



SCIENCE SYMPOSIUM

Next Generation Liquid Biofuels and Co-Products



The *Next Generation Liquid Biofuels and Co-Products* Science Symposium has been sponsored by the Ministry of Business, Innovation, and Employment, and Scion.



Figure 1: ABRN Science Symposium 2014 Attendees.

Introduction

Transportation biofuels and co-products derived from grasses, wood, and algae have the potential to displace a significant proportion of fossil-based fuels and chemicals in New Zealand. To fully exploit this opportunity requires a coordinated scientific research effort across New Zealand's research organisations. As a step along this path, Scion hosted a Science Symposium on Next Generation Liquid Biofuels and Co-Products in December 2010. Out of that first Science Symposium, the New Zealand Advanced Biofuels Research Network (ABRN) was formed. The Network aims to promote better coordination and collaboration across biofuels research in New Zealand. To this end, the Network has organized a further four Science Symposia, held annually, and coordinated through a Steering Committee made up of representatives from key research organizations in New Zealand.

The Symposium series provides a forum for the New Zealand biofuels research community to share their science, engage in scientific debate, and learn about international developments in biofuels. It is intended to complement other fora with a policy or commercial focus to ensure that appropriate synergies between research and development activities are built and that collective work remains both leading edge and relevant to the needs of New Zealand.

The 5th ABRN Symposium was held on 16 October 2014, at the Distinction Hotel in Rotorua. A significant change was made to the format, with the symposium being held for the first time in conjunction with the Appita (Australian and New Zealand Pulp and Paper Technical Association) Fibre Value Chain 2014 Conference and the Bioenergy Association of New Zealand's Conference entitled "Using Commercially Ready Technologies to bring Biofuels and Co-products to Market". As a result, the ABRN symposium was shortened to one day and held as a parallel stream on the second day of the Appita Conference, with the BANZ conference then held on the next day. The ABRN keynote session, which included our two international keynote speakers, was shared with the Appita conference delegates.

Linking these three complementary events together worked well, providing a 3-day event with a total of 312 delegates registering for the three conferences. Many delegates from the Appita and BANZ conferences attended the ABRN symposium, with attendances at the ABRN symposium technical sessions estimated to range between 60 and 90.

This multi-conference format proved an excellent way to profile our research to the broader bioenergy community, including those interested in using and producing biofuels, and for the research community to understand the needs of such companies. For example, the ABRN sessions were well attended by delegates from the pulp and paper industry, and ABRN researchers made a number of presentations at the BANZ conference on the following day. There is a strong interest in biofuels from the pulp and paper industry in the opportunities that biofuels might present for their businesses, as evidenced, for example, by one of the Appita conference keynote speakers, DeWitt Patterson, Director of Biofuels Development at AMEC in the United States. With AMEC heavily involved in engineering design for these new plants, DeWitt provided an authoritative overview of biofuel activities in the United States.

Technical Highlights



Dr Sergios Karatzos from Steeper Energy in Canada provided the first keynote presentation; an overview of a major report prepared for IEA Bioenergy Task 39 entitled “The potential and challenges of drop-in biofuels”. Drop-in biofuels, or bio-hydrocarbons which are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure, are attracting increasing international attention. This presentation gave an overview of the issues, different approaches being investigated globally to produce these biofuels and status of commercial development of these processes. This presentation emphasised the importance of hydrogen, and where it will come from, in the production of drop-in biofuels.



Professor John Ralph, from the University of Wisconsin-Madison in the United States gave the second keynote presentation on work he and his co-workers have recently reported in the journal Science on modifying lignin in the cell wall to make it easier to deconstruct during pulping and biofuel production. This inspiring presentation, the culmination of many years’ work within his research group, showed that a fundamental understanding of how lignin is formed in the cell wall can lead to commercially-useful outcomes.

Professor Shusheng Pang from the University of Canterbury gave a summary of thermochemical methods for the production of biofuels and then summarised his research group’s work undertaken by in the area.

Detailed technical presentations were given by researchers from University of Canterbury, NIWA, University of Waikato, Massey University, CRL Energy Ltd and Scion as highlighted in the appended abstracts. The three presentations by PhD students on their research were a particular highlight.

The Symposium Programme and presentation abstracts are available to registrants on the Advanced Biofuels Research Network website: www.abrn.org.nz.

ABRN Symposium Programme

8.30 am	Registration
8.50 am	Welcome & housekeeping Rupert Craggs , NIWA, Ian Suckling , Scion
<u>SESSION ONE</u>	Chair Ian Suckling , Scion
9.00 am	KEYNOTE SPEAKER – Video link Sergios Karatzos , Steeper Energy Canada <i>The potential and challenges of “drop-in” biofuels</i>
9.45 am	KEYNOTE SPEAKER John Ralph Great Lakes Bioenergy Research Centre USA <i>Designing plant cell walls for deconstruction: Using monolignol ferulate conjugates to introduce ester bonds into the lignin backbone</i>
10.30 am	<i>Morning tea</i>
<u>SESSION TWO</u>	Chair Martin Atkins , University of Waikato
11.00 am	Shusheng Pang University of Canterbury <i>Overview on recent advances and challenges in biomass to liquid fuels through thermochemical processing routes</i>
11.30 am	Tansy Wigley University of Canterbury <i>Biomass pre-treatments to improve the properties of fast pyrolysis bio-oil</i>
12.00 noon	Rupert Craggs NIWA <i>Enhancements of wastewater treatment high rate algal ponds for biofuel production</i>
12.30 pm	<i>Lunch</i>
<u>SESSION THREE</u>	Chair Rupert Craggs , NIWA
1.30 pm	John McDonald-Wharry University of Waikato <i>Carbonaceous materials from the pyrolysis of biomass: Chemistry, properties, and some potential applications</i>
2.00 pm	Georg Ripberger Massey University <i>The intricate relationship between vapour phase residence time and biochar/biofuel yield properties</i>

- 2.30 pm **Rory Bell**
CRL Energy Ltd
Second generation biofuels produced from lignocellulosic feedstocks in a New Zealand context
- 3.00 pm *Afternoon Tea – Symposium Group Photo*
- SESSION FOUR Chair **Shusheng Pang**, University of Canterbury
- 3.30 pm **Lloyd Donaldson**
Scion
Nanoscale interactions of polyethylene glycol with Pinus Radiata biofuel substrate
- 4.00 pm **Martin Atkins**
University of Waikato
Industrial ecology, symbiosis, and process integration – The way forward to a sustainable bio-based energy economy?
- 4.30 pm **Stephan Heubeck**
NIWA
A valuable loop – Anaerobic digestion to reduce waste and internally recycle value within biofuel schemes
- 5.00 pm Conclusion **Ian Suckling**, Scion
- 5.05 pm Close of ABRN Symposium
- 7.00 pm ABRN/BANZ Dinner

Abstracts

Keynote speakers

The potential and challenges of “drop-in” biofuels

Sergios Karatzos, Jim McMillan Jack Saddler

This presentation will outline the main points of a recently published [IEA Bioenergy Task 39 report on drop-in biofuels](#). Fossil-based transportation fuels are finite and are becoming more costly to source and process. At the same time the oil refining sector is increasing parts of its processing capacity to be able to process “heavier and sourer” crude oil. Although biofuels have been advocated as a renewable alternative, current biofuels such as ethanol and biodiesel are too oxygenated to be readily “dropped into” the existing transportation fuel infrastructure (refineries, gas stations, automobile engines, etc.). Less oxygenated and more fungible biofuels have been termed as “drop-in”. These biofuels can be made from various intermediates such as sugars, lipids and “bio/syngas” but they need further processing in order to remove oxygen and yield a hydrocarbon-like biofuel. Most “drop-in” biofuel technologies remove oxygen from biomass by using large amounts of hydrogen gas as an input. As an example, it is estimated that the US would need to triple its current refinery-based hydrogen production capacity to meet the advanced biofuel RFS mandate with pyrolysis-type drop-in biofuels. At the same time a similar amount of additional hydrogen will be needed to meet the projected US oil industry hydrogen requirements for processing crude oils of deteriorating quality. Lipid-based “drop-in” biofuels are already commercial at scale while fermentation-based “drop-in” biofuels appear more problematic (low productivities of 0.1-0.7 g/L/h). Although thermochemical processes show promise (once selectivity and catalyst life issues are resolved) they will require significant hydrogen inputs. The competing technologies, pathways for insertion to oil refineries and potential challenges for “drop in” biofuels, such as the availability of cheap and plentiful hydrogen, will be discussed.

Designing plant cell walls for deconstruction: Using monolignol ferulate conjugates to introduce ester bonds into the lignin backbone

John Ralph

Great Lakes Bioenergy Research Centre

USA

Lignin remains one of the most significant barriers to the efficient utilization of lignocellulosic substrates, in processes ranging from ruminant digestibility to industrial pulping, and in the current focus on biofuels production. Structural studies of lignins in a range of normal plants, as well as in mutants and transgenics misregulated in various plant cell wall pathway genes, have shown that lignification is a remarkably metabolically plastic process. Plant lignins that differ, sometimes strikingly, from those derived from the traditional primary two monolignols, coniferyl and sinapyl alcohol, are now well authenticated. Such changes in lignin composition and structure may positively or negatively impact cell wall utilization. A few approaches hold considerable promise for reducing the severity and energy demands of various processes.

Redesigning lignin, the aromatic polymer fortifying plant cell walls, to be more amenable to chemical depolymerization can lower the energy required for industrial processing. We have engineered plants to introduce ester linkages into the lignin polymer backbone by augmenting the monomer pool with monolignol ferulate conjugates. We will describe the isolation of a transferase gene capable of forming these conjugates, and its xylem-specific introduction into Poplar and other plants. Enzyme kinetics, in planta expression, lignin structural analysis, and improved cell wall digestibility after mild alkaline pretreatment, demonstrate that these trees produce the monolignol ferulate conjugates, export them to the wall, and utilize them during lignification. Tailoring plants to employ such conjugates during cell wall biosynthesis is a promising way to produce plants that are “designed for deconstruction.”

Speakers

Overview on recent advances and challenges in biomass to liquid fuels through thermochemical processing routes

Professor Shusheng Pang

Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

This presentation will firstly introduce the latest R&D progresses at the University of Canterbury on thermochemical conversion technologies for biomass energy and biofuels. The technologies developed include advanced biomass gasification, gas cleaning, liquid fuel synthesis (Fischer-Tropsch), and biomass pyrolysis for biomass densification and for high grade liquid fuel. Issues and challenges will also be discussed towards commercialisation of the bioenergy technologies. Following this, selected international projects on biomass gasification and pyrolysis will be discussed.

Biomass Pre-treatments to Improve the Properties of Fast Pyrolysis Bio-oil

Tansy Wigley, Shusheng Pang, Alex C.K. Yip

Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

The fast pyrolysis process has been recognised as a promising method to produce bio-oil from biomass, which can be used as a potential liquid fuel. However, use of the bio-oil is currently restricted to combustion applications due to the high content of oxygen, inorganics, water, solids and acids. Upgrading bio-oil through catalytic cracking and hydrotreating has been extensively researched, but the high costs and low yields associated with both processes remain challenges for commercialisation. This study experimentally investigated the effects of biomass pre-treatments on the quality of bio-oil. A pre-treatment sequence was developed to incorporate both biomass demineralisation and torrefaction. Demineralisation reduced the inorganic content in raw biomass, while torrefaction targeted at a reduction in the moisture, oxygen and carboxyl content. The liquid produced during torrefaction contains primarily acetic acid, this solution can be recycled as the demineralisation reagent. Biomass was initially leached with a 1 % acetic acid solution followed by torrefaction between 230 and 280 °C for 20 min. Bio-oil from pyrolysis of pre-treated biomass (torrefaction at 280 °C) contained 1.3 and 0.1 wt% water and acetic acid, respectively, compared to corresponding values of 24 and 3.4 wt% for the bio-oil from pyrolysis of untreated wood. These reductions were more pronounced than pyrolysis of only leached or torrefied biomass. This indicates that water, inorganics and carboxylic acids all have a catalytic role during pyrolysis to catalyse secondary reactions of primary pyrolysis vapours, and therefore enhance process water and acids. Further work has been planned to up-grade the bio-oil from pyrolysis of pre-treated wood under a joint PhD project by University of Canterbury and Scion which will be presented separately at ABRN 2014 (Xing et al. 2014).

Enhancements of wastewater treatment high rate algal ponds for biofuel production

Rupert Craggs*, Jason Park, Stephan Heubeck, Donna Sutherland

National Institute of Water and Atmospheric Research Ltd (NIWA), P. O. Box 11-115, Hamilton, New Zealand. (+64-7-8591807; E-mail: rupert.craggs@niwa.co.nz)

High Rate Algal Ponds are part of Enhanced Pond Systems that promote natural biological processes to treat and recover resources from municipal, agricultural and industrial wastewaters. These systems also include Covered Anaerobic Ponds, Algal Harvest Ponds, and Maturation Ponds. Covered Anaerobic Ponds are a cost-effective and easy to operate solids separator and anaerobic digester. The cover enables capture of odour and biogas that would otherwise be released to the atmosphere. Biogas biofuel recovers wastewater solids bioenergy as heat and power. High Rate Algal Ponds harness sunlight energy as algal growth and photosynthetic oxygen production for bacteria to aerobically breakdown the effluent providing nutrient removal and disinfection. Nutrients are assimilated into algal biomass which is then recovered in Algal Harvest Ponds. Maturation Pond treatment provides a high quality final effluent for reuse or discharge. Since the algal biomass is produced and harvested as a by-product of the wastewater treatment process and can also be anaerobically digested, it can be economically used as an additional biogas biofuel feedstock, as well as a fertilizer substitute, or even as a feed supplement depending on the wastewater used. This paper will discuss several biological enhancements that improve the performance of wastewater treatment high rate algal ponds.

Carbonaceous materials from the pyrolysis of biomass: Chemistry, properties, and some potential applications.

John McDonald-Wharry*, Merilyn Manley-Harris*, Kim Pickering*

*University of Waikato, Hamilton, New Zealand

Various types of carbon-rich solid products can be produced as either the primary product or as a co-product from the pyrolysis of biomass. A number of common chemical and structural changes occur within these materials as they are heated to various temperatures. These chemical and structural changes influence a number of material properties and can be detected on a range of different analytical instruments. This talk will give a brief overview of a range of potential applications for these carbonaceous materials and discuss some analytical techniques with potential for quality control. Some important links between processing conditions, product chemistry/structure, product properties, and suitability for various applications will also be briefly explained. Distinctions will be made between the carbonaceous materials which appear to be produced for well-established applications at industrial-scales and those that appear to be currently produced at smaller-scales for the numerous proposed applications which can be found across the existing scientific literature.

The Intricate Relationship between Vapour Phase Residence Time and Biochar/Biofuel Yield Properties

Georg Ripberger, Jim Jones and Tony Paterson

School of Engineering and Advanced Technology, Massey University, New Zealand

Contact: j.r.jones@massey.ac.nz

Long vapour phase residence times and elevated pressures during biomass pyrolysis have been recognized to increase the char yield at the expense of pyrolysis oil by a complex series of secondary reactions. This appears to be advantageous for the manufacture of biochar but not for the production of biofuel. However, an often neglected and not well studied field is their effect on the respective product properties.

Samples of radiata pine were pyrolysed in sealed glass capsules and in open crucibles in a pyrolysis gas chromatograph-mass spectrometer (Py-GC/MS). The pyrograms from the capsules reveal the formation of low molecular weight pyrolysis products and long chain alkanes, alkenes and methyl ketones at the expense of mid-range molecular weight compounds found in the open crucibles. The disappearance of methoxyl groups is also noted, indicating oxygen transfer to low molecular weight gas phase, implying the production of a high quality bio-oil.

Because it is not possible to study the residue char from the Py-GC-MS samples, a separate investigation compared pine char and its respective tar coke produced at 300°C and 600°C. Differences were apparent across a range of measures, e.g. visually, ultimate analysis, and pH. Relating this to biochar production, longer vapour phase residence times will lead to biochars with a higher fraction of tar coke. This most likely explains some of the differences in biochar-soil interaction reported in the literature.

In conclusion, the results reveal that for economic manufacture of pyrolysis products, biochar and biofuel, a holistic approach is needed that includes both slow and fast pyrolysis within the bio-refinery. It outlines the importance of further research in this area.

Second generation biofuels produced from lignocellulosic feedstocks in a New Zealand context

Rory Bell

CRL Energy Ltd

The limitations of first-generation biofuels produced from food crops have caused greater emphasis to be placed on second-generation biofuels produced from lignocellulosic feedstocks. Although progress continues to be made to overcome technical and economic challenges, production will continue to face major constraints to commercial viability. The logistics of providing a competitive, all-year-round, supply of biomass feedstock to a commercial-scale plant is challenging, as is improving the performance of the conversion process to reduce costs. Continued investment in research coupled with appropriate support mechanisms, are essential if full commercialisation is to be achieved any time soon.

Invasive plant species have been introduced either deliberately or accidentally since the first human settlement of New Zealand. These species, almost without exception, have been detrimental to the survival of New Zealand native fauna and flora and are costly to control. Plant species include scotch broom (*Cytisus scoparius*), blackberry (*Rubus fruticosus*) and gorse (*Ulex europaeus*). The last is a major invasive plant species and covers up to 900,000 hectares in New Zealand. Eradication with current technology is expensive, time consuming and virtually impossible; therefore it would be advantageous to exploit these in such a way as to add economic value to the resource. One method to achieve this is to utilise them in the production of a second generation biofuel.

In this study second generation biofuels have been produced from *Ulex europaeus* feedstock utilising a biomass conversion process which results in the removal of water and volatiles through the partial decomposition of wood components (predominately hemicellulose). The biofuels will be evaluated for their potential use as supplement fuels to existing fuel supplies utilising standard energy conversion processes. This includes using the energy densified chars for combustion. The benefits and limitations of exploiting these types of feedstock and associated advanced biofuels, on a scale and in a context relevant to New Zealand, will be discussed and their impact evaluated.

Nanoscale interactions of polyethylene glycol with *Pinus Radiata* biofuel substrate

Lloyd A. Donaldson, Roger H. Newman, Alankar Vaidya

Scion, Te Papa Tipu Innovation Park, 49 Sala Street, Rotorua 3046, New Zealand; telephone +64 7 343 5581; fax +64 7 348 0952;

e-mail: lloyd.donaldson@scionresearch.com

Correspondence to: Lloyd Donaldson

ABSTRACT: Non-productive adsorption of cellulose degrading enzymes on lignin is likely to have a negative effect on the rate and extent of enzymatic conversion of lignocellulosic substrate to sugars. Additives such as polyethyleneglycol (PEG) may reduce this non-productive interaction but the exact mechanism is not known. We have used confocal fluorescence microscopy combined with Förster resonance energy transfer (FRET) as a molecular ruler, to measure nanoscale interactions between lignin present in thermo-mechanically pre-treated *Pinus radiata* substrate, and fluorescently labelled PEG. This work shows that PEG interaction with lignin occurs mainly within particles derived from secondary walls, with little or no penetration into fragments derived from the middle lamella. This information on the PEG-substrate interaction will assist in rationalizing pre-treatment methods to reduce the recalcitrance of softwood biofuel substrates.

KEYWORDS: fluorescence microscopy; FRET; polyethyleneglycol; cellulose; cellulase; radiata pine; biofuel substrate

Industrial Ecology, Symbiosis, and Process Integration – The Way Forward to a Sustainable Bio-based Energy Economy?

M. J. Atkins¹, M. Jack², M. R. W. Walmsley¹, T. G. Wamsley¹

¹ Energy Research Group, School of Engineering, University of Waikato, Hamilton, NZ

² Scion, Rotorua, NZ

matkins@waikato.ac.nz

The fields of Industrial Ecology (IE) and Industrial Symbiosis (IS) have emerged over the past two decades and are based on the premise that to be sustainable industrial production should mimic natural ecosystems with closed-loop, cascading flows of materials and energy. The analogy has its limitations and the methodologies developed to date have largely been qualitative and descriptive in nature and had limited application. By contrast Process Integration (PI), developed independently and concurrently as a distinct branch of chemical engineering, provides holistic or systems approach to process design, synthesis, and optimisation of industrial production. A synthesis of the methods (at least in part) could yield valuable solutions to the areas of energy and process efficiency, water and waste reduction, and improved environmental outcomes. This paper will outline the relationship between these three approaches and offer suggestions as to how they might be beneficially applied to biofuel production via biorefineries. Illustrative examples will be given where to demonstrate the advantages these various approaches.

A valuable loop – Anaerobic digestion for reducing waste and internally recycling value within biofuel schemes

Stephan Heubeck

A broad range of proven and experimental technologies can be employed to convert various biomass resources into transport biofuels. These technologies never convert all of the input biomass into sellable end-products, and often substantial amounts of waste and by-products are co-produced with the biofuel. Increasing the conversion efficiency of the various technologies is important for maximising desirable outputs, but fundamental chemical, physical and biological limits will always provide barriers for maximising conversion efficiencies. In order to maximise input utilisation and reduce the amount of low value wastes and by-products further, the application of internal recycling becomes an important aspect for many biofuel schemes. Internal recycling not only tends to increase the financial attractiveness, but also the environmental performance of many biofuels technologies. Anaerobic Digestion (AD) is a key technology in this regard, which has a proven track record with several established transport biofuel technologies, producing a uniform and versatile fuel – methane-rich biogas – more or less irrespective of the original waste input composition. The methane-rich biogas obtained from anaerobic digestion can often be used to satisfy internal energy demands for steam raising or electricity, while eventual biogas surpluses can be exported relatively easily in the form of electricity or purified methane gas where gas pipeline infrastructure is available. The bio-ethanol industry has used anaerobic digestion of spent liquor for many decades, providing heat energy for ethanol distillation. Both tank and pond digesters are in use in various applications around the world, and there is a great growth potential for this synergetic application in North and South America in particular. Likewise biodiesel manufacture is profiting from the anaerobic digestion of processing wastes and by-products in New Zealand and around the world. Biodiesel glycerol is the main AD feed stock provided by biodiesel manufacture that has recently been successfully tested for low temperature AD in NZ. Internationally the processing of problematic oil fruit cakes such as from i.e. the Castor oil plant provides further scope for synergies between biodiesel manufacture and AD.

In New Zealand hopes for the large scale conversion of woody biomass into transport biofuels are high. In particular the physical / biological conversion pathways (i.e. scarification / fermentation) provide a large scope for synergies with AD, in particular in regards to spent liquor treatment. However woody biomass differs from conventional biofuel production wastes and by-products. None the less the AD process is very adaptable and flexible and offers one of the best options for recovering additional value from wet and / or dilute wastes in particular. In many cases woody biomass processing wastes that cannot be treated in isolation become amenable for AD when co-digested with other waste substrates. Smart management and co-operation, rather than high-tech, may therefore very well be the key for using AD to enhance the financial and environmental attractiveness of transport biofuel manufacture from woody biomass.

Posters

Measuring the cellulose accessibility of steam-exploded *Pinus radiata* wood using the Simmons' stain procedure

Jessica MacAskill¹, Merylyn Manley-Harris¹, Ian Suckling² and John Lloyd²

¹ University of Waikato, Hamilton

² Scion, Rotorua

Forests based on plantation grown *Pinus radiata* offer a readily available lignocellulosic biomass that can be used to produce biofuels. One route for biofuel production involves the enzymatic hydrolysis of biomass into sugars, which are then converted to biofuels. Pretreatments are required for all lignocellulosic biomass, in order to expose cellulose and hemicelluloses to enzymes and increase enzyme digestibility. However, softwoods, such as *P. radiata*, are more recalcitrant in nature towards enzyme hydrolysis and therefore, require more severe pretreatments. The pretreatment type and conditions affect both cellulose accessibility and the formation of inhibitors or compounds that retard enzyme hydrolysis.

As part of a project to evaluate the relative importance of soluble and insoluble fibre components at inhibiting enzyme activity, a series of *P. radiata* substrates were prepared under different conditions, but to a constant cellulose accessibility. One method for evaluating the cellulose accessibility of a substrate is the Simmons' Stain procedure. This method measures how well two dyes with a strong affinity for cellulose are adsorbed by the substrate. The adsorption of the two dyes (direct orange (DO) and direct blue (DB)) to the substrate indicates how many small and large pores are present, and consequently the cellulose accessibility.

This poster will give an overview of the use of Simmons' stain method for evaluating the cellulose accessibility of *P. radiata* that has been steam exploded using a variety of temperatures, times, acid catalysts and levels of ball-milling. Ball-milling is used here to increase the cellulose accessibility without changing the substrate chemistry, thus, allowing the substrates to be compared at a common cellulose accessibility.

A Thermodynamic Analysis of Bio-oil Upgrading via Hydrotreatment

Muthasim Fahmy, Michael Jack and Ferran De Miguel Mercader

Scion, Private Bag 3020 Rotorua 3046

Bio-oils derived from biomass liquefaction technologies such as fast pyrolysis have low energy densities ($\sim 20 \text{ MJ kg}^{-1}$) compared to conventional fossil fuels ($\sim 40 \text{ MJ kg}^{-1}$). In addition to low heating values, such bio-oils have poor quality with undesired properties such as chemical instability and corrosiveness making them unsuitable as a direct substitute for conventional fossil fuels. Upgrading bio-oils through thermochemical treatment to reduce the fuel O/C ratio and increase H/C ratio can increase the heating value as well as mitigate some of these undesirable properties. An appropriate use of thermodynamics that takes into account not only the energy and material flows, but also how the work potential of energy streams are lost during the process is a valuable tool to develop more efficient technologies. Bio-oil upgrading involves transforming fuels with complex composition and with reaction pathways that are often not well understood. Nevertheless, it is possible to apply theoretical and semi-empirical techniques developed for exergy analysis of combustion processes in a manner independent of the reaction pathways to make some general observations on the limits of process efficiency. These techniques are illustrated for a generic hydrotreatment process upgrading bio-oils to less than 2% oxygen content. It is found that up to $\sim 40\%$ of the exergy carried into the process by hydrogen can be lost in such a process. Furthermore, the fuel's initial to final (O/C,H/C) coordinates transitions are restricted by atomic species mass balance and attempts to increase the H/C of lower O/C feedstock will incur larger penalties in exergetic efficiency and resource waste.

APPITA program

WEDNESDAY 15 OCTOBER 2014

FIBRE VALUE CHAIN CONFERENCE OPENING BREAKFAST <i>Rimu/Tawa Combined</i>				
9 am	<p>Welcome Carlo Bigaran Appita President</p> <p>Keynote Presentation <i>Growing and transforming the New Zealand forest industry</i> Warren Parker Chief Executive Officer, Scion, New Zealand</p> <p>Keynote Presentation <i>Effective business strategies for biofuels and biochemicals</i> Dewitt Patterson Biofuels and Biochemicals Program Director, Beca AMEC, USA</p> <p>Keynote Presentation <i>Building innovative capacity through people development</i> Michael Hartman Chief Executive Officer, ForestWorks, Australia</p>			
10 am	Morning tea			
	<p>APPITA TECHNICAL SESSION Efficiency and Process Improvement Chair: Bob Johnston</p> <p><i>Miro</i></p>	<p>APPITA TECHNICAL SESSION Research and Development Chair: Nafty Vanderhoek</p> <p><i>Rimu</i></p>	<p>APPITA TECHNICAL SESSION Engineering and Management Chair: Tony Johnson Proudly sponsored by:</p>  <p><i>Tawa</i></p>	<p>APPITA MEETINGS</p> <p><i>Card Room</i></p>
10 am	<p>Effect of a new high adhesion creping technology on machine stability and tissue quality <i>Spoulos¹, L S Bonday², D Hätzingkoku³, F Liu⁴</i></p> <p>¹Asaleo Care Australia ²Nalco Global ³Nalco W ⁴Nalco WPS</p>	<p>Chemical crosslinking improves creep resistance of corrugated board <i>ES Steen¹, N Dooley, J Capricchio, R Parr, I Suckling</i></p> <p>Scion, New Zealand</p>	<p>Management in tough times <i>Beca AMEC, New Zealand</i></p>	
10 am	<p>Energy saving and sheet formation improvement through monitoring the consistency in forming section <i>Ali, G Cristini</i></p> <p><i>Cristini S</i></p>	<p>Chemical measurement to study the effect of paper and printing variables on linting <i>R Leslani¹, W J Batchelor¹, P B</i></p> <p>¹APPI, A ²Norske Skog, Boyer, A</p> <p>AMEC</p>	<p>End markers for projects <i>erson</i></p>	
10 pm	<p>Effect of feeding strategy on starch performance <i>nanen, J Käyhkö</i></p> <p><i>Mikkeli University of Applied Science</i></p>	<p>Insight into antioxidant capacity of kraft lignin in chemical refining and thermal durability of refined pulp sheets <i>skä, T Vilhelä, T Vuorinen</i></p> <p><i>Aalto University</i></p>	<p>Mill expansion at SAPPi Ngodwana <i>f, K Mukherjee², S Baker²</i></p> <p>¹AMEC ²Beca AMEC, New Zealand</p>	
10 pm	Lunch			
	<p>APPITA TECHNICAL SESSION Efficiency and Process Improvement Chair: Tom Clark</p> <p><i>Miro</i></p>	<p>APPITA TECHNICAL SESSION Resource Management Chair: Gil Garnier</p> <p><i>Rimu</i></p>	<p>APPITA TECHNICAL SESSION Biorefining, Bioenergy, Cogeneration and Bioproducts Chair: Ian Suckling</p> <p><i>Tawa</i></p>	<p>APPITA MILL MANAGERS FORUM Proudly sponsored by the Manildra Group Invitation Only</p> <p><i>Card Room</i></p>
1 pm	<p>High-freeness BCTMP conversion at Pan Pac, New Zealand <i>esuer¹, R Jones², P Allan², C McParland²</i></p> <p>¹Andritz ²Pan Pac, New Zealand</p>	<p>Sign driven world of cellulose – from bulk to luxury? <i>llas¹, P Heikkilä¹, K Kataja¹, J Salmela¹, J Lehmonen¹, J Kataja¹, T Hänttinen¹, A Har</i></p> <p>¹Andritz ²Pan Pac, New Zealand</p> <p>¹VTT Technical Research Centre ²Aalto University ³Tampere University of Technology</p>	<p>Reducing the production cost of urea from black liquor and <i>due eri¹, J Nguyen¹, T Truong¹, K Wagstaff¹, D Wolechowski¹, M Wong¹, Hadley², G G wall¹, A J Dahl¹.</i></p> <p>¹Lulea Univ of Technology, ²Monash University, A</p>	<p>Facilitator - Jim Henneberry</p> <p>Guest Speakers Outi Juntti Principal, Pöyry Management Consulting</p> <p>Todd Saunders General Manager Australia, Sanitarium Health & Well Company</p> <p>Proudly sponsored by:</p>  
1 pm	<p>Benefits of optimisation based production scheduling within integrated pulp and paper operations <i>niainen¹, N Lasslett², C Goulamis², L Gomez²</i></p> <p>¹Greycor Ltd ²Proceq Pty Ltd, A ³Greycor Latin America, A</p>	<p>South Australia Cellulose Value Chain Study <i>derhoek¹, J Kettle², T Ahlqvist²</i></p> <p>¹VTT Technical Research Centre, A ²VTT Technical Research Centre, A</p>	<p>Native resin removal technologies <i>rdson, R Sargent, K Murton</i></p> <p>Scion, New Zealand</p>	
1 pm	<p>Comparison of foaming agents for selective froth flotation of actives from Pinus radiata TMP process water <i>hti¹, T Lewis¹, J Stack¹, D Richardson²</i></p> <p>¹University of T ²Nors</p>	<p>Can biomass satisfy our thirst for liquid fuels? An Australian perspective <i>more</i></p> <p><i>Covey Consulting, A</i></p>	<p>Mass co-firing and refuse derived fuel fired boiler considerations <i>arvey, R M Harvey</i></p> <p><i>Covey Consulting, A</i></p>	
1 pm	Afternoon Tea			
	<p>APPITA TECHNICAL SESSION Efficiency and Process Improvement Chair: Paul Robilliard</p> <p><i>Miro</i></p>	<p>APPITA TECHNICAL SESSION Sustainability Chair: Ralph Coghill</p> <p><i>Rimu</i></p>	<p>APPITA TECHNICAL SESSION Paper and Board Manufacture Chair: Carlo Bigaran</p> <p><i>Tawa</i></p>	<p>APPITA MILL MANAGERS FORUM Proudly sponsored by the Manildra Group Invitation Only</p> <p><i>Card Room</i></p>
1 pm	<p>Technical review of multi-fuel bubbling fluidised bed boilers for paper industry wastes, with predictive models for metals and SO₂ emissions <i>more</i></p> <p><i>Covey Consulting, A</i></p>	<p>Geographically dependent environmental impacts of pulp and paper effluent recovery systems <i>annon, G Garnier, W Batchelor</i></p> <p><i>BiOPRIA, Monash University, A</i></p>	<p>Effect of dissolved organic material on the adsorption of wood preservatives onto bentonite <i>Sk¹, D Heier², D Richardson², T Lewis¹, T Blackstock</i></p> <p>¹University of Tasmania, ²Norske Skog A</p>	<p>Mill Managers Forum is a regular feature of the Appita Technical Conference program.</p> <p>The main aim of the forum is to provide a means for senior managers from the Australian & New Zealand Pulp and Paper Industry to meet and address critical management issues in today's mill environment. It is an invitation only event, and is a consensus agenda – managers select the topics.</p>
1 pm	<p>Online refractometer for controlling COD removal in kraft pulping wastewater treatment plant <i>akainen¹, R Kopra², T Laukkanen¹, T Tarr², O Dahl²</i></p>	<p>Mediation of CCA-treated Pinus radiata as a pulping residue <i>Scion, New Zealand</i></p>	<p>Complete paper plant optimisation and solid waste reduction <i>retorius</i></p> <p><i>Australian Paper, Maryvale Mill, A</i></p>	

	¹ Aalto University ² Mikkeli University			topics are generally wide-ranging, covering culture of safety, water and energy management, industrial relationship skills shortages and lean manufacturing.
pm	aging lime kiln ring formation at Australian Paper, Maryvale Australian Paper Maryvale Mill, A	WBC Highlights anderhoek ¹ , D E Richardson ² ,	ographic printing process for the deposition of latex-based ier dispersion coatings on linerboard ic, R Parr, M Patel Scion, New	
pm	Session close			
pm	APPITA GALA DINNER Proudly sponsored by  Skyline Restaurant, Rotorua			

THURSDAY 16 OCTOBER 2014

am	Advanced Biofuels Research Network (ABRN) Symposium Fuels and Co-Products: The Biorefinery Concept Plenary Session <i>Rimu/Tawa Combined</i>			
am	Welcome Michael Jack, SCION			
am	Chair: Ian Suckling, SCION Keynote Presentation - webcast <i>The potential and challenges of 'drop-in' biofuels</i> Sergios Karatzos Senior Manager Project Development – Steeper Energy Canada Ltd, Canada			
am	Keynote Presentation - webcast <i>Designing plant cell walls for deconstruction: Using monoglignol ferulate conjugates to introduce ester bonds into the lignin backbone</i> Professor John Ralph Great Lakes Bioenergy Research Centre in the US			
10 am	Morning Tea			
	ABRN SYMPOSIUM Chair: Martin Atkins, University Waikato <i>Miro</i>	APPITA TECHNICAL SESSION Engineering and Mill Reliability Chair: Bob Johnston <i>Rimu</i>	SAFETY & OPERATIONS MANAGEMENT Jointly hosted by Appita and the Pulp & Paper Industry Health, Safety & Environment Unit <i>Tawa</i>	APPITA MEETINGS <i>Card Room</i>
10 am	review on recent advances and challenges in biomass to through thermochemical processing routes University of Canterbury, New	VISION: Measure, control, optimise Voith Paper, In	11:00 am Chair: Denise Campbell Burns National Coordinator Health, Safety and Environment Unit, CFMEU Pulp and Paper Workers	Meeting room is available. To book a time see Appita registration desk.
10 am	mass pre-treatments to improve the properties of fast pyro oil eyi, S Pang ¹ , A C K Yip ¹ , F De Miguel Mercader ² , D van de Pas ² ¹ University of Canterbury, New ² Scion, New	er hammer and other pipe transient flow problems ovey, R Patterson Covey Consulting, A	11:05 am Keynote Presentation Working safer – changing the way we manage health and safety at work Karl Simpson, Principal Advisor, Ministry of Business, Innovation & Employment Howard, Chief Inspector, Northern, WorkSafe N land	
10 pm	ancements of wastewater treatment high rate algal pond uel production ggs, J Park, D Sutherland, S Heubeck NIWA, New	sual pressure safety devices ovey, R Patterson Covey Consulting, A	11:45 am Keynote Presentation <i>Building a safety culture in a competitive manufacturing environment - case study</i> Paul McGinn, Senior Projects Manager Major Capital Projects, Fonterra Co- operative Group Limited David Williams, Consultant, Markham Williams a ociates Limited	
10 pm	Lunch			
	ABRN SYMPOSIUM Chair: Rupert Craggs, NIWA <i>Miro</i>	APPITA TECHNICAL SESSION Pulping and Bleaching Chair: Tony Johnson <i>Rimu</i>	SAFETY & OPERATIONS MANAGEMENT <i>Tawa</i>	APPITA MEETINGS <i>Card Room</i>
pm	onaceous materials from the pyrolysis of biomass: mistry, properties, and some potential applications. onald-Wharry, M Manley-Harris and K Pickering University of Waikato, New	ydrolysis-TMP Pulping: an opportunity to reduce refining ry and join the biorefinery race? yst, K D Murton Scion, New	note Presentation <i>Safety - Equipment reliability - maintenance best practices – connect</i> Probst, Consultant, IDCON Australasia	Meeting room is available. book a time see Appita registration desk.
pm	intricate relationship between vapour phase residence ti biochar/biofuel yield properties berger, J Jones and T Paterson Massey University, New	covery boiler reduction degree data review kanen ¹ , J Butler ² ¹ Metso Automation Inc. ² Metso Automation I	ity and competitive manufacturing - making the link Woods, Director, IndustryEdge	
pm	ond generation biofuels produced from lignocellulosic stocks in a New Zealand context CRL Energy Ltd, New	HDRAWN - Effects of CMC on refining of fibres of differ hology eng ¹ , E I Chen Wang ² , S W Tsai ³ ¹ Da-Yeh University ² Taiwan Forestry Research Institute ³ Cheng Loong Corp.	pendent enquiry into safety in the forest industry. ard Miller, Strategic Advisor, FIRST Union	
pm	Afternoon Tea			
	ABRN SYMPOSIUM Chair: Shuseng Pang, University Canterbury <i>Miro</i>	APPITA TECHNICAL SESSION Pulping and Bleaching Chair: Tony Johnson <i>Rimu</i>	SAFETY & OPERATIONS MANAGEMENT <i>Tawa</i>	APPITA MEETINGS <i>Card Room</i>
pm	oscale interactions of polyethylene glycol with Pinus Rad uel substrate aldson, R H Newman and A Vaidya Scion, New	mill and chemical recovery control with advanced analy om trees to final products ng ¹ , G Downes ² ¹ FITNIR Analyzers Inc. ² Forest Quality PIL, A	iting new legislative requirement - machine guarding h Read, New Zealand Manager, Pilz	Meeting room is available. book a time see Appita registration desk.

		Directory paper
duction capacity	(t)	155 000
content	(%)	0

umber of employees: 183

orske Skog Tasman
etcher Avenue
ivate Bag
werau
y of Plenty
ew Zealand

l: +64 7 323 3999
x: +64 7 323 3790

eneral Manager: Peter McCarty

FRIDAY 17 OCTOBER 2014

Bioenergy Association of New Zealand (BANZ) Conference Using Commercially Ready Technologies to Bring Biofuels to the Market	
	Plenary Session <i>Miro Room</i>
am	Welcome and Introduction Brian Cox BANZ Executive Officer
am	Official Opening Mauriora Kingi: Mihi Hon Steve Chadwick Mayor, Rotorua
am	International Keynote Speakers <i>Thermochemical platforms from laboratory to industrial scale</i> Dr Matti Reinikainen Principal Investigator, VTT Technical Research Centre of Finland (by video link)
am	An overview of technologies for the production of advanced biofuels and their progress towards commercialisation Dr Ian Suckling Research Leader Bioenergy and Biofuels, Scion
5 am	Morning tea Proudly sponsored by  Applied Instrument Group <small>Measurement and Control Specialists</small>
Developments in the production and markets of transport biofuels and their co-products	
5 am	<i>Commercial aviation – a guaranteed future market for sustainable biofuels</i> Tony Steer Environmental Fuels Manager Flight Operations and Safety, Air New Zealand
5 am	<i>Renewable fuels for marine transport</i> Peter Wells Manager Shipping Services, Interislander Ferries / KiwiRail, New Zealand
5 am	<i>Co-product opportunities and future directions for the New Zealand pulp and paper industry</i> Dr Tom Clark Manager Technical Services, Carter Holt Harvey Pulp, Paper and Packaging, New Zealand John Reid Strategic Projects Manager, Carter Holt Harvey Pulp, Paper and Packaging, New Zealand
5 am	Maximising revenues and minimising waste in fuel and feed bio-refineries Geoff Bell Chief Executive Officer and Chairman, Microbiogen, Sydney Australia
5 pm	<i>Australian biomass resourcing for biocrude</i> Ross Patterson and Geoff Covey Covey Consulting Pty. Ltd., Australia
5 pm	Lunch Proudly sponsored by  grow ROTORUA <small>ROTORUA REGIONAL DEVELOPMENT AUTHORITY</small>
Commercialising technologies for producing transport biofuels	
pm	<i>Small scale renewable diesel – the future of commercial fuel</i> Peter Brown Miscanthus New Zealand Ltd Adam Bosschieter Everett Hale REEP Development LLC, USA
pm	<i>New technology for biofuel production with Fischer-Tropsch</i> Brendon Miller Consultant, Johnson Matthey Davy Technologies, London UK
pm	<i>Techno-economic assessment of some wood to biofuels options using the WoodScape Model</i> Peter Hall Senior Scientist, Scion, Rotorua New Zealand
pm	<i>Updating Licella's progress towards full commercialisation of its technology</i> Steve Roger Licella, Sydney Australia
pm	Afternoon Tea
pm	<i>Mild hydrotreating of biomass pyrolysis oils to produce a suitable refinery feedstock</i> Bob Baldwin (webcast) Principal Scientist in the National Bioenergy Centre at the National Renewable Energy Laboratory (NREL) Colorado USA
pm	<i>Progress towards commercialisation of AES's Fast Pyrolysis developments</i> Gavin Hedley Alternative Energy Solutions
pm	<i>Opportunities for the use of lignin derived products</i> Kirk Torr Senior Scientist, Scion, New Zealand
pm	Panel Discussion and Closing Remarks Chris Mulcare and Ian Suckling

pm	Conference Close Brian Cox BANZ Executive Officer
pm	Session Close



The Symposium has been sponsored by:



**MINISTRY OF BUSINESS,
INNOVATION & EMPLOYMENT**
HIKINA WHAKATUTUKI

SCION 
forests · products · innovation

Further Symposium details can be found at www.abrn.org.nz. For all enquiries, please email:
biofuels.symposium@scionresearch.com.