

# Promises and challenges for woody biomass to biofuels and biochemicals – a review

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Karlsruhe Institute Technology's demonstration plant of biomass pyrolysis followed by entrained flow gasification (BioliqR project), Karlsruhe, Germany. The biomass feeding rate is 1 oven dry tonne per hour

## Abstract

Biomass has been recognised as the most promising renewable resource for the production of biofuels and biochemicals, which can substitute those presently derived from fossil fuels. However, due to the complicated physical structure and chemical composition of the biomass, there are technical challenges for commercialisation of the new technologies and processes. This review presents recent developments in woody biomass to biofuels and biochemicals using both thermochemical and biotechnology processes, although more focus is given to the thermochemical conversion technologies. Promises and challenges in each pathway are discussed and a future perspective is proposed.

## Introduction

At present, the New Zealand forestry sector harvests 30.5 million m<sup>3</sup> logs p.a. (2016), with 17.4 million m<sup>3</sup> being exported as logs (NZFOA, 2017), which may potentially be used for high-value products in the future. In addition, three million tonnes of forest and wood processing residues are potentially available for new products, which are either lying on the forest floor or used as boiler fuel (Hall & Gifford, 2007). It is shown that the wood availability in New Zealand will steadily increase in the 2020s leading to 35 to 40 million m<sup>3</sup> p.a. (MAF, 2010).

The current wood processing capability in New Zealand is limited and the world markets for most conventional wood products such as timber, medium-

density fibreboard (MDF) and pulp are very competitive. Therefore, exploring new and high-value products from woody biomass is urgently needed for the New Zealand forest industry. On the other hand, the chemicals presently used in the chemical, manufacturing and clothing industries are largely derived from fossil fuel resources (petroleum, natural gas and coal), and this has caused concerns due to reduced reserves and adverse environmental impacts. Biomass has been recognised as the most promising renewable resource to substitute fossil fuels for the production of biofuels and biochemicals.

In the past two decades, extensive research and development has been performed both in New Zealand and globally, and some technologies have been successfully implemented at commercial scale. However, most of the new technologies are still at laboratory or pilot scale and some are at demonstration scale. This review provides a brief description of recent developments and challenges in the utilisation of woody biomass for various biofuels, including gaseous and liquid fuels, and biochemicals, using different conversion technologies. Also, the application of bio-char is discussed due to increasing interest in it applications and rapid advancements.

## Woody biomass to liquid and gaseous fuels

### Liquid biofuels

Extensive research has been conducted to convert biomass to liquid fuels and the pathways include: (1) biomass pyrolysis followed by bio-oil upgrading; (2) biomass liquefaction and bio-liquid and upgrading; (3) biomass gasification followed by gas cleaning, gas reforming and Fischer-Tropsch (FT) synthesis; (4) biomass gasification for mixed methanol and then synthesis for ethanol; and (5) biomass pretreatment, sugar conversion and fermentation for ethanol, just to mention a few. Each pathway has its advantages and disadvantages and these are discussed briefly as follows.

### Pyrolysis and liquefaction

Biomass pyrolysis is a thermochemical process in the absence of oxygen or air to convert biomass to gas, vapours and char. The vapours condense to form a liquid product or bio-oil, thus the final product from biomass pyrolysis includes bio-oil, solid char and non-condensable gas (or simply gas). The product composition (e.g. the fractions of bio-oil, gas and solid char) depends on the heating rate, operation temperature and reaction time. If the target of biomass pyrolysis is for the production of bio-oil, then rapid heating, an operation temperature of 450–600°C and a short reaction time are preferred (Pang, 2019). However, the bio-oil is a very complex mixture consisting of over 300 organic compounds with water content of 20–30% by weight. It is time-consuming to list all the individual compounds, but they can be grouped into alkanes, acetic acid, acetaldehyde, hydroxyacetone, formic acid,

glycolaldehyde, aldehydes, levoglucosan and aromatics (Wigley et al., 2017).

Bio-oil has high viscosity, is chemically unstable, and is immiscible with petroleum-derived fuels. There are some issues in distillation as it cannot be completely vapourised and is chemically unstable with heating because solid residues are formed when it is heated to 100°C. If the bio-oil is used for transport fuel, upgrading is needed, which involves a high temperature and high pressure with an application of catalysts and hydrogen. The bio-oil upgrading is a complex and costly process which hinders commercialisation. However, the bio-oil can be used in other applications, such as boiler fuel and marine engine fuel, after the separation of the aqueous phase.

Biomass liquefaction is a thermochemical process to convert biomass to bio-oil in an aqueous medium to enhance heat transfer to biomass particles, but it operates at higher pressures (5–25 MPa) and lower temperatures (200–400°C) in comparison to biomass pyrolysis (Pang, 2019). The bio-oil from liquefaction has a less complex composition, which makes further fractionation and upgrading relatively simpler than for the pyrolysis bio-oil. Recent research has investigated the application of organic solvents (ethanol, methanol and glycerol) and catalysts in order to improve the bio-oil quality under reduced pressures. Considering the higher operation costs, the bio-oil from liquefaction may be more suitable for higher-valued chemicals and materials than liquid fuel (Cheng et al., 2017).

### Gasification and Fischer-Tropsch synthesis

Biomass gasification is also a thermochemical process in which the biomass is converted to a gaseous product (termed producer gas or product gas) under an oxygen-deficient environment at an operation temperature from 650–1000°C, depending on the gasifier type and gasification agent. In general, the major gas species in the producer gas are hydrogen (H<sub>2</sub>), carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>) and methane (CH<sub>4</sub>). If air or oxygen is used as the gasification agent, the heat needed for desirable gasification reactions is provided by the combustion of combustible gas species and char, which consumes some producer gas. Air is free so many gasification plants use air as the gasification agent.

However, the nitrogen in the air dilutes the useful gas species in the producer gas and increases heat loss, resulting in lower energy efficiency. Oxygen is therefore used as the gasification agent in commercial gasification plants when producer gas with a high calorific value is needed for downstream processes. However, the oxygen is costly, particularly where it needs to be imported to the plant.

Recently technologies using steam as the gasification agent have been developed, which can produce the producer gas with a high H<sub>2</sub> content and at a more competitive operational cost compared to

oxygen gasification. The key technical challenge for steam gasification is the heat transfer process design as a conventional heat exchanger does not work properly due to the low heat transfer coefficient within the gas-solid flow and other engineering problems such as blockage. A dual fluidised bed gasification system with a circulating bed material as a heat carrier has been developed and successfully applied at various scales of plants (Saw & Pang, 2012).

The advantages of this technology are that the producer gas has high H<sub>2</sub> content and high calorific value, and the catalytic bed material can be easily applied for target gas composition. Therefore, it is ideal for the integration of the dual fluidised bed gasification technology with the FT synthesis of liquid fuel, as the ideal mole ratio of H<sub>2</sub> to CO of 2:1 can be achieved in the biomass gasification without the need to add a separate gas reforming reactor (Penniall & Williamson, 2009).

The liquid fuel from the FT process has a desirable composition, which can be refined to diesel grade liquid fuel. The challenge includes high costs and the scale-up limitation for the commercial plant. The gasification-FT synthesis of liquid fuel has been commercialised for coal to diesel (Sasol, 2005), but the system is complex and economically viable only at large scale. For biomass, it is challenging to build a large-scale plant as the collection, transportation and storage of large quantities of the biomass increases rapidly once the size is over a certain level. New FT reactors have been in development which would be suitable for small-to-medium scale plants.

### Fermentation for ethanol

The liquid fuel can be produced from biomass through bioprocessing, namely, fermentation, which is a well-known process to produce highly selective ethanol (Hamelinck et al., 2005; Mohd Azhar et al., 2017). The conventional process of lignocellulosic biomass to ethanol can be summarised in four stages: (1) pre-treatment of the biomass to disrupt the wood structure and to separate non-convertible lignin; (2) acid hydrolysis or enzymatic hydrolysis of cellulose and part of hemicellulose to fermentable sugars, ideally glucose; (3) fermentation of sugars to produce ethanol by microorganisms; and (4) purification of the produced ethanol. The key technical challenges in biomass to ethanol through the fermentation pathway are as follows.

### Conversion rate

Biomass contains about 30% lignin by weight and this is not used as it cannot be transformed into fermentable sugars. However, the lignin content is high in the biomass cell surface acting on adhesives for cell binding, which hinders the access of the hydrolysis agent to the cellulose and hemicellulose for sugar conversion.

Not all of the hemicellulose can be converted to fermentable sugars, and thus the non-fermentable biomass components result in residues in the hydrolysis and fermentation. Research has been conducted to increase the conversion efficiently for the cellulose and hemicellulose to fermentable sugars, and also to explore microorganisms or combined strains, which can ferment both glucose and other sugars such as xylose (Mohd Azhar et al., 2017).

### Challenges in biomass pre-treatment

The pre-treatment of biomass can be physical (grinding, steam explosion), chemical (acid or alkaline) or biological (using fungi to solubilise the lignin). The steam explosion and grinding of the biomass to fine particles do not separate and remove the lignin, but provide increased contact surfaces for effective acid hydrolysis and microorganism access. These physical methods have high energy demand, largely mechanical energy.

The chemical pre-treatment uses an acid or alkaline, although at low chemical concentrations, which increases costs and causes environmental concerns. Biological methods can overcome the above problems, but these may take days to weeks in time. Recent research has been conducted on a combination of the physical, chemical and biological methods to achieve the optimum results (Hamelinck et al., 2005).

### Fermentation

The fermentation process uses microorganisms, generally either bacteria, yeast or fungi, which ferment sugars to ethanol under oxygen-free conditions. Each microorganism has its most preferred sugar to ferment, and at present yeasts are commonly used, which is one of the major costs for the biomass to ethanol bioprocess (Hamelinck et al., 2005; Mohd Azhar, 2017). Recent research and development on the fermentation process has been exploring new yeast strains, or a combination of strains, which can ferment different sugars.

### Ethanol purification

The fermentation reactions occur in aqueous medium and, after the fermentation is complete, the ethanol concentration is 5–10% by weight, which means that 90–95% of water must be removed to produce pure ethanol (Offeman et al., 2008). This is normally achieved through distillation, an energy-intensive process, and the cost for the ethanol purification may account for 60% of the total costs in the commercial production of ethanol from biomass. Recent research has been focused on developing new separation technologies, including membrane separation and ethanol adsorption with zeolite molecular sieves. However, all of these new technologies are still in the development stage.

In summary, biomass to ethanol by a fermentation process can produce a high-purity liquid fuel with some challenges. The recent research and development

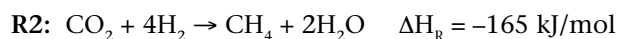
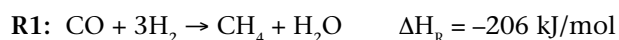
aims to increase the conversion rate to reduce energy consumption and operation costs. Specifically, these studies have been focused on more efficient pre-treatment methods with less energy demand, new strains of microorganisms which can ferment various sugars, and new purification technologies. An important consideration, although not widely reported, is to recover the value of lignin and part of the hemicellulose which are separated from pre-treatment and hydrolysis. This will help to improve the overall conversion rate and the production economy.

## Gaseous fuels

### Gasification for synthetic natural gas

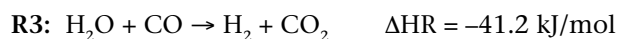
The gasification process has been described under the heading *Gasification and Fischer-Tropsch synthesis*. A typical producer gas composition from biomass gasification using a dual fluidised bed steam gasifier is: 40–45% H<sub>2</sub>, 20–25% CO<sub>2</sub>, 20–25% CO and 10–15% CH<sub>4</sub> by volume (Hongrapipat et al., 2012). This gas can be used for the production of the FT liquid fuel, as discussed already, for synthetic natural gas (or methane, CH<sub>4</sub>) or for pure hydrogen.

When the gas is used for the production of synthetic natural gas, the CO, CO<sub>2</sub> and H<sub>2</sub> in the gas are converted to CH<sub>4</sub> through methanation reactions (R1) as follows:



The CO reaction R1 is exothermic and the catalysts used for this reaction are those based on ruthenium, cobalt, nickel and iron. In fact, the CO reaction R1 is the reverse reaction of steam methane reforming, which converts methane into H<sub>2</sub> and CO under reaction conditions of 1–34 bar and 284–400°C, depending on the catalysts used.

The CO<sub>2</sub> methanation reaction (R2) is also called the Sabatier reaction after the French chemist Paul Sabatier. It is the reaction of H<sub>2</sub> with CO<sub>2</sub> (exothermic) at optimal temperatures of 300–400°C and high pressures in the presence of a catalyst to produce CH<sub>4</sub> and H<sub>2</sub>O. In effect, the Sabatier reaction can be seen as the sum of the CO methanation (R1) as discussed above and the reverse water-gas shift reaction (R3).



The CO<sub>2</sub> methanation process was not commercialised last century due to the complexity of the process and the need for gas compression. However, increasing demands for renewable energy and for using CO<sub>2</sub> provide an opportunity to commercialise this pathway for the production of CH<sub>4</sub>. The key challenges include the control of chemical reactions and reaction kinetics for the production of CH<sub>4</sub> through the optimisation of reaction conditions and the application of catalysts. It is also a key technology issue to clean

the producer gas to retain the catalyst activity over a sufficiently long reaction time.

### Gasification for hydrogen

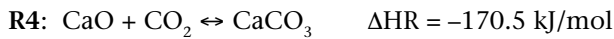
Biomass to hydrogen has attracted increasing interest in recent years due to the high demand for hydrogen as a clean fuel and clean chemical feedstock used for fuel cells, transport fuel, oil refining and urea production. However, over 95% of the hydrogen currently produced is derived from fossil fuels, primarily through steam methane reforming (Anghilante et al., 2018). Hydrogen can be produced from biomass through gasification, preferably by steam gasification. The producer gas from the biomass steam gasification also contains other species (CO, CH<sub>4</sub>), which should be converted to H<sub>2</sub> and CO<sub>2</sub>, and the mixture of H<sub>2</sub> and CO<sub>2</sub> can then be separated to obtain pure H<sub>2</sub>.

If air gasification is applied, the nitrogen present in the producer gas increases the complexity of the



Nongbua dual fluidised bed biomass gasification plant (1 MW electricity, 4 MW biomass input) in Nongbua, Thailand, which uses Güssing Renewable Energy Co. Ltd technology

process due to the need for nitrogen separation in advance, otherwise the reactions for the conversion of CO and CH<sub>4</sub> are adversely affected. Therefore, high hydrogen content and a lesser number of gas species in the producer gas are preferred, which can be achieved by steam gasification using a dual fluidised bed gasifier (Saw & Pang, 2012). Also, in this type of gasifier, catalytic bed material can be added, such as CaO, which can further enhance the hydrogen production and reduce CO<sub>2</sub> content in the producer gas through the carbonation-calcination loop as follows (Saw & Pang, 2012):



The forward reaction is favoured at the relatively lower temperatures which occur in the gasification reactor. This process is also termed carbonation. CO<sub>2</sub> is consumed and the reduced concentration of CO<sub>2</sub> in the gaseous environment enhances the water-gas shift reaction, which produces H<sub>2</sub> and CO<sub>2</sub> from CO and H<sub>2</sub>O. Consequently, overall H<sub>2</sub> concentration is further increased (Saw & Pang, 2012).

The producer gas from the gasifier still contains CH<sub>4</sub>, CO and CO<sub>2</sub>. However, the H<sub>2</sub> content can be increased and concentrations of other species are reduced through optimisation of the operation conditions and the application of catalytic bed materials. Following the gasification process, CH<sub>4</sub> in the producer gas can be converted to H<sub>2</sub> and CO<sub>2</sub> through the reverse methanation reactions as shown in R2. CO in the producer gas and that regenerated from R1 can be transformed to H<sub>2</sub> and CO<sub>2</sub> through the water-gas shift reaction (R3).

Finally, the gas is composed only of H<sub>2</sub> and CO<sub>2</sub>, which can be separated using various separation technologies: (1) solvent scrubbing has been used commercially for the removal of H<sub>2</sub>S and CO<sub>2</sub> from gas streams such as flue gas. It is reported that using mono-ethanolamine as a solvent, with a high purity of CO<sub>2</sub> (>99%), can be achieved; (2) pressure swing adsorption (PSA) is another option in which the gas mixture flows through a packed bed of adsorbent at elevated pressure and the sorbent may be regenerated by reducing the pressure; and (3) membrane separation is also used, which allows one component, such as H<sub>2</sub>, in a gas stream to pass through while retaining the other component (CO<sub>2</sub>).

There are many different types of gas separation membranes, including porous inorganic membranes, palladium membranes, polymeric membranes and zeolites. For a high degree of purity of separated gases (H<sub>2</sub> and CO<sub>2</sub>), multi-stage or combined separation processes are needed.

## Woody biomass to chemicals and materials

At an elemental level, biomass contains hydrogen, carbon and oxygen, with much lower percentages of nitrogen, sulphur and other inorganic elements. The inorganic elements may end up as ash if the biomass is

combusted. When the biomass is converted to energy and fuels, hydrogen and carbon atoms are desirable, but oxygen must be removed through the formation of CO<sub>2</sub> and/or H<sub>2</sub>O. When one atom of oxygen is removed, half of the carbon or two atoms of hydrogen are lost which reduces the energy efficiency and increases the process costs. However, if the biomass is converted to chemicals, the oxygen atom may be useful and in this case there is no need to remove it. In some cases, oxygen is needed to achieve the required chemical and physical properties of the final chemical products, so oxygen in the biomass is desirable.

Many of chemicals used at present are derived from fossil fuels (petroleum, natural gas and coal), and some of these can be substituted by using renewable resources such as woody biomass. The conversion of biomass to these chemicals can be achieved by processing the biomass whole, which would produce complex mixtures of various compounds, and in this case the separation and purification of target chemicals is difficult. Alternatively chemicals can be derived from the processing of each component of biomass, namely, cellulose, hemicellulose and lignin. This concept is also termed a biorefinery.

## Cellulose to chemicals and materials

One of the favourable pathways for converting cellulose to chemicals is through hydrolysis to sugars and then through bioprocessing to produce ethanol as discussed under the *Fermentation for ethanol* heading. The cellulose component can also be used as a feedstock for nano-materials and composite materials. The most likely pathway for the large-scale production of ethylene from bioethanol is through the dehydration or production of butadiene through dehydrogenation, aldol condensation and dehydration. The sugars from cellulose hydrolysis can also be used to produce propylene through a number of processing stages, including reduction and hydrogenolysis, followed by dehydration. With new catalysts developed in recent studies (Han et al., 2019), other chemicals such as methyl glucosides, 5-HMF, gluconic acid, ethylene glycol (EG) and propylene glycol (PG) have been synthesised from cellulose through catalytic liquefactions in solvents. The challenges for these pathways are the low conversion ratio based on biomass feedstock and process complexity, both resulting in high costs.

To make the utilisation of cellulose materials more economically attractive, high-value cellulose-composite materials using cellulosic fibres have been investigated with their advantages of high strength, high stiffness, degradability and compatibility with living bones. A comprehensive review was reported by Huber et al. (2012) in which a new class of monocomponent composites based on cellulosic materials, so-called all-cellulose composites (ACCs), was assessed in detail and their potential applications and challenges proposed. In subsequent studies by the research team led by Staiger, the ACCs were manufactured and their properties

characterised. This pathway shows promising potential due to its relatively simple process and high values (Huber et al., 2012).

## Hemicellulose to furfural

Hemicellulose is a feedstock suitable for the production of furfural, a key platform chemical for useful chemicals that are used in the oil refining, plastics, pharmaceutical and agrochemical industries (Yabushita et al., 2014). The conversion of pure hemicellulose (xylose) is a relatively simple process using catalysts and solvents under high temperatures and pressure, a process similar to liquefaction. However, in practical processing where biomass is the raw feedstock material a two-stage process is proposed. In the first stage, the biomass is pre-treated in organic solvent, such as biomass-derived green solvent ( $\gamma$ -valerolactone or GVL) or water with the addition of acid catalysts, which break down the intermolecular linkages and dissolve the hemicellulose selectively. In the second stage, organic solvent was used and NaCl was applied to enhance the reaction of xylose to furfural in a biphasic system.

The key challenge for the hemicellulose to furfural process is to obtain pure hemicellulose from the biomass. Most of the reported studies are to separate lignin for pulp and paper or for the transformation of cellulose to sugars and then to bioethanol. However, new research has shown that a one-pot process is possible to produce furfural from biomass, in which the simultaneous separation of biomass components and the transformation of hemicellulose to furfural were achieved for most of the biomass species tested by Luo et al. (2019). However, woody biomass is reported to have a low conversion ratio based on starting biomass material (11% by weight).

## Lignin to chemicals and materials

Biomass lignin has the structure of linked aromatic rings. There is a potential to break the macromolecules of lignin into function groups based on the lignin building blocks. In this way, the functionalities of these groups can be maintained or modified through a controlled process. The effective method is to use a liquefaction technique with the application of selected solvents and catalysts.

Yoshikawa et al. (2013) developed a two-stage process for the production of phenols from lignin, in which the lignin was depolymerised in an autoclave reactor using silica-alumina catalysts in a water-1-butanol solvent. In the second stage, the liquid produced from the first stage was further processed with an iron oxide based catalyst to produce phenols and phenolic compounds, such as catechol and guaiacol. The phenols and phenolic compounds can be transformed into bio-aromatics as the chemical platform for various chemical products.

In separate studies, Cheng and his team (2012) developed a hydrothermal technology using various

solvents to convert kraft lignin and hydrolysis lignin to phenols and phenolic compounds. These compounds can substitute for fossil-fuel derived phenols to synthesise the phenol-formaldehyde resins used in the wood processing industry. The lignin can also be directly incorporated into a polyurethane (PU) foam formulation due to the presence of aliphatic and aromatic hydroxyl groups in its structure as the reactive sites, but the substitution proportion is low (20–30%) without modification (Mahmood et al., 2016).

The utilisation of lignin can be incorporated into the pulp and paper industry with bioprocessing technology for the conversion of cellulose to bio-ethanol. In this way, the overall conversion rate and economic returns can be improved.

## Biomass to chemicals

The complex physical structure and chemical composition of woody biomass is the response of trees to natural conditions (wind, snow) and the requirements for growth (sunlight, water and minerals in soil). However, these characteristics complicate the utilisation of biomass for energy, fuels and chemicals. On the other hand, the separation of woody biomass into individual components (cellulose, hemicellulose and lignin) is complicated and costly. Extensive research has been conducted to convert the biomass to various target products, including fuels, chemicals and polymer-based materials, although there are important technical and economic challenges for commercialisation. Pyrolysis and liquefaction have been investigated and have shown encouraging potential to be employed (Bridgwater, 2012). However, the complex chemical composition of the liquid product requires a multi-stage fractionation and purification or upgrading.

A comprehensive review was published by Corma et al. (2007) who assessed various pathways for the transformation of biomass into chemicals, and identified the development of new catalysts to be one of the key areas for further studies. This finding was further reinforced by the review by Besson et al. (2014). Recent studies have been conducted on biomass pre-treatment and catalytic pyrolysis, with the objective to improve the performance of bio-oil composition with an increased yield of the target chemicals (Wigley et al., 2017). The aims are to simplify the liquid product, thus making further separation and upgrading easier.

## Bio-char and bio-char based activated carbon

To fully realise the value of biomass feedstock, byproducts in each processing stage need to be considered for their use and further transformation to more useful products. Bio-char may be regarded as one of the byproducts in biomass pyrolysis where bio-oil is the main product. Bio-char is also produced from low temperature gasification, from which the producer gas is the target product. However, bio-char in some cases is the major product from biomass pyrolysis and

carbonation when the bio-char warrants an attractive return and environmental benefits.

Bio-char generated from both pyrolysis and gasification systems may be directly used in environmental remediation, such as for the removal of organic polluting compounds and toxic metals in aqueous mediums, for water and waste water treatment and for gas cleaning (Oliveira et al., 2017). The organic pollutants, both in the aqueous medium and in the air, include those of agrochemicals, antibiotics/drugs and industrial chemicals, including polycyclic aromatic hydrocarbons and volatile organic compounds. The key driving forces for the removal of these organic compounds are believed to be chemisorption (electrophilic interaction) and physisorption. Therefore, pore structure, surface characteristics and minerals in the bio-char are important factors to be considered in production.

Heavy metals in water and waste water, or other aqueous mediums, are non-biodegradable and thus toxic to living beings above a certain concentration. Bio-char has been tested for the removal of the heavy metals from waste water, and it is found that bio-char with high organic carbon content, specific porous structure and functional groups is more effective, which promotes interactions with heavy metals. The driving forces for such interactions include sorption by ion-exchange, adsorption at the macro-, micro- and nano-porous structures, and the attraction of functional groups and heavy metal ions (Oliveira et al., 2017). Again, the pore structure, surface properties and functionality and pH values of the bio-char all affect the effectiveness of the removal of the heavy metals.

To enhance the effectiveness of contaminant removal by bio-char, conditions for its production can be optimised with a medium operation temperature of 350–550°C for pyrolysis, which considers both the performance of the bio-char and the yield (Oliveira et al., 2017). Pre-treatment of the biomass with dilute acid has also been investigated to improve the pore structure and surface functionality (Wigley et al., 2017).

For significantly improving the desired characteristics of the bio-char, the bio-char produced can be activated either through the physical method or the chemical method (or both), generating activated carbon. The physical activation method is to modify the bio-char surface in addition to the above modification by heating the bio-char in the environment of steam, nitrogen or CO<sub>2</sub>, or a mixture of two gases at temperatures of up to 900°C. This method is mainly to clear the pores and strengthen the pore structure of the bio-char, so that the adsorption capability is increased and the bio-char and physical integrity is improved, meaning it is more durable during use.

Chemical activation uses various chemicals to enhance the bio-char functionality or add reactants for the removal of particular pollutants. This is achieved through a two-stage treatment including: (1) pre-treat

the bio-char with a given chemical; and (2) heat the chemically treated bio-char to different temperatures from 400–900°C and maintain the target temperature for a pre-set duration. The chemicals for the bio-char activation treatment include zinc chloride, potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), potassium hydroxide (KOH) and sodium hydroxide (NaOH). The selection of chemicals, treatment temperature and heating time depends on the biomass type, the operation condition for bio-char generation and the target contaminant(s) to be removed.

In the past decade, research has also been carried out to apply the bio-char for soil amendment or soil amelioration. Biochar has a very porous structure, which allows it to retain nutrients and water for the plant roots when it is applied to soil, improving the retention of nutrients (N by 7%), organic carbon (by 69%) and some minerals significantly, but with no effects on other minerals. Jeffery et al. (2011) reported on data available at that time and found that the results were very diverse, although the crop productivity had a grand mean increase of 10%. They attribute this variability to soil condition, feedstock for bio-char production and bio-char loading.

## Concluding remarks and future perspectives

Woody biomass is a promising renewable resource for future biofuels and biochemicals to substitute for fossil fuels. There is great potential for New Zealand to increase economic returns and remediate environmental concerns around greenhouse gas emissions. Extensive research and development has been conducted on the transformation of woody biomass to biofuels and biochemicals. Commercialisation of the new technologies and processes needs to consider some challenges that are related to the complicated nature of the biomass and the required quality of the target products.

To achieve attractive economic returns and realise the potential environmental benefits, the trend of further research and development in this field is the:

- Development of integrated processes for full utilisation of the feedstock materials. For example, when a bioprocess is developed for ethanol production, the use of lignin from pre-treatment and hydrolysis is critical to improve the overall conversion rate and economic returns
- Development of a system from which multi-products are produced so the overall process could be simplified. For example, if bio-oil from pyrolysis or liquefaction is for chemicals and biofuel, then the bio-oil can be first fractionated and then upgrading can be simplified.

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