Development of Heterogeneous Catalysts for Butyl Butyrate Production.

Thesis presented for the award of Doctor of Philosophy (Ph.D.)

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Declaration

I declare that the work in this thesis is my original research and that it has not been submitted anywhere for any award. Where other sources of information have been used, they have been duly acknowledged.

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Abstract

Butyl butyrate is an environmentally friendly biofuel component that can be produced through the esterification of butyric acid with n-butanol, both of which are obtainable from waste products with a two-step fermentation process. To catalyse the production of butyl butyrate, heterogeneous solid acid catalysts were developed by sulfonation of char obtained from the carbonisation of Miscanthus x giganteus and solid residues derived from the fermentation of brown bin waste (digestate). In the case of Miscanthus derived material, prior to sulfonation, part of the char underwent chemical activation with the purpose of increasing the surface area of the char (from 6.4 to 571 m²·g⁻¹ after chemical activation at 500°C). The catalysts possessing the highest surface area and acid density were shown to have the highest catalytic activity and thus performed better giving competitive results to Amberlyst 15 and H₂SO₄ (96 % yield), after 24 hours reaction. Activated Miscanthus based catalysts and Brown bin waste digestate based catalysts exhibited a superior catalytic activity after usage, and also a better reusability. Realistic kinetic parameters were formulated for the optimum char based solid acid catalyst using two power law models.

A one-step synthesis process of butyl butyrate from butyric acid through hydrogenation and esterification has also been investigated. This process has the potential to replace currently used esterification processes in which both butyric acid and butanol are used. This study focused on the development and characterization of suitable catalysts and on the enhancement of the reaction conditions such as temperature and H₂ pressure.
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Chapter 1

1 Introduction

Currently there is a global push to make major technological advances for the sustainable production of alternatives to petroleum derived liquid transportation fuel components. Biodiesel, an oxygenated fuel that can be derived from biomass (McCormick et al. 2001), is one such alternative being explored by researchers. Increased public awareness of greenhouse gases and the economic security of a stable energy supply have driven this area of research. A number of major economies have supported biofuel production. The EU has committed to a 10% substitution of fossil derived liquid transportation fuels by 2020 and the US has set a target to produce 36 billion litres of renewable fuels per annum by 2022 (Hayes 2009).

Biomass is considered the main potential alternative to fossil fuels because of its ability to be used in the production of biofuel in a manner which operates similarly to conventional oil refinery. Biomass is formed from a variety of chemical compounds which can be used to create higher value products, such as char-based solid acid catalysts. As an alternative to fossil fuels, biomass presents some distinct advantages: it can be decomposed by microorganisms; it is environmentally friendly, organic, renewable, and widely available.

Butyl butyrate is a naturally hydrophobic biofuel component which mixes well with biodiesel and has high potential to support economies looking to meet their environmental targets (Jenkins et al. 2013). Butyl butyrate can be formed through the esterification of butyric acid (BA) with n-butanol. BA and n-butanol can be
produced from biomass (brown bin waste in this case study) through a two-step fermentation process (Ramey and Yang 2005) using Clostridium tyrobutyricum and Clostridium acetobutylicum, respectively.

Esterification to produce butyl butyrate can be supported by a number of catalysts; however, it is often the case that known catalysts have one or more problems related to either product selectivity, environmental protection, high costs, recyclability (or lack thereof) and disposal methods (Hayes 2009).

A new generation of solid acid catalysts has been developed in recent years (Galhardo et al. 2013). These materials are based on carbon created by incomplete carbonisation followed by sulfonation with sulfuric acid. This approach easily enables the use of sulfonated carbon-based solid acid materials which are robust, resistant and insoluble (Lou et al. 2008). These properties make them ideal in catalytic reactions. Investigating the application of these materials is ever more attractive due to their green characteristics, potential recoverability and reliability (Chen and Fang 2011). Carbon-based solid acid catalysts are eco-friendly (Galhardo et al. 2013); they can be created from wastes which can be otherwise difficult to dispose of and can be recycled and reused. Consequently, a number of new materials for carbon-based solid acid catalysts have been developed from the incomplete carbonisation and subsequent sulfonation of carbohydrate and pyrolysis product precursors.

The aim of this work is to develop an environmentally friendly process for the production of butyl butyrate. This is created using heterogeneous char based solid acid (CBSA) catalysts derived from the pyrolysis of biomass feedstock Miscanthus x giganteus (MG), and from brown bin waste digestate (W), the solid
residue obtained during the two steps fermentation process. These CBSA catalysts are employed for the esterification of butyric acid to butyl butyrate with n-butanol.

**Figure 1.1.** Butyl butyrate production via Miscanthus *x giganteus* derived char based solid acid catalyst (Severini et al. 2015);

**Figure 1.2.** Char based solid acid catalysts from brown bin waste to create a green process for the production of butyl butyrate.

The effect of carbonisation temperature on the catalyst's surface area is investigated. A detailed characterisation is carried out to show the link between surface area and catalyst acidity to overall catalyst performance. Once the catalyst
is produced, its capabilities are tested for butyl butyrate production. Kinetic modelling is implemented to establish the kinetic parameters associated with butyl-butyrate production and to describe the reaction mechanism which will further validate these findings.

An important part of this research work is also dedicated to the one-step-hydrogenation-esterification (OHE) of butyric acid to butyl butyrate. The OHE was recently identified as a potential method to solve problems with mass producing biofuels. OHE combines the methods of hydrogenation and esterification into a single step process that does not directly utilize the alcohol component and therefore saves costs. The process requires the use of bi-functional catalysts that operate for both hydrogenation and esterification. In previous work, catalysts containing noble metals such as Ti, Pt, Ni, Pd and Ru have been used for OHE and prior to that for hydrogenation (Wanjin Yu et al. 2011, Tang et al. 2008).

This study is focused on the characterization and application of commercially available Ru and Pd catalysts supported with activated carbon or charcoal; and prepared Ru and Pd catalysts supported with the sulfonated char produced during the first part of this research. All these catalysts are tested with and without mesoporous alumina-silica. Reaction condition such as temperature and H₂ pressure are also investigated.
2 Literature review

2.1 Biomass Feedstock

Biomass may be defined as any material derived from a living or recently living organism (Sources Of Biomass, Biomass Energy Centre, 2015). It is a term that encompasses plant and animal matter and is generally used with the intention of using these biological resources as raw materials for fuel production. The term excludes fossilised biological remains and soil (Bioenergy (Biofuels and Biomass), 2015). Plant based materials not used for food are known as lignocellulosic biomass, consisting of such materials as forestry residue, energy crops (such as short rotation poplar or Miscanthus x giganteus) and agricultural residues (e.g. grain husks, sugarcane bagasse and corn stover) (Sources of Biomass, Biomass Energy Centre, 2015). With the energy stored within biomass, there is the potential to produce renewable energy. This is thanks to the possibility of replenishing biomass resources, as biomass does not require the same time input for regeneration as fossil fuels do.

By virtue of the fact the living biomass takes in carbon from the atmosphere to grow and releases this carbon when used for energy, biomass provides a carbon-neutral source of energy, an environmental advantage over fossil fuels.

Transportation accounts for the major demand on oil, consuming 30% of oil worldwide (Luque et al. 2008). Biomass is seen as potentially the main alternative source of carbon to oil due to the fact that it can be used to produce biofuel which operates similarly to oil derived gasoline and diesel in internal combustion
engines. Biomass also has a number of advantages over other renewable energy sources. For a feedstock to be considered renewable it must have the following characteristics: the raw materials must be renewable for the energy source to be sustainable and the raw materials must be widely available (Melero et al. 2012).

With the threat of a changing global climate and incentives from strategies such as the EU’s 20/20/20 strategy (20% lower use of fossil-based fuels, 20% greater use of biofuels and 20% greater energy efficiency) (2020 Climate & Energy Package, European Commission, 2015) and the Kyoto Protocol, the United Nations international agreement binding its parties into lowering greenhouse gas emissions (‘Kyoto Protocol - United Nations Framework Convention on Climate Change, 2014), biomass provides an excellent source of sustainable, renewable energy which better fits the criteria necessary to meet the world’s environmental protection goals.

Biomass can be converted by thermochemical and biological means into combustible fuels with favourable energy storage properties, known as biofuels (Luque et al. 2008). These can consist of solid, liquid or gaseous fuels and can in theory serve as replacements to coal, oil and gas, all unsustainable fossil fuels.

Thermochemical conversions involve the conversion of plant oils to biofuels, such as biodiesel, via methods including pyrolysis and gasification.

Biological conversions of biomass involve processes such as fermentation that create fuel, such as bioethanol. This involves the hydrolysis and fermentation of sources including sugar cane, corn or non-food plant feedstocks. Many other organic compounds, such as carboxylic acids (e.g. butyric acid) can be obtained
from fermentation of biomass by microorganisms, and products such as these can also be synthesised into biofuels.

Butyric acid is one product of biological biomass conversion with potential as a precursor to a viable biofuel synthesis route (Ramey and Yang 2005).

Until recently, the use of sucrose, starch, and oil crops has been the main source for bio-fuels. The sugar and sucrose crops are easily hydrolysed and fermented leading them to be the original choices for bio-fuel production. These crops are known as first generation feedstock. Good farming practices allow bio-fuel feedstock to be a renewable and sustainable source of fuel, which is a huge advantage over fossil fuels. However it is believed that to make bio-fuels a feasible alternative to crude oil, the economic aspect would need to be improved considerably. The amount of energy bio-fuels are able to produce must far outweigh the cost of the energy input within production (Hayes 2008). For that to be a reality second generation biofuels are needed. These are made from lignocellulosic biomass or woody crops, agricultural residues or waste and are a low-cost, high-yielding biomass feedstock (Carol Sze Ki Lin 2013).

Biomass feedstock can be divided into two categories: oleaginous and carbohydrates.

### 2.1.1 Oleaginous feedstock

It is predominantly oil based feedstock which is composed of triglyceride molecules. Triglyceride compounds consist of glycerine and alkyl-chain fatty acids components. The coupling between these two components is in the ester form. The fatty acids are also long chain compounds containing 8 to 20 carbon atoms. The most common fatty acids in the feedstock contain between 16 to 20
carbon atoms (Melero et al. 2012). Free fatty acids are another form of oleaginous feedstock. Hydrolysis of the triglyceride molecules results in the formation of these free fatty acid compounds. These compounds are mainly found in low grade feedstocks such as residues from organic crops, e.g. waste from fruits, vegetables and grain (Lin et al. 2013).

Algae are an oleaginous feedstock which have recently been researched and are showing some promise (Luque et al. 2008). Although research into this feedstock is at an early stage, initial studies show that there are many advantages to this feedstock. One of the main advantages is that it can be produced on a much larger scale compared to crop or animal waste. The feedstock can also be produced using equipment already built (equipment for fossil fuel production) (Melero et al. 2012). There is also a wide variety of algae which can produce high oil content for biofuel production. These algae would only require small amounts of land compared to other feedstock sources (Luque et al. 2008).

However, there are also limitations for the use of algae feedstocks. The cost of producing this feedstock and also the difficulty with recovering the bio-oil are major limitations. The process of recovering this bio-oil involves significant processing of the algal stock to recover the biomass. The biomass is in a concentrated paste and this paste must be treated with an organic solvent to obtain the bio-oil. Another disadvantage of this feedstock is that the oil produced contains a large amount of long-chain polyunsaturated acids, e.g. eicosapentaenoic (20:5 n-3, EPA). The oxidative stability in biofuel is affected by these polyunsaturated acids and therefore they are an undesirable product (Luque et al. 2008).
2.1.1.1 Brown bin waste feedstock

In recent years, there has been a culture shift in how we dispose of our waste.

This shift has come about due to our desire to improve efficiency by discovering practical uses for our waste. Brown bin waste (figure 2.1) includes any organic matter in waste which can be broken down into carbon dioxide, water, methane or simple organic molecules by micro-organisms and other living things using composting, aerobic digestion, anaerobic digestion or similar processes.

![Figure 2.1. Brown bin waste (source: http://www.islington.gov.uk/services)](image)

Research into the food supply chain waste has shown that this material has the potential to be used as a feedstock to produce biofuels and certain chemicals. Food supply chain waste (FSCW) is organic, i.e. renewable, and widely available. The waste is also composed of a wide variety of chemical compounds: triglycerides, fatty acids, proteins and carbohydrates. These components can also be used to create higher value products, such as bio-adhesives, bio-solvents PVC replacement material, nanocomposites and char (Lin et al. 2013).
Currently food waste is mainly disposed of in animal feed, by composting, incineration or landfill (Lin et al. 2013). Of these various disposal routes animal feed is the most cost effective. Composting is another effective disposal system and is one of the most common. The compounds formed after composting can be used as a fertiliser. Composting is also an environmentally friendly process as it reduces the amount of waste in landfills and reduces the need for incineration. As it produces an environmental fertiliser, it reduces the need for farmers to use mineral fertilisers. These mineral fertilisers, which contain potentially harmful chemicals, can pollute rivers and streams.

Although incineration and landfill are effective at disposing of waste, they are not environmentally friendly. Both of these processes release greenhouse gases, methane and carbon dioxide in particular. Landfills take up large amounts of land which is then polluted by the dumped waste. Incineration requires large amounts of energy to burn the wet waste. Due to the energy required to reduce moisture content via evaporation, energy can’t be recovered from the incineration process (Lin et al. 2013). Fig. 2.2 summarises the advantages of using waste from the food supply chain as a feedstock source.
Figure 2.2. Advantages of food waste as feedstock source (Lin et al. 2013)

Note: Biochemical oxygen demand (B.O.D.) is the milligrams of dissolved oxygen needed by aerobic biological organisms to break down organic material present in one litre of sample at certain temperature (20 °C) over a specific time period (5 days). Chemical oxygen demand (C.O.D.) measures the amount of organic compounds in water. It indicates the mass of oxygen consumed per litre of solution.

2.1.2 Carbohydrates

Carbohydrates are the other form of biomass feedstock and the most abundant in nature. Carbohydrates are composed of carbon, hydrogen and oxygen molecules and have the general chemical formula $C_x(H_2O)_y$. Monosaccharides and polysaccharides are the two groups of carbohydrates. Monosaccharides are simple sugar (i.e. short chain carbohydrates) molecules such as glucose and fructose. Both glucose and fructose have the same chemical formula ($C_6H_{12}O_6$) as they are
structural isomers. Polysaccharides are more complex carbohydrates (i.e. long chain carbohydrates) and examples include starch \((C_6H_{12}O_5)_n\) and cellulose. They are also more common in nature. With regard to the general carbohydrate chemical formula \(C_x(H_2O)_y\), the “\(x\)” denotes the chain length of the molecule. Therefore monosaccharides have a low “\(x\)” value whereas polysaccharides will have a much higher value.

In terms of its use as an energy source, carbohydrates are predominantly used in the production of ethanol via the fermentation process. It is the monosaccharides which are used in this process and therefore polysaccharides require further processing to be used in biofuel production. Polysaccharides can produce simple sugars by undergoing the process of hydrolysis. Starch for example is composed of glucose molecules bonded together, but by hydrolysing starch, glucose molecules can be released and can then be used in biofuel production (Melero et al. 2012).

It is possible to produce large quantities of cellulosic biomass from various crops. These crops are usually non-food crops such as herbaceous plants and short rotation wood crops. A major limitation with these crops is that they compete with food crops for agricultural land. Lignocellulose is another form of biomass which is composed of long chain carbohydrate polymers and lignin. It is formed from wastes and residues and waste wood from industry (paper and forestry industry) (Melero et al. 2012).

It has been estimated that biomass feedstock is composed of 75% carbohydrates, 20% lignin and the remaining 5% is made up of oils, fats and proteins which
makes carbohydrates critically important in the supply of biomass for biofuel production (Melero et al. 2012).

2.1.2.1 Miscanthus x giganteus

A suitable potential feedstock for the production of biofuels can be found with the Miscanthus x giganteus (Figure 2.3). This crop is a highly promising energy feedstock for bio-refinery based processes. Originating in Asia, this perennial C4 rhizomatous grass requires little fertilizer or pesticides and is a fast growing crop that can be harvested in one cut, in a delayed harvest system.

![Miscanthus x giganteus](http://www.irishtimes.com/news)

**Figure 2.3.** Miscanthus x giganteus (source: http://www.irishtimes.com/news)

Its elemental composition, yield, carbohydrate and lignin content are of high importance for biofuel production and development, due to its high yield (about 20 tones ha\(^{-1}\)year\(^{-1}\)), low moisture and ash contents. Miscanthus x giganteus (MG) is a feasible crop for biomass-to-liquid conversion processes in order to produce a range of liquid fuels and chemicals by thermochemical conversion (Brosse et al. 2012), such as pyrolysis.
2.2 Pyrolysis of biomass

Pyrolysis is the process where the biomass feedstock is broken down thermochemically. The pyrolysis of biomass has the potential to produce renewable by-products and solid residue material. The process requires temperatures over 300°C under anaerobic conditions to convert the feedstock into bio-oil, gas and char (Dehkhoda et al. 2010).

![Pyrolysis of biomass feedstock](image)

**Scheme 2.1.** Pyrolysis of biomass feedstock

Pyrolysis oil or thermochemically-derived biomass liquids (bio-oil) has the potential to be used as fuel, and also hold great promise as platform intermediates for production of high-value chemicals and materials. The main pyrolysis gases of biomass are carbon monoxide, carbon dioxide, methane, hydrogen and other hydrocarbons. The yield of these gaseous products can be controlled by adjusting the operating parameters such as solid retention time, pyrolysis temperature, heating rate, and vapour phase residence time. After cleaning and conditioning, the pyrolysis gas can be used in the gas engines for CHP generation with high
efficiency, flexibility, and relatively low investment, particularly in the low-power output range, typically less than 5 MW (Zhang et al. 2015). Char is the solid product of pyrolysis that in addition to being used for improving soil fertilization (bio-char) is an excellent candidate as a low price carbon sequester (Dehkhoda et al. 2010), (Rao et al. 2011).

2.3 Biofuels

Biofuels are crop–based fuels and are seen as the ideal replacement for oil and other fossil fuels. Examples of these fuels include biodiesel and bioethanol. The use and production of biofuels has significantly increased in the last few years as indicated in Figure 2.4. Research into biofuels has predominantly been conducted in its potential use in the transportation sector. The transportation sector is responsible for the emission of vast quantities of greenhouse gases. By replacing traditional petrol and diesel with biofuels it is hoped that emissions of these greenhouse gases can be reduced.
2.3.1 History of Biofuels

Biofuels are not a recent invention in fact their use has been documented since the 19th Century. Since this time, vegetable oils have undergone transesterification to produce biofuels. The first internal combustion engine, invented by Nikolaus August Otto, was originally designed to operate using ethanol. Rudolf Diesel, inventor of the Diesel engine, used biodiesel made from peanut oil in his first demonstration of the engine. Henry Ford designed the Ford 1908 Model T to run on ethanol as he believed that biofuel was the future of the transportation sector. Biofuels were even used by both the Allies and the German armies during World War II to power machinery.
Biofuels were widely used in Diesel engines up until the 1920’s. From then on however, these Diesel engines were modified to run on petroleum as petroleum was widely available, cheap and a convenient energy source. This resulted in the interest in developing biofuel as a viable fuel dwindling.

2.3.1.1 Advantages of Biofuels

There are three main advantages to the production and use of biofuels: energy independence, rural development and climate change (Pickett et al. 2008). The world’s dependence on oil and other fossil fuels is a serious concern. These resources are not renewable and a renewable energy source is required for the future. It is believed that biofuels can, with further research and development, meet some of the world’s future energy demands. Biofuel currently in production can be used in standard Diesel engines without the necessity to modify the engines (Demirbas 2007).

Another major benefit of biofuels compared to fossil fuels is their impact on the environment. Fossil fuels are responsible for the emissions of greenhouse gases which have a severe impact on the environment. Biofuels can be produced from waste materials (e.g. food waste, wood waste), which in itself reduces harmful emissions, and these biofuels have been reported to produce lower amounts of harmful emissions compared to fossil fuels (Luque et al. 2008). Although it has been reported, further research is required to fully understand and calculate the emission of greenhouse gases during every step of biofuel production and combustion.

The increased production and development of biofuels can also help develop rural communities, particularly in third world countries. The feedstock for biofuel
production is generated from the growth of crops, whether they are food crops or non-food crops. As demand for these types of crops increases, the farming incomes will also increase and as a result rural communities will develop and grow.

2.3.1.2 Development of Biofuels

There are presently two generations of biofuels in production, 1st generation and 2nd generation.

1st generation biofuels are generated from predominantly carbohydrates with energy crops such as sugar and starch being the main sources. Oil crops are also used in 1st generation biofuel production. Biodiesel and bioalcohols (bioethanol and biobutanol for example) are the most common forms of 1st generation biofuels. These biofuels can be produced using a number of different processes including via chemical, thermochemical and biological conversion.

Biodiesel, which is the most widely available 1st generation biofuel, is produced using chemical conversion. The traditional mechanism for its synthesis involved the transesterification of triglycerides from vegetable oils. This was carried out in the presence of short chain alcohols such as methanol. This process resulted in the formation of fatty acid methyl esters and also glycerol was formed as a by-product. The use of different feedstocks in the production of biodiesel has also been widely reported in literature.

Biodiesel is mainly produced with the aid of a suitable catalyst, whether that catalyst is acid or base, homogeneous or heterogeneous. Biodiesel has also been synthesised without the use of such catalysts. This process involves the use of methanol, in a supercritical state (the temperature and pressure of the methanol is
above its critical point), in the esterification of fatty acids and transesterification of triglycerides (Marchetti et al. 2007). The esterification and transesterification reactions proceed simultaneously. The use of supercritical methanol is imperative to the process as it gives the methanol a combination of its gas and liquid properties and as a result a relatively high reaction rate is obtained. If standard methanol was employed in the reaction there would be a low reaction rate (Demirbaş 2002). Although this non-catalytic route is effective in producing a high yield of biodiesel, the supercritical conditions increase the production costs significantly.

Bioalcohols are produced using biological conversion. Bioethanol is mainly used as an additive in traditional diesel and petroleum (Luque et al. 2008). Bioethanol production incorporates the use of carbohydrates as feedstocks. The production of bioethanol is a two-step process: hydrolysis and fermentation. The hydrolysis step is only required if starch, a polysaccharide, is used as the feedstock. The hydrolysis is used to transform the starch into simple sugar molecules.

The fermentation process involves the use of yeast, such as Saccharomyces Cerevisiae, to form ethanol (Balat et al. 2008). It has recently been reported in literature, that bacteria has been used as an alternative to yeast in the fermentation process. The bacterium used was Zymomonas Mobilis. The use of this bacteria resulted in a higher yield of ethanol produced with a higher alcohol tolerance (Huber et al. 2006).

Biofuels can also be produced via thermochemical conversion (Brosse et al. 2012). This requires the process of fast pyrolysis of vegetable oil. Fast pyrolysis is the process of exposing these oils to medium or high temperatures (300 – 500°C).
These temperatures cause vaporisation and the high molecular weight compounds in the feedstock to break down resulting in the formation smaller compounds. The vapours generated are condensed back into 2 liquid fractions/layers, an aqueous layer and an organic layer. The organic layer is transformed into the biofuel by catalyst.

Second generation biofuels are produced via the same conversion processes as 1\textsuperscript{st} generation biofuels (i.e. chemical, biological and thermochemical). The only significant difference between the two generations of biofuels is the feedstock used in the production process. The feedstocks for 2\textsuperscript{nd} generation biofuels are non–food crops and waste vegetable oils and fats. Although many 2\textsuperscript{nd} generation biofuels are still only in the development stage and not yet widely commercially available, it is believed that these biofuels have a number of advantages over 1\textsuperscript{st} generation biofuels. These advantages include the ability to produce higher biofuel share with these feedstocks using a more cost effective and sustainable production system, as illustrated by Figure 2.4 (Luque et al. 2008). The use of waste materials as feedstock is also environmentally friendly as it reduces waste levels while also producing an environmentally fuel.
Figure 2.4. Potential development pathways for 1st and 2nd generation biofuels.

For the chemical conversion process for the production of biodiesel, feedstocks such as Brassica Carinata and Jatropha Curcas are used (Achten et al. 2007). The use of the Jatropha crop is of particular interest as it has been reported to produce a high yield product while also being beneficial to the surrounding environment. Compared to 1st generation biodiesel, it produces around 27–40% w/w higher yield while requiring less feedstock (Luque et al. 2008). This crop can be grown in soil and land which is not suitable for the food crops. It therefore doesn’t compete for agricultural land with food crops which was one of the concerns about the development of biofuels (Heger et al. 2012). The Jatropha crop also helps to create topsoil.

The production of 2nd generation bioethanol via biological conversion requires the use of cellulosic biomass as a feedstock. This biomass includes woody biomass, grasses and agricultural waste (Russo 2006). The general process for bioethanol is the same as for 1st generation with one key difference. The feedstock contains
cellulose and hemicelluloses and as a result enzymes are required in the hydrolysis step. When using the woody feedstocks, lignin is produced as a by-product. This can be combusted to produce heat and power, throughout the production plant to power machinery (Luque et al. 2008).

2.3.1.3 Butanol

Butanol is seen as one of the most significant biofuels for the future. This is due to the fact that butanol has many desirable fuel properties (Luque et al. 2008). Similar to ethanol, butanol is produced via a fermentation process. The traditional fermentation process is ABE fermentation (Acetone-Butanol-Ethanol) which uses the bacteria Chlostridium Acetobutylicum (Kang et al. 2011, Chen et al. 2013). Other bacteria examples include Chlostridium Beijerinckii and Chlostridium Saccharobutylicum (Luque et al. 2008).

There are many advantages to the use of butanol as a transportation fuel. It has been reported that butanol contains 85% of the energy content of traditional petroleum, whereas ethanol contains only 70% (Luque et al. 2008). Butanol can also be used in unmodified car engines. Ethanol, on the other hand, can only be used as a fuel additive in unmodified car engines and only up to 85% concentrations of ethanol (Luque et al. 2008).

Butanol also has a better fuel mileage compared to ethanol and has lower polluting emissions (Kang et al. 2011). It is also a safer fuel to handle than ethanol and as such, butanol doesn’t need devices for storage and transport unlike ethanol.(Kang et al. 2011) Butanol also has a lower vapour pressure (Luque et al. 2008) which reduces the chance of a vapour lock forming inside the engine (Kang et al. 2011). A vapour lock could potentially damage the engine. butanol
production can be carried out with infrastructure already used for the production of traditional transportation fuels (Luque et al. 2008). The development of butanol production plants is already underway in the USA while BP have developed a biobutanol production plant in the UK (Luque et al. 2008).

The major benefit of butanol over the use of ethanol is the interaction between ethanol and water. Ethanol is primarily used as an additive to petroleum and when water enters the system, it interacts with the ethanol-petroleum blend (Luque et al. 2008, Kang et al. 2011). The water dissolves in the blend and the ethanol and water separate from the petroleum. Butanol, on the other hand, does not absorb water and therefore does not separate out when water enters the fuel system (Kang et al. 2011). Butanol is therefore a more desirable fuel additive than ethanol.

Butanol also has a similar air to fuel ratio to traditional petroleum. This allows for a higher concentration of butanol to be added to butanol-petroleum blends without damaging the engine (Kang et al. 2011). The properties of butanol, ethanol and petroleum (gasoline) are summarised in Table 2.1.
Table 2.1. Properties of Ethanol, Butanol and Petroleum (Gasoline).

<table>
<thead>
<tr>
<th>Property</th>
<th>Ethanol</th>
<th>Butanol</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in water</td>
<td>Miscible</td>
<td>9.1 cm³·100 cm³</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Molecular Weight, g·mol⁻¹</td>
<td>46</td>
<td>74</td>
<td>-</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>C₂H₅OH</td>
<td>C₄H₉OH</td>
<td>C₄~C₁₂</td>
</tr>
<tr>
<td>Density @20°C, g·cm⁻³</td>
<td>0.79</td>
<td>0.81</td>
<td>0.72</td>
</tr>
<tr>
<td>Boiling Point, °C.</td>
<td>78</td>
<td>117</td>
<td>32~210</td>
</tr>
<tr>
<td>Flash Point, °C.</td>
<td>12</td>
<td>35</td>
<td>-20</td>
</tr>
<tr>
<td>Heat Value, Kcal·L⁻¹</td>
<td>5,075</td>
<td>6,404</td>
<td>7,700</td>
</tr>
<tr>
<td>Evaporation Heat, Kcal·Kg⁻¹</td>
<td>200</td>
<td>142</td>
<td>86</td>
</tr>
<tr>
<td>Sensible Heat, Kcal·L⁻¹·°C⁻¹</td>
<td>0.62</td>
<td>0.56</td>
<td>0.5</td>
</tr>
<tr>
<td>Air to Fuel Ratio</td>
<td>9</td>
<td>11.2</td>
<td>14.6</td>
</tr>
<tr>
<td>Blending Octane Number</td>
<td>120</td>
<td>95~100</td>
<td>91~99</td>
</tr>
<tr>
<td>MON (Motor Octane Number)</td>
<td>96</td>
<td>78</td>
<td>81~89</td>
</tr>
<tr>
<td>Vapour Pressure at 20°C, kPa</td>
<td>5.95</td>
<td>0.79</td>
<td>-</td>
</tr>
</tbody>
</table>

Although butanol has a number of significant advantages over bioethanol, it also has some limitations. Butanol has a high octane number (shown in Table 1 above) which is almost identical to petroleum. This, results in ethanol being more suitable to be used as an octane number booster as opposed to butanol. Butanol also has a higher production cost which is caused by the large amount of energy required to separate and concentrate the butanol obtained during the fermentation process. Butanol is also toxic to the bacteria used in the fermentation process, which limits the yield of butanol (Kang et al. 2011).
2.3.1.4 Two-step fermentation process

The high production cost and toxicity of butanol lead to a new production mechanism being developed. Conventional acetone–butanol–ethanol (ABE) fermentation generates low levels of butanol from biomass. The production of butanol can be limited by severe product inhibition. Butanol concentrations are often lower than 13 g·L⁻¹ in conventional ABE fermentations. Cell growth is extremely limited which reduces fermentation when the concentration is 10 g·L⁻¹ or less. Typically ~15% (w/w) of butanol is yielded during fermentation and amounts rarely exceed 25% (0.8 – 0.14 dm³·dm⁻³ of biomass).(Ramey and Yang 2005) Low butanol yield and butanol concentration has made the production of butanol from biomass uneconomical when produced by way of ABE fermentation (Maddock 1989).

The fibrous-bed bioreactor and the two step fermentation process produced a maximum yield of 49% (0.27 dm³·dm⁻³) with an estimated production cost of $0.28 per dm³ of butanol. This approach would theoretically produce a maximum yield of 0.3 dm³ of butanol per dm³ of available biomass. The result is a 25% increase of power (joules) derived from biomass when compared to those derived from ethanol (Ramey and Yang 2005).

In the first step of the two-step fermentation process the biomass is fermented using Chlostridium Tyrobutyricum. This results in the formation of butyric acid. This butyric acid, in a second step is then fermented using Chlostridium Acetobutylicum to form butanol at higher yields than the traditional ABE fermentation process (Kang et al. 2011, Chen et al. 2013). The yield of butanol can be further enhanced by the conversion to butyl butyrate.


### 2.3.2 Butyl butyrate

Butyl butyrate is a pleasant smelling ester formed via the esterification of n-butanol and butyric acid which is given by the following chemical equation:

\[ \text{C}_3\text{H}_7\text{COOH} + \text{C}_4\text{H}_9\text{OH} \rightarrow \text{C}_3\text{H}_7\text{COOC}_4\text{H}_9 + \text{H}_2\text{O} \]

This compound has many uses in different industries. It has been used for years as a food additive, used to flavour confectionaries, baked goods and alcoholic beverages with its fruity, pear-pineapple aroma (Burdock 2009).

Thanks to the ester’s flammable nature, it has been gaining interest in recent years as a potential biofuel. Due to the widely known issue of petroleum resources depletion and market price instability, an increasing amount of research is being conducted in the area of alternative fuel sources (Dwidar et al. 2012).

Butyl butyrate is a desirable product as it has excellent fuel properties. It is far more hydrophobic than butanol which allows for easier extraction from the reaction mixture. The extraction of butanol from the fermentation mixture is one of the contributing factors causing the high production cost of butanol (Kang et al. 2011). By converting butanol to butyl butyrate, the product can be easily extracted thereby reducing production costs. Diesel and kerosene can be employed as extraction agents. By using these fuels as extraction agents, they become enriched with the butyl butyrate. This can be then used as a fuel without the need of further processing and as a result production costs are again reduced.

Other benefits of butyl butyrate include the use of waste feedstocks in its production and the fact that as the process requires low energy levels, there are only low amounts of CO\(_2\) emissions. Also the octane number of butyl butyrate is
the same as that of butanol which means that butyl butyrate can be added, as an additive, to petroleum in the same way as butanol. The flash point of butyl butyrate is lower than for butanol which means it is a safer fuel while its cetane number is similar to the cetane number of diesel (Kang et al. 2011). These properties, which are summarised in Table 2.2, indicate that butyl butyrate can be used as a new form of biofuel.

**Table 2.2.** Properties of Butanol and Butyl Butyrate (Kang et al. 2011).

<table>
<thead>
<tr>
<th></th>
<th>Butanol</th>
<th>Butyl butyrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility in water cm³·cm⁻³</td>
<td>9.1/100</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Molecular Weight, g·mol⁻¹</td>
<td>74</td>
<td>144</td>
</tr>
<tr>
<td>Density @20°C, g·cm⁻³</td>
<td>0.81</td>
<td>0.87</td>
</tr>
<tr>
<td>Boiling Point, °C</td>
<td>117</td>
<td>165</td>
</tr>
<tr>
<td>Flash Point, °C</td>
<td>35</td>
<td>49</td>
</tr>
<tr>
<td>Blending Octane Number</td>
<td>95−100</td>
<td>95~100</td>
</tr>
<tr>
<td>Blending Cetane Number</td>
<td>0</td>
<td>24~30</td>
</tr>
</tbody>
</table>

Butyl butyrate can also be converted back to butanol by the process of hydrogenolysis. Therefore depending on which biofuel you want to produce, the production process can be modified. If butanol is the desired biofuel, a portion of butanol can be recovered as a final product while the remainder undergoes esterification with butyric acid forming butyl butyrate (Kang et al. 2011). Similarly, a portion of the butyl butyrate produced can be removed as final product, with the remainder undergoing hydrogenolysis back to butanol thus creating a production cycle.
For this esterification reaction to proceed at a reasonable reaction rate, a catalyst, either homogeneous or heterogeneous, is required. The examples of homogeneous catalysts which may be used are sulfuric acid, hydrochloric acid and nitric acid (Kang et al. 2011). There are a wide range of heterogeneous catalysts which can be used. These catalysts are mainly acid catalyst such as ion exchange resins, zeolite, alumina silica and heteropolyacid (Kang et al. 2011). One-step hydrogenation-esterification is a recently developed synthesis route for the same product using fewer reactants (Wanjin Yu et al. 2011).

2.3.3 Catalysts for biofuels production

The primary function of a catalyst is to increase the rate of the chemical reaction without being deactivated in the reaction. The catalyst lowers the activation energy required for the reaction to proceed. A good catalyst usually has a high surface area with a high density of active sites. The esterification reaction for the production of biofuel can be aided by a number of different catalysts: acid homogeneous (Lotero et al. 2005), alkali homogeneous (Vicente et al. 2004), acid heterogeneous (Melero et al. 2009), alkali heterogeneous (Lee et al. 2009), biocatalysts (Ha et al. 2007). Supercritical conditions in absence of catalyst were also investigated (Cao et al. 2005).

2.3.3.1 Homogeneous Catalysts

Sulfuric acid and hydrofluoric acid are the main homogeneous catalysts used in industry (Sharma et al. 2011). Both of these acid catalysts are highly corrosive and can cause serious environmental hazards. There are also problems with the recovery of the catalyst and as a result the catalysts reusability. The poor reusability of these catalysts causes production costs to increase as more catalyst
has to be produced to run every new reaction. During the recovery of the catalyst, the biofuel-catalyst mixture must be washed with water. This causes some of the biofuel to be lost and also generates a significant amount of waste water (Sharma et al. 2011).

In the production of biodiesel, sulfuric acid is a commonly used catalyst. The main problems associated with its use in biodiesel production are that it is not environmentally friendly and it results in high production costs (Luque et al. 2008, Toda et al. 2005). The catalyst has to be separated from the reaction mixture which requires large amounts of energy and cost. The reaction mixture also must be neutralised and washed with water (Luque et al. 2008, Hara 2010). This generates large volumes of waste water and salts which require further processing. The process also prevents the catalyst being reused (Luque et al. 2008). This contributes to a high biodiesel production cost. The alkali homogeneous catalysis has shown the limitation of the water poisoning effect. Relevant attention has been focused on homogeneous catalysis replacement. The ideal process would involve a continuous flow reaction that neither deactivate nor consume the catalyst and that minimize or eliminates the need for separation and purification in the final stage of the process (Helwani et al. 2009).

These limitations resulted in increased research into heterogeneous catalysts for biofuel production

2.3.3.2 Heterogeneous Catalysts

Although they have less activity than there homogeneous counterparts, solid acid catalysts are used extensively in industrial processes due to their varied active sites containing both BrØnsted and Lewis acids.
Production of biodiesel, derived from vegetable oil, using solid heteropolyacids, shows that heterogeneous catalysts are capable of producing 99% yield even with low catalyst concentrations, with a low methanol to oil ratio in a short time at a low temperature (Helwani et al. 2009). Using HYSYS to simulate four continuous processes of biodiesel production, at a rate of 8,000 tonnes a year, a simulation showed that the process utilising heterogeneous catalysts and supercritical processes were the simplest and most effective. The heterogeneous acid catalyst was shown to be the most economical with the lowest total capital investment (West et al. 2008).

For the production of biodiesel, the catalyst must be selective and specific while also having the ability to, simultaneously, perform esterification and transesterification reactions (Sharma et al. 2011). These reactions must also have a high conversion and yield of biodiesel. The physical properties of these catalysts should include having a high surface area with a high stability and also a hydrophobic surface (Sharma et al. 2011).

Acid and alkali heterogeneous catalysts have a number of advantages compared with their homogenous counterparts. A major asset of heterogeneous catalysts, especially acid catalysts, is that these catalysts can be easily separated from the product yield. This means that there is not a loss of product and also there is no waste water generated (Dehkhoda et al. 2010). The catalyst can be separated by simple filtration and cleaned with a small amount of water. The catalyst can then be reused. Solid base/alkali catalysts are beneficial catalysts as they have a high efficiency rate i.e. they have a high conversion rate and therefore generate a high yield of biofuel (Sharma et al. 2011). Examples of solid base catalysts include
zeolites, hydroxides with alkaline earth metal compounds and hydrotalcites (Sharma et al. 2011). The selectivity of these catalysts limits their use as they are sensitive to free fatty acids which may be present in the reaction mixture.

The catalysts discussed above have a number of limitations associated with them from environmental problems, high production costs, loss in product, and selectivity and the reusability of the catalyst. Many heterogeneous acid catalysts used in esterification reaction producing biofuels have some of these characteristics also. Ion-exchange resins, in particular cation exchange resins, have been investigated for their efficiency in catalysing esterification reactions.

Feng et al. (2010) researched a cation exchange resin, NKC-9, which proved to be efficient in catalysing the esterification reaction involving feedstock with a high acid value (Feng et al. 2010). This catalyst was found to have the following characteristics: a high capacity for water absorption and a high average pore diameter. The high average pore diameter results in a larger number of active sites for the reactants to adsorb to, and a large conversion of biofuel. Another major benefit of this catalyst is its reusability. Its catalytic activity increased after it was reused and it is believed that this is due to the fact that the resin particles broke down as a result of mechanical agitation (Sharma et al. 2011). The mechanical agitation was beneficial as it increased the total surface area of the catalyst.

The application of heterogeneous catalysts for biodiesel production in the industrial perspective warrants a minimal energy requirement. This can be accomplished if the heterogeneous catalysts are easy to prepare and need moderate reaction conditions. Heterogeneous catalysts have shown very good performance compared to sulphuric acid in the production of biodiesel. However
the solid catalysts sensitivity to water, tedious preparation methods and less activity at lower temperatures has given it drawbacks (Rao et al. 2011). The leaching aspect is another important criterion that governs the suitability of a particular catalyst. Therefore, there is a need for development of heterogeneous catalysts that can produce biodiesel at conditions (e.g. temperature and pressure) comparable to that used in homogeneous catalysis (Kiss et al. 2010).

2.3.3.3 The Role of Carbon in Heterogeneous Catalysis

In the production of biodiesel, several processes use esterification with a liquid acid catalyst. However, this method requires a high energy input and the removal of the catalyst from the homogeneous reaction mixture is expensive and wasteful. A sturdy carbon material made of small aromatic sheets can be produced through the pyrolysis of products such as sugar starch and cellulose. Once this material can be sulphonated, a high density stable solid with several active sites can be created. Thus, a high performing catalyst can be produced, cheaply. High quality biodiesel has been produced through the esterification of oleic acid with stearic acid with the use of a solid acid catalyst. It was shown that a sulphonated carbon catalyst had a reaction activity of more than half that of liquid sulphuric acid and was better than some commercial heterogeneous catalysts. This catalyst was easily recovered by decanting and showed no loss in activity after repeated use in reactions between 80°C and 180°C. Carbon supported catalysts produced from starch and cellulose have also shown successful activity. It seems to be the case that all saccharide molecules could be suitable for use in the preparation of catalysts (Toda et al. 2005).
More than 90% of the world’s chemical manufacturing processes utilise a catalytic process. It is possible that carbon as a catalyst support can offer a superior range of options when designing a catalyst to meet specific needs. For a catalyst to be successful, its chemical composition, surface area, stability, and mechanical properties must be optimised. Using a support, such as carbon, allows the active phase to distribute throughout the pore network, thus allowing a larger surface area per unit weight to be obtained. Inertness, stability under reaction, sufficient mechanical properties, high surface area, porosity, and chemical characteristics are the most important combinations that will achieve a desirable catalyst support. A carbon based support does have its limitations. Gasification may occur above 430°C producing methane or, in the presence of oxygen, produce carbon dioxide anywhere above 230°C. Depending on the precursor and its treatment, carbon tends to be a disorganised structure built mainly of small aromatic sheets with few bonded heteroatoms, usually oxygen and hydrogen. However, with pyrolysis, many of those heteroatoms are disposed of as they are volatilised due to the intense heat. This in turn leaves the residual carbon stacked in sheets. As these sheets are highly disorganised, it creates gaps and spaces that become the micro-, meso-, and macro-pores. Micropores tend to be any size up to 2nm; mesopores between 2 and 50nm; and macropores anything greater than 50nm. Adsorption of molecules onto the carbon support generally takes place within the micropores. However, the meso- and macropores play a vital role also, in creating the pathway from the micropore to the surface. The high disorganisation of the activated carbon leads to a higher-than-normal edge area. This edge area is where the in-plane bonding cease, leaving unpaired electrons to attract other molecules (Rodríguez-reinoso 1998).
2.3.3.4 Char based Catalysis

Char based catalysts are a new promising form of catalyst, which is formed by the pyrolysis of a biomass feedstock (Dehkhoda et al. 2010). As previously stated in section 2.2, Char can also be utilised as a soil amendment as it is a carbon sequester and can improve some soil properties (Malghani et al. 2013), as was first seen within the Tera Preta of South America. The source of biomass feedstock decides the adsorption capacity and surface area of the char. Any char rich in organic material can be used as a carbon precursor.

Most wood-derived char has surface area and requires activation (Wang et al. 2013). Char is activated through the physical and chemical creation of pores in the material. They tend to have relatively high volatile content and low ash content. Potassium hydroxide is a common activating agent; however the chemical activation of carbon materials is not well understood. Although, it is believed the agent dehydrates the sample and enhances the yield of carbonised material. The agent’s ions can be removed by washing with distilled water (Azargohar and Dalai 2008). Solid acid catalysts are typically rarer compared to solid base catalysts (Furuta et al. 2004). The development of high porosity requires relatively high activation temperatures. However, if the temperature is too high, the carbon structures will burn-off and the micro-, meso-, and macro- pores are all widened (Lua and Yang 2004).

In order to transform the char into a fully functional solid acid catalyst, the char must undergo a sulfonation process which consists in attaching the sulfonic groups in the carbon network base of the material.
The sulfonation of the char forms a more robust solid catalyst with a high density of active sites. This leads to the formed catalyst performing with high efficiency. The presence of the SO$_3$H groups means that the catalyst also has the potential to be used as a proton conductor (Toda et al. 2005). Catalysts with the highest surface area and acid density proved to have the best conversion rates (Dehkhoda et al. 2010). Toda et al. (2005) used sulfonated naphthalene in order to form ethyl acetate.

The char was carbonized at temperatures between 200 and 250°C. Although the solid acid catalyst was successful in the formation of ethyl acetate, the material was soft while the active sites of the catalyst were removed during liquid reactions where the temperature exceeded 100°C (Toda et al. 2005). This resulted in this catalyst having poor reusability.

Sulfonated biochar has recently been used in the production of biodiesel (Rao et al. 2011). Shu et al. synthesised a solid acid catalyst for biodiesel production (Sharma et al. 2011). The catalyst was designed from biochar obtained from the pyrolysis of vegetable oil asphalt.

Zheng et al. (2002) used potassium hydroxide activation and sulphuric acid sulfonation in the preparation of a heterogeneous catalyst from petroleum coke.
(Zheng et al. 2002). The esterification of oleic acid with methanol was used to investigate the effectiveness of this catalyst. The raw material was first treated with KOH and then pyrolysed in a horizontal cylinder furnace for 1 hour and then brought to a higher temperature for a further 1 hour. The activated carbon was then washed with HNO$_3$ and any free ions were washed away with distilled water until the pH returned to 6. The activated coke was dried and then sulphonated with H$_2$SO$_4$ in a N$_2$ atmosphere for 10 hours with 100 ml acid per 1g coke. The mixture was then filtered and dried to obtain the solid acid catalyst (Zeng et al. 2013).

2.4 Esterification reaction

The esterification reaction is the formation of esters from carboxylic acids and alcohols in the presence of homogeneous or heterogeneous acid catalysts which act as proton donors (Fischer and Speier 1895).

The overall reaction is reversible; to drive the reaction to completion, it is necessary to exploit Le Châteliers principle, which can be done either by continuously removing the water formed from the system or by using a large excess of the alcohol (Bellamy and Clarke 1968).

2.4.1 Reaction Mechanism

The reaction mechanism can be divided into six steps as follows. In the first step (1), the carboxylic acid takes a proton (a hydrogen ion) from the acid catalyst. The proton becomes attached to one of the lone pairs on the oxygen of the carbonyl group (C=O). One of the lone pairs of the alcohol molecule oxygen functions as the nucleophile, attacking the electrophilic C in the C=O, with the electrons
moving towards the oxonium ion (2), creating the tetrahedral intermediate. At this stage (3) the proton (a hydrogen ion) is transferred from the alcoholic oxygen atom to one of the other species in the mixture. The $-\text{OH}$ is converted into a leaving group by protonation (4) and the electrons of an adjacent oxygen help to form a neutral molecule of water (5). In the final step (6), the deprotonation of the oxonium ion reveals the ester (Fischer and Speier 1895).

Scheme 2.2. Esterification reaction mechanism. B is the conjugate base $A^-$ of the acid catalyst, or a C=O group (as in step 1), or an R-OH group as in step 4, or a water molecule as in step 6.

2.5 One step hydrogenation esterification (OHE)

One-step hydrogenation esterification (OHE) is a method that combines the processes of hydrogenation and esterification into a single step. In one step hydrogenation esterification, the alcohol is formed as an intermediate compound for the ester production and has potential to replace the traditional esterification
process. OHE reactions usually take place in a vacuumed, stainless steel autoclave vessel for lab scale processing.

One-step hydrogenation esterification requires the use of a bifunctional catalyst (a catalyst which operates for both processes).

OHE has many uses besides the production of esters including the upgrading of bio-oils i.e. the replacement of acid an aldehyde contaminants furfural and acetic acid with stable, combustible compounds.

2.5.1 OHE for bio-oil upgrading

The one step hydrogenation esterification reaction has potential in upgrading bio oil derived from pyrolysis of biomass (Yang Tang et al. 2010). This bio oil is seen as a potential replacement for petroleum to be used as a fuel and in processing of chemical products (Xiong et al. 2011). Bio oil has some unfavourable properties also, such as high acidity, high viscosity, poor heating value and poor stability due to high oxygen content (Mohan et al. 2006). Processes to remove or reduce the oxygen concentration are therefore desirable to produce better quality oil to reach the properties of petroleum. The upgrading of crude bio oil can be accomplished by a variety of methods including catalytic esterification, catalytic hydro-processing and catalytic cracking (Elliott and Hart 2009). Physical methods include char removal, hot vapour filtration, liquid filtration and solvent addition. The catalyst is a key factor in the upgrading process with homogeneous and heterogeneous types available.

A number of heterogeneous catalysts were already applied including zeolites. Mono and bifunctional catalysts, e.g. mesoporous materials doped with
noble/transitional metals can produce high quality bio oil, with low oxygen and water content (Stöcker 2008). Some catalysts, for example the copper-chromium (Cu-Cr) oxide catalyst used in many commercial processes, may cause severe environmental problems. In order to combat this, investigations were successfully undertaken over the use of titanium oxide (TiO\textsubscript{2}) supported Adkins catalyst (produced by sonification) in the selective hydrogenation of furfuryl alcohol to decrease the chromium content without affecting the catalytic activity (Huang et al. 2007).

Tang et al. (2008) developed a model upgrading method called one OHE to convert acids and aldehydes in bio oil to stable combustible compounds. They used acetaldehyde (butyl aldehyde) and acetic acid as model components for OHE over bifunctional platinum (Pt) catalysts. Bifunctional catalysts have both hydrogenation and esterification properties and are widely used for OHE (Xueqin Wang et al. 2005). It was found that catalysts with large surface area, large pore size distribution, smaller metal particles and strong acid sites may be beneficial for the OHE reaction. The OHE reaction involved the reaction of molecular hydrogen, aldehyde and alcohol to form an ester and water. Two platinum catalysts were developed with an acidic support of HZSM-5 for the first and amorphous aluminium silicate (Al\textsubscript{2}(SiO\textsubscript{3})\textsubscript{3}) for the second, with a weight percentage of 5 % platinum in both cases. Their findings show that platinum/aluminium silicate catalysts had far higher activity for ester formation with far less by product formed. The group proposed that this was the case for the reasons listed above (large surface area, large pore size distribution, smaller metal particles and strong acid sites).
2.5.2 Catalysts for OHE

2.5.2.1 Bifunctional hybrid heterogeneous catalysts

Bifunctional hybrid heterogeneous catalysts are suggested by literature as suitable candidates suitable for OHE reactions (Tang et al. 2010). What is meant by „hybrid catalyst” here is a catalyst comprised of organic and inorganic components, in order to better satisfy the needs for the OHE to be successful, as outlined below:

The inorganic component is comprised of a noble metal catalyst and this concerns the hydrogenation component of the OHE step. Possible candidates include some Group VIII transition metals of the periodic table, namely Ru, Rh, Pd, Pt, Ni and Co (Tang et al. 2010). These are used because transition metals, in particular those in the Ni, Pd and Pt series, are typically used in hydrogenation reactions (Brieger and Nestrick 1974). These Group VIII metals are used because they have unpaired $d$ electrons and this is particularly conducive to catalysis of hydrogenation reactions (Bond 1968).

Pd seems to be of most interest in OHE studies, appearing to give the best catalytic performance (Wanjin Yu et al. 2011).

The organic component would normally be a homogeneous acid catalyst, and these are not favourable for reasons listed above. A porous solid acid catalyst (i.e. zeolites, resins, zirconium sulphate, sulfonated-carbon composites and mesoporous silica) is instead used. These solid catalysts contain acid functional groups on the surface of the macromolecule; these constitute the catalyst active sites. According to L.F. Giraldo et al. (2007), the adequate diffusion of molecules
through the catalyst pores allows the direct interaction with the acidic sites on the wall surface, promoting the conversions (Giraldo et al.).

The high surface area and adjustable pore size of mesoporous silica makes it an excellent candidate for the heterogeneous acid catalyst (Tang et al. 2010, Giraldo et al.).

The use of bifunctional palladium (Pd) catalysts supported by Al-SBA-15 for OHE of furfural and acetic acid as a model for bio oil upgrading was studied by Yu et al. (2011). With the aid of NH$_3$-TPD (Ammonia-Temperature Programmed Desorption) and catalytic performance analysis, the group investigated the performance of the catalyst. Their findings showed that the medium ratio of AlSi favours the OHE reaction between furfural and acetic acid.

**2.5.3 OHE of carboxylic acids**

F.A. Pesa et al. (1983) experimented on vapour phase hydrogenation of carboxylic acids to their corresponding alcohols in the presence of steam and various mixed metal catalysts comprising of ruthenium, one of nickel or cobalt and optionally one of cadmium, zinc, copper, iron, rhodium, palladium, osmium, iridium or platinum. Tests were done on the following catalyst: RuCoMZ$_{0.4}$O$_x$ where M= palladium or nickel, it was found that palladium gave better percentage conversion, yield and selectivity over temperatures or 200-215°C and pressures of 69-86 bar.

Wilbur A Lazier (1932), designed a process of direct catalytic hydrogenation of acids to alcohols and esters. He used molecular hydrogen (H$_2$) as a reducing agent in the presence of a suitable catalyst to achieve this. The method worked on the
following mechanism: One molecule of hydrogen removes the oxygen of the C=O (Carbonyl) group of the acid to generate water, while another hydrogen atom takes the place of the oxygen atom. A secondary reaction (esterification) then takes place between a portion of the alcohol formed and a portion of the unchanged acid. Lazier conducted his process at higher temperature and pressure that the liquid phase hydrogenation used at that time in the hardening of fats and fatty acids. The process was conducted to favour ester and alcohol products. Nickel catalysts were then used to separate products and bring them to the same level of H₂ saturation.
Chapter 3

3 Materials and methods

3.1 CBSA catalysts for butyl butyrate production

MG and BBW digestate are the original source of biomass for the production of char by carbonization in the process of slow pyrolysis. This form of pyrolysis utilizes a long vapour residence time in order to maximize char yields (Kwapinski et al. 2010).

MG was supplied by JHM Crops Ltd. (http://www.jhmcrops.ie), in Adare, Co. Limerick, Ireland. It was received as chipped cane with particle size less than 2 cm.

The BBW digestate used in this study was prepared in the Prof. Vincent O’Flaherty lab at the University of Galway by Corine Nzeteu from the university’s Microbiology Department. The n-butanol (ACS reagent, ≥99.4 %, 360465-2.5L) and butyric acid (≤99 %, B103500-2.5L) were purchased from Sigma-Aldrich (Ireland).

Potassium hydroxide (Sigma-Aldrich, 90 % flakes) and hydrochloric acid (Merck, 37 %) were used in the activation of the carbon support, and sulfuric acid (Sigma-Aldrich, ACS reagent, 95-98 %) was used in the sulfonation step. The same sulfuric acid and Amberlyst-15 (Sigma-Aldrich, Moisture≤ 1.5 %) were used as comparison catalysts in the esterification reactions. For the gas chromatography, n-heptane (Sigma-Aldrich, CHROMASOLV, ≥ 99 %) was used as a solvent, along with 1-octanol (Fluka, 95446) as the internal standard for butyl butyrate. All
injections were made using a Hamilton Bonaduz 10 µl syringe. Total acidity testing was done through back titration. Hydrochloric acid, sodium hydroxide (Sigma-Aldrich, Anhydrous Pellets, reagent grade ≥ 98 %), and potassium carbonate (Fluka, Anhydrous, Ultra ≥ 99 %) were used as titrants.

3.2 Catalyst preparation

There were three steps to prepare the catalysts.

3.2.1.1 Pyrolysis/Carbonisation

In this work a Carbolite tubular furnace with a quartz tube was used. Char was produced at three temperatures; 400, 500, and 600°C. To achieve anaerobic conditions, a nitrogen pressure of 1.6 atm was maintained in the reactor. The MG and BBW digestate samples were placed inside a metal gauze basket and then inserted into the heated part of the furnace for 20 min after which it was removed from the heated region, but kept in a nitrogen atmosphere until it cooled to room temperature.

Figure 3.1. Pyrolysis apparatus setup.

Once the char were collected, they were ground and sieved to between 180 and 600 µm (smaller particles size would not improve the performance of the material and would be too dusty to be managed properly). With regards to MG, part of its
char underwent chemical activation in order to increase the total surface area, while the remainder underwent sulfonation directly.

### 3.2.1.2 Chemical activation

Chemical activation was undertaken to increase the surface area of the material.

The char was mixed with 7.0 M KOH in a ratio of 300 ml to 36 g. A magnetic stirrer was used to mix the KOH/char mixture for 2 hours at room temperature in a glass beaker, after which it was placed in an oven (Memmert, 100 800), overnight, at 105°C. The 20 g of the prepared sample was then placed in the cylinder inside the furnace under a flow of nitrogen, which was heated to 300°C at 20 °C/min, and held at this temperature for 1 hour to prevent carbon loss through the direct attack of steam (Azargohar and Dalai 2008). The temperature was then increased to the desired temperature for activation which was the same as that used during carbonization. The chemical activation was carried out for 2 hours before cooling down. Afterwards, the products were thoroughly washed with water and placed in an oven for 12 hours at 105°C. When the activated char was removed from the oven it was added to 0.1 M hydrochloric acid (HCl), at a ratio of 300 ml to 36 g of char, and stirred for 1 hour with a magnetic stirrer, at 100°C. Afterwards, the samples were filtered and washed with distilled water to remove the soluble salts and the potassium compounds due to acid washing, until the washing water reached pH = 7, and dried overnight in oven at 105°C (Azargohar and Dalai 2008).

### 3.2.1.3 Sulfonation

In order to produce the catalytic acid materials, 20 g of char (activated or non-activated) was placed in a 500 ml flask with 200 ml of concentrated (95-97 %)
sulfuric acid. The mixtures were heated at 150°C for 24 h on magnetic hotplate stirrers, fitted with J-type PTFE coated thermocouples. The slurries obtained were then filtered and washed several times with distilled water until the pH became neutral (Dehkhoda et al. 2010). The materials were subsequently dried overnight in an oven at 105°C and sieved to particles between 180 and 600 µm. Aliquots of sample were collected for characterization at every stage. All procedures were repeated for each pyrolysis process temperature.

3.2.2 Characterisation techniques

Structural information about the prepared samples were obtained by: scanning electron microscope (SEM), Brunauer-Emmet-Teller surface analyser (BET), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), elemental analyser (EA) and total acid density test.

3.2.2.1 SEM

A visual observation was performed with the Hitachi SU-70 Scanning Electron Microscope (SEM) from the Materials & Surface Science Institute in order to gain knowledge of the morphology and pores size of the materials.

SEM high definition pictures were taken of the structures of the char each step of the preparation with an acceleration voltage of 20 kV.

A very small sample of char was placed on this pad and then gold was dusted on to the sample to compensate for any moisture and thus improve resolution. The sample was then scanned with the microscope for the most ideal photos and interesting pieces.
Once the sample is placed inside the SEM, a voltage is applied to a filament loop of tungsten. This filament then acts as a cathode and emits a beam of electrons towards the anode. Some of the beams will accelerate past the anode, down the column, and hit the sample. Through a condenser lens, very close-up and precise pictures can be taken of the sample. When the beam of electrons hit the sample, secondary electrons are emitted from the sample. These electrons are picked up by a backscatter detector and this signal is converted to a voltage which is then turned into an image on the computer screen that is identical to that of the face of the sample.
All materials collected at each stage of the preparation of the catalysts were also analysed using the energy-dispersive (EDS) detector (Oxford Instruments) integrated into the SEM. INCA software was used to examine the energy spectrum in order to determine the abundance of specific elements and to give an overall view of the composition of the samples.

Figure 3.2. SEM configuration (source: Hitachi company).
3.2.2.2 BET

The purpose of the Brunauer-Emmett-Teller (BET) theory is to quantify the specific surface area and pore-size distribution of the samples of char that have been produced. The BET theory attempts to explain how gas molecules adsorb to the surface of a porous solid and thus gives a way to analyse the specific surface area.

The surface area of the carbon carriers prior to chemical activation, following chemical activation and after sulfonation was determined with nitrogen adsorption–desorption isotherms at −196°C using Micrometrics Gemini 236 BET analyser. Around 0.1 g of char sample was placed in a sample tube and then outgassed in nitrogen atmosphere (1 bar) for 12 h at a temperature of 200°C.

The technique is based on the isotherm derived by Brunauer, Emmett and Teller (BET) for physical multilayer adsorption onto a surface.

\[
\frac{P}{V(P_0 - P)} = \frac{1}{V_mC} + \frac{C - 1}{V_mC} \frac{P}{P_0}
\]

\(P = \) equilibrium pressure.

\(P_0 = \) saturation pressure of the adsorbate at the measured temperature.

\(V = \) corresponding gaseous volume at the pressure \(P\) of adsorbed molecules.

\(V_m = \) volume \(V\) required for a monolayer coverage of adsorbate.

\(C = \) constant, related to the enthalpy of adsorption.

The \(\frac{P}{P_0}\) range used for the BET measurement in the equation above was 0.05-0.3.
3.2.2.3 FTIR

The catalyst surface functional group chemistry was investigated by attenuated total reflectance FT-IR spectrometry (Agilent Technologies Cary 630).

Infrared spectroscopy is a non-destructive, qualitative and quantitative analysis of samples. Within each spectrum produced from the instrument, there will be a number of bands corresponding to a particular vibration of a molecular structure. The frequency at which this band is produced will depend entirely on its bond structure, the size of the atoms involved, the configuration of the sample, and what state the sample is in. Thus, other than enantiomers, each molecular structure has its own specific fingerprint. This allows for identification of the main structural features of molecules and materials.

As it is considered the most useful range to work in, the spectra were recorded over the range from 4000 to 650 cm$^{-1}$ with a resolution of 1 cm$^{-1}$.

A small amount of each compacted sample was placed on the FT-IR stage and a light beam of varying frequency of the range stated was sent towards the sample, this beam then travelled to a detector and through a Fourier transform device, was converted to an FT-IR spectrum. The spectrum was then analysed for potential active sites within the sample.

3.2.2.4 XRD

X-ray diffraction (XRD) was used for the structural characterization of the catalysts. The XRD diffractograms were collected using an X”PERT MPD-Pro Pan Analytical, the Netherlands. Ground samples were loaded into a circular cavity holder and the instrument operated at 40 kV and 35 mA using a Cu source of $\lambda=1.54$ nm, a nickel filter and a beam mask.
XRD is a multi-purpose, non-destructive analytical tool in identifying the various possible crystalline structures within a sample. This is achieved by comparing the diffractogram received from a sample to the computer database, HighScore.

**Figure 3.3.** Schematic diagram of the XRD

A crystalline structure is an arrangement of the atoms within a sample that is periodic and predictable in shape. Due to the periodic shape, a crystal can be broken down into a unit cell and then built through stacking of these cells. Within a sample, there could be several different phases of crystals as well as amorphous compounds. A broad shallow rise, known as a background hump, in the diffractogram indicates amorphous material, while a crystalline structure is defined by sharp peaks. The width of the peak is inversely proportional to the size of the crystalline structure. The concentration of a specific phase is proportional to the area of its corresponding peaks.

As the char material is already in powder form, the sample needed only to be placed in the holder and then placed within the diffraction unit. To do this, a soft metal O-ring was placed on a holding stage. A small sample of char was placed at the centre of the ring and patted flat with a stamp. The back of the O-ring was
then fixed on top of the char sample and the whole unit was flipped. The holding stage was removed and the char sample was ready for analysis.

3.2.2.5 Total acidity test

The total acid density originated from SO$_3$H + COOH + OH functional groups was estimated by standard acid-back titrations.

The amount of acid that has been adsorbed by the catalyst should give a clear indication of how successful the catalyst should be in an esterification reaction. The total acidity of the catalyst will also give a clear indication as to how well the sulfonation step was carried out. In total, the development of this technique was crucial to understanding the catalyst, its abilities, and its weaknesses.

The total acidity test was a form of the back titration method. A standard burette and a pH meter (HI 9126 pH/ORP Meter – HANNA, USA) along with a magnetic stirrer and stir plate (Yellow Line, MSH Basic) were used for this technique. A very pure sample of potassium carbonate (K$_2$CO$_3$) was used as the base comparison for the titration of everything else. 0.2M of the potassium carbonate was produced by mixing 2.76 g with 1 litre of distilled water in a volumetric flask. However, to ensure absolute accuracy, the potassium carbonate was placed in the oven at 105°C for 2 hours and then desiccated for a further 1 hour.

A 0.050M hydrochloric acid solution was produced. To ensure the absolute accuracy of the hydrochloric acid, it was titrated with the known molarity of potassium carbonate. This gave a more accurate prediction of the molarity of the hydrochloric acid. For the remainder of the back titration, the hydrochloric acid acted as the titrant in the reaction with 10 ml of titrate.
A 0.037 M NaOH solution was produced. The hydrochloric acid solution was titrated with the sodium hydroxide solution and the actual molarity of the sodium hydroxide was calculated. 20 ml of the sodium hydroxide solution was mixed for 30 minutes with 0.1 g of the heterogeneous catalyst. The acidity of the catalyst would neutralise part of the basicity of the sodium hydroxide. However, as there were more moles of base than acid (predicted) in the mixture, the catalyst would not be able to neutralise the entire base. The catalyst was filtered from the mixture and 10 ml of it was titrated against standardized 0.050 M HCl. To set the titration end point, the pH meter was employed. As the molarity of the sodium hydroxide and the hydrochloric acid were already elucidated, the difference between the molarity of the sodium hydroxide and the catalyst mixture is comparable to the moles of NaOH consumed in the catalyst mixture. The value that was obtained was then converted to mmol of H₂SO₄ per g of catalyst, meaning that the catalyst had the same acidity of a certain number of millimoles of sulfuric acid per grams of catalyst. Titrations were carried out in triplicate.

Here is a summary of how the calculations were carried out:

\[
Molarity\ of\ unknown\ Solution\ (M) =
\]

\[
= \left( \frac{\text{solution of known molarity (L)}}{\text{solution of unknown molarity (L)}} \right) \times \text{Molarity of known solution (M)}
\]

\[
\text{Molarity of consumed NaOH in the catalyst mixture (M)} =
\]

\[
= \text{Molarity of NaOH (M)} - \text{Molarity of the catalyst mixture (M)}
\]

\[
\text{Moles of consumed NaOH per 1 g catalyst} =
\]

\[
= \frac{\text{Molarity of consumed NaOH (M)} \times \text{volume of NaOH mixed with the catalyst (L)}}{\text{weight of catalyst}}
\]
### 3.2.2.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a technique in which the mass of a substance is measured as a function of temperature, while the substance is subjected to a controlled temperature programme and was employed to demonstrate the influence of the catalyst preparation on the weight changes of the materials derived from the pyrolysis of Miscanthus x giganteus (MG) and brown bin waste digestate (W). For this analysis a TGA/DSC instrument (Setaram Labsys, USA) was utilized. The samples were heated under a flow of nitrogen (flow rate of 500ml/min) at a constant heating rate of 10°C/min.

![Schematic diagram of the TG-DTA system](image)

**Figure 3.4.** Schematic diagram of the TG-DTA system (Naoharu et al. 2012).

As shown in Figure 3.4, two alumina crucibles were used with one for reference and the second one for holding sample. Approximately, 5 ± 1 mg of the sample was loaded in the sample crucible. The crucible was tapped gently on a hard and
clean surface to evenly distribute the sample in the crucible. It was then loaded on the holder carefully. The programmed heating was started after the furnace was closed and the gas streams were applied. After the programme

3.2.2.7 Proximate Analysis

Proximate analysis conducted in this study involved the determination of moisture and ash content according to standards methods (BS EN 14774-3, I.S. EN 14775:2009, I.S. EN 15148:2009).

3.2.2.7.1 Moisture

The moisture content of a feedstock is very important with regards to thermal treatment technologies. It is the parameter which most influences the energy balance. Once samples are dried the moisture content can still change during storage and treatment practices depending on its hygroscopic nature. Therefore, the moisture content was completed alongside other analytical measurements.

Procedure:

The moisture content was determined according to BS EN 14774-3 (2009). At least three replications were performed each time. A crucible was dried at 105 ± 2 °C for at least two hours and subsequently cooled to room temperature in a desiccator. Around 1 g of each sample was added to the crucible and weighted to an accuracy of 0.1 mg. For char samples the weight was 0.5 g each. The crucibles containing the samples were heated over night at 105 ±2 °C left to cool to r.t. the following day in a desiccator and finally the crucibles containing the dry sample were weighed.

Calculation:
MC = \frac{((m_3-m_1))/((m_2-m_1))}{100}

Where:

MC = Moisture Content at 105 °C (wt. %)

m_1 = mass of empty crucible (g)

m_2 = mass of empty crucible and initial sample (g)

m_3 = mass of empty crucible and dried sample (g)

3.2.2.7.2 Ash

The ash content represents the inorganic part of the sample which remains after combustion.

The ash content of the samples was carried out in accordance with BS EN 14775 (2009). At least three replications were carried out for each sample. Prior to ash content determination the moisture content was analysed. The porcelain crucible and samples were heated in a furnace from r.t. to 250 ± 10 °C at a heating rate of 5°C min\(^{-1}\) with a residence time of 60 min. Then the furnace was raised to 550 ± 10 °C at a heating rate of 5 °C min\(^{-1}\) and kept at this temperature level for at least 120 min (overnight for biochar samples) until complete incineration was achieved. The crucible was allowed to cool in the furnace until 105 °C and then placed in a desiccator to cool to room temperature before weighing to the nearest 0.1 mg.

Calculation:

A = \frac{((m_3-m_1))/((m_2-m_1))}{100 x 100/(100-MC)}

Where:
A = ash content on dry basis (wt.%)  

$m_1$ = mass of empty crucible (g)  

$m_2$ = mass of empty crucible and initial sample (g)  

$m_3$ = mass of empty crucible and ashed sample (g)  

MC = moisture content (wt.%) of the initial sample  

### 3.2.2.8 Ultimate analysis

Ultimate analysis was conducted to determine the elemental composition of the samples. Carbon, hydrogen, nitrogen and sulphur were analysed with an Elemental Vario EL Cube analyser.

The analysis was conducted according to BS EN 15104 (2011). Sulphanilamide was used as a standard. Oxygen was calculated by difference, subtracting the percentage of C, H, S and ash from 100%.

**Procedure:**

Approximately 10 ± 1 mg of finely ground sample was weighted to the nearest 0.01 mg into an aluminium boat, which was then sealed carefully, formed to a ball shape, and placed into an integrated carousel. Each sample entered a ball valve, flushed with helium gas to remove atmospheric nitrogen and then dropped into a combustion tube. Catalytic combustion of the samples was carried out at 1150 °C with oxygen and tungsten trioxide (WO$_3$). Furthermore, WO$_3$ is used to prevent the formation of non-volatile sulphates and bind alkali metals, which interfere with the results and damage the instrument. Water was removed with Sicapent (phosphorus pentaoxide). Then the gases passed through a reduction tube using helium as a carrier gas, where compounds such as NO$_x$ and SO$_3$ were reduced to
N₂ and SO₂ by hot copper wires. Excess oxygen was adsorbed, while volatile halogen compounds were trapped by silver wool at the entrance to the reduction tube. The formed analysis gases (CO₂, H₂O, and SO₂) were separated by adsorption to three separate columns, while N₂ entered the thermal conductivity detector (TCD) directly. The trapped gases were desorbed one by one from the columns by heat exposure, which are then also detected and quantified using the TCD.

A basic schematic of the instrument is given in Figure 3.5

![Figure 3.5. Schematic of elemental analyser (Elemental Vario EL Cube)](image-url)
3.2.3 Esterification reaction

The esterification reactions were used not only to test the abilities of each solid catalyst, but also to test the amount of catalyst needed to get the optimum production of butyl butyrate. Previous works had shown that a 2:1 (n-butanol : butyric acid) ratio is the optimum for esterification reactions (Waddington and Finlay 1981). Esterification reactions were carried out using 1, 2 and 5 % catalyst loading. An electronic pipette (HandyStep) with pipette dispenser tips were used to place 20.0 ml of n-butanol and 10.0 ml of butyric acid in a 50 ml round-bottom flask fitted with a magnetic stirrer and condenser. The round-bottom flask was heated using a silicone oil bath with a magnetic stirrer to increase heat transfer throughout the bath and to reduce the external mass transfer resistance between liquid and the catalyst. The reaction was carried out under reflux at 110°C for 24 hours and the time started when the apparatus had been placed in the silicone bath and the temperature had reached 110°C (~15 min).

The magnetic stirrer was set to 150 rpm. Samples (around 0.01 g) were taken at 1, 2, 4, 6, 8, and 24 hours using a Pasteur pipette and were added to an Eppendorf tube with a known amount of 1-octanol and n-heptane. Samples were then placed into a 5 ml Terumo Syringe fitted with a filter (VWR, 0.45 µl PTFE filter), and then filtered into an Eppendorf tube before being placed in the freezer to avoid evaporation. After each experiment the CBSA catalysts were filtered by decanting onto filter paper and washed several times with distilled water. The catalysts were dried in an oven at 105°C overnight, collected and reloaded to perform other experiments. Each reaction was repeated three times with the standard deviation from the mean represented by uncertainty bars in the related figures.
The mass of the solution at the beginning and at the end of each experiment was noted to check whether there were any losses. Calculated losses were at most 1%.

3.2.3.1 GC

The stock solutions were analysed by gas chromatography (Agilent 7890A, Agilent Tech., USA) equipped with a flame ionization detector system. The separations were carried out on Restek Stabilwax column (30 m x 0.25 mm x 0.25 µm). The temperature of the column was held at 100°C for 2 min, increased to 160°C at a rate of 15°C/min, held for 1 min and increased to 180°C at a rate of 10°C/min for a total time of 9 min. The split ratio was 7.5:1 and the carrier gas used was nitrogen. The injection inlet and the detector were held at 250°C and injection volume was 1.0 µl.

3.2.3.1.1 Internal standard calibration

Heptane acts as a solvent for both octanol and butyl butyrate and as such was suitable for the gas chromatography of these two molecules. Five calibrated samples were made using butyl butyrate (Fluka analytical standard, 67367-1ML), at 10, 8, 6, 4, and 2 mg/ml. In a 100ml volumetric flask, 1g of butyl butyrate, 1g of butanol and 1 g of butyric acid were added using a Sartorius BP121S balance. The remainder of the flask was filled to the mark with heptane. In another 100 ml volumetric flask, 1 g of octanol (internal standard) was added and the rest of the flask was filled with heptane to the mark in order to have an octanol concentration of 10mg/ml. In five 10ml volumetric flasks were prepared dilutions of butyl butyrate, butanol, butyric acid/heptane mixture, corresponding to the desired concentrations. At this stage, 0.75 ml of each dilution was added in a different Eppendorf tubes in which 0.25 ml of the octanol/Heptane solution were poured.
Each sample was injected to the GC (Agilent Technologies, 7820A GC System) three times and an average of each compound peak area was calculated.

Tables 3.1 and 3.2 and Figure 3.6 below shows the calculation for the calibration of the standard.

**Table 3.1.** Concentration of prepared and injected solutions

<table>
<thead>
<tr>
<th></th>
<th>Butyl butyrate [mg/ml]</th>
<th>Butyric acid [mg/ml]</th>
<th>Butanol [mg/ml]</th>
<th>Octanol [mg/ml]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prepared</td>
<td>Injected</td>
<td>Prepared</td>
<td>Injected</td>
<td>Prepared</td>
</tr>
<tr>
<td>1.96</td>
<td>1.47</td>
<td>1.98</td>
<td>1.48</td>
<td>2.07</td>
</tr>
<tr>
<td>3.91</td>
<td>2.93</td>
<td>3.96</td>
<td>2.97</td>
<td>4.13</td>
</tr>
<tr>
<td>5.87</td>
<td>4.40</td>
<td>5.93</td>
<td>4.45</td>
<td>6.20</td>
</tr>
<tr>
<td>7.82</td>
<td>5.87</td>
<td>7.91</td>
<td>5.93</td>
<td>8.27</td>
</tr>
<tr>
<td>9.78</td>
<td>7.33</td>
<td>9.89</td>
<td>7.42</td>
<td>10.3</td>
</tr>
</tbody>
</table>

**Table 3.2.** GC Area of injected solutions (average over 3 runs)

<table>
<thead>
<tr>
<th></th>
<th>Butyl butyrate</th>
<th>Butyric acid</th>
<th>Butanol</th>
<th>Octanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>2292</td>
<td>1541</td>
<td>2526</td>
<td>4637</td>
<td></td>
</tr>
<tr>
<td>3931</td>
<td>2479</td>
<td>3366</td>
<td>4005</td>
<td></td>
</tr>
<tr>
<td>6460</td>
<td>4280</td>
<td>6039</td>
<td>4454</td>
<td></td>
</tr>
<tr>
<td>7943</td>
<td>5253</td>
<td>7302</td>
<td>4132</td>
<td></td>
</tr>
<tr>
<td>10125</td>
<td>6821</td>
<td>9196</td>
<td>4228</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.6. X, Y values for standard calibration

Where

\[
X \text{ ratio} = \frac{\text{Concentration of injected solution}}{\text{Concentration of injected internal standard}}
\]

\[
Y \text{ ratio} = \frac{\text{GC Area of injected solution}}{\text{GC Area of injected internal standard}}
\]

Each of the hourly samples from the esterification reaction was removed from the freezer and analysed at the GC. The resulted areas where used with the equation above to calculate the ratio between the concentration of injected solutions and the concentration of injected internal standard.

The X ratio values for each sample were therefore: \(X_{BB}\), \(X_{BA}\), and \(X_{BT}\).

Since the reflux apparatus was perfectly sealed, and the water was not considered escaping from the reactor, the \(XH_2O\) value was calculated based on the fact that the moles of Butyl butyrate produced are the same as the moles of water formed.
The $X$ ratio values were converted into the corresponding mass fraction (WF) with the following formula:

$$WF_{BB} = \frac{X_{BB}}{X_{BB} + X_{BA} + X_{BT} + X_{H_2O}}$$

By dividing each WF by the correspondent molecular weight, the number of moles per 1 g of solution where calculated. At this point, this last value was multiplied by the actual weight of the solution and divided by its volume in order to obtain the concentration of the compound at every stage of the reaction.

The butyl butyrate yield was calculated using eq.(3.1).

$$\text{yield} = \frac{\text{final moles butyl butyrate}}{\text{initial moles butyric acid}}$$ \hspace{1cm} (3.1)

### 3.2.4 Kinetic model

To establish the kinetic parameters associated with butyl-butyrate production with CBSA catalysts, two separated elementary power law kinetic models: model 1 (m1) and model 2 (m2), were implemented for the esterification reaction. The models describe the reactions numerically and provide provisional estimations of the phenomenological reaction rates involved. These models assume there is no deactivation of the catalytic material during reaction.

To achieve this, two mole balance equations were defined (equations 2 and 3) by considering a reversible reaction mechanism, where

**m1:**

$$\frac{d C_{Am1}}{dt} = - \frac{d C_{Bm1}}{dt} = - \frac{d C_{Mm1}}{dt} = - \frac{d C_{Dm1}}{dt} = k_f C_{Am1} C_{Bm1} + k_r C_{Mm1} C_{Dm1} \hspace{1cm} (2)$$

$$C_{Bm1} = C_{Am1} + C_{B0} - C_{A0}$$
and by applying a generic power law model with a non-defined reaction order

\[ m_2: \]

\[ \frac{d C_{Am2}}{dt} = -k C_{Am2}^\alpha \]  

(3)

where

\[ C_{c_2} - C_{c0} = C_{a0} - C_{Am2}. \]

\[ C_{c0} = 0 \]

\( C_A \) is the concentration of butyric acid, \( C_B \) is the concentration of butanol, \( C_C \) is the concentration of butyl butyrate, \( C_D \) is the concentration of water, \( k_f \) is the rate constant of the forward reaction and \( k_r \) is the rate constant of the reverse reaction.

All of these were calculated for each of the nine experiments conducted with a CBSA catalyst, at three different catalyst loadings and at three different temperatures: 70°C, 90°C and 110°C. The equilibrium constants (\( K_{eq} \)) for each temperature were calculated using HSC software:

\[ K_{eq} = e^{-\frac{(\Delta H - T\Delta S)}{RT}} \]  

(4)
Table 3.3. Equilibrium constants for the esterification reaction of butyric acid with butanol.

<table>
<thead>
<tr>
<th>T, °C</th>
<th>ΔH, kJ</th>
<th>ΔS, J/K</th>
<th>ΔG, kJ</th>
<th>K&lt;sub&gt;eq&lt;/sub&gt;</th>
<th>log(K&lt;sub&gt;eq&lt;/sub&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>-4.46</td>
<td>7.98</td>
<td>-7.19</td>
<td>12.4</td>
<td>1.10</td>
</tr>
<tr>
<td>90</td>
<td>-4.22</td>
<td>8.64</td>
<td>-7.36</td>
<td>11.4</td>
<td>1.06</td>
</tr>
<tr>
<td>110</td>
<td>-3.97</td>
<td>9.29</td>
<td>-7.54</td>
<td>10.7</td>
<td>1.03</td>
</tr>
</tbody>
</table>

Based on the equilibrium constants, the conversions at equilibrium have also been calculated.

Figure 3.7. Conversion of butyric acid at equilibrium with different ratio of reactants (butanol: butyric acid), and formation of butyl butyrate at equilibrium (butyl butyrate: water).

Figure 3.7 shows that the butyric acid conversion with 1:1 molar ratio (butanol: butyric acid) goes from 78 % to 77 % in a temperature range from 70°C to 110°C. However, butyric acid conversion increases significantly with increasing molar ratio. The conversions at equilibrium with the ratio 2:1 (molar ratio used in our work) go from 94 % to 93 % in the temperature range from 70°C to 110°C.
The kinetic parameters associated with each reaction were determined by minimising an objective function (obj) using *lsqcurvefit* of Matlab (eq.5).

\[
\text{obj} = \sum_{i=1}^{N} (C_{\text{A exp},i} - C_{\text{A mod},i})^2
\]  

(5)

\(N\) is the number of experimental data points considered for each reaction and \(C_{\text{A mod},i}\) is the analytical solution of the differential equation of kinetic model 1 (eq.6) and kinetic model 2 (eq.7), respectively.

Model 1 equations are defined as follows:

\[
C_{\text{A m1}} = \frac{-S_2 \ H \ e^{-k_f(t(S_1-S_2))} + S_1}{1 - H \ e^{-k_f(t(S_1-S_2))}}
\]  

(6)

where

\[
k_f = A \ e^{\frac{-E_{af}}{RT}}; \quad S_1 = \frac{-b + \sqrt{\Delta}}{2a}; \quad S_2 = \frac{-b - \sqrt{\Delta}}{2a}; \quad H = \frac{C_{A0} - S_1}{C_{A0} - S_2}
\]

\[
a = 1 - \frac{1}{K_c}; \quad b = (C_{B0} - C_{A0}) + \frac{2C_{A0}}{K_c}; \quad c = -\frac{C_{A0}^2}{K_c}
\]

and for model 2 are:

\[
C_{\text{A m2}} = \left[ -k(1 - \alpha)t + C_{A0}^{1-\alpha} \right]^{\frac{1}{1-\alpha}}
\]  

(7)

\[
k = A_{m2} \ e^{-\frac{E_{am2}}{RT}}
\]

\(E_{af}\) is the activation energy of the forward reaction, \(A\) is the pre-exponential factor, \(C_{A0}\) is the initial concentration of butyric acid, \(C_{B0}\) is the initial concentration of butanol and \(E_{am2}\) is the activation energy of model 2.

The best representation of the experimental data was enabled by linking the mass of the catalyst to the constant rate term \(k_f\) (for model 1) and \(k_{m2}\) (for model 2).
\[ k_f = \left( \frac{A}{g \text{ of catalyst}} \right) e^{\frac{E_a}{RT}} \]  

\[ k_{m2} = \left( \frac{A}{g \text{ of catalyst}} \right) e^{\frac{E_{a,m2}}{RT}} \]  

3.3 OHE of butyric acid into butyl butyrate

3.3.1 Catalysts

Several catalysts were either purchased or prepared in order to investigate the OHE of butyric acid to butyl butyrate; four commercial catalysts were obtained from Sigma Aldrich and two were prepared in-house using the sulfonated char \( \text{MG}_500 \) previously prepared in this research work. The alumina-silica support was also characterised.

The samples involved are thus:

- Alumina-Silica catalyst support, grade 135 (AlSi)
- Palladium, 5 % on activated carbon powder (Pd/C)
- Ruthenium, 5 % on activated carbon powder (Ru/C)
- Ruthenium, 5 % on activated charcoal (Ru/Charcoal)
- Palladium, 5 % on sulfonated char \( \text{MG}_{500} \) (Pd/\( \text{MG}_{500} \))
- Ruthenium, 5 % on sulfonated char \( \text{MG}_{500} \) (Ru/\( \text{MG}_{500} \))
- Physical mixture of Pd/C + AlSi (50/50 weight %)
- Physical mixture of Ru/C + AlSi (50/50 weight %)
- Physical mixture of Pd/\( \text{MG}_{500} \) + AlSi (50/50 weight %)
- Physical mixture of Ru/\( \text{MG}_{500} \) + AlSi (50/50 weight %)

3.3.1.1 Catalyst preparation

The Pd/\( \text{MG}_{500} \) Ru/\( \text{MG}_{500} \) catalysts were prepared with the wet impregnation method. The amount of Tetramminepalladium (II) chloride monohydrate (Pd compound) and Ruthenium (III) Chloride hydrate, 99.98 % metals (Ru
compound) required to prepare a 5 % noble metal over sulfonated char support was calculated as follows:

$$\frac{x}{x + 1 \text{ (g of support)}} = 0.05 \rightarrow x = 0.053 \text{ g of noble metal}$$

$$\text{Molecular mass of noble metal} = MNM \text{ g·mol}^{-1}$$

$$\frac{0.053 \text{ g of noble metal}}{MN M \text{ g·mol}^{-1} - 1} = \text{moles of noble metal}$$

$$\text{Molecular mass of noble metal compound} = MNMC \text{ g·mol}^{-1}$$

$$\text{g of compound required} = \text{moles of noble metal} \times MNMC \text{ g/mol}$$

When the appropriate amount of noble metal was found, 50ml of ethanol was added and the mixture was sonicated for 10 minutes. The catalyst support was then added to the mixture, magnetically stirred, recovered with paraffin and sealed 0 for 16 hours. After removal of the magnetic stirrer and paraffin, the sample was transferred to the RotoVap (rotary evaporator) platform and the necessary valves (water, compressor, rotation etc.) were turned on. The catalyst sample was heated at 80°C for 15-20 minutes. The sample was extracted and dried in an 80°C oven after this period.

### 3.3.2 Calculation procedures

#### 3.3.2.1 Conversion and yields

The conversions and yields were determined by the calculation of the concentrations from the product peaks from the GC. For the one step hydrogenation esterification of butyric acid to butyl butyrate there were no other products besides butanol and butyl butyrate. It was therefore considered that only two reactions took place during the OHE:
Based on this assumption, the reaction conversion was calculated by the equation

\[ \text{Conversion} = \frac{\text{initial moles of butyric acid} - \text{final moles of butyric acid}}{\text{initial moles of butyric acid}} \]

the yield of butanol was calculated by the equation

\[ \text{butanol yield} = \frac{\text{final moles of butanol}}{\text{initial moles of butyric acid}} \]

while the yield of butyl butyrate was calculated by the equation

\[ \text{butanol yield} = \frac{\text{final moles of butyl butyrate}}{\text{initial moles of butyric acid}} \]

### 3.3.2.2 Turnover frequency (TOF)

The turnover frequency (TOF) of reaction was also calculated to describe the reaction rate across a number of different catalysts. Typically, the TOF is defined as the number of molecules reacted or produced per catalytic active site per unit of time. In this work, all the surface metal atoms exposed to the reactant were assumed to be active sites and so the TOF’s reported in this work are the number of reacted molecules per surface atom of metal per second. On the basis of the assumption that all the catalysts particles seen in TEM images (see Section 4.2) are ideal spheres, the number of surface atoms was calculated by the steps described in the following paragraph.
3.3.2.3 Specific metal surface area, $A_s$

Assuming that all the atoms of the noble metal are on the surface forming a monolayer, the specific metal surface area $A_s$ (m$^2$g$^{-1}$) is determined by the size of the particles of the catalysts determined by electron microscopy as described below. It can be calculated by dividing the average surface area of the noble metal particles $S_p$ (m$^2$), by the weight of noble metal particles in the catalyst $W_p$ (g); $W_p$ is calculated by multiplying the volume of the noble metal particles $V_p$ (m$^3$) by the density $\rho_m$ (g m$^{-3}$), these values being determined from the mean particle size $d_p$ (m) obtained from TEM images.

\[
S_p = \pi d_p^2
\]

\[
V_p = \frac{\pi d_p^3}{6}
\]

\[
W_p = V_p \rho_m
\]

\[
A_s = \frac{S_p}{W_p} = \frac{6}{d_p \rho_m}
\]

Alternatively, the specific metal surface area could also be determined from the number of surface metal atoms $N_s$ by multiplying the atomic area $S_a$ (m$^2$ atom$^{-1}$) of the noble metal by the number of surface metal atoms $N_s$ per metal weight used for the sample $W_M$ (g).

\[
A_s = \frac{S_a N_s}{W_M}
\]

Hence, the number of surface metal atoms in the samples is determined by the equation below.
Table 3.4. Metal parameters used for $N_s$ and $A_s$ calculations

<table>
<thead>
<tr>
<th></th>
<th>Pd</th>
<th>Ru</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight, (g mol$^{-1}$)</td>
<td>106.4</td>
<td>101.1</td>
</tr>
<tr>
<td>Atomic cross sectional area $S_a$, (nm$^2$)</td>
<td>0.060</td>
<td>0.067</td>
</tr>
<tr>
<td>Density $\rho_m$, (g cm$^{-3}$)</td>
<td>12.02</td>
<td>12.37</td>
</tr>
</tbody>
</table>

Note: Metal parameters were considered according to Cordero et al. (2008).

3.3.2.4 Metal surface area, $A_M$

The metal surface area $A_M$ is calculated by dividing the total surface of the noble metal by the grams of catalyst utilised for a reaction.

$$A_M = \frac{S_a N_s}{g \text{ of catalyst}}$$

3.3.3 Average molecular reaction rate, $R_t$

The average molecular reaction rate $R_t$ (mole s$^{-1}$) is the total number of molecules produced per unit time. It is determined by the total amount of butanol produced with hydrogenation (mol) divided by reaction time (s$^{-1}$). The $N_A$ is the Avogadro constant.

$$R_t = \frac{\text{Butanol produced with hydrogenation (mol)} \cdot N_A}{4 \text{ (h)} \cdot 3600 \text{ (s}\cdot\text{h}^{-1})}$$

The turnover frequency (TOF) was then calculated by the equation below.

$$TOF = \frac{R_t}{N_s}$$
3.3.4 Characterisation techniques

3.3.4.1 XRD

XRD analysis was carried out with the aid of a PANalytical Monochromatic Diffractometer (X-PERT MPD PRO) with CuKα radiation at a wavelength of 1.5406Å scanning 40KV and 40mA in the 2θ range from 20°-90° and a step size and step time of 0.017° and 120 seconds respectively. Each of the 10 mm catalyst samples were prepared in sample cups in powdered form and analysed at room temperature. Results were generated in the form of peak intensity vs 2θ graphs for each sample. These were subsequently analysed for the presence/absence of Ruthenium or Palladium.

3.3.4.2 TEM

The catalyst samples were prepared and left to dry overnight following a procedure of mashing, dilution with isopropanol, addition of a glass recipient and the application of a sample drop to a grid. Analysis was carried out using a JEOL STEM (Scanning Transmission Electron Microscope).

Figure 3.8. Schematic of a TEM (Encyclopaedia Britannica 2016)
Samples were loaded onto a multiple specimen holder allowing the analysis of three consecutive samples. Once three samples were loaded, the instrument was used to focus electron beams onto the sample with the CCD camera transferring the image to the adjacent computer. Ten catalyst samples and the alumina silica catalyst support were analysed with images taken at magnification ranging from 20KX to 1.5MX. The images obtained were analysed with GATAN Digital Micrograph software for estimation of particle diameter as well as specific metal surface area and later turnover frequency (TOF).

3.3.4.3 BET
Surface area analysis (B.E.T) was used to establish surface area, pore volume and pore radius analyses of the catalysts by nitrogen physisorption using a Quantachrome Autosorb AS-1. For each analysis, 0.1 g of sample was outgassed under vacuum at 200°C for 12 hours to remove water and other atmospheric contaminants followed by analysis consisting of measurement of absorption and desorption of nitrogen gas on the sample conducted at -196°C. Analysis produced an equilibrium isotherm when the volume of nitrogen gas adsorbed was plotted against P/P₀ where P is the pressure and P₀ is the saturation pressure at the measured temperature. The surface area was subsequently calculated using the BET (Brunauer, Emmett and Teller) equation.

3.3.4.4 Atomic Absorption Spectroscopy
Atomic Absorption Spectroscopy is a simple, highly specific and highly sensitive technique used to determine the atomic content of a sample. AAS was used to discover what exact percentage of noble metal was present in the Pd₉MGS500 and Ru₉MGS500 catalysts samples as an extra characterization technique to ensure that
the value was close to 5%. Analysis was carried out on a SpectrAA 220 Atomic Absorbtion Spectrometer.

![Diagram of a single beam flame atomic absorption spectrophotometer](http://www.experts mind.com)

**Figure 3.9.** Schematic diagram of a single beam flame atomic absorption spectrophotometer (http://www.experts mind.com)

A sample of the noble metal catalysts was taken from the stock container and 0.05 g were extracted and transferred to a 100 ml glass container to which 10 ml of HCl was added. The sample was then heated for 18 hours at 60°C. Dilutions of 1 ppm, 10 ppm, 50 ppm and 100 ppm were made and Lanthanum suppressant was added to have a concentration of 2000 ppm in each flask (the unknown sample was diluted by a half). A blank was prepared containing Lanthanum suppressant and water. When each of the standards were run through the AAS instrument a calibration plot of intensity vs Ruthenium Concentration was fitted with the aid of the computer attached to the instrument. The unknown catalyst sample was then run through the instrument and a concentration of the unknown noble metal concentration of the sample was determined by the instrument’s software. As the
unknown sample was diluted \( \frac{1}{2} \), this concentration value was multiplied by 2 to find the actual concentration. This value was then converted into mg/100ml and expressed as a weight percentage of the original 0.05 g/100 ml to find the percentage of noble metal on the catalysts supported by CBSA_{MGS500}.

### 3.3.5 OHE reaction

The One-Step Hydrogenation Esterification reaction was carried out in a 600 ml stainless steel vessel. With the application of high temperatures and H\(_2\) pressure, the conversion of butyric acid to butyl butyrate was attempted and the results were recorded. This investigation focused on a two-step process involving the reduction of the catalyst followed by hydrogenation esterification.

![Autoclave reactor](image.png)

**Figure 3.9.** Autoclave reactor

The amount of catalyst utilised for these reactions was the same for each material: 0.2 g of noble metal supported by carbon, char or MS500; or 0.2 g of noble metal supported by carbon, char or MS500 plus 0.2 g of AlSi to create a 50/50 weight % physical mixture.
The catalyst was placed in the autoclave and flushed with argon followed by the introduction of hydrogen. Reduction of the catalyst was carried out at 300°C and 20 bar hydrogen pressure for 2 hours. The system was vented and flushed with argon prior to the addition of the solvent, 90 ml of cyclohexane (Lennox, AO782, 2500, pure) or toluene (Sigma-Aldrich, ACS reagent, ≥ 99.7%) and the substrate butyric acid (10 ml) to the reactor. The reactor was flushed with argon and brought to the desired reaction temperature and hydrogen pressure. The reaction mixture was stirred continuously at 400 rpm for 4 hours. The sample was collected from the reactor at room temperature and was subsequently analysed by GC.
Chapter 4

4 Results and discussion

4.1 CBSA catalysts for butyl butyrate production

4.1.1 Characterisation

A detailed characterization of the CBSA catalysts produced in this work was carried out in order to understand their properties arising from their chemical and physical features.

4.1.1.1 SEM

Visual observation was performed by SEM to assess the materials morphology throughout the production process. There was no visible difference between untreated chars prepared at various temperatures and those converted to CBSA catalyst. All Miscanthus (MG) char-based analysed materials presented an inner, well developed, honeycomb structure with a highly complex network of pores, channels and fibrous ridged surfaces (Figure 4.1).
Figure 4.1. SEM images of Miscanthus-based material carbonized at different temperatures (500 and 600°C) and then Activated and Sulfonated.

At the contrary, all analysed Brown bin waste digestate based (W-based) materials presented ridged surfaces with few visible pores (Figure 4.2).
**Figure 4.2.** SEM images of W-based material carbonized at different temperatures (400 and 500°C) and then and Sulfonated.

All materials collected at each stage of the preparation of the catalysts were also analysed using the energy-dispersive (EDS) detector integrated into the SEM. INCA software was used to examine the energy spectrum in order to determine the abundance of specific elements and to give an overall view of the composition of the samples. Spectra of all CBSA catalysts showed the presence of sulfur due to sulfonation, small traces of silica, oxygen and an abundance of carbon (Figure 4.3 and Figure 4.4).
Figure 4.3. EDS spectrum of CBSA catalyst derived from activated Miscanthus x giganteus carbonised at 500°C.

Figure 4.4. EDS spectrum of CBSA catalyst derived from brown bin waste digestate carbonised at 400°C.
4.1.1.2 BET

The BET results for each stage of the preparation of carbonized, activated, and sulfonated MG-based materials are listed in Table 4.1.

Table 4.1. Surface area of MG-based materials throughout the production.

<table>
<thead>
<tr>
<th>Carbonisation temperature, °C</th>
<th>Carbonised (C)</th>
<th>Activated (A)</th>
<th>Sulfonated (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>4.2</td>
<td>-</td>
<td>6.3</td>
</tr>
<tr>
<td>500</td>
<td>6.4</td>
<td>-</td>
<td>17.9</td>
</tr>
<tr>
<td>600</td>
<td>7.0</td>
<td>-</td>
<td>15.3</td>
</tr>
<tr>
<td>400</td>
<td>4.2</td>
<td>7.2</td>
<td>10.5</td>
</tr>
<tr>
<td>500</td>
<td>6.4</td>
<td>571.0</td>
<td>317.0</td>
</tr>
<tr>
<td>600</td>
<td>7.0</td>
<td>554.0</td>
<td>548.0</td>
</tr>
</tbody>
</table>

Note: MG – derived from Miscanthus; C – carbonized; A – activated; S – sulfonated e.g. sample mA500 was carbonized at 500°C and then was activated; and sample mAS600 was carbonized at 600°C, then was activated and sulfonated, while sample mS600 was carbonized at 600°C, then only sulfonated.

In the case of MG-based materials, an increase in carbonization temperature lowers the yield of char while it increases the relative carbon concentration (Table 4.2). There are many resulting products formed during the chemical activation process by reactions between KOH, carbon and nitrogen (Robau-Sánchez et al. 2005). At higher temperatures, some of these products are removed from the carbon material by evaporation and are released from the reactor as effluent gases leading to an increase of the BET surface area (Azargohar and Dalai 2008). As expected, chemical activation results in an increase of the surface area for each carbonaceous material (Table 4.1). For activated \( MG A400 \) and for non-activated samples, the sulfonation process led to a further increase of the surface area, probably due to the harsh conditions capable of breaking the C-C linkage between the carbon layers (Dehkhoda and Ellis 2013). This behaviour was not encountered
in the \textit{MG}A500 samples where the surface area decreased after sulfonation \textit{(MGAS500)} suggesting that a small part of the pore space was occupied by the grafted \textit{SO}_3H groups (Liu et al. 2010). In the \textit{MG}A600 sample the surface area was not influenced by the sulfonation process \textit{(MGAS600)}.

**Table 4.2.** Elemental composition and ash content of MG-chars and MG-CBSA catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>O</th>
<th>ASH</th>
<th>H/C</th>
<th>O/C</th>
<th>S/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{MG}C400</td>
<td>0.81</td>
<td>72.0</td>
<td>3.19</td>
<td>0.04</td>
<td>16.6</td>
<td>7.35</td>
<td>0.044</td>
<td>0.231</td>
<td>0.001</td>
</tr>
<tr>
<td>\textit{MG}S400</td>
<td>0.52</td>
<td>59.1</td>
<td>0.39</td>
<td>1.91</td>
<td>29.2</td>
<td>8.88</td>
<td>0.007</td>
<td>0.495</td>
<td>0.032</td>
</tr>
<tr>
<td>\textit{MG}S400_R</td>
<td>0.40</td>
<td>48.2</td>
<td>1.43</td>
<td>1.05</td>
<td>43.0</td>
<td>5.90</td>
<td>0.030</td>
<td>0.892</td>
<td>0.022</td>
</tr>
<tr>
<td>\textit{MG}A400</td>
<td>0.77</td>
<td>77.8</td>
<td>2.37</td>
<td>0.00</td>
<td>18.3</td>
<td>0.76</td>
<td>0.031</td>
<td>0.235</td>
<td>0.000</td>
</tr>
<tr>
<td>\textit{MG}AS400</td>
<td>0.57</td>
<td>64.0</td>
<td>0.97</td>
<td>1.66</td>
<td>32.1</td>
<td>0.65</td>
<td>0.015</td>
<td>0.501</td>
<td>0.026</td>
</tr>
<tr>
<td>\textit{MG}AS400_R</td>
<td>0.62</td>
<td>69.4</td>
<td>1.99</td>
<td>1.45</td>
<td>25.0</td>
<td>1.45</td>
<td>0.029</td>
<td>0.361</td>
<td>0.021</td>
</tr>
<tr>
<td>\textit{MG}C500</td>
<td>0.85</td>
<td>78.3</td>
<td>2.42</td>
<td>0.05</td>
<td>8.8</td>
<td>9.56</td>
<td>0.031</td>
<td>0.112</td>
<td>0.001</td>
</tr>
<tr>
<td>\textit{MG}S500</td>
<td>0.64</td>
<td>70.0</td>
<td>1.31</td>
<td>3.84</td>
<td>23.4</td>
<td>0.74</td>
<td>0.019</td>
<td>0.335</td>
<td>0.055</td>
</tr>
<tr>
<td>\textit{MG}S500_R</td>
<td>0.60</td>
<td>73.7</td>
<td>2.02</td>
<td>2.24</td>
<td>20.7</td>
<td>0.73</td>
<td>0.027</td>
<td>0.281</td>
<td>0.030</td>
</tr>
<tr>
<td>\textit{MG}A500</td>
<td>0.78</td>
<td>77.3</td>
<td>0.86</td>
<td>0.00</td>
<td>19.4</td>
<td>1.67</td>
<td>0.011</td>
<td>0.251</td>
<td>0.000</td>
</tr>
<tr>
<td>\textit{MG}AS500</td>
<td>0.54</td>
<td>69.3</td>
<td>0.81</td>
<td>1.05</td>
<td>27.4</td>
<td>0.89</td>
<td>0.012</td>
<td>0.396</td>
<td>0.015</td>
</tr>
<tr>
<td>\textit{MG}AS500_R</td>
<td>0.55</td>
<td>72.8</td>
<td>1.69</td>
<td>1.03</td>
<td>22.3</td>
<td>1.70</td>
<td>0.023</td>
<td>0.306</td>
<td>0.014</td>
</tr>
<tr>
<td>\textit{MG}C600</td>
<td>0.81</td>
<td>79.7</td>
<td>1.91</td>
<td>0.05</td>
<td>6.5</td>
<td>11.0</td>
<td>0.024</td>
<td>0.082</td>
<td>0.001</td>
</tr>
<tr>
<td>\textit{MG}S600</td>
<td>0.52</td>
<td>62.3</td>
<td>1.72</td>
<td>2.95</td>
<td>31.1</td>
<td>1.34</td>
<td>0.028</td>
<td>0.500</td>
<td>0.047</td>
</tr>
<tr>
<td>\textit{MG}S600_R</td>
<td>0.62</td>
<td>75.9</td>
<td>1.59</td>
<td>3.36</td>
<td>18.0</td>
<td>0.55</td>
<td>0.021</td>
<td>0.237</td>
<td>0.044</td>
</tr>
<tr>
<td>\textit{MG}A600</td>
<td>0.67</td>
<td>82.8</td>
<td>0.55</td>
<td>0.00</td>
<td>14.2</td>
<td>1.84</td>
<td>0.007</td>
<td>0.171</td>
<td>0.000</td>
</tr>
<tr>
<td>\textit{MG}AS600</td>
<td>0.58</td>
<td>78.3</td>
<td>0.34</td>
<td>0.62</td>
<td>19.1</td>
<td>1.00</td>
<td>0.004</td>
<td>0.244</td>
<td>0.008</td>
</tr>
<tr>
<td>\textit{MG}AS600_R</td>
<td>0.58</td>
<td>74.3</td>
<td>1.60</td>
<td>0.26</td>
<td>21.3</td>
<td>1.95</td>
<td>0.022</td>
<td>0.286</td>
<td>0.004</td>
</tr>
</tbody>
</table>

BET results for W-based materials are shown in table 4.3.
Table 4.3. Surface area of W-based materials at each stage of the preparation.

<table>
<thead>
<tr>
<th>Carbonisation temperature, °C</th>
<th>BET single point surface area, m²·g⁻¹</th>
<th>Carbonised (C)</th>
<th>Sulfonated (S)</th>
<th>Recovered (R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td></td>
<td>6.2</td>
<td>8.9</td>
<td>7.8</td>
</tr>
<tr>
<td>500</td>
<td></td>
<td>4.4</td>
<td>6.05</td>
<td>5.7</td>
</tr>
<tr>
<td>600</td>
<td></td>
<td>2.7</td>
<td>3.54</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: W – derived from brown bin digestate; C – carbonised; S – sulfonated; R – recovered; e.g. sample \( \text{W}_C500 \) was carbonised at 500°C; sample \( \text{W}_S600_R \) represents the recovered catalyst that was carbonised at 600°C and sulfonated.

Notably, for these, an increase of carbonisation temperature resulted in a lower surface area; likely a result of the collapse in the structure of the material (Lua and Yang 2004). This behaviour was not encountered in other works where this range of carbonisation temperatures was used. The opposite, in fact, took place in the study conducted using \( \text{Miscanthus x giganteus} \) as a catalyst precursor where the surface area increased as the temperature was increased (table 4.1) (Severini et al. 2015). When studying MGs, it was noted that the structural collapse of material is only observed when temperatures exceed 800°C.

In all W-based samples, the sulfonation process resulted in an increase in the surface area. Harsh conditions enable the breaking of C-C links between the carbon layers and is probably the cause for the increase in surface area (Dehkhoda and Ellis 2013).

4.1.1.3 FTIR

IR spectroscopy was carried out to obtain an understanding of the changes to the surface chemistry during the catalyst production.

During carbonization, the biomass is degraded and rearranged producing phenolic and polyaromatic rings. Some of these functional groups such as hydroxyl and
aromatic rings will then undergo sulfonation reactions with sulfuric acid producing sulfonic groups (Rao et al. 2011).

All spectra of MG-based material represented in the following figures show the presence of the alkyne functional groups at around 2117 cm$^{-1}$ persisting throughout all processes. The C=O stretching at 1699 cm$^{-1}$, attributable to the carboxylic groups are present in most of the samples.

The spectra of the carbonized MG (Figures 4.5a and 4.5b) show peaks at around 1600, 1200 and 1100 cm$^{-1}$.

Figure 4.5. FTIR spectra for char and CBSA catalysts produced from MG. a) carbonized, sulfonated and recovered catalyst after esterification reaction; b) carbonised, activated, sulfonated and recovered catalyst.

The peak at 1100 cm$^{-1}$ shows the presence of C-O bonding, while the peak at 1600 cm$^{-1}$ is characteristic of the C=C bonds of polyaromatic structures (Rao et al. 2011). The variation of band intensities in carbonized MG spectra, between 1700 and 1500 cm$^{-1}$ show that the rise in temperature from 400 to 500°C produced an increase in C=O and aromatic C=C bonds. The spectra of carbonized MG at 600°C did not show the C=O stretching due to a lower level of oxygen groups that
can be attributed to an increase in temperature (Gomez-Serrano et al. 1996). The sulfonated MG-chars show peaks at around 1600 cm$^{-1}$ and 1100 cm$^{-1}$. Vibration bands at around 1100 (SO$_3$ stretching) and peaks at 1028 and 1160 cm$^{-1}$ (SO$_2$ stretching) indicate the presence of SO$_3$H groups in the catalyst (Rao et al. 2011). In contrast to the carbonized MG spectra, peaks within this wavelength range were obscured due to the strong absorption of SO$_3$H. From the results of the recovered MG-CBSA catalysts it is possible to notice the same vibration bands and peaks for the sulfonated samples, confirming the acidic nature due to the presence of SO$_3$H groups.

Similarities were encountered for W-based material spectra that exhibited the presence of alkyne functional groups at around 2117 cm$^{-1}$ which persisted throughout all processes (Figure 4.6b).

**Figure 4.6.** FTIR spectra for char and CBSA catalysts produced from BBD. a) carbonised at 400°C, 500°C and 600°C; b) carbonised at 400°C, sulfonated and recovered catalyst.

The spectra of the carbonised brown bin waste digestate showed peaks at around 3000 1600, and 1100 cm$^{-1}$. The peak at 1100 cm$^{-1}$ showed the presence of C-O
bonding, while the peak at 1600 cm\(^{-1}\) was characteristic of the C=C bonds of polyaromatic structures (Rao et al. 2011).

The variation of band intensities between 2700 cm\(^{-1}\) and 3000 cm\(^{-1}\) suggests the rise in temperature from 400°C to 600°C resulted in a decrease in aromatic and aliphatic groups (Figure 4.6a). The sulfonated W-chars showed peaks at around 1600 cm\(^{-1}\) and 1100 cm\(^{-1}\) (Figure 4.6b). Vibration bands at around 1100 (SO\(_3^\cdot\) stretching) and peaks at 1028 cm\(^{-1}\) and 1160 cm\(^{-1}\) (SO\(_2^\cdot\) stretching) indicate the presence of SO\(_3^\cdot\) H groups in the catalyst (Rao et al. 2011). Results of the recovered W-CBSA catalysts showed the same vibration bands and peaks for the sulfonated samples, confirming the presence of SO\(_3^\cdot\) H groups.

4.1.1.4 XRD

XRD patterns of MG-based analysed samples have shown that most of the carbonized material was populated with crystalline structures as presented in Figures 4.7a and 4.7b.

![Figure 4.7](image)

**Figure 4.7.** XRD patterns of carbonized MG, activated char, sulfonated char and recovered catalysts, derived at different carbonization temperatures.
It can be seen that through activation and sulfonation, any crystalline structures which were in the carbonized sample became amorphous. Broad C (002) diffraction peaks between 2θ = 15-30° with broad and weak C (101) diffraction peaks between 2θ = 40-50° indicate the presence of an amorphous solid carbon structure.

It is also important to notice that there is no substantial difference between the activated and sulfonated XRD patterns which suggests that the microstructure of the carbon material was not affected by the chemical activation process.

XRD patterns of W-based analysed samples (Figure 4.8) also showed the carbonised material was populated with crystalline structures.

![Figure 4.8. XRD patterns of carbonised W, sulfonated char and recovered catalysts, derived at different carbonisation temperatures.](image)

Through sulfonation the crystalline structures became amorphous, showing the same diffraction peaks of the MG-based catalysts. Literature indicates that this might be significant in relation to the activity of the catalysts throughout esterification reactions (Zong et al. 2007).
4.1.1.5 TGA

The thermal stability of the catalytic materials was studied by thermo gravimetric analysis in a nitrogen atmosphere. It can be seen that the increase of carbonization temperature improved the thermal stability of the material (Figure 4.9).

*Figure 4.9. TGA of MG-CBSA catalysts derived at different carbonization temperatures.*

\(_{MG}S500\) and \(_{MG}S600\) CBSA catalysts showed moisture desorption between 20 and 120°C followed by almost a plateau to 250°C and a gradual weight loss up to 900°C (Figure 4.9a). Activated MG-CBSA catalysts (Figure 4.9b) were all characterized by moisture desorption to 130°C after which it almost plateaued to 300°C, followed by weight loss to about 700°C. The loss of weight at high temperatures was due to the gradual desorption and thermal decomposition of the \(SO_3H\) groups that are the active sites of the catalyst (Zong et al. 2007). The recovered samples showed the same trend as their respective fresh CBSA catalysts except for a smaller weight loss at lower temperatures that was observed due to a reduction of porosity which resulted in a decrease in moisture content.

All W-based catalysts (Figure 4.10), as \(_{MG}S500\) and \(_{MG}S600\), showed moisture desorption between 20°C and 120°C followed by a quasi-plateau to 250°C and
then a gradual weight loss as the temperature rose to 900°C (due to the thermal decomposition SO$_3$H groups). It is also important to point out that after 200°C there is still an important loss suggesting that the surface might not be clean for N$_2$ adsorption during BET analysis.

![Figure 4.10. TGA of W-CBSA catalysts derived at different carbonization temperatures.](image)

Compared to the fresh W-based catalysts (Figure 4.10a), recovered samples showed a smaller weight loss at high temperatures (Figure 4.10b). This variation was likely due to the presence of fewer sulfonic groups which leached during the esterification reaction (high temperature) or during the recovery procedure (J. T. Yu et al. 2011).

### 4.1.2 Reactions study

The effect of catalyst loading and reaction time was studied for all CBSA catalysts. With a constant molar ratio 2:1 (n-butanol: butyric acid) the catalyst loading varied comprising of: 1, 2 and 5 % of the original butyric acid (BA) weight. These results showed that an increase in the amount of catalyst led to an increase in yield (Figure 4.11a, Figure 4.12).
Figure 4.11. Butyl butyrate yield after 4 hours of reaction. a) MG-CBSA catalysts loading comparison; b) evaluation of recovered and fresh MG-CBSA catalysts. Uncertainty bars represent the standard deviation from the mean.

Figure 4.12. Butyl butyrate yields at different reaction times. W-CBSA catalysts loading (1, 2 and 5 %) comparison and evaluation of reusability with 2 recovery cycles (rec 1 and rec 2).

The mass balance for each reaction was obtained by calculating the ratio of the mass consumed by the reactants at a certain time to the mass of the products at that time (Table 4.4).
Table 4.4. Mass balance between the reactants consumed and the product formed.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>No catalyst</th>
<th>H₂SO₄</th>
<th>Amberlyst 15</th>
<th>MGS400</th>
<th>MGS500</th>
<th>MGS600</th>
<th>MGS600 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.946</td>
<td>1.023</td>
<td>1.049</td>
<td>0.871</td>
<td>1.044</td>
<td>0.971</td>
<td>0.931</td>
</tr>
<tr>
<td>120</td>
<td>0.978</td>
<td>1.003</td>
<td>1.017</td>
<td>0.971</td>
<td>1.008</td>
<td>0.971</td>
<td>0.931</td>
</tr>
<tr>
<td>240</td>
<td>0.989</td>
<td>1.003</td>
<td>1.017</td>
<td>0.971</td>
<td>1.017</td>
<td>0.971</td>
<td>0.931</td>
</tr>
<tr>
<td>360</td>
<td>0.996</td>
<td>1.003</td>
<td>1.017</td>
<td>0.971</td>
<td>1.017</td>
<td>0.971</td>
<td>0.931</td>
</tr>
<tr>
<td>480</td>
<td>0.996</td>
<td>1.003</td>
<td>1.017</td>
<td>0.971</td>
<td>1.017</td>
<td>0.971</td>
<td>0.931</td>
</tr>
<tr>
<td>1440</td>
<td>0.996</td>
<td>1.003</td>
<td>1.017</td>
<td>0.971</td>
<td>1.017</td>
<td>0.971</td>
<td>0.931</td>
</tr>
</tbody>
</table>

| F1s (I) and second (II) recovery cycle of CBBA catalysts.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>MGS400 1%</th>
<th>MGS400 2%</th>
<th>MGS400 5%</th>
<th>MGS500 1%</th>
<th>MGS500 2%</th>
<th>MGS500 5%</th>
<th>MGS600 1%</th>
<th>MGS600 2%</th>
<th>MGS600 5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>1.093</td>
<td>1.093</td>
<td>1.093</td>
<td>1.093</td>
<td>1.093</td>
<td>1.093</td>
<td>1.093</td>
<td>1.093</td>
<td>1.093</td>
</tr>
<tr>
<td>360</td>
<td>1.115</td>
<td>1.115</td>
<td>1.115</td>
<td>1.115</td>
<td>1.115</td>
<td>1.115</td>
<td>1.115</td>
<td>1.115</td>
<td>1.115</td>
</tr>
<tr>
<td>480</td>
<td>1.122</td>
<td>1.122</td>
<td>1.122</td>
<td>1.122</td>
<td>1.122</td>
<td>1.122</td>
<td>1.122</td>
<td>1.122</td>
<td>1.122</td>
</tr>
<tr>
<td>1440</td>
<td>1.129</td>
<td>1.129</td>
<td>1.129</td>
<td>1.129</td>
<td>1.129</td>
<td>1.129</td>
<td>1.129</td>
<td>1.129</td>
<td>1.129</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction condition: 2% Catalyst loading, 110 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MGS400</td>
</tr>
<tr>
<td>60</td>
</tr>
<tr>
<td>120</td>
</tr>
<tr>
<td>240</td>
</tr>
<tr>
<td>360</td>
</tr>
<tr>
<td>480</td>
</tr>
<tr>
<td>1440</td>
</tr>
</tbody>
</table>
Overall, CBSA catalysts with higher acid density, such as \( \text{MG} \text{S}500 \), gave better performances both in terms of their initial formation rate (Table 4.5) and yield (Figure 4.11, Figure 4.12, Figure 4.13).

**Table 4.5. CBSA catalysts comparison.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Total acid density ( \text{mmol} \cdot \text{g}^{-1} )</th>
<th>Surface area ( \text{m}^2 \cdot \text{g}^{-1} )</th>
<th>Initial formation rate, ( \text{mmol} \cdot \text{dm}^3 \cdot \text{min}^{-1} ) 1%*</th>
<th>2%*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{MG} \text{S}400 )</td>
<td>0.43</td>
<td>6.30</td>
<td>4.95</td>
<td>5.03</td>
</tr>
<tr>
<td>( \text{MG} \text{S}500 )</td>
<td>2.72</td>
<td>17.9</td>
<td>16.5</td>
<td>29.5</td>
</tr>
<tr>
<td>( \text{MG} \text{S}600 )</td>
<td>2.45</td>
<td>15.3</td>
<td>17.9</td>
<td>22.5</td>
</tr>
<tr>
<td>( \text{MG} \text{S}500 _ \text{R} )</td>
<td>1.31</td>
<td>7.10</td>
<td>-</td>
<td>9.61</td>
</tr>
<tr>
<td>( \text{MG} \text{S}600 _ \text{R} )</td>
<td>0.66</td>
<td>6.40</td>
<td>-</td>
<td>6.16</td>
</tr>
<tr>
<td>( \text{MG} \text{AS}400 )</td>
<td>2.05</td>
<td>10.5</td>
<td>11.5</td>
<td>16.2</td>
</tr>
<tr>
<td>( \text{MG} \text{AS}500 )</td>
<td>1.35</td>
<td>317</td>
<td>8.52</td>
<td>10.1</td>
</tr>
<tr>
<td>( \text{MG} \text{AS}600 )</td>
<td>1.74</td>
<td>548</td>
<td>9.98</td>
<td>14.2</td>
</tr>
<tr>
<td>( \text{MG} \text{AS}400 _ \text{R} )</td>
<td>1.62</td>
<td>9.20</td>
<td>-</td>
<td>12.7</td>
</tr>
<tr>
<td>( \text{MG} \text{AS}500 _ \text{R} )</td>
<td>0.85</td>
<td>28.4</td>
<td>-</td>
<td>7.28</td>
</tr>
<tr>
<td>( \text{MG} \text{AS}600 _ \text{R} )</td>
<td>0.52</td>
<td>20.2</td>
<td>-</td>
<td>5.39</td>
</tr>
<tr>
<td>( \text{WS}400 )</td>
<td>1.93</td>
<td>8.90</td>
<td>7.82</td>
<td>11.3</td>
</tr>
<tr>
<td>( \text{WS}500 )</td>
<td>0.69</td>
<td>6.05</td>
<td>5.20</td>
<td>6.02</td>
</tr>
<tr>
<td>( \text{WS}600 )</td>
<td>0.00</td>
<td>3.54</td>
<td>3.73</td>
<td>-</td>
</tr>
<tr>
<td>( \text{WS}400 _ \text{R} )</td>
<td>1.35</td>
<td>7.80</td>
<td>6.64</td>
<td>-</td>
</tr>
<tr>
<td>( \text{WS}500 _ \text{R} )</td>
<td>0.58</td>
<td>5.70</td>
<td>4.98</td>
<td>-</td>
</tr>
<tr>
<td>Amberlyst 15</td>
<td>4.80</td>
<td>52.0</td>
<td>16.6</td>
<td>28.7</td>
</tr>
<tr>
<td>( \text{H}_2\text{SO}_4 )</td>
<td>20.4</td>
<td>n.a.</td>
<td>53.7</td>
<td>56.7</td>
</tr>
</tbody>
</table>

*Note: *Catalyst loading

For example, after 24-hour (1440 minutes) reaction \( \text{MG} \text{S}500 \) gave a yield of 94.5% close to that achieved with \( \text{H}_2\text{SO}_4 \) (96 %), similar results were reported by Kang et al. (2011).
Figure 4.13. Acidity vs butyl butyrate yields.

The figure above displays the acidity of the catalysts presented in table 4.5 in relation to the butyl butyrate yield achieved at three different sampling hours at certain reaction conditions: 2 % catalyst loading; 150°C. It is notable, as the results suggested that there is almost linearity between total acid density and yields and thus the performance of each catalyst.

The pyrolysis temperature, apart from improving the surface area of the char, plays a crucial role in the formation of aromatic rings that are related to the formation of SO$_3$H groups during the sulfonation process (Rao et al. 2011). In the case of brown bin waste digestate derived material it can be argued that as the carbonization temperature increased the amount of polycyclic aromatic rings available decreased. This position is supported by the elemental analysis (Table 4.6).
Table 4.6. Elemental composition of chars and CBSA catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>N</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>O</th>
<th>Ash</th>
<th>Atomic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>H/C</td>
</tr>
<tr>
<td>wC400</td>
<td>5.31</td>
<td>74.8</td>
<td>6.43</td>
<td>0.00</td>
<td>5.09</td>
<td>8.36</td>
<td>0.086</td>
</tr>
<tr>
<td>wS400</td>
<td>4.74</td>
<td>66.7</td>
<td>3.55</td>
<td>4.72</td>
<td>17.3</td>
<td>2.98</td>
<td>0.053</td>
</tr>
<tr>
<td>wS400_R</td>
<td>4.57</td>
<td>70.1</td>
<td>3.23</td>
<td>4.02</td>
<td>15.5</td>
<td>2.59</td>
<td>0.046</td>
</tr>
<tr>
<td>wC500</td>
<td>5.76</td>
<td>72.8</td>
<td>3.31</td>
<td>0.00</td>
<td>3.97</td>
<td>14.1</td>
<td>0.045</td>
</tr>
<tr>
<td>wS500</td>
<td>5.68</td>
<td>70.1</td>
<td>2.89</td>
<td>2.76</td>
<td>13.9</td>
<td>4.64</td>
<td>0.041</td>
</tr>
<tr>
<td>wS500_R</td>
<td>5.15</td>
<td>73.7</td>
<td>2.46</td>
<td>2.42</td>
<td>12.4</td>
<td>3.82</td>
<td>0.033</td>
</tr>
<tr>
<td>wC600</td>
<td>5.40</td>
<td>70.7</td>
<td>2.49</td>
<td>0.00</td>
<td>0.38</td>
<td>21.1</td>
<td>0.035</td>
</tr>
<tr>
<td>wS600</td>
<td>5.75</td>
<td>71.2</td>
<td>1.74</td>
<td>1.65</td>
<td>2.23</td>
<td>17.5</td>
<td>0.024</td>
</tr>
</tbody>
</table>

A decrease in the H/C ratio as carbonisation temperatures increased caused more heteroatoms to evaporate from the carbon rings. As a result, wS500 had a lower density of active sites.

For the case of Miscanthus derived material, the formation of aromatic rings occurs between 300 and 500°C (Gomez-Serrano et al. 1996). Though the KOH activation was successful in increasing the surface area of the MG-char, the chemical inertness of the activated carbon (Gomez-Serrano et al. 1996) resulted in a lower density of SO$_3$H groups in the activated $^{\text{MG}}$-CBSA catalysts compared to the non-activated materials and therefore to an inferior performance. It can be argued that the prolonged treatment at high temperatures, as in the case of $^{\text{MG}}$AS500 and $^{\text{MG}}$AS600, did not allow the production of more polycyclic aromatic carbons available to be functionalized. This argument is supported by the elemental analysis of activated char samples (Table 4.2) which showed a decrease in the H/C ratio as the activation temperature increased, causing more heteroatoms to evaporate from the carbon rings (J. T. Yu et al. 2011).
Due to leaching of SO$_3$H groups during the reaction, all recovered catalysts presented a lower catalytic activity compared to their fresh CBSA. This was confirmed by elemental analysis which revealed reduced oxygen and sulfur and by lower values of total acid density (Table 4.2 and Table 4.6). There are two probable reasons for the active site leaching in carbon-based catalysts: washing with solvent and/or high temperature/pressure condition (J. T. Yu et al. 2011). The coking effect was not observed during characterization with SEM and therefore was not considered as one of the reasons for catalyst deactivation. A second recovery test of all CBSA catalysts was performed at the same reaction conditions as for the first cycle (Figure 11b)). Apart from the CBSA$_{MGAS400}$ and CBSA$_{MGAS500}$ catalysts which seemed to suffer the leaching of the active sites in a smaller scale, the other MG-based catalysts gave similar results to those achieved without catalyst (21% butyl butyrate yield after 4h of reaction). Probably due to the chemical stability of activated carbon (Rodríguez-reinoso 1998), MGAS recovered catalysts showed less loss of activity compared to the non-activated material. MGAS400 lost only 21% of its acid density after the first recovery cycle, and achieved comparable results to the other MG-CBSA catalyst (Table 4.5). On the other hand Both W-based catalysts, however, only lost around 20% of their acid density after the first recovery cycle reached the same final conversion of their fresh counterparts, achieving comparable results to other W-CBSA catalysts (Figure 4.12) (Severini et al. 2015).

As part of this work the CBSA catalytic activity was compared to a heterogeneous commercial acid catalyst and concentrated sulfuric acid, each with the loading that gave the highest yields of butyl butyrate. A reaction in the absence of any catalyst
was run to act as a control. The yields achieved by the tested catalyst are shown in Figure 4.13 and detailed features of the materials are reported in Table 4.5.

![Figure 4.14. Butyl butyrate yields of various acid catalysts.](image)

**Figure 4.14.** Butyl butyrate yields of various acid catalysts.

\textsuperscript{MG}S500 catalyst showed higher catalytic activity than Amberlyst 15 and especially during the early stage of the reaction. \textsuperscript{MG}S600 performed slightly better than the commercial catalyst, while activated \textsuperscript{MG}AS400 did not show any enhancements, although it gave comparable results. Catalyst \textsuperscript{w}S400 showed comparable catalytic activity to activated catalyst \textsuperscript{MG}AS400 and Amberlyst 15. The yield achieved after 24 hours reaction also gave comparable results to sulfuric acid.

4.1.2.1 Kinetic modelling

Two power law kinetic models were tested for the esterification reaction, to establish the kinetic parameters (Table 4.7) associated with the production of butyl-butyrate with CBSA catalysts. The models describe the reactions numerically and provide a provisional estimation of the phenomenological reaction rates involved.
Table 4.7. Kinetic parameters of CBSA catalysts

<table>
<thead>
<tr>
<th>Catalyst loading</th>
<th>T, °C</th>
<th>(k), (k_f) [mol·min(^{-1}·g^{-1})]</th>
<th>(E_a) (\text{[kJ·mol}^{-1})]</th>
<th>(R^2)</th>
<th>(E_a) (\text{[kJ·mol}^{-1})]</th>
<th>(R^2)</th>
<th>(E_a) (\text{[kJ·mol}^{-1})]</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(\text{MG S500})</td>
<td>(\text{MG AS400})</td>
<td>(\text{wS400})</td>
<td>(\text{wS500})</td>
<td>(\text{wS400})</td>
<td>(\text{wS500})</td>
<td></td>
</tr>
<tr>
<td>1 %</td>
<td>70</td>
<td>110 (\text{k} \cdot 10^5)</td>
<td>55.0 (\text{k} \cdot 10^5)</td>
<td>54.3 (\text{k} \cdot 10^5)</td>
<td>19.5 (\text{k} \cdot 10^5)</td>
<td>184 (\text{k} \cdot 10^5)</td>
<td>50 (\text{k} \cdot 10^5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>306 (\text{k} \cdot 10^5)</td>
<td>180 (\text{k} \cdot 10^5)</td>
<td>168 (\text{k} \cdot 10^5)</td>
<td>62.6 (\text{k} \cdot 10^5)</td>
<td>594 (\text{k} \cdot 10^5)</td>
<td>172 (\text{k} \cdot 10^5)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>766 (\text{k} \cdot 10^5)</td>
<td>520 (\text{k} \cdot 10^5)</td>
<td>460 (\text{k} \cdot 10^5)</td>
<td>178 (\text{k} \cdot 10^5)</td>
<td>1689 (\text{k} \cdot 10^5)</td>
<td>520 (\text{k} \cdot 10^5)</td>
<td></td>
</tr>
<tr>
<td>2 %</td>
<td>70</td>
<td>94.7 (\text{Ea} = 53.11)</td>
<td>34.3 (\text{Ea} = 61.39)</td>
<td>35.3 (\text{Ea} = 58.4)</td>
<td>11.2 (\text{Ea} = 60.6)</td>
<td>122 (\text{Ea} = 60.6)</td>
<td>28.8 (\text{Ea} = 63.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>264 (\text{Ea} = 57.8)</td>
<td>112 (\text{Ea} = 63.9)</td>
<td>109 (\text{Ea} = 60.7)</td>
<td>35.9 (\text{Ea} = 60.7)</td>
<td>393 (\text{Ea} = 60.7)</td>
<td>98.7 (\text{Ea} = 63.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>661 (\text{Ea} = 57.8)</td>
<td>323 (\text{Ea} = 63.9)</td>
<td>299 (\text{Ea} = 60.7)</td>
<td>102 (\text{Ea} = 60.7)</td>
<td>1121 (\text{Ea} = 60.7)</td>
<td>298 (\text{Ea} = 63.9)</td>
<td></td>
</tr>
<tr>
<td>5 %</td>
<td>70</td>
<td>87.4 (\text{Ea} = 57.8)</td>
<td>22.4 (\text{Ea} = 63.9)</td>
<td>24.4 (\text{Ea} = 60.7)</td>
<td>6.37 (\text{Ea} = 60.7)</td>
<td>87.1 (\text{Ea} = 60.7)</td>
<td>16.4 (\text{Ea} = 63.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>244 (\text{Ea} = 57.8)</td>
<td>73.1 (\text{Ea} = 63.9)</td>
<td>75.8 (\text{Ea} = 60.7)</td>
<td>20.5 (\text{Ea} = 60.7)</td>
<td>280 (\text{Ea} = 60.7)</td>
<td>56.6 (\text{Ea} = 63.9)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>610 (\text{Ea} = 57.8)</td>
<td>211 (\text{Ea} = 63.9)</td>
<td>208 (\text{Ea} = 60.7)</td>
<td>58.5 (\text{Ea} = 60.7)</td>
<td>800 (\text{Ea} = 60.7)</td>
<td>170 (\text{Ea} = 63.9)</td>
<td></td>
</tr>
</tbody>
</table>
From Table 4.7 it can be observed that the rate constants for butyl butyrate formation, calculated by the kinetic models, numerically highlight the higher activity of the catalysts. They are faster for the \( w_{S400} \) catalyst compared to the \( w_{S500} \) and for \( M_{S500} \) compared to \( M_{AS400} \).

Figures 4.15-4.18 show that the models fit well with the experimental data and therefore were considered valid for this study. The coefficients of determination (\( R^2 \)) are also displayed in Table 4.7.

**Figure 4.15.** Species fractions for reactions undertaken with \( M_{S500} \), at 70, 90 and 110°C and 1%, 2% and 5% catalyst loading. Experimental values—symbols, model 1 calculations—lines.
Figure 4.16. Species fractions for reactions undertaken with MGAS400, at 70, 90 and 110°C and 1 %, 2 % and 5 % catalyst loading. Experimental values–symbols, model 1 calculations–lines.
Figure 4.17. Species fractions for reactions undertaken with $\text{WS400}$, at 70, 90 and 110°C and 1 %, 2 % and 5 % catalyst loading. Experimental values—symbols, model 1—lines, model 2—dashes.
Figure 4.18. Species fractions for reactions undertaken with WS500, at 70, 90 and 110°C and 1 %, 2 % and 5 % catalyst loading. Experimental values—symbols, model 1—lines, model 2—dashes.

In the generic power law model (M2), fitted only for the case of W-based catalysts, the reversible reaction mechanism is incorporated into the alpha values. Non integer numbers of this value suggests that the reaction is not elementary (as it was for the method adopted for M1) and intermediate steps are occurring. The two models calculated very similar activation energies (Table 4.7). This result supports the fact that the reaction mechanism, the activation energies and the reaction order of different catalysts with the same functional groups (such as in M2) should be the same. To validate this, as depicted in Table 4.7, similar activation energy values were calculated for MG-CBSA catalysts in which the
small variation between $E_a$ is attributed to mass transfer effects (Severini et al. 2015).

In future work it can be relatable to develop a Langmuir–Hinshelwood model for catalytic reactions to further discuss in detail the mechanism of the esterification and intrinsically link the result of the catalyst characterization to butyl butyrate formation as has been done by Ju et al. (2011).

## 4.2 OHE of butyric acid into butyl butyrate

### 4.2.1 Characterisation results

#### 4.2.1.1 AAS

**Table 4.8.** AAS parameters and results of $\text{Pd}/_\text{MG}S500$ and $\text{Ru}/_\text{MG}S500$.  

<table>
<thead>
<tr>
<th></th>
<th>$\text{Pd}/_\text{MG}S500$</th>
<th>$\text{Ru}/_\text{MG}S500$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst (g)</td>
<td>0.051</td>
<td>0.052</td>
</tr>
<tr>
<td>Hydrochloric Acid (mL)</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Dilution (mL)</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Concentration (mg/L)</td>
<td>32.8</td>
<td>21.6</td>
</tr>
<tr>
<td>% of metal on Catalyst</td>
<td>6.50</td>
<td>4.20</td>
</tr>
<tr>
<td>Sample Preparation</td>
<td>Heat at 60°C+ 18 h agitation</td>
<td></td>
</tr>
</tbody>
</table>

Atomic absorption spectroscopy was used to determine the exact amount of Palladium in the $\text{Pd}/_\text{MG}S500$ catalyst to ensure that the value was close to the target value of 5 %. It was calculated that there was 6.5 % Pd in the catalyst. This value is slightly higher than the desired value but is acceptable for the purposes of the investigation. The analysis of the $\text{Ru}/_\text{MG}S500$ catalyst by AAS gave a value of 4.2 % for the Ruthenium in the catalyst. This value is slightly lower than the
target value of 5% but is an acceptable value permitting future use of this catalyst. As is the case for the Pd\(_{\text{MG}}\)S500 sample, any value too distant from the desired amount of 5% would deem the catalyst unsuitable for use for the purposes of the autoclave reaction experiment.

4.2.1.2 XRD

The XRD patterns of alumina silica and all the palladium catalysts used in this investigation are displayed in Figure 4.18.

![XRD Patterns](image)

**Figure 4.18.** Graphical results for four Palladium catalysts and for the Alumina Silica supports.

The alumina silica support produced only one broad peak at 2\(\theta\) = 22.5°. This peak is diagnostic for the amorphous structure of AlSi. The width of the peak is due to the scattering of X-rays in multiple directions (Wanjin Yu et al. 2011). No other peaks were detected for the analysis of the alumina silica which gives reassurance that there are no XRD detectable contaminants present in the support. In the case of Pd/C four peaks can be identified at 2\(\theta\) values of 40.3°, 46.6°, 68.5° and 81.5°
which are the characteristic diffraction peaks of crystal planes of metallic palladium. The Pd/C + AlSi catalyst shows two small peaks visible at 2θ values of 26.5° and 40.3°. These are also present for the Pd/C catalyst with the first peak (26.5°) being diagnostic of the activated carbon amorphous structure. The second peak at 2θ = 40.3° is also diagnostic for metallic palladium. No other peaks are clearly distinguishable in the Pd/C + AlSi catalyst but Pd was detected by other characterisation techniques (TEM and AAS) and this leads to the conclusion that palladium is highly dispersed throughout the catalyst.

The analysis of catalyst Pd/MgS500 produced many peaks between 2θ values of 20° to 60°. Only the peaks at 42.1° and 46.3° were found to be representative of Pd. The numerous other peaks most likely represent support particles. As expected, the same peaks are shown for Pd/MgS500 + AlSi however, with a lower intensity than Pd/MgS500.

Figure 4.19. Graphical results for XRD analysis for the five ruthenium catalysts.
On close examination of the XRD intensity vs 2θ plots for the five Ruthenium catalysts displayed in figure 4.19, it is clear that there is a pattern of repeating peaks for the commercial catalysts at 2θ values of 26.6°, 36.5°, 39.4°, 43.5°, 50.0°, 59.9° and 68.0°. These peaks are characteristic of polycrystalline structures of activated carbon and charcoal. No characteristics peaks corresponding to metallic Ru particles were detected for these samples. Ruthenium was detected by other characterisation techniques, namely AAS and TEM, implying that the metal particles are highly dispersed on the charcoal and activated carbon supports (Upare et al. 2011). The XRD patterns of Ru/MG500 and Ru/MG500 + AlSi also show the absence of ruthenium peaks. As for the case of the commercial Ru catalysts, this information leads to the conclusion that the Ruthenium is finely dispersed across the entire catalyst structure and therefore any peaks are too small to be detected with XRD.

### 4.2.1.3 BET

**Table 4.9.** Surface area, pore size and pore radius of AlSi, Ru and Pd catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface Area (m²·g⁻¹)</th>
<th>Pore Volume (cm³·g⁻¹)</th>
<th>Pore Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlSi</td>
<td>70.9</td>
<td>0.73</td>
<td>18.6</td>
</tr>
<tr>
<td>Ru/C</td>
<td>132</td>
<td>0.63</td>
<td>18.5</td>
</tr>
<tr>
<td>Ru/C + AlSi</td>
<td>138</td>
<td>0.70</td>
<td>18.5</td>
</tr>
<tr>
<td>Ru/MG500</td>
<td>10.4</td>
<td>0.03</td>
<td>18.8</td>
</tr>
<tr>
<td>Ru/MG500 + AlSi</td>
<td>21.1</td>
<td>0.04</td>
<td>18.3</td>
</tr>
<tr>
<td>Ru/Charcoal</td>
<td>119</td>
<td>0.49</td>
<td>19.5</td>
</tr>
<tr>
<td>Ru/Charcoal + AlSi</td>
<td>129</td>
<td>0.54</td>
<td>19.6</td>
</tr>
<tr>
<td>Pd/C</td>
<td>94.4</td>
<td>0.35</td>
<td>18.4</td>
</tr>
<tr>
<td>Pd/C + AlSi</td>
<td>109</td>
<td>0.54</td>
<td>18.8</td>
</tr>
<tr>
<td>Pd/MG500</td>
<td>10.2</td>
<td>0.02</td>
<td>15.9</td>
</tr>
<tr>
<td>Pd/MG500 + AlSi</td>
<td>30.8</td>
<td>0.04</td>
<td>18.6</td>
</tr>
</tbody>
</table>
The main values of interest from the BET analysis were the surface area ($\text{m}^2 \cdot \text{g}^{-1}$), the pore volume ($\text{cc} \cdot \text{g}^{-1}$) and the pore radius ($\text{Å}$). Catalyst supports are used to achieve a higher surface area and therefore higher activity for the catalyst. Surface area, porosity, chemical inertness and oxygen surface groups are the four main factors that affect preparation, resistance to sintering, catalytic activity and selectivity of the catalyst (Rodríguez-reinoso 1998). Large surface area, wide pore size distribution, smaller metal particles and strong acid sites may be beneficial to the OHE reaction (Yang Tang et al. 2008). These properties are very desirable in catalysts for the OHE reaction and are the reason why catalyst supports are used as they provide them. The support spreads the active phase of the catalyst over a much wider area and greatly improve the activity while pores allow the diffusion of reactants through them, reducing sintering of the catalyst, aiding dissipation of heat and lowering potential for poisoning of the catalyst (Rodríguez-reinoso 1998).

Activated carbon and alumina-silica provide a huge surface area and porosity increase to the catalysts and by spreading the active phase over a much larger area, greatly improve the conversion of substrate and yield of product. Table 4.9 displays the values of surface area, pore volume and pore radius obtained for each of the catalyst samples and the alumina-silica support. The purchased Ruthenium and Palladium catalysts all achieved values for surface area near or greater than 100 $\text{m}^2 \cdot \text{g}^{-1}$ with the highest being the physical mix of Ruthenium, activated carbon and alumina-silica (Ru/C + AlSi) at 138.45 $\text{m}^2 \cdot \text{g}^{-1}$. The three purchased Ruthenium catalysts (Ru/C + AlSi, Ru/C and Ru/Charcoal) also had the three highest surface area values. The four prepared catalysts, with the ($\text{MG}_{500}$) sulfonated char, gave low values for surface area with the highest ($\text{Pd}_{\text{MG}_{500}}$ +
AlSi) at only 30.77 m²·g⁻¹. Both catalysts supported with MG₅S500 without alumina-silica had the lowest surface area values of 10.17 m²·g⁻¹ and 10.44 m²·g⁻¹ respectively while the catalysts with MG₅S500 and alumina-silica achieved surface area values of 21.12 m²·g⁻¹ and 30.77 m²·g⁻¹. These values suggest that the alumina-silica is providing a boost to the surface area but the surface area remains too low. There are numerous possibilities for values of surface area for the prepared catalysts being substantially lower than the purchased catalysts including problems with the analysis method, parameters of the BET instrument e.g. higher outgassing temperature required or possible loss of sample during analysis. The fact that the lower values occurred only for the MG₅S500 char prepared catalysts and none of the purchased catalysts does not appear coincidental and the low values must be related to the composition, method of preparation of these catalysts or unsuitability to the chosen analysis parameters of BET.

The pore volume values obtained have a similar pattern to those of the surface area values. The five purchased catalysts and the solo alumina-silica support had pore sizes of between 0.353 and 0.731 cubic centimetres per gram (cc/g) while the four prepared catalysts (Pd/MG₅S500, Pd/MG₅S500 + AlSi, Ru/MG₅S500 and Ru/MG₅S500 + AlSi had pore volume values of 0.024, 0.039, 0.033 and 0.041. These values seem to follow the same pattern as the surface area and suggest that the pore sizes of the prepared catalysts are also much lower than the purchased catalysts. The value for the Ru/MG₅S500 + AlSi catalyst however, has a pore size competing with some of the purchased catalysts and when examining the catalysts, the ones that have activated carbon and/or alumina-silica together have the highest pore volume. When comparing the Ru catalysts with the corresponding Pd catalysts, it seems that Ru permits higher pore volumes. The
pore radius values are fairly similar in most cases with values ranging from 15.86Å to 19.52Å for each catalyst and the highest being for the Ruthenium on activated charcoal catalyst. These values are fairly close, apart from the Pd + MgS500 catalyst which had a slightly lower pore radius. This contributed to that same catalyst having the lowest pore volume value also.

In comparison to the results of Yu et al. (2011) in terms of the surface area of Pd catalysts, there are significant differences in surface area between their Pd/C catalyst boasting a surface area of 1020 m²·g⁻¹ and their Pd/Al-SBA-15 catalysts obtaining values between 647 and 795 m²·g⁻¹. The highest surface area obtained during this study for Pd catalysts was the Pd/C + AlSi catalyst with a surface area of 138.45 m²·g⁻¹. This surface area value is much lower than those of Yu et al. and shows that the active phase of each of their catalysts is dispersed over a much wider area than the catalysts involved in this study. Their Pd/AlSi catalyst also showed higher surface area (170 m²·g⁻¹) in comparison to the Pd/C + AlSi used in this study, which further emphasised the point that a much wider distribution of the active phase was achieved.

Zheng et al. (2002) studied the thermal and oxidative treatments of activated carbon on its surface and its surface structure and suitability as a support for barium promoted ruthenium catalysts for ammonia synthesis. A BET surface area of 74.55 m²·g⁻¹ and a total pore volume of 0.046 cm³·g⁻¹ was achieved for their C1600 catalyst support while the activated carbon catalyst support achieved much larger values of 825.62 m²·g⁻¹ surface area and 0.48 cm³·g⁻¹, over 10 times better. This value is over 6 times the highest surface area achieved by any catalyst in this study.
Huang et al. (2015) studied the biosynthesis of ruthenium nanoparticles supported on nitric acid modified activated carbon for liquid-phase hydrogenation of 2,2,4,4-tetramethylcyclobutane-1,3-dione (TMCB). They compared ruthenium supported on activated carbon catalysts which were treated with HNO$_3$ (nitric acid) with regular Ru/activated carbon catalysts in terms of characterisation and then hydrogenation for the production of TMCB. For their BET results, surface areas of 806 and 731 m$^2$·g$^{-1}$ were observed for their 1 and 2 % Ru/C catalysts while their HNO$_3$ treated 1 and 2 % Ru/C catalysts recorded values of 803 and 785 m$^2$·g$^{-1}$. These values are much larger than those achieved for any of the catalysts in this study, with the Ru/activated carbon catalyst only achieving a surface area of 131.99 m$^2$·g$^{-1}$. In terms of pore volume, Huang et al. (2015) achieved values of 0.83, 0.75, 0.65 and 0.69 cm$^3$·g$^{-1}$ respectively. These values are similar to the values obtained during this study with a pore volume of 0.632 cm$^3$·g$^{-1}$ obtained for the Ru/C catalyst. The results of these comparisons also show that the active phase is spread over a much wider area for the Huang et al. catalysts compared to the catalysts in this study.

4.2.1.4 TEM

A minimum of 100 measurements were taken for each image. The diameter of each particle detected was measured using Fiji digital micrograph software. A representative image and the particle size distribution are shown for each catalyst.

Figure 4.20 displays the image and the particle size distribution of Ru/C catalyst. This catalyst has around 70 % of the particle between 1 and 2 nm and it is the catalyst with the lowest particle size average in this investigation.
Figure 4.20. TEM images (left) and particle size distribution (right) of the catalysts reduced in hydrogen: 5 wt.% Ru/C.

The particle size distribution of Ru/MGS500 catalyst (Figure 4.21) shows that the majority of the particles detected have a diameter between 1 and 3 nm.

Figure 4.21. TEM images (left) and particle size distribution (right) of the catalysts reduced in hydrogen: 5 wt.% Ru/MGS500.

Figure 4.22 shows the TEM results obtain for the catalyst Ru/Charcoal and its article size distribution in which it is observed that over 75 % of the particles have a diameter between 2 and 3 nm.
Figure 4.22. TEM images (left) and particle size distribution (right) of the catalysts reduced in hydrogen: 5 wt.% Ru/Charcoal.

Figure 4.23 and Figure 4.24 present the results of Pd/C and Pd/MG500 catalysts respectively. While the majority of the Pd/C palladium particles size are between 2 and 3 nm, for the case of Pd/MG500 they vary from 2 to 3 nm (27 %) and from 3 to 4 (52 %).

Figure 4.23. TEM images (left) and particle size distribution (right) of the catalysts reduced in hydrogen: 5 wt.% Pd/C.
Figure 4.24. TEM images (left) and particle size distribution (right) of the catalysts reduced in hydrogen: 5 wt.% Ru/MgS500.

4.2.2 OHE reactions study

All the catalysts were tested for the one-step hydrogenation esterification of butyric acid to butyl butyrate. At the beginning of this work, the reactions were undertaken for 4 h with a reaction temperature of 250°C and a pressure of 40 bar. Once the catalyst that allowed for higher conversion and yield was identified, the further experiments were carried out to study the effect of temperature and pressure.

Overall, high surface area (Table 4.9) together with high TOF (Table 4.10) can lead to high butyric acid conversion and butyl butyrate yield (Figure 2.26).

Table 4.10 shows the reaction conditions used with the catalysts, the metal surface area (As) and the TOF. Results highlights that Ru/C catalysts have the highest metal surface area meaning that there are more active sites exposed to the reactant. Higher TOFs were achieved with ruthenium supported with carbon or charcoal at 250°C and 40 bar. The TOF value for the Ru/Charcoal catalyst is
slightly higher than the one for Ru/C and both of them are from 3 to 5 times higher than the rest of the catalysts used under the same reaction conditions.

**Table 4.10. TOF of the catalysts**

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction conditions</th>
<th>Metal surface area, $A_M$ (m$^2$ g$^{-1}$)</th>
<th>TOF (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/C</td>
<td></td>
<td>13.7</td>
<td>0.220</td>
</tr>
<tr>
<td>Ru/C + AlSi</td>
<td></td>
<td>13.7</td>
<td>0.217</td>
</tr>
<tr>
<td>Ru/Charcoal</td>
<td></td>
<td>9.90</td>
<td>0.278</td>
</tr>
<tr>
<td>Ru/Charcoal + AlSi</td>
<td></td>
<td>9.90</td>
<td>0.283</td>
</tr>
<tr>
<td>Ru/MgS500</td>
<td></td>
<td>9.26</td>
<td>0.081</td>
</tr>
<tr>
<td>Ru/MgS500 + AlSi</td>
<td>250°C, 40 Bar</td>
<td>9.26</td>
<td>0.099</td>
</tr>
<tr>
<td>Pd/C</td>
<td></td>
<td>9.25</td>
<td>0.051</td>
</tr>
<tr>
<td>Pd/C + AlSi</td>
<td></td>
<td>9.25</td>
<td>0.067</td>
</tr>
<tr>
<td>Pd/MgS500</td>
<td></td>
<td>9.87</td>
<td>0.039</td>
</tr>
<tr>
<td>Pd/MgS500 + AlSi</td>
<td></td>
<td>9.87</td>
<td>0.040</td>
</tr>
<tr>
<td>Ru/C + AlSi (toluene)</td>
<td>225°C, 40 Bar</td>
<td>13.7</td>
<td>0.022</td>
</tr>
<tr>
<td>Ru/C + AlSi</td>
<td>200°C, 40 Bar</td>
<td>13.7</td>
<td>0.043</td>
</tr>
<tr>
<td>Ru/C + AlSi</td>
<td>250°C, 30 Bar</td>
<td>13.7</td>
<td>0.088</td>
</tr>
<tr>
<td>Ru/C + AlSi</td>
<td>250°C, 20 Bar</td>
<td>13.7</td>
<td>0.018</td>
</tr>
</tbody>
</table>

*Note: where not stated, the experiments were undertaken with cyclohexane as a solvent, e.g. Ru/C + AlSi (toluene) was undertaken using toluene.*

Butyric acid conversions with the catalysts at same reaction conditions are shown in Figure 4.25. It is notable that the Ru/C, Ru/Charcoal and their physical mixture with AlSi gave the better conversions. Furthermore, the introduction of AlSi promoted the esterification reaction, as expected, and therefore allowed for a higher conversion of butyric acid. The rest of the catalyst didn’t perform at the same level but the same behaviour is found by adding AlSi which favoured the esterification reaction and therefore consumed more butyric acid. A test using toluene was undertaken to study the influence of the solvent and the conversion were found to be significantly lower than that obtained with the same catalyst and reaction conditions using cyclohexane.
Figure 4.25. Butyric acid conversion of different catalysts at 250°C and 40 bar.

*Note: all experiments were undertaken with cyclohexane unless stated differently.*

Figure 4.26 shows the yields of butanol and butyl butyrate with all the catalysts used in this work. The catalysts that gave the highest butyric acid conversions are the same as those which gave the best butyl butyrate yields: Ru/C and Ru/Charcoal catalysts. The introduction of AlSi lowered the yields of butanol compared to the reaction undertaken with the same catalyst without AlSi and increased the yields of butyl butyrate. This confirms that adding AlSi promotes the esterification and accelerates the consumption of butanol and therefore it decreases its yields.
Figure 4.26. Butanol (left) and butyl butyrate (right) yields of different catalysts at 250°C and 40 bar.

The influence of reaction conditions were investigated for the most active catalyst, Ru/C + AlSi. With a constant pressure of 40 bar, the temperature varied from 250 to 225 and 200°C. These results (Figure 4.27) showed that decreasing the temperature results in a lower conversion of butyric acid and lower yields of butanol and butyl butyrate. The same trend was found by experimenting with a constant temperature of 250°C and by decreasing the reaction pressure from 40 to 30 and 20 bar (Figure 4.28).

Figure 4.27. Butyric acid conversion at different temperatures (left), butanol and butyl butyrate yields at different temperatures (right).
Due to instrumentation limitation, our autoclave could have not been used with a pressure over 40 bar. F.A. Pesa et al. (1983) reported in their work that over 60% butyric acid conversions was achieved within the reaction pressure around 80 bar and temperatures between 200 and 250°C. In the future work, higher pressure conditions will be investigated for these reactions.

Figure 4.28. Butyric acid conversion at different pressures (left), butanol and butyl butyrate yields at different pressures (right).
Chapter 5

5 Conclusion

Heterogeneous solid acid catalysts were produced by sulfonation of char obtained from the slow pyrolysis of Miscanthus x giganteus and brown bin waste digestate at different carbonization temperatures. All char based solid acid catalysts were successfully employed in the esterification of butyric acid with butanol.

An increase in catalyst loading was found to accelerate the rate of butyl butyrate yield especially during the early stage of the reaction. CBSA catalysts with higher acid density performed better. Compared to Amberlyst-15, non-activated MG-CBSA catalyst produced from carbonization of Miscanthus at 500°C was considerably better while most of the other MG-CBSA catalysts gave similar results. Chemical activation, undertaken for MG-materials only, increased the surface area of the char but, the prolonged treatment at high temperatures (500 and 600°C), did not allow the production of more polycyclic aromatic carbons available to be functionalized. This resulted in a lower total acid density and an inferior performance in comparison to the non-activated counterparts. Conversely, activated MG-CBSA catalysts after use and recovery have generally shown an inferior loss of activity and better reusability.

In the case of brown bin waste digestate chars, increasing the carbonisation temperature didn"t increase the surface area of the material, a different result to the study undertaken with Miscanthus x giganteus. This difference is likely due to a structural collapse that for MG occurs when it reaches temperatures over 800°C. This also did not allow the production of more polycyclic aromatic carbons
available to be functionalized resulting in a lower acidity and an inferior performance of the catalysts derived from brown bin waste carbonised at higher temperatures (500 and 600°C). On the other hand, both wS400 and wS500 have generally shown a good level of reusability.

The main disadvantage of CBSA catalyst was found to be the leaching of sulfonic groups during esterification reactions. These acid characteristics can be regenerated by additional sulfuric acid treatment (Rao et al. 2011), or the used material can be disseminated or applied, e.g. as an adsorber (Severini et al. 2015).

Realistic kinetic parameters were formulated for the optimum CSBA catalyst using two power law models. The models fitted very well the experimental data and calculated very similar activation energies for all the catalysts employed thus validating the study. A small variation between Ea was noticed for MG-catalysts and was attributed to mass transfer effects (Severini et al. 2015).

Commercial Ru and Pd catalysts supported with activated carbon or charcoal; and prepared Ru and Pd catalysts supported with sulfonated char MGS500 were characterized and tested for the one-step hydrogenation esterification of butyric acid to butyl butyrate at 250°C and 40 bar using cyclohexane as solvent.

Generally, high surface area together with high TOF led to high conversions and yields in total. Ru/C, Ru/Charcoal and their physical mixture with AlSi gave the best performances among the catalysts investigated in this work. The results implied that the introduction of AlSi promoted the esterification reaction and accounted for a higher conversion of butyric acid and of butyl butyrate yields by accelerating the consumption of butanol.
The investigation of different reaction conditions showed that decreasing the temperature and pressure resulted in lower conversions and yields. To further test these noble metal catalysts, higher pressure will be applied in a future work.
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