INTRODUCTION

Environmental sustainability and greenhouse gas (GHG) mitigation are two of the greatest challenges currently facing the global distilled spirits industry. Regulatory bodies around the world are in the process of placing stretching environmental targets upon domestic distilled spirits production. For example, the Scotch Whisky Association’s environmental strategy has placed environmental targets upon the industry as a whole, including GHG mitigation, improved energy efficiency and specific renewable energy utilisation targets of 20% by 2020, rising to 80% by 2050 (Scotch Whisky Association 2012). In light of this, the area of environmental sustainability and renewable energy utilisation is one of intense research interest. There is significant opportunity to contribute to environmental targets through the utilisation of co-products in the generation of bioenergy. This approach has several potential advantages, those being greenhouse gas (GHG) mitigation through the substitution of conventional fuel sources (e.g. gas and heavy fuel oil) with those of a renewable nature, alongside a reduction in discharges to the local environment. This Chapter discusses the production, characterisation, management and utilisation of co-products from malt whisky distilleries.
have been allowed to run off, with a second batch of water being mashed in, the temperature raised to around 70°C and the wort again being allowed to run off. The procedure is repeated for a third time with the temperature being raised to around 80°C (Dolan, 2003). The wort collected during the mashing process is cooled prior to being used as the fermentation medium in the production of the spirit. Subsequent to wort filtration the residual solid cereal component is now referred to as distiller’s SG or draff. Annual production volumes at a typical Scottish malt distillery equate ~2,400 tonnes per million litres of alcohol produced (Table 1).

Distillation in a malt distillery comprises a traditional two-stage batch distillation using copper pot stills. The wash (fermented wort) produced during fermentation, usually at 8-9% ABV (alcohol by volume), is used to charge the wash still. Heating is commenced with the wash beginning to boil at around 92°C, at which point the ethanol in the wash vaporises, rises through the swan neck and is condensed before being collected in the low wines receiver. The residue in the wash still, referred to as pot ale, represents the second most abundant co-product produced during malt whisky production (by weight). The low wines typically have an ethanol content of 20-23% ABV and are used as the charge for the spirit still during the second stage spirit distillation which typically results in the production of spirit at 68-70% ABV. Spent lees are the second co-product generated during distillation and comprise the residue remaining in the spirit still subsequent to final distillation. A typical distillery will produce around 10,000 m³ of pot ale and around 3,000 m³ of spent lees, per million litres of alcohol produced annually (mla) (Table 1).

**CO-PRODUCT COMPOSITION**

**Spent grains**

Spent grains from malted barley comprise mainly lignocellulose, protein, residual starch and ash. The majority of the weight of freshly produced spent grains comprises water imparted during the mashing process (Figure 2). Lignocellulose is a matrix comprising cellulose, hemicellulose, and lignin (see Chapter 15). Cellulose is a polysaccharide of glucose subunits joined by $\beta-1, 4$ glycosidic bonds (Fan et al., 1982), whilst hemicellulose is a branched heteropolysaccharide consisting of various co-polymers: the pentoses D-xylose and L-arabinose, and the hexoses D-glucose, D-mannose and D-galactose (Saka, 1991). Additionally,
Hemicellulose is heavily acetylated, with high levels of acetyl functional groups found along its side chains. Lignin is a complex hydrophobic aromatic polymer containing phenylpropanoid monomers, principally p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol.

The component parts of the lignocellulose matrix form a complex structure which is found in the plant cell wall. Hydrogen bonding packs the cellulose chains together into a structure termed a micro-fibril. Hemicellulose occupies the outer region of the microfibril attached via covalent linkages to the cellulose chains. Adjoining fibrils are bound to each other by lignin and other polymers such as pectin which are bonded to the hemicellulose, creating a bundle of tightly packed micro-fibrils referred to as a macro-fibril. Lignin occupies the outer of region of the micro-fibril and surrounds the cellulose and hemicellulose chains. It provides structural strength to the macro-fibril and protects the polysaccharide component from external attack.

**Pot ale and spent lees**

Pot ale primarily contains water, intact (but dead) yeast cells, yeast cellular residues (eg. cell wall material), soluble protein and carbohydrates, alongside other compounds such as polyphenols, phosphorus, sulphur, phytate and copper (Table 2). Spent lees typically contain a dilute solution of a range of organic acids and alcohols, alongside high levels of copper and low levels of phosphorus and sulphur (Table 2).

**Figure 2. Overview of the typical composition of malt distillery spent grain**

(Derived from Mussato et al. (2006) and Bennett (2013)).

**Table 2. Typical composition of pot ale and spent lees**

<table>
<thead>
<tr>
<th></th>
<th>Pot ale</th>
<th>Spent lees</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD (mg/L)</td>
<td>50,000 – 75,000</td>
<td>1,500 – 4,000</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>25,000 – 35,000</td>
<td>500 – 2,000</td>
</tr>
<tr>
<td>SO$_4^{2-}$ (mg/L)</td>
<td>100 – 450</td>
<td>&lt;40</td>
</tr>
<tr>
<td>PO$_4^{3-}$ (mg/L)</td>
<td>150 – 600</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>2 – 12</td>
<td>8 – 50</td>
</tr>
<tr>
<td>Cd (mg/L)</td>
<td>0 – 0.035</td>
<td>0</td>
</tr>
<tr>
<td>Al (mg/L)</td>
<td>0.03 – 0.150</td>
<td>0.01 – 0.08</td>
</tr>
<tr>
<td>Solids (%wt/wt)</td>
<td>4 – 7</td>
<td>0.02 – 0.175</td>
</tr>
<tr>
<td>Total Nitrogen (mg/L)</td>
<td>2,000 – 4,000</td>
<td>100 – 150</td>
</tr>
</tbody>
</table>
production range from simple discharge to the local environment, through to production of fertiliser or as a substrate for the production of agricultural feed (Pass and Lambert, 2003). Spent lees are typically treated on site utilising conventional aerobic biological treatment before being discharged to local water courses. Pot ale represents a higher value co-product than spent lees and there are a number of avenues the distiller can exploit to derive value from it. These include use as an agricultural fertiliser or the production of pot ale syrup or barely dark grains to be used as a feedstock for cattle. Pot ale syrup is produced through the evaporation of pot ale to produce syrup with a dry matter content of 40-50% and has commercial value as a feed for pigs and cattle (Pass and Lambert, 2003). However, the market for pot ale syrup is fairly limited and it is usually combined with spent grains and dried in pellet form to produce barley dark grains which are marketed as a feed for cattle and horses.

**MANAGEMENT AND USE OF MALT WHISKY CO-PRODUCTS: NOVEL METHODS**

**Composting**

Agricultural use of spent grains through the production of compost is commonly applied in the brewing and distilling industries. Spent grains are more amenable to composting than the other co-products of the alcoholic beverage industry due mainly to their relatively low moisture content. With 70-80% moisture content and C/N ratio of 10-17, more effective composting can be carried out following a pre-drying stage and mixing with high carbon materials (Seefeldt, 2015). Their high protein and fibre content makes the final product suitable for a wide range of applications as soil conditioner and organic fertiliser. This can be carried out in open heaps (windrows), aerated piles and vessels or in vermicomposting systems. Many small scale distillers and brewers use their homemade compost from spent grains to fertilise their fields.

**Production of biofuels**

**Biogas**

Biogas is one of the by-products of anaerobic digestion (AD) of organic residues. AD is a natural biological process that converts materials containing organic matter in the absence of oxygen into biogas. This process can be summarised in four distinct phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis, as shown in Figure 3.

When an AD system is operating efficiently the biogas produced contains about 60% methane (CH₄) and 40% carbon dioxide (CO₂) plus traces of other

![Figure 3. Scheme of the anaerobic biodegradation steps of complex organic matter (adapted from Gujer and Zehnder, 1983).](image-url)
Co-products from malt whisky production and their utilisation

...gas, such as hydrogen sulphide and hydrogen (Gallert and Winter, 2008). The biogas can either be combusted onsite, in a gas engine or turbine, to raise steam or electricity or further refined for use as vehicular fuel or for municipal and industrial heating. Additionally, a rich nutrient resource as soil conditioner, called digestate, is also produced.

Various reactor designs have been proven to be effective in the anaerobic digestion of distillery effluent at the lab scale include; upflow anaerobic sludge blanket (UASB) (Goodwin and Stewart, 1994; Goodwin et al., 2001; Gao et al., 2007), upflow anaerobic filter (UAF) (Kida et al., 1999; Tokuda et al., 1999) and anaerobic baffled reactor (GRABBR) (Akunna and Clark, 2000). Many of these reactor designs are commercially available. Figure 4 shows a typical system configuration of an AD system treating distillery effluent.

Anaerobic digestion has been shown to be effective in the treatment of liquid distillery co-products, however the technology is significantly less developed in terms of dealing with solid distillery residues (e.g. spent grains). This centres upon the fact that the structural components, particularly lignin, within the grains make it resistant to rapid digestion and necessitates long reactor retention times for effective digestion. Hence, the hydrolysis is the limiting step for spent grain digestion. Research on anaerobic digestion of the grains focus mainly on enhancing the step through the use of various pre-treatments such as chemical (acid and alkaline), physical (thermal, ultrasound, grinding, etc.) biological (e.g. use of enzymes) processes and combinations of these processes prior to anaerobic digestion. The application of these processes are widely reported in the literature (e.g., Bennett et al., 2015, Bochmann et al., 2007, 2011, Malik et al., 2010, Rieker et al., 1992, Behmel et al., 1993, Beldman et al., 1987).

**Second generation bioethanol**

The conversion of lignocellulose based feedstocks is an area which has been of intense research interest in recent years, particularly with regards to the production of 2nd generation fuel ethanol which has the potential to replace fossil fuel derived liquid transportation fuels (see Chapters 15 and 16). Sources of lignocellulose for the production of ethanol are extremely varied with spent grains being one potential substrate. As previously discussed, lignocellulose comprises lignin, cellulose and hemicellulose, with these components coming together to form a complex structure which is found within the plant cell wall. The structure of lignocellulose dictates that in order to extract fermentable carbohydrate from the biomass, it must first be pre-treated to render it susceptible to enzymatic hydrolysis (Figure 5). The presence of lignin within spent grains results in the material being extremely resistant to hydrolysis and sugar extraction. The pre-treatment degrades lignin bound to the cellulose fraction (Mosier et al., 2005) and results in partial hemicellulose hydrolysis, causing the release of pentose sugars, chiefly xylose and arabinose. Additionally it results in increasing...
cellulose accessibility, thus rendering it susceptible to enzyme attack.

Following pre-treatment, the material is further digested enzymically, typically with a mix of cellulase, xylanase and β-glucosidase. Cellulase enzymes form a major component of the range of enzymes that are critical in the enzymolysis of pre-treated lignocellulose. Cellulase enzymes fall under two main classes; exocellulase and endocellulase. Endocellulase acts to cleave internal glycosidic bonds at random points along the cellulose chain, thus exposing individual chains to further hydrolysis (Henrissat et al., 1998). Exocellulase comprises two enzymes - CBHI and CBHII, which cleave cellobiose subunits from the reducing and non-reducing ends of the cellulose chain, respectively (Bommarius et al., 2008). Subsequent to cellobiose release, β-glucosidase hydrolyses the disaccharide to free glucose. Xylanase hydrolyses residual hemicellulose, not degraded during pre-treatment, to glucose, arabinose, xylose and low levels of galactose and mannose.

Following pre-treatment and enzymatic digestion, the resulting hydrolysate contains a variety of fermentable sugars. The range and concentration of the component monosaccharides vary dependent on biomass type. In the case of spent grains, the hydrolysate typically contains high levels of glucose, arabinose and xylose, with low levels of mannose and galactose (White et al., 2008). The sugars in the hydrolysate can be used as fermentation substrate for the production of fuel ethanol. Standard distilling strains of S. cerevisiae can ferment the glucose within spent grain hydrolysates. However, they lack the capability to metabolise the pentose sugars (arabinose and xylose). Various strains of wild-type yeast species possess the capability to ferment both the hexose and pentose sugars present within spent grain hydrolysates, these include; Pichia (Scheffersomyces) stipitis, Kluyveromyces marxianus, Candida shehatae and Pachysolen tannophilus.

**Biobutanol**

Traditionally butanol has been derived commercially from fossil fuels through hydroformylation of propene to butyraldehyde which is subsequently reduced with hydrogen to butanol (Green, 2011). Biobutanol differs from conventional butanol in that it is derived through the bioconversion of biomass and as such is deemed to be renewable. Biobutanol is produced through the conversion of biomass sugars to butanol utilising bacterial acetone-butanol-ethanol (ABE) fermentation, with feed-stocks usually being either starch (Al-shorgani, Kalil and Yusoff, 2012) or cellulose based (Ranjan et al., 2013). The process usually involves *Clostridium* spp. bacteria (e.g. *Clostridium acetobutylicum*) which ferment biomass sugars in an anaerobic fermentation similar to yeast fermentation, with products produced at a ratio of around 3:6:1 (acetone: butanol: ethanol) (Garcia et al., 2011).

It is anticipated that biobutanol may eventually become a more attractive replacement for liquid transportation fuels than bioethanol. Biobutanol displays a number of advantages over ethanol including having a higher energy content and lower water absorption (Durre, 2007). However, biobutanol is seriously disadvantaged by a number of factors, specifically extremely low yields, which

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**Figure 5.** Process steps in the production of bioethanol from lignocellulose.
in turn increases feedstock costs and leads to energy intensive distillation (Green, 2011). That being said, the process is deemed to be commercially viable and pilot scale facilities which convert malt distillery co-products to biobutanol are currently operational (Celtic Renewables, 2016).

**Microbial fuel cells**

Microbial fuel cells (MFCs) generate electrical energy through the anaerobic oxidation of organic material by bacteria. During the oxidation of the organic material within the feed, the bacterial population within the MFC produce protons and electrons, which are then harnessed using electrodes to produce an electrical current. Whilst the technology is relatively novel in terms of treatment of distillery co-products, their use in the context has been proven at the lab scale (Feng et al., 2008; Mohana et al., 2010). That being said, MFCs contain a number of disadvantages when compared with AD, including being unable to deal with the high solids component within pot ale, as well as being less efficient at COD reduction.

**Thermal energy**

**Combustion**

Combustion of spent grains is an area which is coming under increased focus within the alcoholic beverage industry. The technology relies upon the utilisation of spent grains as a fuel source within a biomass boiler, thence reducing the amount of externally purchased energy sources required for the industrial process. A number of full scale plants are currently in operation highlighting that direct combustion of spent grains is more effective if pre-dried (less than 55% moisture content), and this is a readily applicable technology that is already commercially available. However, the technology is currently expensive particularly when applied in small to medium size industries, the most prevalent challenge being the high energy requirement for the pre-drying stage and the treatment of toxic gas emissions, which can contain high concentrations of dust, nitrogen and sulphur oxides (Meyer-Pittroff, 1988, Keller-Reinspach, 1989, Mussato et al., 2006).

**Pyrolysis**

Pyrolysis is a process of thermal decomposition of organic matter under pressure and in an oxygen deficient atmosphere where the feedstock is heated from 350°C to 500°C. Most organic materials are unstable when applying high temperature, resulting in thermal cracking and additional processes taking place. The products produced from the pyrolysis process consist of charcoal (bio-char), bio-oil which is a liquid fraction containing tar and pyrolytic oil (high molecular weight) and syngas which is a mixture of combustible compounds (carbon monoxide, methane, hydrogen, ethane) and non-combustible (carbon dioxide, water, nitrogen (gases). These by-products have potential as a boiler fuel source, with the bio-char having additional commercial value as a soil additive (Sanna et al., 2011). Variation in the physical parameters observed during thermal conversion can be used to tailor the chemical composition of the bio-oil/bio-char. The application of the process in the beverage industry is still under development, mainly in its effectiveness compared to direct combustion.

**FUTURE DEVELOPMENTS**

Whilst animal feeds production is a tried and tested method for deriving value from distillery co-products, it does little to alleviate the pressures being placed upon the Scottish distilled spirits industry to meet environmental and renewable energy targets. The use of distillery co-products in the production of renewable energy is gaining increased traction and it is likely that this trend will continue in future. However, the challenge is on how to identify the most appropriate treatment technologies at specific plant locations.

All of the technologies discussed in this Chapter have the potential to generate value added products from co-products generated during malt whisky distillation; however there is a marked difference between the efficiencies of each particular technology. In terms of treatment of the liquid co-products produced by malt whisky distillation such as pot ale and spent lees, anaerobic digestion technology is significantly more developed than any of the other technologies discussed here. It also displays much higher energy yields, with generation of ~2,400 MWh per annum being typical if a 5 mla distillery were to switch to converting all of its pot ale to biogas via anaerobic digestion (Bennett et al., 2015). This compares favourably to other technologies such as a microbial fuel cell with quoted potential yields of around 700 MWh per hour obtainable by treatment of pot ale at the same distillery (Bennett et al., 2015). In
light of this, anaerobic digestion is likely to remain the treatment option of choice for the liquid co-products produced by malt whisky production and it is likely that its application will increase in coming years. This is more so because the other promising technologies, notably the Microbial fuel cells (MFC), are still to be proven effective at industrial scale.

The situation with regards to spent grains is significantly more complex. Whilst anaerobic digestion has the potential to generate ~15,000 MWh of renewable energy for a typical 5 mla distillery (Bennett et al., 2015), the technology is hampered by the, as yet, unsolved issue with regards to unfeasibly long retention times within the reactor, thereby requiring expensive pre-treatment stages for more efficient application. Spent grain combustion is a more proven technology with regards to production of renewable energy with typical energy yields of ~14,000 MWh per annum being feasible. Pyrolysis and second generation bioethanol production display significantly less energy generation potential than either combustion or anaerobic digestion, with typical annual energy yields of around 1000 MWh and 3000 MWh respectively (Bennett et al., 2015). As such, if there is to be increased diversion of spent grains from animal feeds production towards renewable energy generation, combustion is likely to be a more attractive technology unless reduction in anaerobic digestion retention times can be addressed more cost-effectively than is currently the case.

REFERENCES


