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# A Study of the Importance of Secondary Reactions in Char Formation and Pyrolysis

A dissertation presented in partial fulfilment
of the requirements for the degree of

Doctor of Philosophy
in
Process Engineering

at Massey University, Manawatū,
New Zealand.

**Georg Dietrich Ripberger**

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# Abstract

Anthropogenic climate change, caused primarily by excessive emissions of carbon dioxide, has led to a renewed interest in char, the solid product of pyrolysis. When applied to soil as biochar it can both sequester carbon and improve soil function. To make its manufacture environmentally friendly and economically viable it is important to maximise char yield, which can be done by promoting secondary reactions.

This research shows that secondary reactions, which are enhanced by prolonged vapour-phase residence time and concentration, not only increase the char yield but are the source of the majority of the char formed. All four biomass constituents (extractives, cellulose, hemicellulose and lignin) undergo secondary reactions concurrent with primary reactions over the entire pyrolysis range ≈ 140 to 500 °C, which makes it practically impossible to separate them. Secondary char formation was confirmed to be exothermic which affects the overall heat of pyrolysis. Impregnating the feedstock with the elements K, Mg and P, which are plant macro-nutrients naturally present in biomass, resulted in the catalysis of secondary char formation. The results reveal that a first order reaction model does not describe pyrolysis accurately when char formation is enhanced by catalysis and secondary reactions.

Secondary char can be enhanced by increasing the particle size but there is a limit due to increased cracking and fracturing of the pyrolysing solid. This limitation is overcome by pyrolysis in an enclosed vessel, termed autogenous pressure pyrolysis, which was discovered to cause significant changes in the volatile pyrolysis products; indicating the co-production of a high quality liquid. This process, however, negatively affects the char properties relevant for biochar like the surface area, similar to self-charring and co-carbonisation of condensed volatile pyrolysis products. To increase research capabilities a unique high temperature/ high pressure reactor (600 °C at 20 MPa) was designed to allow the detailed characterisation of all three pyrolysis product classes under extreme pyrolysis conditions. This was demonstrated to be invaluable for understanding the underlying pyrolysis mechanism and physical processes at play.

# Acknowledgements

Doing research is a bit like a quest into the unknown. Over the past few years I embarked on my own journey to discover the unknown, and shed some light onto it. There are a few people who helped me along the way, who I would sincerely like to thank:

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Like an expedition into the wild, this journey was not a single person’s effort. One can only be as good as the team that supports them; imparting their knowledge, wisdom, and insight along the way. Thus, journeys are not defined by reaching the finish line, but rather by the experiences we gain, the people we meet, and the friendships we develop. I have been privileged to be part of a great team that made this journey possible to whom I am greatly indebted.

# Statement of Contribution to Doctoral Thesis Containing Publications

## List of Publications

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[PhD Confirmation Report]

**Conference presentations:**

Ripberger, G. D., Jones, J. R., Paterson, A. H. J., & Holt, R. (2015, September/October). *Is it possible to produce biochar at different highest treatment temperatures in the pyrolysis range?—The exothermic nature of pyrolysis*. Paper presented at the APCChE 2015 Congress incorporating Chemeca 2015, Melbourne, Australia.

[Conference Oral Presentation & Peer Reviewed Paper; Speaker: Georg Ripberger]

Ripberger, G. D., Jones, J. R., Paterson, A. H. J., & Holt, R. (2013, September). *Temperature regime of secondary char forming reactions in the pyrolysis of radiata pine*. Paper presented at the Chemeca 2013: Challenging Tomorrow conference, Brisbane, Australia. Paper retrieved from http://www.conference.net.au/chemeca2013/papers/25402.pdf

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[Conference Oral Presentation; Speaker: Georg Ripberger]

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[Conference Poster; Presented by Georg Ripberger]

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Ripberger, G. D., Kirwan, C., Jones, J. R., & Paterson, A. H. J. (2014, May). *Effect of autogeneous pressure on volatile pyrolysis products*. Poster presented at the Pyro2014 20th International Symposium on Analytical and Applied Pyrolysis, Birmingham, United Kingdom.

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[Oral Presentation; Speaker Georg Ripberger]

# Statement of Contribution

These outputs were distributed over the time of Georg Ripberger's PhD study. They represent the state of knowledge at the time. The final opinions are contained in the thesis which, in some cases, are different to those expressed in the publications and presentations. In other words, the work has evolved over time. Georg had ownership of his PhD project and the work contained is entirely his. The role of the supervisors, Jim Jones and Tony Paterson, was to mentor him. A number of honours research projects were conducted alongside the PhD; these were supervised by Georg Ripberger and Jim Jones. We discussed many of the ideas presented in the publications, but emphasise that they are the work of Georg. Percentages are hard to ascribe, but as supervisors, we can only attribute ourselves a small percentage commensurate with mentoring.

Signed

Jim Jones, Principal Supervisor

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