark Waterland,^e James Clark^{a*}

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 microwave (MW) biomass pyrolysis is described for the first time. The presence of natural 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 the 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 requires increasing land area to be dedicated to non-food energy or chemical crops.^{1,2} 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 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.³

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.⁴ Moreover, the use of plants to remediate polluted land presents an aesthetically pleasing approach with high public acceptance. 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 the surrounding soil.^{5,6} When the biomass of these plants is harvested to recover the metals, this process is called phytomining.⁴

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,^{7,8} with this technology mainly developed for nickel-contaminated soils.⁹ 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.⁹

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.¹⁰ One pathway to recover the metal from such plants involves their thermal treatment to produce catalysts for use in organic chemistry,^{11,12} metal or its salts.^{13,14}

Several reported studies have focused on the catalytic effect of different transition metals on the thermal conversion of plant biomass to platform chemicals.^{15,16} 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.¹⁷ 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

^a Department of Chemistry, The University of York, Heslington, York, YO10 5DD, United Kingdom

^b Materials Chemistry Research Center, Department of Chemistry and Center of Excellence for Innovation in Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen, 40002, Thailand

^c Department of Biology, The University of York, Heslington, York, YO10 5DD, United Kingdom

^d School of Agriculture and Environment, Massey University, Auckland, New Zealand

^e Institute of Fundamental Science, Massey University, Auckland, New Zealand
Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

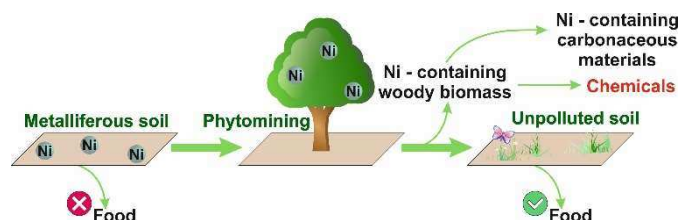


Fig. 1. The concept of the work and characterisation of the ground leaf materials used in this study

some reductive conversions of biomass.^{18,19} The Ni-impregnated catalysts demonstrated good thermal stability and reduced oxygenate breakthrough.¹⁹ Extrapolating from this result, it is likely that the catalytic activity of naturally accrued nickel in plant hyperaccumulators could improve biomass valorisation processes (see Figure 1). 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^{20,21}. Microwave (MW) heating has a number of advantages over conventional types of heating including the selective activation of the principal components of the biomass.^{22,23} Herein, the initial results studying the effect of hyperaccumulated nickel on biomass pyrolysis using microwave activation have been 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 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

Table 1. Characterisation of the ground leaf materials used in this study

Sample	Ni content, wt%	H ₂ O content, wt%	Ash residue, wt%
<i>Stackhousia tryonii</i>	0.93	5.3	4.2
<i>Alyssum bertolonii</i>	0.35	6.1	4.6
<i>Stackhousia Control</i>	0	5.0	3.8
<i>Alyssum Control</i>	0	5.1	3.7
Ni-doped <i>Stackhousia Control</i>	0.93	6.5	4.4
Ni-doped <i>Alyssum Control</i>	0.35	6.8	4.6

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, non-hyperaccumulator species sweet alyssum (*Alyssum maritimum*) and *Lobelia sp.* purchased from a commercial

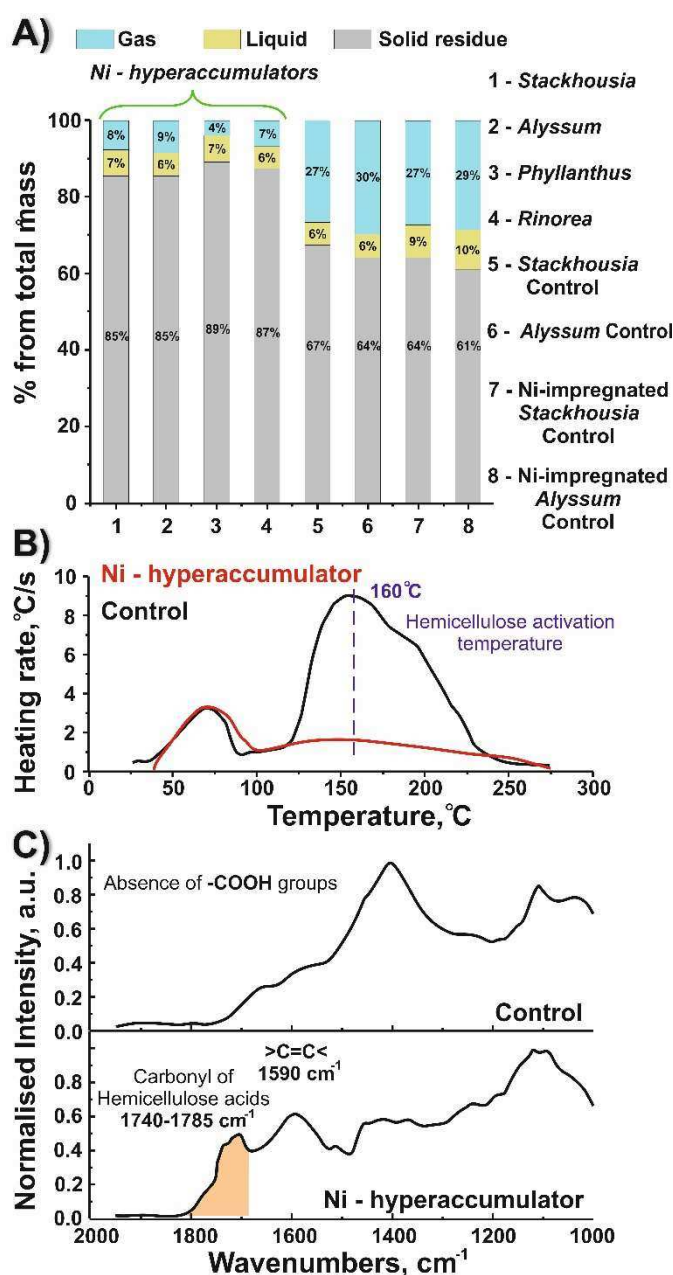


Fig. 2. A) Mass balance for all the samples; B) MW traces; C) ATR-FTIR spectra of the Ni-hyperaccumulator and its control

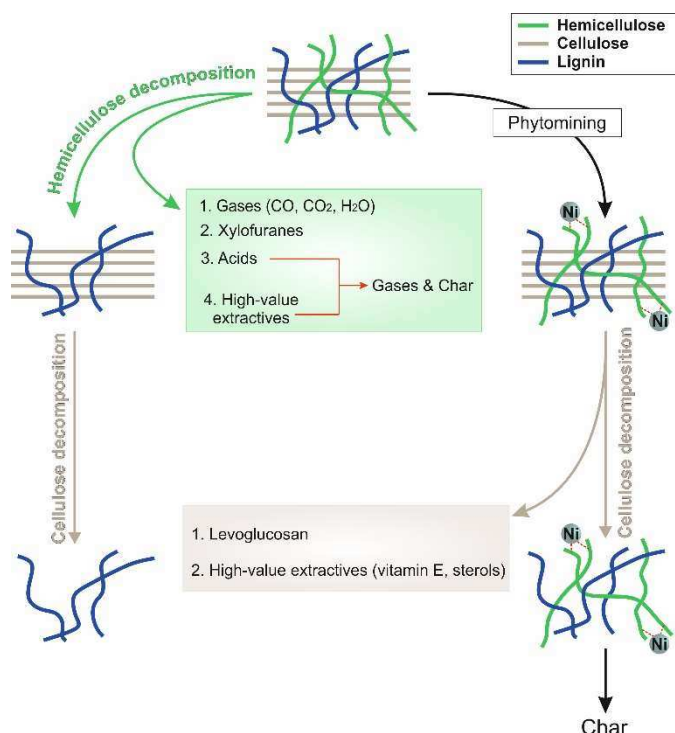


Fig. 3. Proposed role of naturally accrued nickel found in hyperaccumulator species during microwave-assisted pyrolysis

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 NiCl₂·6H₂O aqueous solution to achieve final nickel concentrations equivalent to the 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 determined using Microwave Plasma Atomic Emission Spectroscopy (see Table 1). 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 nickel role in the MW pyrolysis, we extended the range of the natural Ni-containing plants including 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 and artificially Ni-doped materials. 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 is 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.²⁴ Remarkable, 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 possible that the presence of nickel inhibits the decomposition of hemicellulose. The presence of substantial amounts of hemicellulose 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.²⁵ Nickel has a high affinity for oxygen and nitrogen centres as ligands.^{26,27} Moreover, the d-block elements tends to accumulate in the hemicellulose part of the plant.²⁸ Thus nickel could be acting as a stabiliser in hemicellulose, preventing its decomposition. This stabilisation effect is not seen with the artificially impregnated control plants, and could be due to the accumulation of the metal on

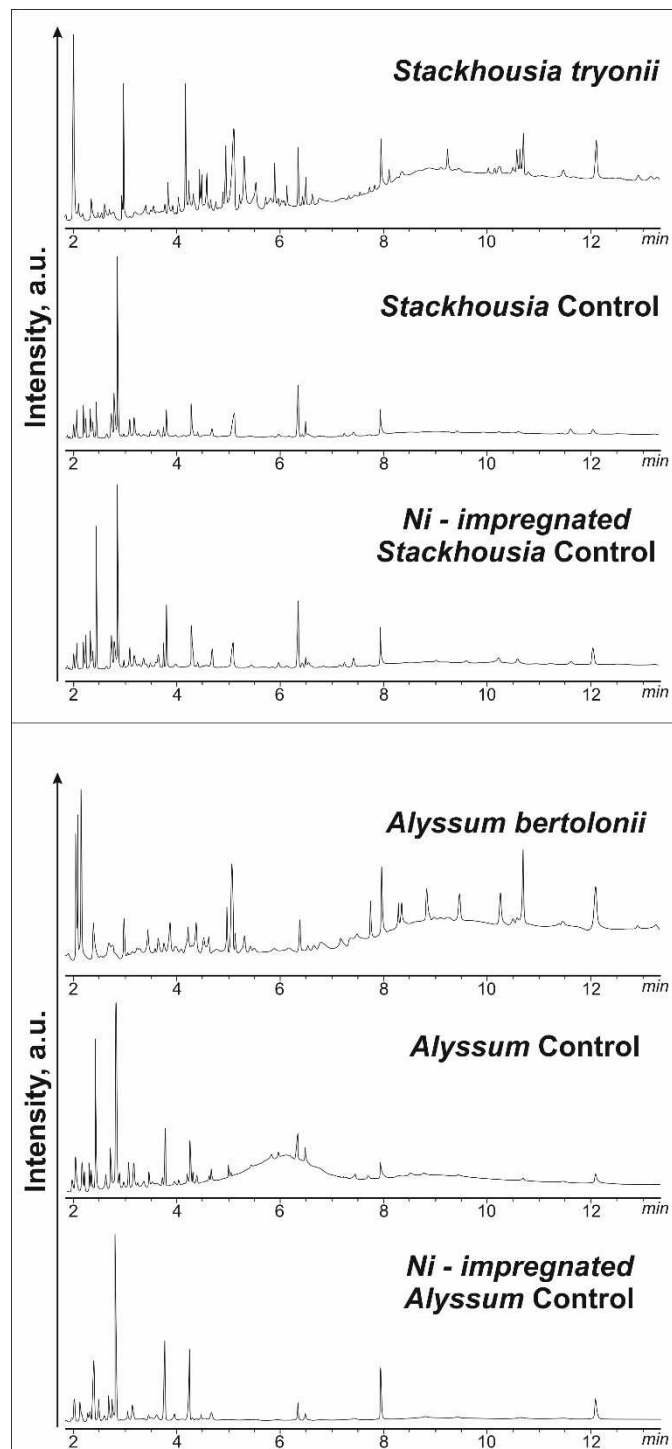


Fig. 4. GC-FID spectra of all the investigated samples

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 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 one²⁹: 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. This unique selectivity 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 are known products of biomass pyrolysis.³⁰ The CHN analysis of the bio-oil has also demonstrated that nitrogen is 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.

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 biorefinery including 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.

Acknowledgments

The authors acknowledge the financial support of the New Zealand Government through the MBIE Catalyst Fund Global Strategic Partnerships Programme 'PhytoCat: high-value products from metal-rich biomass' (MAUX1508) and the assistance of the Dr. Antony Van der Ent of the University of Queensland, Australia in the field collection of hyperaccumulator species

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