Brewing, winemaking and distilling: an overview of wastewater treatment and utilization schemes (Part IV - Chapter 35)

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Brewing, winemaking and distilling: overview of wastewater treatment and utilisation schemes

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35.1 Introduction

Food industries, due to the nature of their production, are identified as important consumers of high-quality water. Likewise, their wastewater production is high, and this forces the food industry to consider water resource preservation as a strategic and vital priority. Water cannot be considered as a common fluid, but as a fundamental raw material to ensure the quality and safety of products (Mathieu-André, 2000). At each level (production, cleaning, cooling, etc.), water management consists in controlling and reducing water consumption and reducing effluent. Whatever the potential ways to reduce water consumption, by acting on the production process or on the effluent treatment, ready-to-use or plug-and-play solutions do not exist. Each process and each product requires specific analysis to match different motivations and constraints (cost control or reduction, environmental constraints).

The brewing, winemaking and distilling industries produce alcohol as a beverage, industrial solvent or fuel. These three processes exhibit strong similarities (fermentation and separation operations) and stand as important water consumers and wastewater producers. In the food industry, the brewing, winemaking and distilling (spirit production) sectors hold a strategic economic position with world production estimated at 159.8 $10^9$ L beer, 26.7 $10^9$ L wine and 7.0 $10^9$ L spirits expressed in LPA/y (LPA = litre of pure alcohol) in 2004 (see Table 35.1).

Beer is the fifth most widely consumed beverage in the world behind tea, carbonates (sodas), milk and coffee and it continues to be a popular drink with an average consumption of 23 L/y per person. In Europe, the total contribution of the brewing sector to the European economy in terms of
added value is €57.5 billion, generating jobs for 164 000 employees in breweries, while 2.6 million jobs can be attributed to the brewing sector (Ernst and Young, 2006). The brewing sector is one of the few in which several European based companies are amongst the leading companies in the world (among the seven largest brewers, four are European). There are also very dynamic and innovative small and medium sized companies and breweries estimated at 2800 in 2005. This market masks the high degree of heterogeneity in the production capacity (Ciancia, 2000; Levinson, 2002). In 2004, the world’s 10 largest brewing groups shared almost 58 % of the world production (production capacity superior over 1.0 \times 10^9 \text{L/y}^{-1}), while a microbrewery may start its activity with an annual production of around 1000 hl (Verstl, 1999).

World-wide wine production is 26.7 \times 10^9 \text{L}, 70 % of which are produced in Europe (France, Italy, Spain, etc.), 17.2 % in America (USA, Argentina, Chile), 5 % in Asia (China), 4 % in Oceania (Australia) and 3.8 % in Africa (South Africa) (OIV, 2005). The world-wide wine market represented $99.6 billion in 2003 and the forecast for 2008 is $114 billion, whereas the wines and spirits market reached 250 billion dollars in 2003 (VINEXPO IWSR/GDR, 2005). Water consumption may appear to be erratic with ratios varying from 0.3 to 10 \text{L water/L wine}, depending on the winery. The establishment of regulations and the levying of taxes on winery effluents, the implementation of water purification treatments and the improved awareness of operators in relation to water management have contributed to reducing water consumption to approximately 0.8 \text{L/L} (Rochard et al., 1996; ITV, 2000; Rochard, 2005).

Agricultural alcohol may be distilled from many plants that produce either simple sugars directly (cane, beet, sweet sorghum) or starch (corn, grain, sorghum). The distribution, according to Berg (2006), between beverage, industrial utilisation and fuel ethanol is given in Fig. 35.1. The oldest use of alcohol is as a beverage (rum, whisky, vodka, etc.). Demand for distilled spirits in most developed countries is stagnating and even declining, due to increased health awareness, around 7.0 \times 10^9 \text{LPA/y} in 2004. These tendencies and figures are unlikely to change in the near future. According to the European

<table>
<thead>
<tr>
<th>Area</th>
<th>Beer (10^9 L)</th>
<th>Wine (10^9 L)</th>
<th>Spirits (10^9 L pure alcohol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>America</td>
<td>50.29</td>
<td>4.6</td>
<td>na</td>
</tr>
<tr>
<td>Europe</td>
<td>54.33</td>
<td>18.7</td>
<td>na</td>
</tr>
<tr>
<td>Asia</td>
<td>45.65</td>
<td>1.3</td>
<td>na</td>
</tr>
<tr>
<td>Africa</td>
<td>7.42</td>
<td>1.01</td>
<td>na</td>
</tr>
<tr>
<td>Oceania</td>
<td>2.11</td>
<td>1.07</td>
<td>na</td>
</tr>
<tr>
<td>World</td>
<td>159.8</td>
<td>26.7</td>
<td>7.0</td>
</tr>
</tbody>
</table>

na = not available
spirits organisation (CEPS, 2006), the EU is the leading exporter world-wide of spirit drinks. The annual value of EU export is € 5.4 billion. Spirit drinks make a positive contribution of € 4.5 billion to the EU’s balance of trade. This contributes 10 % of total EU food and drink exports. It is significantly larger than the figure for wine exports and more than double the figure for beer.

Besides the beverage production, the second large market for ethanol is in industrial applications as solvents that are primarily utilised in the production of paints, coatings, pharmaceuticals, adhesives, inks and other products (≈ 6.5 \times 10^9 \text{ LPA/y}). Production and consumption is concentrated in the industrialised countries in Northern America, Europe and Asia (Berg, 2004). The last usage category is fuel alcohol, which is either used in blends or pure. Its production has been increasing sharply since 2000 as it was approximately 18 \times 10^9 \text{ L/y} in 2000, 28 \times 10^9 \text{ L/y} in 2004 and is projected to reach 60 \times 10^9 \text{ LPA/y} in 2010). In 2003, around 61% of world ethanol production was produced from sugar crops, be it beet, cane or molasses, while the remainder was produced from grains where maize or corn was the main feedstock. Leaving aside biomass as a feedstock, the raw material accounts for around 70–80 %, of the overall cost of fuel ethanol. Therefore, its relative abundance plays a crucial role in getting the fuel alcohol industry started in a particular country. By 2013, fuel ethanol will be produced in North America (the USA and Canada), in South America, Africa, India and Australia from cane sugar (juice and molasses) and in the European Union from beet sugar (juice and molasses) and wheat (Berg, 2004). Two main sectors are then considered: ethanol from sugar (cane and beet) and ethanol from grain (corn and wheat).
The role of environmental technology for industry has greatly evolved over the past decades. Since the mid-seventies, the general trend is to consider that pollution from industrial processes should be cleaned up. ‘The polluters pay’ remains the basis of regulations. During beer, wine or alcohol production, the product goes through a whole series of chemical and biochemical reactions (mashing, boiling, fermentation, distillation, evaporation) which require solid–liquid separations, cleaning, other water processes and energy. The brewing, wine and alcohol industries have grown from ancient tradition but stand as a dynamic sector open to new technological and scientific developments. These agro-industries recognise that business success should depend upon consumer perception of company reliability. To be considered reliable by consumers, they are making efforts to establish compliance statements, to guarantee the quality of their product, to build consumer satisfaction and confidence, and to actually practice ecoship and sustainability management. Ecoship management can be defined as an attitude and policy towards environmental issues. The aim is to take advantage of natural energy sources, to promote reuse of packaging and recycling waste, to reduce waste and to promote diversification (Kawasaki and Kondo, 2005).

In 1996, the European Union approved the Integrated Pollution Prevention and Control (IPPC) directive 96/61/EC (EC, 1996). The IPPC directive constitutes an important tool to identify and quantify the environmental impact of production with life-cycle analysis (LCA), and to define the best available techniques (BAT) under both economically and technically viable conditions (CBMC, 2002; Koroneos et al., 2005).

Brewers, winemakers and ethanol producers are very concerned that the techniques they use are the best in terms of product quality, cost-effectiveness and environmental impact (Fig. 35.2). Consequently energy consumption, water use and wastewater generation constitute real economic opportunities for improvements in the existing process. Our present analysis is designed to highlight the emerging and existing constraints in relation to water and waste management in these industries and to give an overview of resource consumption. The most common treatments and the associated constraints and advantages are reported and possible biological and technical alternatives to reduce water consumption and waste production are discussed. Higher efficiencies and tighter environmental restrictions stand as a new framework for environmental technology, in which sustainability and economy are the keywords.

### 35.2 Water use: the Origin and nature of effluents in the brewing, wine and distilling industries

#### 35.2.1 Brewing industry

The main ingredients for the production of beer are barley malt, adjuncts, hops and water. The brewing process includes wort production, fermentation,
Brewing, winemaking and distilling: overview of wastewater 933

beer processing and packaging. A brewery utilises energy in the form of both heat and electricity. To run a brewery, utility installations involve boiling, cooling, water treatment, CO2 recovery, N2 generation and air compression (CBMC, 2002; Koroneos et al., 2005). The basic input and output in the brewing process are quantified in Table 35.2 and the most common waste treatments are illustrated in Fig. 35.3.

Rising costs of energy require rational use by improving energy conversion efficiencies, by reducing losses in conversion and by recovering heat. Average energy costs were estimated at 0.0282 €/L in 2002 (Schu and Stolz, 2005), water and effluent costs usually dominate (40.1 %), followed by heat (34.7 %) and electrical power (25.2 %). Wouda and Seegers (2005) performed a world-wide benchmark study on specific energy consumption (SEC) in the brewing industry in 2003. 158 breweries (production capacity: 0.05–1.2 109 L/y), representing 26 % of the world’s production, have an average SEC of 2.39 ± 0.6 MJ/L (for 10 %, 50 % and 90 % of breweries, the SEC is lower than 1.76, 2.33 and 2.90 MJ/L, respectively) which represents a reduction of 14 % with respect to 1999 data.

Food and beverage processing, including brewing, are large water consumers. Water management and waste disposal have become significant cost factors and an important aspect in the running of a brewery operation (Unterstein, 2000; Perry and De Villiers, 2003). Every brewery tries to keep

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**Fig. 35.2** Best available techniques (BAT) applicability scheme.
waste disposal costs low and the legislation imposed on waste disposal by the authorities is becoming increasingly more stringent (Knirsch et al., 1999). Water consumption in a brewery is not only an economic parameter but also a tool to determine its process performance in comparison with other breweries (Unterstein, 2000; Perry and De Villiers, 2003). Furthermore, the position of beer as a natural product leads the brewers to pay attention to their marketing image and to take waste treatment (wastewater, spent grains, Kieselguhr sludge and yeast surplus) into account. The average water consumption in a brewery is estimated to be 5–6 L water/L beer and the most voluminous solid waste is identified as spent Kieselguhr, surplus yeast and brewers grain. Spent grain represents the largest quantity of all the by-products: 0.18–0.24 kg/L beer, which is above surplus yeast: 0.025 kg/L beer and whirlpool trub: approximately 0.008 kg/L beer and spent Kieselguhr: 0.004–0.008 kg/L.

Several legal requirements carry weight in decisions in the beverage industry:

- For industrial waste, the stringency of waste management requirements in the beverage industry (including brewing) has been increased in Europe in recent years. The consequences are an increasing cost factor due to treatment or dumping. In brewing, diatomaceous earth (Kieselguhr) is increasingly scrutinised because legislation about dumping has come into effect since 2002. In Germany, legislation was reinforced in 2005 by a technical regulation related to domestic waste and material recycling law.

### Table 35.2  Typical resources consumption (Moll, 1991; CBMC, 2002; Fillaudeau et al., 2006)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Malt</td>
<td>g/L</td>
<td>100–200</td>
</tr>
<tr>
<td>Hops</td>
<td>g/L</td>
<td>0.1</td>
</tr>
<tr>
<td>Water consumption</td>
<td>L/L</td>
<td>4–10</td>
</tr>
<tr>
<td>Ferment</td>
<td>L/L</td>
<td>0.01–0.1</td>
</tr>
<tr>
<td>Processing aids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PVPP, siligel, etc.</td>
<td>g/L</td>
<td>0.1</td>
</tr>
<tr>
<td>Kieselguhr</td>
<td>g/L</td>
<td>1–2</td>
</tr>
<tr>
<td>Energy supply</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heat consumption</td>
<td>MJ/L</td>
<td>1.7–3.0</td>
</tr>
<tr>
<td>Electricity consumption</td>
<td>kWh/L</td>
<td>0.08–0.12</td>
</tr>
<tr>
<td>Waste</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wastewater discharge</td>
<td>L/L</td>
<td>2.2–8.7</td>
</tr>
<tr>
<td>Solid waste</td>
<td>g COD/L</td>
<td>8–25</td>
</tr>
<tr>
<td>Spent grain</td>
<td>g/L</td>
<td>&lt;10–240</td>
</tr>
<tr>
<td>Surplus yeast</td>
<td>g/L</td>
<td>180–240</td>
</tr>
<tr>
<td>Whirlpool trub</td>
<td>g/L</td>
<td>8</td>
</tr>
<tr>
<td>Spent Kieselguhr</td>
<td>g/L</td>
<td>4–8</td>
</tr>
</tbody>
</table>

COD = chemical oxygen demand  
PVPP = polyvinyl polypyrrolidone
From a public health point, the use of Kieselguhr sludge with spent grain as livestock feed is not a long-term solution and is not always viable.

In terms of water management, strict legislation favours a reduction of water consumption and wastewater production in order to reduce the volume to treat.

**Water and wastewater**

Breweries have a specific consumption of water ranging from 4–10 L water/L beer including brewing, rinsing and cooling water. The largest volume of...
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water is used as rinsing water in the brewing house (during the production) and in the bottling plant. In addition to the hot water required for the brewing process (depending on the mashing programme and mash water cycles 0.9–1.1 L/L including false bottom rinsing, product displacement and vessel cleaning), additional quantities of hot water are needed in the plant for cleaning and sterilisation operations. Specific hot process water requirements fluctuate widely between 0.2 and 1.5 L/L of cast wort (Schu and Stolz, 2005). Cooling and brewing water only comprise a small part of the water consumption: cooling water is usually only needed as supplementation water in a closed circuit; the brewing water is essentially the basis of the end-product (Braeken et al., 2004).

In brewing, the average water consumption is correlated to beer production for industrial breweries (Perry and De Villiers, 2003). Water consumption is divided into 2/3 used in the process and 1/3 in the cleaning operations (Moll, 1991). In the same way, the effluent to beer ratio is correlated to beer production. It has been shown that the effluent load is very similar to the water load since none of this water is used to brew beer and most of it ends up as effluent (Perry and De Villiers, 2003). The wastewater discharge will be equal to the water supply minus the beer produced, water evaporated in brew house and utility plants, and the water present in the by-products and solid-wastes (spent Kieselguhr, surplus yeast and spent grains). Water loss along the process is estimated to be 1.3–1.8 L water/L beer.

\[
\frac{\text{Water}}{\text{Beer}} = 2.89 + \frac{8731200}{\text{Beer}} \quad \text{For } 30 < \text{Beer} < 60 \times 10^6 \text{ L/month}
\]

\[
\frac{\text{Effluent}}{\text{Beer}} = 2.21 + \frac{54589200}{\text{Beer}} \quad \text{Beer [L/month] with}
\]

Effluent/Beer and Water/Beer, [L/L beer]

The brewing process generates a unique, high-strength wastewater as a by-product. The wastewater typically has a high biochemical oxygen demand (BOD) from the carbohydrates and protein used in brewing beer. The wastewater from the brewery is usually quite warm (over 38 °C). Both these specificities make brewery wastewater an ideal substrate for anaerobic treatment. Anaerobic digestion of brewery wastewater is a proven process with more than 250 full-scale systems in operation (Totzke, 2005).

Spent grain

The mashing process is one of the initial operations in brewing, rendering the malt and cereal grain content soluble in water. After extraction, the spent grains and wort (water with extracted matter) are called mash and need to be separated. The amount of solid in the mash is typically 20–30 % but can reach 40 %. At present, spent grains, often mixed with yeast surplus and cold break (trub separation after cooling of wort), are sold as ruminant livestock feed with an average profit close to 5 €/t (min: 1 €/t, max: 6 €/t, Knirsch et al., 1999). Anaerobic fermentation can be an attractive alternative to waste disposal since it provides a gain of energy, although the composition of spent grain (Table 35.3) requires a specific degradation process.

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Yeast surplus

Maturation and fermentation tank bottoms constitute another source of sludge estimated at 0.025 kg/L beer. Low-fermentation beer is produced through two fermentation steps, the primary fermentation being when 90% of the fermentable matter is consumed. Rapid cooling of the tank stops this fermentation and causes the flocculation of insoluble particles and the sedimentation of yeast. The tank bottom becomes full of yeast and ‘green beer’. At present, the fermentation tank bottom generates a beer loss of around 1–2% of production (Nielsen, 1989; Reed, 1989).

In brewing, surplus yeast is recovered by natural sedimentation at the end of the second fermentation and maturation. The yeast can be sold to the animal feed industry. This brewing by-product has dry matter content close to 10% (w/w) and generates beer losses (or waste) of between 1.5 and 3% of the total volume of produced beer.

Kieselguhr sludge

Diatomaceous earth has various advantages for filtration in the brewing process as reported by Baimel et al. (2004). The conventional dead-end filtration with filter-aids (Kieselguhr) has been the standard industrial practice for more than 100 years and will be increasingly scrutinised from economic, environmental and technical standpoints in the coming century (Hrycyk, 1997; Knirsch et al., 1999). Approximately two-thirds of diatomaceous earth production is used in the beverage industry (beer, wine, fruit juice and liqueurs). The conventional dead-end filtration with filter-aids consumes a large quantity of diatomaceous earth (1–2 g/L of clarified beer) and carries serious environmental, sanitary and economical implications (Modrok et al., 2006). At the end of the separation process, diatomaceous earth sludge (containing water and organic substances) has more than tripled in weight. From the environmental point of view, the diatomaceous earth is recovered from open-pit mines and constitutes a natural and finite resource. The resources of good-quality Kieselguhr are limited and brewers are facing problems with the continuously increasing iron content of the raw material. After use, recovery, recycling and disposal of Kieselguhr (after filtration) are a major difficulty.
due to its polluting effect and the increasing cost of disposal. From a health perspective, the diatomaceous earth is classified as ‘hazardous waste’ before and after filtration (The World Health Organization defines the crystalline silica as a cause of lung disease) and its use requires safe working conditions. From an economic standpoint, the diatomaceous earth consumption and sludge disposal generate the main cost of the filtration process ranging between 0.0025 and 0.007 €/L. In Europe, the economic aspect is strengthened because its consumption is higher (around 1.7 g/L of clarified beer). The disposal routes of Kieselguhr sludge are into agriculture and recycling with an average cost of 170 €/t. Disposal costs vary widely from one brewery to another with a positive income of 7.5 €/t up to a maximum charge of 1100 €/t of Kieselguhr purchased (Knirsch et al., 1999).

35.2.2 Wine industry
The wine industry can be divided into two sectors of activity:

- wine production (winemaking) within the wineries that creates winery effluents and co-products: pomace, lees;
- transformation/recycling of winery co-products within wine distilleries (alcohol distillation, extraction of components, etc.), whose wastewaters consist mainly of stillage.

These two sectors can be differentiated by the highly different production processes and raw materials used, leading to different types of effluent produced and treatment and recycling methods specific to each one (Fig. 35.4).

One of the main characteristics of winery effluents is linked to the seasonal character of the production with heavy pollution loads discharged over a short period of time (grape harvest, winemaking). The transformation of the by-products resulting from wine production (pomace, lees) by distilleries leads to the production of highly polluted wastewater (stillage).

The range of methods for treating and eliminating effluent (spreading, biological wastewater treatment, aerobic and anaerobic techniques, heat concentration, etc.) was transposed to the wine sector. However, constraints linked to the characteristics of the effluents and the companies involved resulted in the emergence of suitable treatment methods: aerated storage, aerated lagooning, natural evaporation for winery effluents, anaerobic digestion for stillage, etc. (OIV, 1999; ITV, 2000).

Winery wastewater
Water use and wastewater
Winery wastewater mainly consists of the water used to wash and clean winery equipment and facilities used for destalking, pressing, racking, alcoholic and malolactic fermentation, clarifying, tartaric stabilisation, filtering and bottling operations. The organic pollution of the effluent is due to the contribution of matter from wash water and product loss.
Fig. 35.4  Overview of wine industry processes and waste water production.
Wineries vary considerably, in production capacity – from several tens of thousands to several tens of millions of litres of wine – and as a result of the extremely varied vinification methods and techniques used. They also vary as to their water resources – underground and/or drinking water systems – as well as to the wastewater treatment methods that they use and to the level of awareness of the operators responsible for water management. All these differences lead to water consumption levels that vary considerably from one establishment to another: from 0.3–10 L of water per litre of wine produced (Duarte et al., 1998; Picot and Cabanis, 1998; ITV, 2000). The establishment of regulations and the levying of taxes on winery effluents, the implementation of water purification treatments and the improved awareness of operators in relation to water management have contributed to the reduction of water consumption to approximately 0.8 L/L (Rochard et al., 1996; ITV, 2000; Rochard, 2005). The amount of taxes levied on waste depends on the country; the French and Italian wine industries generate six times less effluents than those of Spain where taxes are lower (Prodanov and Cobo Reuters, 2003; Bustamante et al., 2005). The seasonality of wine production activity is an important factor to be taken into consideration in the management of wastewater treatment. Of the annual volume of effluents 60 % is produced over a period of approximately two months (harvest/vinification) and waste production is maximal from the start.

Water management

After separating rain water from uncontaminated process water (cooling water), efforts to reduce water consumption focused on washing and cleaning operations, the choice of materials and the intrinsic consumption of the various operations involved. Since the washing of facilities (tanks, equipment, floors) is a major source of water consumption in wineries, the use of high-pressure blowers (> 50 bars) or medium-pressure blowers (20–40 bars) that are just as efficient but without the disadvantages (less splattering, aerosols and abrasion), makes it possible to reduce water consumption (Seegers, 2006). The nature and the quality of tank construction materials are also considered in terms of water management. For example, the use of electropolished-type stainless steel for tanks not only reduces the quantity of water required for washing but the pollution load discharged into the water as well, as a result of decreased adherence and retention of matter on the tank surface. Concerning cleaning (disinfecting) of equipment, the application of chemicals (biocides) in the form of foams is recommended to limit product consumption and to increase efficiency.

Among the different vinification operations, the filtering of musts and wines is an important step in the management of water and waste. Membrane filtering processes (tangential microfiltration) applied to wine production are a considerable improvement in terms of the environmental impact of vinification processes (Moutounet and Vernet, 1998). Some of the advantages offered by membrane filtration as opposed to clay filtration are: the suppression
of filtration waste (using clay), whose elimination is increasingly difficult; the decrease in raw material loss (loss of wine through imbibitions), and the reduction of the pollution load in effluents. Nevertheless, water consumption for membrane filtration, linked to cleaning-in-place (CIP) procedures, is not actually less than that of clay filtration (Kerner et al., 2004). Moreover, the substitution of mineral filtration additives with substances suitable for reconditioning (Salame et al., 1998) or biodegradation (Erbslöh, 2006) contributes to the improved management of filtration residues.

Tartaric stabilisation of wines is a very specific operation and necessary if the wine is to conform to quality criteria. It is often carried out by cooling the wine at temperatures below freezing (−4 °C) for around eight days, and then filtering it to eliminate potassium acid tartrate precipitates. This process consumes a great deal of electrical energy (5 kWh/m³ wine) and produces considerable quantities of waste (filtration clay: 2 kg/m³ wine). Electrodialysis is a new technology used for the tartaric stabilisation of wine (Escudier et al., 1993) with a better environmental record: energy consumption is greatly reduced (0.5–1 kWh/m³) and filtration wastes are eliminated. Water consumption in the electrodialysis brine circuit (0.1 L/L wine) can be reduced through reverse osmosis (RO) of the brine and by recycling the permeate in the process (Bories et al., 2006).

Organic load and composition of winery wastewaters

Studies on winery effluents have generally focused on the evaluation of overall pollution loads on the basis of pollution measurement criteria – chemical oxygen demand (COD), biological oxygen demand (BOD), suspended solids (SS), etc. This research has shown that there is a wide disparity between winery effluents depending on the winery, the activity and the production period. On average, winery effluents have a COD close to 15 g O₂/L, and this organic load is easily biodegradable (COD/BOD < 1.5). Low nitrogen and phosphorus contents are observed and contribute to an insufficient BOD/N/P ratio in aerobic biological treatment. The quantity of sugars (glucose and fructose) in musts – 200–250 g/L – and ethanol in wines – 100–120 g/L – that present a similar COD (# 250 g O₂/L), contribute to the high organic load of effluents. Cleaning and disinfecting chemicals mainly consisting of caustic soda and biocides (hypochlorite, hydrogen peroxide, quaternary ammonium), very occasionally lead to a high level of alkalinity of the effluents (pH > 10) that are generally acidic (pH 3.5–5).

The detailed composition and the proportion of the different components of the pollution load of winery effluents have recently been studied (Bories et al., 1998; Colin et al., 2005). Ethanol is the major organic component and accounts for up to 90 % of the COD, except during the grape harvest when it is mainly sugars (Table 35.4). Winery effluents may contain almost 1 % (vol/vol) ethanol, corresponding to a wine diluted ten-fold. A close correlation has been shown between the COD of winery effluent and ethanol content.
The recovery of alcohol by wine distilleries through the distillation of winery co-products – pomace and lees – leads to the production of wastewater: pomace stillage and lees stillage (Fig. 35.4). Brandy production and the distillation of excess wine production generate wine stillage. Taking the alcohol content of co-products into account (5–12 % v/v), the stillage volume (dealcoholised product + condensed steam) represents approximately 10–20 L/L of pure alcohol.

Water consumption in wine distilleries is obviously linked to the production of steam for distillation and cooling (condensers, exchangers), as well as to the extraction of alcohol from the pomace by steeping with water. The recycling of pomace stillage for the extraction of pomace alcohol is used to reduce water consumption. Contrary to wineries whose waste production is concentrated over short periods of time, distillery activity is spread out over a large part of the year as a result of the chronology of the production of co-products – pomace, lees, wine – and their storage.

Table 35.4 Composition and breakdown of the COD of winery waste water

<table>
<thead>
<tr>
<th>Concentration (g/L)</th>
<th>% COD/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.0</td>
</tr>
<tr>
<td>Suspended solids (g/L)</td>
<td>3.3</td>
</tr>
<tr>
<td>COD raw (g O₂/L)</td>
<td>14.6</td>
</tr>
<tr>
<td>COD dissolved (g O₂/L)</td>
<td>12.7</td>
</tr>
<tr>
<td>Ethanol (g/L)</td>
<td>4.9</td>
</tr>
<tr>
<td>Glucose + fructose (g/L)</td>
<td>0.87</td>
</tr>
<tr>
<td>Glycerol (g/L)</td>
<td>0.32</td>
</tr>
<tr>
<td>Tartaric acid (g/L)</td>
<td>1.26</td>
</tr>
<tr>
<td>Malic acid (g/L)</td>
<td>0.07</td>
</tr>
<tr>
<td>Lactic acid (g/L)</td>
<td>0.16</td>
</tr>
<tr>
<td>Acetic acid (g/L)</td>
<td>0.30</td>
</tr>
</tbody>
</table>

1except pH
COD = chemical oxygen demand

Winery stillage

Water use and wastewater

The dissolved organic components found in stillage are glycerol, organic acids (tartaric, malic/lactic, succinic, acetic) and other wine components (phenolic compounds, nitrogenous matter and polysaccharides). The absence of ethanol in the stillage clearly differentiates it from winery effluent. Three types of stillage – lees, pomace and wine – have very distinct characteristics (Table 35.5).

Lees stillage is rich in suspended matter (50–100 g SS/L): yeasts and crystals of potassium hydrogen tartrate, giving it a particularly high raw COD (80–120 g O₂/L). Of the dissolved organic matter in detartrated lees stillage (COD d # 30 g O₂/L) 45 % is due to simple compounds (glycerol,
Brewing, winemaking and distilling: overview of wastewater

Table 35.5 Composition of stillages from wine distillery (Bories, 2006)

<table>
<thead>
<tr>
<th></th>
<th>Pomace stillage</th>
<th>Lee stillage</th>
<th>Wine stillage (White wine)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Not recycled</td>
<td>Recycled</td>
<td>Without tartrate recovery</td>
</tr>
<tr>
<td>pH</td>
<td>3.8</td>
<td>3.7</td>
<td>4.9</td>
</tr>
<tr>
<td>Suspended solids (g/L)</td>
<td>0.69</td>
<td>2.4</td>
<td>86.9</td>
</tr>
<tr>
<td>COD raw (g O₂/L)</td>
<td>17.3</td>
<td>46.8</td>
<td>100</td>
</tr>
<tr>
<td>COD dissolved (g O₂/L)</td>
<td>15.2</td>
<td>44.9</td>
<td>36.1</td>
</tr>
<tr>
<td>Ethanol (g/L)</td>
<td>0</td>
<td>0.13</td>
<td>0</td>
</tr>
<tr>
<td>Glucose + Fuctose (g/L)</td>
<td>0.6</td>
<td>6.8</td>
<td>0</td>
</tr>
<tr>
<td>Glycerol (g/L)</td>
<td>3.69</td>
<td>4.28</td>
<td>2.58</td>
</tr>
<tr>
<td>Tartaric acid (g/L)</td>
<td>4.64</td>
<td>5.66</td>
<td>30.0</td>
</tr>
<tr>
<td>Malic acid (g/L)</td>
<td>0</td>
<td>0</td>
<td>0.447</td>
</tr>
<tr>
<td>Lactic acid (g/L)</td>
<td>1.13</td>
<td>13.0</td>
<td>4.88</td>
</tr>
<tr>
<td>Acetic acid (g/L)</td>
<td>0.58</td>
<td>2.64</td>
<td>2.87</td>
</tr>
<tr>
<td>Sulfate (SO₄) (g/L)</td>
<td>0.264</td>
<td>0.62</td>
<td>0.885</td>
</tr>
</tbody>
</table>

COD = chemical oxygen demand

organic acids), and 55% is due to complex substances (phenolic compounds, polysaccharides, nitrogenous compounds). Lees stillage has a relatively low BOD/COD ratio of 0.36, highlighting the limited biodegradability of the organic load.

Pomace stillage resulting directly from the extraction of alcohol and sugars by washing with water has a COD of 15–20 g O₂/L, whereas recycled pomace wine stillage is characterised by a high organic load (COD: 30–50 g O₂/L).

Almost 70% of the organic load of wine stillage (COD: 20–30 g O₂/L) consists of glycerol and organic acids. The BOD/COD of wine stillage is the highest (0.44–0.52) and testifies to its satisfactory biodegradability in relation to the high proportion of simple substances.

Concerning the nitrogen and phosphorus composition, pomace and lees stillage have BOD/N/P ratios of 100/3.2/2.0 and 100/3.8/1.6, respectively (Bories, 1978). However, wine stillage is characterised by a ratio of 100/0.6/0.4 that clearly reveals the deficiency in N and P for aerobic biological treatment.

Concerning the mineral composition of stillage, potassium is the major element. It can be very highly concentrated in lees stillage (8–10 g K/L). Moreover, detartrated lees stillage is rich in sulphate (8–10 g SO₄/L) or chloride, depending on the reagents used for the extraction of calcium tartrate: lime/calcium sulphate or lime/calcium chloride.

35.2.3 Distilling industry

A project launched in 2002 between Indian organisations and Europe demonstrated that distilleries are one of the 17 most polluting industries
listed by the Central Pollution Control Board (Nataraj et al. 2006). For each litre of alcohol produced, the molasses-based distilleries would usually have water consumption per litre of alcohol produced of 14–22 L in process applications (yeast propagation, molasses preparation, steam generation) and 100–240 L in non-process applications (cooling water, steam generation). They generate about 8–15 L of wastewater.

In all the schemes, it is possible to distinguish two types of wastewater:

- wastewater with high solids concentrations as spent wash (named also stillage or vinasse) removed from the bottom of the column receiving the fermented broth,
- wastewater with very low solids concentration as cooling water used to evacuate the heat from the fermentation and distillation steps and the condensates from the stillage concentration plants.

The treatment of the first is very dependent on the raw material used for the fermentation. In contrast, in the second case their characteristics are the same.

Spent wash from the distillation column
The main difficulty comes from the spent wash issued from the bottom of the column receiving the fermented broth. Its composition, treatment and recycling schemes depend on the raw material used to produce the alcohol. The process, with cane and beet sugar products, is nearly the same and reported in Fig. 35.5.

The distilleries that ferment cane juice produce spent wash with a low concentration of solids (2–4 % solids) but high COD level (14–34 g/L) (Table 35.6) (Decloux and Bories, 2001). Their biodegradability is high (BOD/COD > 0.6) as 87 % of the COD of the cane juice stillage is represented by simple compounds: glycerol, organic acids. The glycerol alone represents 38 %. Direct land application, anaerobic biodigestion, aerobic treatment and discharge in aquatic environments are the main post-treatments.

Fermentation units working with cane molasses or green cane syrup need dilution water to decrease the sugar concentration to 16 % before fermentation. They produce stillage (8–10 % solids) of variable chemical composition with high mineral and organic matter content. Its COD is between 60 and 120 g/L. The BOD/COD ratio (0.3–0.35) demonstrates the limited biodegradability of the organic load. Substances which are not easily biodegradable represent a large proportion of the COD. It is made up of complex compounds (hetero-polymers) responsible for the dark brown colour of molasses stillage (phenolic compounds, mixtures of caramels, melanoidins and products of the alkaline degradation of hexoses). The mineral load is mainly made up of potassium (4–12 g/L), magnesium (2–3 g/L), calcium (2–3 g/L) sulphate (4–8 g/L) and chloride (5–6 g/L). Cane molasses stillage is rich in glycerol. Direct land application, anaerobic digestion, aerobic treatment, livestock feed production and other forms of recycling are the main post-treatments.
Fig. 35.5  Typical distilling process with cane and beet products.
Almost all the distilleries using beet juice are located alongside a sugar beet factory. The spent wash is recycled into the beet diffuser. Outside the beet harvest period, distilleries produce alcohol principally from molasses, green syrup (intermediate crystallisation products) or sugar syrup. As the total dissolved solids of the raw material is around 75 %, a mixture of water and backset stillage is used to dilute the broth to about 16 % sugar before fermentation. The amount of backset stillage is limited by the increasing osmotic pressure induced. The excess must be treated. Stillage from beet molasses fermentation has an acid pH, a dry matter content of about 100 g/L including 60 % of organic matter, a COD of around 60 g/L and a BOD of about 30 g/L (Table 35.7). The potassium content (K₂O) is high (8 g/100 g solids) as well as the glycerol (6 g/L) and betaine (15–20 g/L). The main utilisation is to concentrate it to produce liquid fertiliser (syrup with 55 % solids) with, in certain cases, an extraction of potassium sulphate crystals. Other forms of recycling are in study. The main cereals used to produce ethanol are maize in the USA and wheat in Europe and Australia. The general process is represented in Fig. 35.6.

There are two main production processes differentiated by the initial treatment of the grain. In the first one, the whole grain is used to produce the mash: the entire corn kernel or other starch grain is first ground into flour and processed without separating out the various component parts of the grain. Water is added to form a ‘mash’. This slurry is then treated with a liquefying enzyme called α-amylase to hydrolyse the cereal to dextrins, which are a mix of oligosaccharides. The hydrolysis is done above the
temperature of gelatinisation of the cereal by cooking the mash at an appropriate temperature to break down the granular structure of the starch. The dextrins are further hydrolysed to glucose in the saccharification process using the exo-enzyme glucoamylase. Then the mash is cooled and transferred to fermenters where yeast is added. After fermentation, the resulting ‘beer’ is transferred to distillation columns where the ethanol is separated. The stillage extracted at the bottom of the column is sent through a centrifuge that separates the coarse grain from the solubles that are then concentrated to about 30% solids by evaporation, resulting in condensed distillers solubles (CDS) or ‘syrup’. The coarse grain and the syrup are then dried together to produce dried distillers grains solubles (DDGS), a high-quality and nutritious livestock feed. Most of the new corn distilleries use this process or a minor variation of it. In the second process, the different parts of the grain are separated before hydrolysis of the starch. For the wheat, the separation process is the same to produce the flour, and then the fibre and the gluten are removed and processed separately. The advantage of this process is a better recycling value of the co-products and easier fermentation, but the disadvantage is a drop in the yield as the recovery of the starch is not complete.

For maize the grain needs to be soaked or ‘steeped’ in water and dilute sulphurous acid for 24 to 48 hours to facilitate the separation of the grain into its many component parts. After steeping the grain slurry is processed through a series of grinders to separate the germ. The remaining fibre, gluten and starch components are further segregated using centrifugal, screen and hydroclonic separators. The steeping liquor is concentrated in an evaporator and co-dried with the fibre component. It is then sent to the livestock industry. The gluten component (protein) is filtered off and dried to produce the gluten meal co-product. This process requires large volumes of water (1.3 m³/
Fig. 35.6  Typical distilling process with cereal products.

1. Fermentation
2. Distillation
3. Evaporator

Beer Distilling process with cane and beet products

CO₂
Alcohol
Condensate
Acetic treatment
Digestion
Reverse osmosis
Water recycling in fermentation.

Concentrated stillage

DDGS

DDG (distiller grains with solubles)

Livestock feed
Thin stillage backset

Milling + liquefaction + saccharification

Temperature regulation
Water
Mixing
Cooling water
Pumping

Outlet corn wheat
t of maize) involving large volumes of diluted solutions to concentrate. The starch and any remaining water from the mash can then be processed in one of three ways: fermented to ethanol, dried and sold as dried or modified corn starch, or processed into corn syrup. The fermentation process for ethanol is very similar to the cane or beet juice process described previously.

In the USA, most fuel ethanol is produced from maize following either the dry-grind (67 %) or the wet-mill (33 %) process. Theoretically, 1 kg of corn can yield a maximum of 0.44 LPA. Realistically, however, a yield of between 0.37 and 0.41 LPA/kg is common, although the newest plants can achieve up to 0.42 LPA/kg (Rosentrater and Kuthukumarappan, 2006). The production of DDGS is 0.30 kg/kg maize. The chemical properties of maize distillers dried grains with solubles were reviewed by Rosentrater and Kuthukumarappan (2006) and are reported in Table 35.8.

Until now, recycling of the co-products was mainly in the form of livestock feeds as DDGS. A potential market exists in the world’s animal feed industry where traditionally-used sources of protein such as animal by-products and fish meal have been either eliminated due to concern surrounding mad cow disease (BSE) or have become less available and more costly. The combined protein and energy value of ethanol by-products gives them tremendous potential in animal feeds across the world. Nevertheless, research is being continued to find better reuse opportunities and the bio-refinery concept where the parameters are chosen not only for the ethanol production but also for the valorisation of the co-product is generally accepted. (Dawson, 2003).

As new technologies are implemented, adding value to co-products is essential to the profitability of the fuel business. This will require a more holistic approach to ethanol in dry-grind plants. Optimisation of co-products as well as ethanol yield must be considered.

**Wastewaters with very low solids contents**

As highlighted previously, ethanol is produced by fermentation of a must containing fermentable molecules from which it is separated by distillation. For fuel alcohol dehydratation a step using molecular sieves is added. In all cases, the plant needs cooling water to evacuate the heat from the fermenters.

---

**Table 35.8** Chemical properties of corn (Rosentrater and Kuthukumarappan, 2006)

<table>
<thead>
<tr>
<th>Property</th>
<th>Reported values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter %</td>
<td>86.2–93.0</td>
</tr>
<tr>
<td>Protein % solids</td>
<td>26.8–33.7</td>
</tr>
<tr>
<td>Fat % solids</td>
<td>3.5–12.8</td>
</tr>
<tr>
<td>Nitrogen free extract %</td>
<td>33.8–54.0</td>
</tr>
<tr>
<td>Starch % solids</td>
<td>4.7–5.9</td>
</tr>
<tr>
<td>Total dietary fiber %</td>
<td>25.0–39.8</td>
</tr>
<tr>
<td>Ash % solids</td>
<td>2.9–9.8</td>
</tr>
</tbody>
</table>
and from the top of the distillation columns. To prevent any decrease in fermentation kinetics, water cooler than 30°C is necessary. In the condensers of the distillation columns, the cooling water temperature must be lowered as the distillation pressure is lowered, but generally not lower than 45°C. The dehydration step also needs cooling water at about 50°C.

Some small distilleries may be on the coast or near a river and use the cooling water in an open loop (pumping in cold water and sending the heated water back into the sea or river). However, with the increasingly stringent environmental rules, this scheme is less and less used. The distillery plants must have a cooling system to recycle the water. Most of them use an air-cooling exchanger. This implies evaporation of water into the air and hence the necessity to replace it with fresh water. Furthermore, to prevent salt accumulation in this cooling loop, a small flux of water must be regularly removed from the system. Thus a consumption of fresh water is necessary to ensure heat removal from the distillation columns. The main problem of this circuit is not the water consumption or the water quality even if disinfectant treatments are needed to prevent bacterial development, but the difficulty in reaching sufficiently low temperatures, in particular in warm countries with humid air. In some very large fuel plants an electrical cooling system may be the solution.

The concentration of stillage by evaporation generates large volumes of condensate which cannot be discarded without treatment because of its COD which ranges from 1–10 g/L (Morin et al., 2003). It is mainly used as water for irrigation. However, tight regulations make this utilisation has easy than it looks. Furthermore, alcoholic fermentation requires a major input of water. Some treatments are in study to allow the recycling of this water in fermenters are being studied.

35.3 Most widely used treatment methods: Livestock feed, discharge, anaerobic and aerobic treatments, incineration

Several techniques can be considered as existing industrial practice, but livestock feed, discharge in soil, and biological (aerobic and anaerobic) treatments stand as the most widely used. The specificity of the brewing, winemaking and distilling industries leads to different levels of development for each technique (Table 35.9). Their levels of development, advantages and constraints are reported. The choice of wastewater treatment techniques is based on numerous parameters:

- knowledge of process and product specificities;
- characterisation of the effluent (nature, composition, concentration, flowrate);
- historical, economical and environmental constraints;
- efficiency of the technique in agreement with BAT selection.
<table>
<thead>
<tr>
<th></th>
<th>Brewing industry</th>
<th>Wine industry</th>
<th>Distilling industry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Spent grain</td>
<td>Yeast surplus</td>
<td>Kieselguhr sludge</td>
</tr>
<tr>
<td></td>
<td>(mash)</td>
<td>(tank bottoms)</td>
<td></td>
</tr>
<tr>
<td>Livestock feed</td>
<td>I–CP</td>
<td>I–CP</td>
<td>I–CP</td>
</tr>
<tr>
<td>Direct land application</td>
<td>I–CP</td>
<td>I–CP</td>
<td>I–CP</td>
</tr>
<tr>
<td>Fertiliser</td>
<td>I–CP</td>
<td>I–CP</td>
<td>I–CP</td>
</tr>
<tr>
<td>Composting</td>
<td>A–PP</td>
<td>A–PP</td>
<td>I–CP</td>
</tr>
<tr>
<td>Dumping/offshore dumping</td>
<td></td>
<td></td>
<td>I–CP</td>
</tr>
<tr>
<td>Evaporation in pond</td>
<td>I–CP</td>
<td></td>
<td>I–CP</td>
</tr>
<tr>
<td>Anaerobic digestion</td>
<td>I–CP</td>
<td>I–CP</td>
<td>I–CP</td>
</tr>
<tr>
<td>Aerobic treatment</td>
<td>I–CP</td>
<td>I–CP</td>
<td>I–CP</td>
</tr>
<tr>
<td>Incineration</td>
<td>A–PP/I–ND</td>
<td></td>
<td>I–CP</td>
</tr>
</tbody>
</table>

Table 35.9 Most widely used techniques – synthesis of biological and technological pathways to minimize effluent production and water consumption (A–L: academic work on the laboratory scale; A–PP: academic work on the pilot-plant scale; I–ND: industrial application – new development; I–CP: Industrial application – current process)
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In the brewing and distilling industries, the most common treatment is livestock feed, discharge in soil and biological treatment. In wine production, the choice of wastewater treatment techniques is based on the seasonal nature and dependent on winery production capacities. Spreading and natural evaporation were among the first treatments to be implemented since they suit the variability of the pollution load and the technical and economic context of the sector (limited operating costs and investment). With the development of biological wastewater treatment technologies, companies with large production capacities (distilleries, wineries) began using aerobic and anaerobic biological processes. The specificities of the composition of winery effluents were also a determinant factor in the study and development of new treatment methods (fractionation, membrane separation) and valorisation (molecule production/extraction).

35.3.1 Livestock feed

In breweries, the livestock feed is limited by several economical, technological and biological constraints. The fibre content of spent grain is 150–160 g/kg DM (dry matter) making them unsuitable as a feed for non-ruminant animals (pork, poultry). Spent grain is bulky, due to its high water content (70–80 % w/w) making handling and transport inefficient. In wet form the spent grain is not stable and must be consumed within two or three days otherwise a biological degradation takes place. The production of spent grain is high in summer when the demand for cattle feed is low, and in certain areas (Africa, Singapore) the cattle feed market does not exist.

Heineken Technical Service and 2B Biorefineries (Bruijn et al., 2001; Schwencke, 2006) adapted a grass separation method for use with spent grains, which is environmentally sustainable, applicable world-wide and economically viable. The process separates spent grains into two useful fractions, a ‘protein concentrate’ and a ‘fibre concentrate’ and produces a wastewater stream. Wet spent grains (0.18–0.2 kg/L beer with 20–25 % w/w DM) are collected in a tank from which it is measured into an impeller mixed tank. Water (0.54–0.80 kg/L beer) at 80 °C is added to obtain a suspension of 5 % w/w DM. This suspension is pumped through a vibrating screen, which separates water and small particles (70 % vol/vol with 1.5–2 % w/w DM) and the coarse material (30 % vol/vol with 16–18 % w/w DM). After separation, the fibre material is fed into a screw press for water removal to reach 40 % w/w DM (0.095–0.140 kg/L beer), and the protein fraction is fed into a scroll-type decanter, where it can be dehydrated to 30 % w/w DM (0.030–0.050 kg/L beer). The liquid stream coming from the screw press and the decanter is recirculated to the mixing tank and extracted as drain (0.60–0.85 L/L beer with an estimated COD 0.02 kg/L). In 2001, the protein concentrate fetched 170 €/t (88 % w/w DM) and the fibre concentrate, 20 €/t (45 % w/w). The value of the protein product is the most important factor and determines the success and applicability of a spent grain separation.

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process. Three scenarios can be investigated: (i) direct cattle feed with spent grain; (ii) press and burn all spent grain without separation; (iii) separate spent grain, combus the fibres (see Section 35.3.5) and sell the proteins as wet product (30 % DM) or spray-dried (80 % DM). Schwencke (2006) reports promising results with nutritional trials of 180 piglets (diet with 30 % protein coming from spent grains). The protein content could be included in diet formulation with a net and metabolisable energy value of 117 and 18.0 MJ/kg DM, respectively.

At an experimental level, the incorporation of brewery waste (spent grain) into fish-feed (carp) was investigated by Kaur and Saxena (2004) in India. The better growth performance in fish fed on diets containing brewery waste is attributed to the availability of good-quality protein, as the waste contains more essential amino acids such as lysine, arginine and methionine than fish meal and about three times the level of these amino acids present in rice bran. In beet and cane molasses alcohol production, because of the high salt, particularly potassium, content stillage used in ruminants is limited to 10 % of the diet to avoid laxative effects (Decloux and Bories, 2002; Nguyen, 2003).

In contrast, for cereal alcohol production, cattle feed is the main utilisation of DDGS. Over the years, numerous research studies have been conducted in order to optimise their use in feed rations and, as reported by Rosentrater and Kuthukumarappan (2006), these studies have been comprehensively reviewed by Aines et al. (1986) and UMN (2006). However, today’s DDGS feed customers are asking for more information than the traditional moisture, protein, fat and fiber analyses. Animal nutritionists want complete nutrient profiles of the ingredients and they want to know the variability of these nutrients as well as the ability to select nutrients they need. Research projects are underway that would modify the amino acid composition, protein composition or phosphors content of DDGS. DDGS market expansion beyond cattle to swine, poultry and aquaculture is dependent on improving the quality and consistency of the DDGS coproduct.

35.3.2 Discharge in soil or ground water

Most of the effluents from various industrial sources were usually discharged directly in the soil or in ground water. However, this possibility is decreasing due to stringent environmental restrictions. World-wide scarcity of water is another incentive for recovering pure water from such industrial effluents.

Direct land application

In the brewing industry, spent grain can be dumped; however, in addition to restrictions or expense, an economical and ecologically feasible solution is required. Legal restriction for landfill materials such as maximum organic carbon content of 5 % strengthens these limitations. The spreading characteristics of winery effluents are linked to the C/N (carbon/nitrogen)
ratio; this is generally very high and can result at any given moment in a considerable mobilisation of nitrogen in the soil, with a heavy organic load that can precipitate aerobic and anaerobic phenomena capable of leading to the release of calcium, magnesium, iron and manganese, as well as to a concentration in heavy metals (Debroux et al., 2004; Peres et al., 2004; Bustamante et al., 2005).

The practice of fusing cane or beet distillery stillage for spray irrigation is long established by ethanol production units. Nguyen (2003) highlights the way in which it is trucked as far as economically possible to spray irrigate on cane and beet plantations. The practice varies with the raw material (cane juice or molasses) and the country. The advantages of direct return include formation of an initial buffer to the soil with calcium and magnesium, and improved soil physical properties, increased water and salt retention capacity and an increased soil microflora population. The disadvantages include problems of strong smell, insect invasion, possible increase in soil acidity, salt leaching and putrefaction. Another reported problem is the buildup of sulphates. These sulphates are reduced in the soil to hydrogen sulphide (bad odour), which is then oxidised into sulphuric acid by sulphur bacteria in the soil. Mahimairaja and Bolan (2004) demonstrated that in India spent wash application at doses higher than 250 m$^3$/ha is detrimental to crop growth and soil fertility, but its use at lower doses (250 m$^3$/ha) remarkably improves germination, growth and yield of dryland crops.

As far as molasses stillage is concerned, direct land application of spent wash from molasses fermentation is no longer carried out in Europe. The law distinguishes between categories of effluent depending on the C/N ratio (Decloux and Bories, 2001). Indeed all nitrogen fertiliser of organic origin is mineralised at varying rates depending on the presence or absence of mineral nitrogen (essentially ammonium) and organic nitrogen close to mineral nitrogen (urea, uric acid). The C/N ratio is the main factor of evolution since it conditions the mineralisation rate. The volumes and possible periods of land application are not the same depending on the category of effluent.

Concentration and land application as fertiliser

Industrial waste from breweries, especially of organic origin, has a high potential for several agricultural uses as reported in numerous works on laboratory (in vitro or in vivo) or industrial scales. Firs, the use of brewery wastes in arid or semi-arid regions, where the organic matter content of soils is rather low, may contribute to reducing environmental problems and enriching the soil. Second, soil-less substrates are used in horticulture for growing seedlings, plant propagation, vegetable production and the production of ornamental plants in pots; brewery wastes could be used as compost. Third, spent grains and yeast extracts are a source of complex carbohydrates that may have biological activity in order to fortify plants or stave off disease with various reported rates of success.

In Turkey, Kütük et al. (2003) investigated the effects of beer factory
sludge (BFS) mixed with soil on soil properties and sugar beet growth. Increasing doses of brewery sludge has a significant effect on the vegetative growth of sugar beet plants. However, the effect of BFS on leaf growth was more pronounced than on root growth. The best application level seems to be 10 t ha$^{-1}$ considering root growth, this being the economic part of the sugar plant. Application above 10 t ha$^{-1}$ negatively affected the root quality, possibly due to high levels of organic acids, $\text{NH}_4^+$-$\text{N}$ and $\text{NO}_3^-$-$\text{N}$, all released during mineralisation. BFS should be applied to the soil over six or seven months.

Garcia-Gomez et al. (2002) evaluated the use of compost (mixture of BFS (yeast and malt), 2.5 % and lemon tree prunings, 97.5 %) in the preparation of substrates for ornamental plants in pots, as peat substitutes and as an alternative to commercial composts used as substrates, and to determine any limitation to their use. Substrates were prepared by combining each compost with Sphagnum peat (p) or commercial substrates (CS) in different proportion (0, 25, 50 and 75 %). The authors demonstrate that compost of agro-industrial origin can be used for growing ornamental plants, provided the mixture contains at least 25 % peat or CS (up to 75 % with peat and 50 % with CS for calendula, and up to 50 % with peat or CS for calceolaria).

Rogers et al. (2001) studied the effects of formulations based on yeast fractions, spent grains fractions and hops extract, on commercial turf, growth and health. Liquid and dry BioTurf were composed of soluble and particulate fractions from spent grains, combined with yeast extract and glucan, and between 3 and 6 kg/100 m$^2$ were applied in agricultural field trials. In all cases, BioTurf improved the visual appearance, the rate of growth and the resistance to disease. The biological components can provide basic nutrition in the form of N, P and K and are particularly active in restricting the growth of plant fungal pathogens, *Microdochium*, *Rhizoctonia* and *Fusarium* species.

In the beet molasses industry, concentrated beet stillage is mainly used as fertiliser. Researches have demonstrated the fertiliser value of stillage which is classified as an NPK fertiliser. These fertilisers must contain more than 10 % of ($\text{N} + \text{P}_2\text{O}_5 + \text{K}_2\text{O}$) with a minimum of 3 % nitrogen and 6 % potash ($\text{K}_2\text{O}$) and do not contain more than 2 % chlorine. The nitrogen of stillage is almost totally in organic form: amino acids, glutamic acid salts, betaine (2–4 %). Fertilising sugar beet with concentrated beet stillage improves the yield per hectare. Beet molasses stillage enjoys a particular status since it is a natural fertiliser produced on a large scale and whose quality is acknowledged unanimously. Concentrated beet stillage can also be used in organic farming in conformity with the European directive CEE 2092/91. The stillage is concentrated at the output of the distillation column in multiple effect evaporators to 55 % solids. The final dry matter content is limited by the risks of spontaneous crystallisation of the potassium sulphate and the deposit at the bottom of the storage reservoirs. However, the application of concentrated stillage cannot be made on all types of land and it requires a concentration phase which is accompanied by a production of condensates with a COD (1–10 g/L) above the discharge norm. These condensates are most often treated...
in lagooning or in aeration ponds. Research is being conducted on their
treatment to enable their recycling in fermentation (see later).

As explained by Decloux and Bories (2002) during the concentration of
beet molasses stillage, large quantities of potassium tend to crystallise and
clog up the evaporators. To limit this spontaneous formation of potassium
sulphate crystals during the concentration stage or during the storage of the
concentrated stillage, many distilleries acidify the fermentation must with
hydrochloric acid instead of sulphuric acid, potassium chloride being much
more soluble than potassium sulphate. It is, however, possible to promote
and control the crystallisation of potassium sulphate that is then used as
fertiliser. Moreover, potassium sulphate crystallisation is a legal requirement
when using stillage for cattle feed. It must in this case contain less than 2–
3 % of potassium per unit dry matter and have a total nitrogen content
(measured by mineralisation and multiplied by 6.25) at least equal to 39 %.
To obtain complete precipitation of potassium and be within the acceptable
limits for using stillage in cattle feed, it is necessary to add sulphate ions,
most of time ammonium sulphate (\(\text{NH}_4\))_2\text{SO}_4 that increase the total nitrogen
content of the concentrated stillage. The cost of the ammonium sulphate is
thus in part compensated by a better utilisation of the stillage. Few beet
molasses distilleries go as far as to crystallise out the potassium sulphate. On
the other hand, several distilleries do extract crystals from concentrated
stillage, but only to avoid deposits in the storage reservoir.

Composting
To integrate stillage into compost it is necessary to have solid matter available.
In the case of wine distilleries, the stillage can be mixed with the grape. In
the case of cane alcohol industry, Liu et al. (1995) have shown the utility of
compost composed of stillage and bagasse. A technique of inoculating the
stillage has been developed by Alfa-Laval. The sugar-distillery Yestwant in
the Maharstra in India mixes the cooled stillage with a foam (flocculate
resulting from the purification by sulphitation and filtration in the presence
of bacilli) then inoculates the mixture with bacteria and fungi. It is then
spread over a large surface in the sun to dry. The compost is regularly (once
a week) turned over for aeration with a specially designed machine with a
large capacity (> 1000 m³/h). The total duration of composting is 11 weeks.
All the stillage is treated before the rainy season. The compost is a much
sought fertiliser. More often, press mud generated from the sugar mill is
simply mixed with distillery effluent (Nagaraj and Kumar, 2006).

In the beet industry, according to Madejon et al. (2001), direct application
of concentrated stillage on agricultural land may lead to economical and
environmental problems due to high salinity, low P content and high density.
Then composting of stillage with other solid agricultural residues would be
used to overcome these disadvantages by producing compost that is easily
handled, with higher potassium content and lower salinity.
Direct dumping in ground water and sea
Some cane juice distilleries send their stillage into the sea at more or less depth. In the French West Indies these discharges led to unacceptable problems of pollution on the coast and most distilleries have had to build a biological treatment plant.

Evaporation in ponds
Natural evaporation of winery effluents is a relatively simple treatment technique that has been developed in regions with temperate and dry climates, particularly in the south of France, where approximately 180 ponds exist in the largest wine producing region (Languedoc Roussillon: 1.6 \times 10^9 L wine). Effluents are stored in water-tight ponds (clay) until total evaporation, where the height of the water is determined by the difference between the evaporation capacity and the rainfall. This treatment technique is in agreement with the aims of sustainable development (no consumption of fossil fuel, evaporation via wind and sun). Storage in evaporation ponds is not subject to variations in flow or pollution load, a major advantage for the treatment of winery effluents. The evaporating capacity can be improved using accelerated evaporation by splashing the wastewater on supports with a large surface area (Duarte and Neto, 1996; Stock and Capelle, 1998).

The main disadvantage is the risk of noxious odours due to the fermentation and transformation of organic matter into volatile fatty acids (VFA) and other volatile compounds (Guillot et al., 2000; Desauziers et al., 2002; Bories, 2005). Nevertheless, the formation of foul-smelling compounds can be prevented by the addition of nitrate and the use of anaerobic respiration (denitrification) for the degradation of carbon compounds (Bories, 2005).

Generally speaking, the problem of noxious odours linked to effluents (storage, treatment, etc.) is becoming increasingly important in the agrifood sector (Paillier, 2005). Preventive treatments such as the inhibition of fermentation with biocides or nitrate, or curative treatments such as degradation or neutralisation of foul-smelling compounds, as well as the modification of processes (elimination of sulphate in distilleries), have been particularly studied for the wine and oil industries (Le Verge and Bories, 2004; Bories, 2006; Chrobak and Ryder, 2006).

35.3.3 Anaerobic digestion
Anaerobic treatment is an accepted practice, and various high-output anaerobic reactor designs have been tested at the pilot scale and under fully-operational conditions. The use of this process is increasing on a daily basis.

The brewing industry has been at the origin of one BAT in particular, that of anaerobic technology. The anaerobic microbial conversion of organic matter into biogas is state-of-the-art at this time. Wastewater with a high organic load is preferably treated using anaerobic digestion, for example waste and wastewater produced by the food industry. The fact that anaerobic
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treatment systems produce biological sludge at a low rate is a key factor, in addition to their ability to reduce chemical and biological oxygen demand (COD, BOD) without energy consumption. The biological treatment of brewery effluents is not really complex and the anaerobic processes used and related performance aspects are well understood and described in the literature. Compact wastewater treatment systems able to produce high-quality effluents and to handle nutrient removal are of major industrial interest. However, wastewater from breweries is highly variable (Table 35.10); depending on the step of the brewing process, pH, temperature, quantity, organic load, solids contents, cleaning and disinfecting agents can all change. Volumetric conversion capacities of the biological reactor are defined by (i) the biomass conversion capacity (bacterial kinetic parameters, physicochemical environment), (ii) mass transport (hydrodynamics, reactor geometry) and (iii) biomass concentration (retention of biomass, settler system, viscosity).

Considering the heavy organic load of distillery wastewater, anaerobic digestion has long been considered to be an ideal technique, combining the advantages of being both a primary treatment for depolluting the organic load and energy-producing due to the large production of biogas reusable for distillation (Bories and Maugenet, 1978; Chabas et al., 1990). Now used principally for the treatment of industrial liquid effluents, it has been the subject of numerous studies in France since the 1980s. Its efficiency for treating carbon pollution has aroused particular interest in the agrifood and pulp industries (Perillat and Boulenger, 2000). Approximately 50 units operate in France in the agrifood industry at this time; they are most prevalent in brewing and malting industries, wine distilleries and wineries. However, the

| Table 35.10 Effluent properties in the brewing industry (Pesta and Meyer-Pittroff, 2005; Totzke, 2005) |
| Flow | 1.5–7.5 L/L beer |
| Total BOD | 3–6 g/L beer |
| Total COD | 3.7–22.4 g/L beer |
| COD/BOD | 1.5–1.8 |
| Total nitrogen | 25–85 mg/L |
| Total phosphate | 5–35 mg/L |
| Soluble COD | 4.7 g/L |
| Soluble BOD | 3.0 g/L |
| Total SS | 0.74–2.92 g/L beer |
| FOG | 0.05 g/L |
| Settling sediment | 0.15–1.5 g/L |

BOD = biological oxygen demand
COD = chemical oxygen demand
FOG = fats, oils and grease
SS = suspended solids
wide disparity in the composition and production conditions between different
distillery stillage makes it difficult to generalise about the different data
available in each of the sectors. For example, effluents from a cane distillery
may have a high BOD/COD, which would lead to the destruction by micro-
organisms that are useful in biodegradation. In their efforts to conform to the
discharge standards, Indian distilleries use various forms of primary, secondary
and tertiary treatment. The typical treatment sequence is screening or
equalisation, followed by biomethanisation. The biomethanisation effluent
is occasionally subjected to a single- or two-stage aerobic treatment using
activated sludge, trickling filters or even a second stage of anaerobic treatment
in lagoons.

Digestion conditions
The anaerobic digestion process includes several microbiological stages to
transform the organic matter: (i) a hydrolysis phase of complex substrates
(polysaccharides, proteins) using hydrolytic bacteria, (ii) a fermentation stage
to convert simple substrates into alcohol and VFA, such as acetic, propionic
and butyric acids, using acidogenic fermentative bacteria, (ii) a phase of
conversion of fatty acids or alcohols into acetic and hydrogen (acetogenesis)
using acetogenic bacteria (syntrophic bacteria or OHPA – obligate hydrogen-
producing aceticogenic – bacteria, homoacetogenic bacteria, sulphate-reducing
bacteria), (iii) a final stage of methane production exclusively from acetate,
formate, H₂ and CO₂ using methanogenic bacteria.

In the case of breweries, it is feasible to use a biogas plant to treat
concentrated wastewater with a COD higher than 3.5 g/L. Treating wastewater
by anaerobic digestion converts more than 90% of the initial organic carbon
into biogas (CH₄, CO₂). Fermentation residues (1–5% of carbon) require
an advanced effluent treatment by aeration. The aerobic step generates 1–3
% of CO₂, 1–3% of sludge residual and 1% organic carbon in the
effluent. An optimised process is used that includes a pre-treatment and a
two-step fermentation process. Upstream solid separation and a blending–
buffering tank make it possible to separate solid and grainy contraries. This
provides a constant wastewater for a steady-going feeding of the fermentation
tank. A two-step fermentation process provides the opportunity to exert an
influence on single degradation processes that take place in different fermenters.
The hydrolysis fermenter (pH = 5.6–6.5) degrades the organic matter by
encouraging the action of acidifying bacteria and repressing that of
methanogenic bacteria. Acidified wastewater flows through the methanogenesis
fermenter, where biogas is produced. The biogas is a mixture of methane
(CH₄, 50–85% v/v), carbon dioxide (CO₂, 15–50% v/v) and trace gases
(H₂O, H₂S or H₂). Before utilisation, water and hydrogen sulphide need to
be removed. The calorific value of biogas depends on its CH₄ content and
varies between 4 and 7.5 kWh/m³.

In the case of media that are rich in fermentable substrates such as distillery
stillage, the acidogenic phase is very active and leads to a high VFA
concentration (Bories, 1981). Glycerol, a major compound of stillage, is easily fermented into propionic acid by propionic bacteria or butyric acid and 1,3-propanediol by clostridia (Claret, 1992; Barbirato et al., 1997; Colin et al., 2001). Since methanogenesis is the limiting stage of the anaerobic digestion of stillage, the equilibrium of the fermentation must be controlled to avoid the accumulation of VFA and the acidification of the digester, which would inhibit methanogenesis. The separation of the acidogenic and methanogenic phases in two distinct digesters is a practice proposed to control these phenomena (Ghosh and Klass, 1978; Massey and Pohland, 1978; Bories, 1980). The high sulphate contents (the case for molasses stillage and wine stillage treated with calcium sulphate) pose a problem (Karhadkar et al., 1987). The sulphate-reducing bacteria form sulphide with a high concentration both in the biogas (3–6 °% in H₂S) and in the liquid phase where the free, non-dissociated (H₂S) form inhibits anaerobic bacteria at concentrations of about 200 mg S⁻²/L. The cations (Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺) are inhibitors at high concentrations as is sometimes the case in molasses stillage. Often considered as difficult to biodegrade, and even reported to act as inhibitors in biodegradation processes, phenolic compounds, in their monomeric forms, can be degraded by the microflora of anaerobic digestion (Bories and Allaux, 1989a,b). For the complex polyphenolic forms, adsorption by the microorganisms in the purification systems leads to a partial elimination. Wine stillage has a high degradation rate (% of eliminated COD) by anaerobic treatment (85–90 °), as does cane juice stillage (90–98 °%), which is not the case for molasses stillage that is being studied in many countries in order to optimise fermentation conditions (Decloux and Bories, 2002a).

**Biodigestion technology**

Treatment by anaerobic digestion involves various systems, extensive or intensive, selected in relation to the nature of the wastewater (biodegradability, load) and the industrial context (capacity, seasonality of the production, etc.).

Treatment in anaerobic lagoons

Treatment in anaerobic lagoons is the simplest solution with lagoons at ambient temperature and a long residence time. This method has been applied to cane molasses stillage in India with residence times of 60 to 100 days. However, the biogas cannot be recovered.

Treatment in mixed digesters

Treatment in mixed digesters at a controlled temperature was developed in wine distilleries in Italy in the 1970s and is particularly well adapted to treating stillage with high suspended matter content (lees stillage). The residence times vary from 15 to 25 days and the volume load is from 1–2 kg COD m⁻³ d⁻¹.
The anaerobic contact procedure
The anaerobic contact procedure involves a mixed digester coupled with the recycling of the microbial biomass separated by static decantation (clarificator). This makes it possible to increase the biomass concentration in the digester and to decrease its volume. The volume load reaches 4–6 kg COD m⁻³ d⁻¹, and the hydraulic residence time (HRT) varies from six to ten days. Two plants, each with two anaerobic contact digesters, have been operating for approximately 15 years in wine distilleries in France (Table 35.11).

Fixed biomass on immobile media procedures
Fixed biomass on immobile media procedures consists of anaerobic digesters where the biomass is immobilised on plastic media with a large developed surface area and a low dead volume. The circulation of the liquid is either in the upflow (anaerobic filter) or downflow direction. These digesters have been developed in wine distilleries (Bories et al., 1982) and molasses distilleries.

Table 35.11 Examples of French anaerobic digestion plants of distillery and winery wastewaters

<table>
<thead>
<tr>
<th>Plant</th>
<th>REVICO (Cognac)</th>
<th>UCVA (Coutras)</th>
<th>ECLIPSE (Limoux)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste water</td>
<td>White wine stillage (pre-concentrated and detartrated) and lee stillage</td>
<td>Lee, pomace and wine stillages</td>
<td>Winery effluents/stillages</td>
</tr>
<tr>
<td>Flow (m³/d)</td>
<td>2000</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Organic load (kg COD/d)</td>
<td>80 000</td>
<td>35 000</td>
<td></td>
</tr>
<tr>
<td>Digester process</td>
<td>Mixed tanks: 19 500 m³ (6000 + 5500 + 4500 + 3500 m³)</td>
<td>Mixed tanks (3000 + 6000 m³)</td>
<td>UASB (700 m³)</td>
</tr>
<tr>
<td>Secondary treatment</td>
<td>Aerated lagoon (10 000 m³)</td>
<td>Thermal evaporation (evaporator 15 T/h)</td>
<td>Activated sludges (1600 m³)</td>
</tr>
<tr>
<td>Biogas production (m³/d)</td>
<td>24 000</td>
<td>12 000</td>
<td></td>
</tr>
<tr>
<td>Biogas use</td>
<td>Steam production for distillation and preconcentration of stillage</td>
<td>Steam production (30 % of distillery and treatments needs)</td>
<td>Boiler, heating effluent/digester</td>
</tr>
<tr>
<td></td>
<td>Heat water (1.2 MW) for temperature control of digester and greenhouse</td>
<td>Mixed boiler biogas/natural gas</td>
<td></td>
</tr>
</tbody>
</table>

COD = chemical oxygen demand
UASB = upflow anaerobic sludge blanket
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(Bolivar, 1983; Bories et al., 1988; Bazile and Bories, 1989, 1992). Revico (Cognac, France) has two fixed biomass digesters (PVC rings) of 6000 and 4000 m³ for white wine stillage (Table 35.11). However, because of the development of calcium tartrate recovery from pre-concentrated white wine stillage, these anaerobic filters have been converted to mixed digesters to avoid clogging by mineral precipitates of calcium salts. Revico’s anaerobic digestion plant comprises four mixed digesters (6000; 5500; 4500 and 3500 m³) at the current time and its capacity is 300 000 m³ of wine stillage/year (2000 m³/d) (Table 35.12). The biogas (800 m³/h) is used on three steam generators for lees and wine distillation and pre-concentration of stillage.

The digester of the SIS (Société Industrielle de Sucre) distillery in Guadeloupe, with a fixed biomass (PVC rings) and a volume of 1700 m³ was the first French plant to use anaerobic treatment of cane molasses stillage in 1986. A second anaerobic filter (6000 m³) was added to the plant in 2003. Several dozen similar plants have been set up in molasses distilleries in India (Proserpol). A distillery in Martinique is presently being equipped with a digester to treat cane juice stillage. The use of lignocellulosic materials as supports for micro-organisms in anaerobic filters has been considered for winery wastewater and cane stillage treatment (Bories and Moulon, 1995; Bories et al., 1997b).

Upflow anaerobic sludge blankets
Upflow anaerobic sludge blankets (UASB) are digesters where the liquid circulates from the bottom to the top and where the biomass is mobile. Due to a phenomenon of flocculation and agglomeration, the biomass is in the form of granules in the fluid state. These digesters can treat loads of up to 30 kg COD m⁻³ d⁻¹. Digesters in which everything is in circulation make it possible to prevent the sludge blanket from clogging (Fama, 2001).

Taking the moderate COD concentration (< 5.5 g/L) into account, the easy biodegradability of brewery wastewaters and the high daily volume to be treated, treatment with UASB has been extensively applied, with 265

<table>
<thead>
<tr>
<th>Table 35.12 World-wide installations of anaerobic system in the brewing industry.</th>
<th>Technology</th>
<th>Number</th>
<th>Area</th>
<th>Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lagoon</td>
<td>3</td>
<td>Africa</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Contact</td>
<td>3</td>
<td>Asia</td>
<td>137</td>
<td></td>
</tr>
<tr>
<td>Filter</td>
<td>6</td>
<td>Europe</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>Hydrid</td>
<td>5</td>
<td>America</td>
<td>142</td>
<td></td>
</tr>
<tr>
<td>UASB</td>
<td>265</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EFB</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>405</td>
<td>Total</td>
<td>405</td>
<td></td>
</tr>
</tbody>
</table>

EFB = expanded fluidised bed
UASB = upflow anaerobic sludge bed
Brewing, winemaking and distilling: overview of wastewater

plants, representing 65 % of the total of anaerobic brewery plants in operation (Table 35.12) (Totzke, 2005). This process has also been used in Brazil to treat different types of effluent, but very little stillage up until now, although the procedure is technically efficient (Cortez et al., 1999). Because of the limited flow and seasonal production of winery effluent, the development of anaerobic treatment with UASB digesters has been limited (Andreottola et al., 1998; Müller, 1998). An example of a treatment plant of mixed winery effluents and stillage with UASB digester is presented in Table 35.11.

Expanded fluidised beds

Expanded fluidised beds (EFB) are based on the microbial colonisation of media (sand, zeolith, etc.) with high specific area (size < mm), which are maintained in suspension by a high recirculating flow. EFB are well suited to the anaerobic treatment of brewery wastewater: a total of 123 digesters (30 % of the total number of anaerobic plants) was reported by Totzke (2005). UASB and EFB are high-output processes requiring a pre-acidification stage to obtain optimal acidogenesis and to permit the control of the pH in order to avoid inhibition of the methanogenic micro-organisms.

Since 1984, the number of anaerobic facilities for the treatment of brewery effluent has rapidly increased to more than 400 (Table 35.12). Reactor configurations have improved and the spin-off of these projects has led to the widespread application of anaerobic technology in other industries (Vereijken and Driessen, 2001; Totzke, 2005). Industrial anaerobic digestion plants are currently operational and their specificities are fully described in the literature (Etheridge and Leroff, 1994; Kormelinck, 2003; Nordskjold and Stippler, 2003; Muroyama et al., 2004; Li and Mulligan, 2005; Pesta and Meyer-Pittroff, 2005; Totzke, 2005).

Energy optimisation

In addition to the degradation of the organic load, biodigestion produces two utilisable fluids: methane and the effluent still loaded in salts. Methane production by anaerobic digestion results in 350 L CH4/kg degraded COD. The biogas produced has a CH4 content of 60–65 %. This gas (65 % methane) has a net heating value of 1450 kJ/m3 and can be burned to produce steam or electricity. Depending on the organic load and the nature of the stillage, methane production ranges from 7–20 m3 CH4/m3 of stillage. The higher the organic load of the stillage, the closer we get to becoming almost totally energy independent. In wine distilleries, methane production covers almost half of the energy requirements (Bories, 1982). Each year, the Revico plant produces 4000 tonnes equivalent petroleum (TEP) (Menier, 1996). Anaerobic digestion of distillery stillage therefore appears to be the primary treatment for effective depollution improving the reduction of BOD from 85 to over 95 %. According to Inamdar (1998) and Shibu et al. (1999), 70 % of distilleries in Asia apparently use biodigestion. According to Nagaraj and Kumar (2006), the post-methanisation effluent from Indian distilleries, if used carefully for
irrigation of agricultural crops, can provide 245 000 t of potassium, 12 500 t of nitrogen and 2100 t of phosphorus annually. However, technical, environmental and economic problems still arise when stillage is treated by anaerobic digestion (Cortez et al., 1999) and it requires further treatment in order for the effluent produced, particularly in the case of molasses stillage, to comply with discharge standards.

### 35.3.4 Aerobic treatment

In the cases of breweries, aerobic treatment combined with anaerobic sludge stabilisation could be considered for dilute effluents. Biological wastewater treatment in municipal sewage plants is usually an aerobic process, then the sludge surplus can be stabilised by anaerobic digestion. The carbon mass balance indicates that 100 % of organic carbon in the wastewater influent is lost: 50 % through CO2 production in the aerobic step and 50 % through biomass and sewage production. Sludge is stabilised by anaerobic digestion and generates 28–36 % of biogas (CH4, CO2) and 13–21 % of residual sludge (Pesta and Meyer-Pittroff, 2005). Only 1 % of organic carbon ends up in the effluent.

Sludge production and energy costs are the limiting factors in relation to the aerobic treatment of concentrated wastewaters, such as those produced by distilleries. The aerobic biological purification parameters of stillage from wine distilleries were studied by Bories and Maugenet (1978), who also studied the performance and cost of treatment on an industrial scale. As a result of the heavy organic load, the deficiency in nutrients, the seasonal nature and the variability of winery wastewater production, the design of aerobic wastewater treatment processes has either tended towards extensive approaches such as one- or two-stage aerated lagooning (Canler et al., 1998; Racault et al., 1998), aerated storage (Rochard et al., 1998) with different reveals of discharge, and mixed treatment with domestic waste (Badie, 1998), and activated sludge (Bolzonella et al., 2006) or towards intensive systems such as two-stage activated sludge (Racault et al., 1998), two-stage bacterial filters (Andreottola et al., 2005), or very heavy-load mono-stage pre-treatment (Ehlinger et al., 1994). The study of microbial population dynamics during treatment of synthetic winery wastewater with a rotating biological contactor illustrates the involvement of yeasts and bacteria in the biofilm and the role of yeasts in the degradation of the COD (Malandra et al., 2003) that had also been observed by Ehlinger et al. (1994) and Lefebvre (1998). Lalane et al. (1996) and Rols (1996) studied the biological treatment of rum distillery stillage by aerobic digestion, in particular with the system of aeration by hydro-ejectors. It is possible to reduce 90 % of the soluble COD and more than 95 % of the BOD in only one stage, provided that the pH of the stillage is neutralised, that it is cooled to 30 °C, and that the nutritive balance (nitrogen and phosphorus) is guaranteed, followed by a second stage to reduce the production of sludge.
The good degradability of the organic load leads to high degradation rates for the dissolved COD, and the main problem with aerobic treatment lies in the difficulties related to sludge flocculation and sedimentation. Membrane bioreactors (MBR) are capable of resolving this problem. Artiga et al. (2005) on a pilot MBR with synthetic winery wastewater (diluted white wine, COD < 4 g O₂/L) obtained a high output (97 % COD) and a low residual COD (< 100 mg O₂/L); however, the accumulation of biomass in the reactor decreased the oxygenation capacity. The combination of aerated storage and membrane filtration offers new treatment possibilities for small wineries (#3000 hL) (Racault and Stricker, 2004). For distillery wastewater with a low organic load (1 g COD/L), Zang et al. (2006), studied a calefactor (30–45 °C) aerobic MBR equipped with a stainless steel membrane (0.2 µm). The COD removal efficiency was 94.7 % with a HRT of 10–30 h and a volumetric load rate of 0.6–2.8 kg COD m⁻³ h⁻¹.

35.3.5 Pre and post-treatments

Although biological treatments are well suited to the degradation of dissolved organic load, the presence of suspended matter and complex substances such as phenolic compounds, melanoidins, etc., particularly in stillage, has led to the design of pre- or post- physicochemical treatments. Molasses stillage from the digester still has a COD of 30–40 g/L equivalent to that of products usually treated in digesters. Numerous studies deal with post-treatment, an obvious necessity.

**Coupling anaerobic digestion with an aerobic treatment**

Most of the authors referred to have studied the combination of anaerobic digestion followed by an aerobic treatment, which makes it possible to reduce the BOD to about 0.5 g/L and the COD to about 5 g/L for molasses stillage (Inamdar, 1998) or malt whisky wastewater (Uzal et al., 2003). The final effluent can then be discharged into the river (Maiorella et al., 1983). The use of a membrane reactor for this final stage of aerobic degradation could be worth exploring. However, in certain cases, the colour of the effluent is still too dark (Shibu et al., 1999).

**Degradation of the colouring and recalcitrant COD by micro-organisms**

Various laboratory studies have been conducted on the biodegradation of the recalcitrant compounds in stillage. They have shown that certain microorganisms (the fungi Deuteromycetes, Basidiomycetes, Eurotiomycetes) enable the partial elimination, under specific conditions, of these compounds from molasses stillage undergoing anaerobic and aerobic digestion, with *Coriolus* (*Trametes*) versicolor, *Aspergillus* sp (Ohmomo et al., 1985, 1987; Siriamunpiboon et al., 1988a,b; Gonzales Benito et al., 1997; Shayegan et al., 2005). García García et al. (1997) suggested carrying out the aerobic treatment with *Aspergillus terreus* or *Geotrichum candidum* before the
anaerobic treatment, in order to reduce the phenol concentration from 60 to 70 %. Research on the selection of strains capable of destroying these pigments continues (Fitz-Gibbon et al., 1998; Nakajima-Kambe et al., 1999; Patil et al., 2001) as well as studies aimed at understanding the degradation mechanism (Miyata et al., 1998). The aerobic degradation of beet molasses stillage with Penicillium sp strains and Aspergillus niger, before anaerobic digestion, resulted in a degree of higher COD removal and increased the decolourisation of the wastewater (Jiménez et al., 2003). Finally, Shibu et al. (1999) showed that the bacteria Lactobacillus casei reduces the colouring by 54–57 % and results in a simultaneous production of lactic acid in batch fermentation over five days at a rate of 113 mg/L of lactic acid with immobilised cells. Lactic acid has a market in India, since 70 % is imported from other countries such as Japan.

This research shows the microbiological perspectives of biodegrading recalcitrant forms of COD in stillage, but implementing these cultures on an industrial scale still seems a long way off for treating molasses stillage. Contrary to the majority of studies on the degradation of colours with aerobic cultures, Mohana et al. (2007) isolated a bacterial consortium from soil that contains Pseudomonas aeruginosa PAO1, Stenotrophomonas maltophilia and Proteus mirabilis, and that is able to decolourise anaerobically-treated spent distillery wash under static conditions. The colouring matter and the recalcitrant COD are less of a problem in the case of wine stillage than in molasses stillage. However, the polyphenolic compounds from grape (anthocyanins, tannins) contribute to the final colouring and the residual COD of the treated effluent. The bioremediation of winery waste by means of white-rot fungi has recently been reported (Strong et al., 2006).

Decolouration by ozonation and/or oxidative treatment

Dhamankar et al. (1993) studied ozonation and showed that it is more effective when sodium hydroxide is added to modify the pH (decolourising of 26 %, 68 % and 92 % at a pH of 4.3, 7 and 10, respectively) in the presence of 1.2 % H₂O₂. Gehring et al. (1997) studied different modes of ozonation (alone or combined with γ rays). Beltrán et al. (1999) also showed that ozonation of wine stillage improves its biodegradability and makes its subsequent decolouration more complete. However, degradation levels are highly dependent on the pH of the wastewater because pH affects the double action of ozone on the organic matter, that may be a direct or an indirect (free radical) oxidation pathway (Beltrán et al., 2001). The degradation of phenolic compounds is not necessarily complete, but it contributes to the bleaching of the effluents and improves the biodegradability of the degradation products (Bijan and Mosheni, 2005). The inclusion of an ozonation step prior to treatment in an anaerobic sequencing batch reactor was found to be useful for the treatment of cherry stillage, since more than 75 % of the polyphenols could be removed by ozone and an improvement in the parameters of the anaerobic treatment (COD removal rate, higher organic load rate (OLR),
higher biomethanation and good stability) was observed (Álvarez et al., 2005). The pre-treatment of molasses stillage by ozone combined with UV light and titanium oxide increased the yield coefficient and the mean specific rate of the anaerobic digestion by 25% (Martín et al., 2002).

Decolouration by treatment on activated coal or nanofiltration
Serikawa et al. (1993) showed that it is possible to remove the colour from dilute stillage (from 1 to 0.1% weight) on activated coal, but the procedure is long and nothing was mentioned about the cost of regenerating the coal. Cartier et al. (1997) showed that the colorants in the brine used to regenerate the decolourising resins of syrup are effectively retained by nanofiltration (NF), whereas the saline fraction passes into the permeate. We can therefore hope that the colouring of stillage before or after anaerobic digestion will also be retained, especially since Jaouen et al. (2000) succeeded with pen inks.

Physicochemical treatments
The clarification of lees stillage can be achieved, for example, with centrifugation upstream of the heat concentration step or by flocculation/flotation upstream of anaerobic digestion. Sales et al. (1986) studied the precipitation of acids with sodium hydroxide or lime coupled with separation by centrifugation. The treatment is valid on lees stillage where the deposit contains more than 80% of the COD. Similarly, Pandiyan et al. (1999) studied the addition of ferrous sulphate (FeSO₄·7H₂O) and ferric chloride (FeCl₃·6H₂O) in stillage in order to precipitate propionic acid. According to Lalov et al. (2000), anaerobic digestion is apparently not well suited to solutions that are not particularly concentrated, such as wine stillage, for example. They therefore studied the concentration of organic matter by retention on biodegradable anionic exchangers made of chitosan and its biodigestion with or without prior hydrolysis, after saturation with organic acids. Photocatalytic oxidation with Fenton’s reagent (mixture of H₂O₂ and Fe²⁺) has recently been studied for winery wastewater pre-treatment and total organic carbon (TOC) removal reached 50% (Mosteo et al., 2006a,b). Experiments on the laboratory scale were carried out to reduce colour and COD in distillery wastewater using electro-oxidation processes (anode made from a titanium sponge, pH = 1; additives: H₂O₂ and NaCl) with stillage diluted 10-fold (Piya-areetham et al., 2006). It was shown that approximately 92, 89, 83, 38 and 67% of colour, COD, BOD, total dissolved solids (TDS) and total solids (TS), respectively, were removed, with an energy consumption of 24–28 kWh/m³.

Coupling anaerobic digestion with thermal evaporation
Despite the perspectives shown by secondary biological or chemical treatments, the high organic matter content and the poor biodegradability of the stillage from anaerobic digestion do not make it possible in all cases to reach the
recommended level for discharge into a river. Coupling the anaerobic digestion of stillage with a secondary treatment by thermal evaporation of digested stillage provides an interesting solution to this problem. The SIS distillery in Guadeloupe initiated treatment by thermal evaporation of cane molasses stillage produced by anaerobic digestion in 2004. The condensate resulting from the evaporation presents a very high level of purification in terms of COD, colour, mineral content and suspended matter. The concentrate from digested stillage can be highly concentrated because of its low organic load, and is used for agronomic purposes (spreading, composting). The thermal concentration of effluent from anaerobic digestion of wine stillage has been recently achieved at the UCVA distillery (Coutras, France) for secondary treatment in order to obtain high-quality final wastewater for discharge into a river. The condensate from the evaporator (15 t/h, multiple effects) that treats digested stillage (pomace, wine, lees) has a low COD (< 300 mg/L) and is colourless, demineralised and has no suspended matter or microorganisms. The energy for the thermal evaporation is provided by steam generators using biogas produced at the anaerobic stage.

35.3.6 Incineration

In the brewing process, spent grain is a by-product (0.18–0.20 kg/L beer) with a high water content (70–80 % w/w). The constraints involved in using it as ruminant cattle feed or landfill material were described on pp. 000–000. Brau Union Autria and Lueben university (Kepplinger and Zanker, 2001) developed a process associating the combination of mechanical pre-drying and combustion in a biomass vessel. The wet spent grains (20–30 % w/w DM) are stored in a butter vessel to compensate for fluctuating production and then press-filtered up to 42 % w/w DM. The dried matter is stable and can be stored in a tank before combustion in a biomass vessel. The wastewater could be processed by anaerobic treatment. In the process proposed by Heineken Technical Service and 2B Biorefineries (Bruijn et al., 2001; Schwencke, 2006), the fibres extracted from spent grain could be sent to a furnace, where the heat of combustion from the fibre product is used to generate steam. In both processes, the heat of combustion of the spent grains is similar to that of lignite coal or dry wood, i.e. approximately 21 MJ/kg. The exact heat of combustion depends on the water content because of the relatively high vaporisation energy of water: \( H = 21000 \cdot (1 – w) – 2250 \cdot w \). Above 40 % w/w DM, the combustion properties improve considerably. Combustion also produces ash, which is another valuable product. Its high phosphorus pentoxide (P\(_2\)O\(_5\)) content is of great value as a fertiliser additive and can be added to standard NPK-fertilisers. Wet cleaning of the flue gas is normally not necessary, the discharge of exhaust gases (NO\(_x\), SO\(_2\), CO\(_2\)) that are emitted from the combustion of spent grains or fibres is below the standards set by the European governments.

In alcohol production, the incineration of stillage can be an attractive
means of recovering mineral matter and energy with the total combustion of
organic matter, and it seems to be common practice in India (Inamdar, 1998;
Nagaraj and Kumar, 2006). In this process, the raw spent distillery wash is
first neutralised with lime and filtered. This is further concentrated to 60 %
solids in multiple-effect with forced circulation evaporators. Then this thick
liquor is burnt in an incinerator and converted to ash. The heat of combustion
of the liquor is 8600 kJ/kg solids (Maiorella et al., 1983; Nagaraj and Kumar,
2006) and a positive return in energy can be obtained. The resulting ash is
found to contain about 37 % potash (K₂O) and 2–3 % phosphate (P₂O₅), and
their reuse makes it possible to balance the economic viability of the process.
However, special boilers are necessary, firstly to recover the ash and secondly
to limit the temperature to below that of potassium sulphate fusion which is
only about 700 °C. Because of increasingly strict air pollution guidelines,
incineration has to be considered carefully for any new proposal, which
should include an electrostatic precipitator system. In Australia, direct
combustion of cane stillage was carried out for several months but was
finally abandoned (Nguyen, 2003).

35.4 Alternative treatments and re-engineering
processes with the best available techniques
(BAT) approach: industrial reality and
alternative treatments

Implementing environmental management systems in the brewing, winemaking
and distilling industries requires the efficient and effective integration of
risks and opportunities. The Integrated Pollution Prevention and Control
directive 96/61/EC (EC, 1996) is a key stage in environmental legislation
and defines BAT selection. The word ‘available’ in this context means available
under circumstances which are both economically and technically viable,
and ‘techniques’ means not only the technology but also its operation on the
ground. Any BAT candidate judged to be positive in terms of environmental
benefits must then be studied with respect to its effects on product quality,
food, land occupation and industrial safety. Its economic impact needs to be
assessed and this depends on existing or new plants and their size.

The environmental impact is analysed on different geographical scales
(global, regional, local) and can be divided into three groups: availability of
(resources water, fossil fuels, raw materials, chemicals), nuisance factors
(emission of noise, odour, and dust) and toxic effects (health considerations).
Alternative treatments and re-engineering processes and techniques (Table
35.13) are proposed for the brewing, winemaking and distilling industries.
However, a wide heterogeneity in development levels is noticeable from
laboratory scale up to industrial application. ‘Real issues’ or differences
between industrial reality and scientific/academic approaches must be identified
### Table 35.13 Alternative treatments and re-engineering processes with the BAT approach – synthesis of biological and technological pathways to minimize effluent and water consumption (A–L: academic work on the laboratory scale; A–PP: academic work on the pilot-plant scale; I–ND: industrial application – new development; I–CP: industrial application – current process)

<table>
<thead>
<tr>
<th></th>
<th>Brewing industry</th>
<th>Wine industry</th>
<th>Distilling industry</th>
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<tbody>
<tr>
<td></td>
<td>Spent grain (mash)</td>
<td>Yeast surplus (tank bottoms)</td>
<td>Kieselguhr sludge</td>
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<td><strong>Treatment of effluent:</strong></td>
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<tr>
<td>alcohol/sugar</td>
<td>A–PP</td>
<td>A–PP</td>
<td>A–PP</td>
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<td><strong>Specific molecule</strong></td>
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<td>extraction:</td>
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<tr>
<td>Glycerol, betaine, organic acids</td>
<td>A–L</td>
<td>A–L</td>
<td></td>
</tr>
<tr>
<td>Tartaric acid</td>
<td>A–L / A–PP</td>
<td>I–CP</td>
<td></td>
</tr>
<tr>
<td>Colouring and phenolic compounds</td>
<td>A–L</td>
<td>A–L/I–ND</td>
<td></td>
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<tr>
<td><em>Heavy metals</em></td>
<td>A–L</td>
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<tr>
<td><strong>Bioproduction of molecules</strong></td>
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<td>Yeast, enzyme, fungi, algae</td>
<td>A–L</td>
<td>A–L</td>
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<tr>
<td>Organic acids</td>
<td>A–L</td>
<td>A–L</td>
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<tr>
<td>Complex organic compounds</td>
<td>A–L</td>
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<tr>
<td><em>Regenerable filter-aids</em></td>
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<td>Membrane process:</td>
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<td></td>
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<tr>
<td>ED: Salt extraction</td>
<td>A–L / A–PP</td>
<td>A–PP</td>
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<tr>
<td>Of: Water condensate re-use</td>
<td>A–PP</td>
<td>A–PP</td>
<td></td>
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<tr>
<td>UF/MF: Loss reduction</td>
<td>A–L</td>
<td>I–CP</td>
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<tr>
<td>UF/MF: Technical alternative</td>
<td>A–L</td>
<td>I–CP</td>
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<td>ED =</td>
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<td>Of =</td>
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<td>mF = micro filtration</td>
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<td>UF = ultra filtration</td>
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**Notes:**
-ED = EDI = OI =
-mF = micro filtration
-UF = ultra filtration
35.4.1 Industrial reality

Treatment of effluents containing alcohol and sugars

The presence of ethanol as the major component of effluent generated by the alcoholic beverage industry (wine, etc.), and of sugars in the case of canneries for fruit and sweetened beverages (fruit juice and syrup) underscored the specificity of their composition and made it possible to find treatments adapted to their specific makeup (Bories et al., 1998; Bories, 2000). In the case of winery effluents, distillation of the effluent alone is an effective treatment (elimination of COD: # 85 %), making it possible to discharge the dealcoholised effluent into the wastewater system and to recover the ethanol (Colin et al., 2005). The combination of distillation and concentration of the dealcoholised effluent ensures a highly effective and complete treatment with production of: (i) purified evaporation condensate (COD < 300 mg/L, demineralised, bleached, germ-free) that can be reused as industrial water or discharged directly into the receiving environment; (ii) ethanol (energy recovery); and (iii) a concentrated co-product (> 5 % of the initial volume of effluent) that can be spread, composted or used in distilleries (recovery of tartaric acid) (Bories et al., 1998, 1999; Colin et al., 2005).

For effluents containing sugars (glucose, fructose, sucrose, maltose), the transformation of sugars into alcohol must be done beforehand. Alcoholic fermentation can be initiated at the level of effluent storage by yeast inoculation (S. cerevisiae). Thanks to the use of mechanical steam compression, energy consumption for concentration and distillation is reduced (15–20 kWh/m³). For effluents with a heavy organic load (COD > 20 g/L), it is competitive with that of biological treatment processes. This process, operational at maximal load as soon as it is started up and insensitive to variations in the pollution load, is the solution to the problem of seasonal activities. The absence of wastewater sludge is another important advantage of this physical fractionation technique applied to effluents.

Extraction of specific molecules or compounds

Separation of glycerol, betaine and organic acids

Stillage contains large quantities of glycerol, betaine in the case of beet stillage and organic acids. The glycerol is commonly used in industry as a solvent, emollient and antifreeze. The betaine is used in the pharmaceutical industry as a complement to other compounds against muscular deficiencies and weakness, as a complement in animal feed (enables water retention in the muscle tissues) and in crop protection. Glycerol can be separated by precipitation with lime (CaO) or by ethanol treatment. Cheryan and Parekh (1995) have studied the separation of glycerol from the organic acids of molasses stillage by electrodialysis after a prefiltration on a 0.2 µm ceramic
membrane. However, it is chromatography techniques which have been
developed on the industrial scale, particularly with regard to molasses.
Numerous authors have published on the subject with patents pending (Kampen,
1990; Kampen and Saska, 1999a, b) for the University of Louisiana. Most of
the patents involve stillage concentration phases, potassium removal by
crystallisation, clarification and one or several chromatography techniques
depending on the number of compounds to separate.

Extraction of tartaric acid
Tartaric acid is present in all wine distillery effluents (Mourgues et al., 1996)
and represents from 4–30 % of the pollutant load. Extracting tartaric acid
from lees stillage by precipitation in the form of calcium tartrate salt is a
widespread practice in wine distilleries (Mourgues and Maugenet, 1975;
Mourgues et al., 1993). Moreover, the recovery of tartaric acid is essential
before concentrating stillage. To precipitate tartaric calcium salt, the stillage
is first made neutral with calcium carbonate milk or quick lime to pH 4.5–
5, then calcium sulphate (CaSO4) is added to have a full precipitation and to
avoid the potassium tartrate (K2C4H4O6) formed during the neutralisation
process from remaining in solution. There are two main types of procedure,
which have been described by Mourgués (1986). Distilleries recover 4–6 kg
of tartaric calcium salt per hL of lees received. The products obtained contain
48–53 % of tartaric acid. Particular attention must be paid to the impact of
tartaric acid extraction on subsequent treatments, in particular biodigestion
where the sulphate can indirectly inhibit fermentation. It is therefore preferable
to reduce the tartaric acid extraction rate but to avoid adding sulphate ions if
biodigestion takes place. However, in order to maintain optimal recovery of
tartaric calcium salt and to prevent the formation of soluble tartaric potassium
salt, the sulphate (a mixture of lime and calcium sulphate) is replaced by
nitrate (lime and nitric acid). Moreover, this process change is advantageous
for the treatment of lees stillage by natural evaporation, since nitrate reduces
the production of odorous compounds (Bories, 2006). Other procedures for
extracting tartaric acid have been studied, as explained below.

Liquid–liquid extraction has been envisaged in the laboratory using wine
effluent and synthetic solutions of tartaric, malic or lactic acids with the
solvents tributyl-phosphate-n-dodecane and triisocyclamine-octanol-1
(Smagge, 1991; Malmary et al., 1994; Marinova et al., 2004). It has the
advantage of eliminating the intermediate precipitation in the form of tartaric
calcium salt.

Extraction of colouring anthocyanic matter and
phenolic compounds
Mourgues et al. (1996) mentioned the separation of colouring matter from
grape pomace before distillation, either by extraction by diffusion in the
presence of SO2 or by adsorbing resins. The industrial production of
concentrated anthocyanic extracts (E163) has rapidly expanded these past
Brewing, winemaking and distilling: overview of wastewater

years in wine distilleries (Salgues, 1980; Usseglio-Tomasset, 1980). The production of antioxidant extracts with nutraceutical properties constitutes a new way of using wine by-products (Shrikhande 2000; Tobar et al., 2004).

**Loss reduction with ultra and microfiltration**

In breweries, loss reduction concerns mainly beer recovery from tank bottoms (fermentation and maturation vessels). The membrane-separated permeate can be recycled in the wort or in the maturation vessels (Reed, 1989; Nielsen, 1989) for fermentation tank bottoms. The beer recovered from the maturation tank bottom may be returned into the maturation vessel or sent for final clarification. However, the different compositions of the tank bottom beer may prevent a direct dilution into the rough beer before filtration (Cantrell et al., 1985; Le, 1987; O’Reilly et al., 1987). Tank bottom concentrates may be sold as livestock feed.

Two fundamental differences exist among tank bottoms: (i) the fermentation vessels have high yeast cell content and high viscosity; (ii) the maturation vessels have high protein and polyphenol content, and fewer yeast cells and are characterised by low viscosity (close to that of beer). In order to recover ‘green beer’ and ‘rough beer’ from tank bottoms, natural sedimentation, centrifugation and a filter-press may be used. However, centrifugation is expensive and may damage the permeate quality because of yeast cell degradation. Filter-presses provide a relatively low-moisture solid discharge and consequently high extract recovery. However, sufficient clarification of the filtrate is not obtained. The use of micro filtration (MF) is designed to produce: a permeate of acceptable quality with respect to both flavour and haze (defined by the European Brewery Convention norm, Analytica EBC, 1987), with minimal loss of original gravity, colour and bitterness while processing a retentate of between 2 and 4 % dry weight to a minimum of 20 %; to operate at low temperatures (close to 0°C); to achieve economically sound flux and hygienic beer recovery. The presence of cloudiness or haze in beer is one of the more obvious quality defects discernible to the consumer. Several substances can cause haze in beer, but the most frequently encountered problem is due to a cross-linking of polyphenol (tannin) and protein.

Almost all the membranes installed in breweries around the world are dedicated to the recovery of beer from fermentation and maturation tank bottoms. These membrane applications have almost become industrial standards. The biggest challenge today is more a problem of commercialisation than a food-engineering problem. Since 1994 numerous industrial applications (Methner et al., 2004; Fillaulteau et al., 2006) have been reported in addition to scientific papers. Micro filtration enables a 20–30 % w/w concentration to be reached, and several industrial units already use it. More than 50–60 % of the yeast sediment is recovered as a high-quality beer (equivalent to a volume reduction ratio of between 2 and 3). Membrane filtration becomes competitive in comparison to the filter-press for waste reduction. The recovered permeate, recycled in the brewing process at a rate of 2–5 %, allows beer loss and costs
to be reduced. Various systems are in use and it has been shown that ceramic (0.4–0.8 µm, Schlenker, 1998) or polysulfone (0.6 µm, Wenten et al., 1994) membranes concentrate solids from 12–15 % to 20–22 %. The payback is less than two years regarding the recovery of sterile beer from yeast beer with 0.4–0.8 µm pore diameter multichannel ceramic membranes installed in 1 MHL capacity breweries. Bock and Oechsle (1999) explained that brewing plants are running with ceramic membranes made of α-aluminium oxide (multichannel membrane: 19 channels, length: 1020 mm, mean pore diameter: 0.80 µm). Surplus yeast can be processed with about 17–20 L h⁻¹ m⁻², up to a concentration of 20 % w/w (transmembrane pressure up to 3 bar) and three process options exist: batch, semi-batch and continuous. This material can be cleaned in place since it is resistant to caustic, acid and oxidising sterilants even at high temperature (above 90° C).

Snyder and Haughney (1999) and Methner et al. (2004) described a new system called VMF (vibrating membrane filtration) produced by PallSep™ (Pall Corporation, USA). The system differs from traditional cross-flow filtration systems in that the shear at the membrane surface is generated mechanically by vibrational energy and not from high cross-flow rates. VMF enables uncoupling of pressure differential from cross-flow velocity, with a reduced installed pump capacity, a minimum energy input, reduced mechanical and thermal stressing of yeast cells and a compact design of filter module operating without backwashing. The system operates with a transmembrane pressure (TMP) of 500–800 mbar, with 0.45 µm polytetrafluoroethylene (PTFE) membranes, under an oscillation of around 50 Hz and amplitude of 20 mm at the outer rim (diameter 800 mm). Recovery of beer from surplus yeast can achieve an average flux of 18–22 L h⁻¹ m⁻² with an industrial module of 40 m² (energy input: 6 Wh/L) with solids concentration of 10.5–18 % w/w.

Process modification with ultra and microfiltration
In breweries, MF can be utilised as a technological alternative in three applications: mash separation, clarification of rough beer, cold-sterilisation of clarified beer before conditioning. Scientific studies and industrial applications essentially concern the clarification of rough beer and sterile filtration of clarified beer. Modrok et al. (2006) reported that the filtration technologies in breweries use diatomaceous earth (91 %), trap filters (68 %), sheet and fine filters to reduce the level of micro-organisms (32 %) and sterile filtration with membranes (8 %).

Cold-sterilisation of clarified beer
The clarification of rough beer is usually followed by heat treatment so as to ensure its microbiological stability and conservation. Currently, heat treatment is mainly performed by flash pasteurisation (72–74 °C during 15–30 s with a plate heat exchanger or at 60 °C in a tunnel pasteuriser) before conditioning. Conventional heat treatment requires water loops to heat and cool the product and also induces additional water and energy consumption.
Sterile filtration appears interesting and eliminates the organoleptic problems caused by heat processing (Gaub, 1993; Leeder, 1993). Micro filtration will have to face several challenges: to produce a microbe-free beer without a negative change in beer quality, whilst operating at low temperatures (close to 0 °C); to ensure beer stability (biological, colloidal, colour, aroma and flavour, foam stability); to achieve economic flux. Provided it fulfils these considerations, MF can be a truly operational alternative to pasteurisation and dead-end filtration with cartridges. Cold-sterile filtered beer (draught beer or bottled beer) corresponds to a strong demand from consumers for quality and natural products. The objective of eliminating heat treatment of the finished product is achieved with membrane cartridge systems (dead-end filtration) installed directly upstream of the filling system. However, cold-sterilisation by cross-flow membrane is under trial and is feasible in an industrial context (Fillaudeau and Carrère, 2002; Scanlon, 2004). Krottenthaler et al. (2003) reported that the technical developments of membrane filtration (membrane lifetime, running time, cleaning procedure, cost reduction) as well as market indicate constant improvement. Organic membrane filtration (0.45 µm nylon or 0.55 µm polyvinylidene fluoride, PVDF) offers safe and careful product stabilisation for the brewing industry. Financially MF is becoming increasingly attractive; for instance the cost of flash pasteurisation is assumed to be 0.20 €/hl whereas membrane filtration is around 0.26 €/hl of clarified beer.

Clarification of rough beer

Beer clarification is probably one of the most important operations, when rough beer is filtered in order to eliminate yeast and colloidal particles responsible for haze. In addition, this operation should also ensure the biological stability of the beer. It should comply with the haze specification of a lager beer in order to produce a clear bright beer. Standard filtration consists of the retention of solid particles (yeast cells, macrocolloids, suspended matter) during dead-end filtration with filter-aids. The variety of compounds (chemical diversity, large size range) to be retained makes this operation one of the most difficult to control. However, membrane processes should satisfy the same economic and qualitative criteria (O’Reilly et al., 1987; Wackerbauer and Evers, 1993) as conventional dead-end filtration. Micro filtration should be able: to produce a clear and bright beer with similar quality to a Kieselguhr filtered beer; to perform separation in a single-step without additives; to operate at low temperature (0 °C); to achieve economic flux.

Among the potential applications of cross-flow microfiltration, the clarification of rough beer represents a large potential market (approximately 200 000 m² surface area of membrane). Industrial experiments, however, encountered two main problems: (i) the control of fouling mechanisms and (ii) the enhancement of permeate quality (Fig. 35.3). Micro filtration suffers from a low permeate flux in comparison to the conventional dead-end filtration with filter-aids such as diatomaceous earth (usual flux ranges from 100–
500 L h⁻¹ m⁻²). Since 1995, a lot of reports have mentioned the economic and scientific stakes of the clarification of rough beer. Recent scientific and industrial studies (e.g. Fillaudau et al., 2007) have dealt with (i) fouling mechanisms, (ii) the relationship between quantitative and qualitative performance, (iii) the development of alternative membrane filtration such as membrane structure and dynamic filtration and (iv) industrial applications.

Since 2000, the first industrial plants have started to run with three membrane systems proposed by Norit Membrane Technology/Heineken Technical Service (Schuurman et al., 2005a,b), Alfa-Laval AB/Sartorius AG (Modrok et al., 2004, 2006), and Pall Food & Beverage/Westfalia Food Tech (Denniger and Gaub, 2004; Höflinger and Graf, 2006; Rasmussen et al., 2006). Norit/Heineken (Schuurman et al., 2005a,b) reported several industrial processes running with a MF unit for rough beer clarification with a capacity above 10 000 L/h. The filtration unit contains between 10 and 24 hollow fibre modules X-Flow R-100 (pore size: max 0.50 µm, length: 1 m, inner diameter: 1.5 mm, filter area: 9.3 m², material: polyethersulfone, PES). The key to the process is based on a specific cleaning procedure patented by Heineken and Norit Membrane Technology. It combines a caustic step, an acidic step and a strong oxidative step (two hours in duration), which is successful in achieving a run time between seven and 20 hours for about 120 runs. Filtration is accomplished at 0°C, 1.5–2 m/s flow velocity and up to 1.6 bar transmembrane pressure. During filtration, 10 minute periods of back-flushing are applied every two hours to remove the reversible fouling that has built up. The flux is maintained at 100 L h⁻¹ m⁻² and clarified beer fulfils the European Brewery Convention (EBC) standard in terms of turbidity (close to 0.6 EBC units), bitterness, total extract, colour, and protein content. In 2005, the cost of membrane filtration for bright beer was estimated to be between 0.20 and 0.40 €/hL, i.e. identical to Kieselguhr filtration 0.20–0.40 €/hL. By 2007, the total cost of membrane filtration is expected to be 20–30 % cheaper than Kieselguhr filtration (Schuurman et al., 2003).

In the Alfa-Laval/Sartorius cross-flow filtration process (Modrok et al., 2004, 2006), the rough beer goes from the maturation tank to a high-performance centrifuge, which is directly followed by the cross-flow system. From there the beer goes to a bright beer tank and then on to sterile cartridge filtration before conditioning. The filtration unit contains up to six holding devices with up to 72 filter Sartocon® cassetes (20 membranes, dimension: 175 × 210 mm, small channel spacers: 120 µm, filter area: 0.7 m², material: PES). Filtration steps are accomplished with a combination of normal filtration, feed reverse to loosen the clogging and back-flushing with the product. An intermediate cleaning (duration: 15 min) is done every three to five hours and maintains high and constant flux rates (80–120 L m⁻² h⁻¹). The costs are estimated at 0.46 €/hL and can roughly be divided into 22 % for the running costs, 48 % for the membranes, and 30 % for the system.

PROFi® technology is a joint project of Westfalia Food Tec and Pall Food & Beverage (Denniger and Gaub, 2004; Höflinger and Graf, 2006; Rasmussen...
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et al., 2006) and is based on a combination of a centrifuge and a hollow fibre membrane filter system. The centrifuge separates most of the coarse solids like yeast and colloids with a high dry substance from the beer; the membrane system afterwards separates the remaining yeast and fine-forming colloids effectively. The membrane system is a patented polyethersulfone hollow fibre cross-flow system operating in a dead-end mode. No retentate tank or recirculation line is necessary, which makes the system design and control simple. The industrial system is designed to reach a constant flux of 36–48 000 L/h and consists of five independent and identical blocks operating in a sequential mode (three to four blocks in filtration mode, one or two blocks in cleaning and standby mode). Operating runs last between five and ten hours, if one block has reached the maximum pressure difference of 2 bar, it is emptied and cleaned. Beer losses for the complete line are at 0.02 % extract; the water consumption is surprisingly low with 0.043 L/L beer and energy consumption less than 0.40 kWh/L.

35.4.2 Alternative treatments including scientific and academic approaches

Regenerable filter-aids

In breweries, reduction of Kieselguhr consumption may be achieved by optimising the existing process in different ways (Freeman and Reed, 1999): selection and characteristic of filter-aids, pre-coating and multistage-filtration, automation of filtration system and filter-aid dosage, increasing filtration capacities, saving water for cleaning and regeneration by chemical and thermal treatment. However, the use of regenerated Kieselguhr appears to be of limited occurrence in industrial practice. The opportunity to carry out the filtration with alternative and regenerable filter-aids seems very attractive. The filter-aid should satisfy food process requirements, resist caustic solutions and temperatures up to 100 °C (conventional regenerative conditions), exhibit specific mechanical properties (inert and rigid material), present a low specific surface area but a high retention capacity (clarification) together with a high filtration efficiency. Regeneration of the spent filter medium should not modify its initial performances. Recent results have been reported at a pilot-plant scale but none in industrial conditions. Below, we describe the filter-aids used by Bonachelli et al. (1999) and Rahier and Hermia (2001).

The regenerable filter-aid developed by Interbrew and UCL (Université Catholique de Louvain, Belgium) is composed of polymer granules (Rahier and Hermia, 2001) with specific properties (density, particle size, pore size, diameter, shape and specific surface). The material, in combination with poly vinyl poly pyrrolid one (PVPP), was used successfully for the clarification and stabilisation of beer. The advantages reported for this material are a single clarification–stabilisation step with high specific flow rate and long run times.

Meura company (Bonachelli et al., 1999) developed a filter-aid composed
of a mixture of synthetic polymer or special cellulose fibres and 44–88 µm microbeads coated with a polymer which improves surface properties. The mixture combines the mechanical properties of the microbeads (incompressibility, low porosity) with the qualities of the fibres. Filtration performance is reported to be similar to conventional Kieselguhr filters.

Bioproduction of added-value molecules

Industrial and agricultural by-products and waste can often be used as substrates in fermentation processes. Their complex composition, containing carbon, nitrogen and mineral supplies, is accurate for the growth of micro-organisms. The aim of the bioprocess may be the production of biomass, or its metabolic products (i.e. organic acids), flavour and aroma compounds or enzymes. The carbon components of stillage can be considered as substrates for the production of molecules of interest to industry via biotechnological pathways. Tibelius and Trenholm (1996) have published a whole report on recycling the co-products from cereal fermentation and Decloux and Bories (2001) a literature survey on uses for stillage from molasses fermentation. They mentioned several examples of bioproduction of added value molecules that may be grouped in three categories

Yeast, enzymes and algae

The production of yeast in aerated medium is an efficient means for reducing the pollutant load of stillage originating from alcohol production either from cane or beet. This technique, developed on an industrial scale, however, consumes a lot of energy to ensure the oxygen supply and the cooling of the fermenter. It is possible to produce 16 kg of Torula yeast (Candida utilis) per tonne of stillage and to consume non-fermentable sugars, hence increasing the ratio which can be recycled to fermentation and, similarly, to decrease the quantity of water to be evaporated during concentration. The residual BOD is reduced to 10–15 g/kg (Maiorella et al., 1983). According to Lee and Lee (1996), Candida utilis yeasts, generally used for producing SCP (single cell proteins) are not very well adapted to stillage. After screening tests, they selected a thermoresistant strain Candida rugosa. Shojaosadati et al. (1999) studied the culture of the Hansenula yeast strain in continuous culture on beet stillage and showed that it is possible to reduce the COD by 31% and to produce 3–5 g/L of biomass with a protein content of 39.6% without any addition to the culture medium. Other compounds such as glycerol, acetic acid and the rest of the ethanol can also be consumed (Maiorella et al., 1983).

The production of enzymes is also under study. In breweries, Zvauya and Zvidzai (1996) found that an aerobic and spore forming Bacillus sp. produces hydrolytic extracellular enzymes when cultured on opaque brewery wastewater supplemented with defatted soya, spent yeast and malt flour. The strain produced endo-1-4-α-glucanase, amylase, polygalacturonase, xylanase and protease. Hatvani and Mecs (2001) investigated the mycelial growth (biomass
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Production) and the extracellular production of *Lentinus edodes* on the malt-containing by-product of the brewing process. They demonstrated that this substrate is a suitable medium for mycelial growth. Laccase and manganese peroxidase purified from the cultures of *L. edodes* can be immobilised and employed in enzyme bioreactors for the non-specific oxidation of organopollutants (e.g. phenolics). Couto *et al.* (2004) demonstrated the potential of barley bran as a support for laccase production by the well-known laccase producer *Trametes versicolor* under solid state condition. In the wine industry, enzymes (amylases) or fungi (*Penicillium natatum*) can be developed to increase the level of vitamin B (Maiorella *et al.* 1983). Tests for producing fungi on stillage have apparently been carried out at the laboratory stage in Brazil (Cortez *et al.*, 1998).

The culture of filamentous fungi has been studied in wine distillery stillage (white wines) in the mid 1970s and an industrial unit was created following this research (Biovina/Remy Martin, Cognac), but it only operated for a short period. The culture of green algae in Turkey has been tested to produce pigments from a medium enriched in molasses stillage (Kadioglu and Algur, 1992).

**Organic acids**

Commercial utilisation of natural ferulic acid has been limited by its availability and cost. It can be used as a preservative due to its ability to inhibit peroxidation of fatty acids, and constitutes the active ingredient in many skin lotions and sunscreens. Faulds *et al.* (1997) isolated and purified a number of novel microbial esterases, which can cleave ferulic acid from sugar residues in agro-industrial waste. They showed that after treatment of wheat bran with a *Trichoderma fungus*, followed by treatment of the dissolved material with *Aspergillus niger* FAE-III, ferulic acid can be obtained. L-lactic acid production from brewery spent grain with immobilised lactic acid bacteria, *Lactobacillus rhamnosus*, was investigated by Shindo and Tachibana (2004). Spent grains were liquefied by a steam explosion treatment (30 kg/cm², 1 min) to obtain liquefied sugar (60 g/kg wet spent grain) and treated with glucoamylase, cellulase and hemicellulase enzymes before bioreaction.

In propionibacteria (*Propionibacterium acidipropionici*), the fermentative pathway of glycerol leads to the production of propionic acid in very advantageous conditions with regard to the results obtained from glucidic substrates: increase in yield and propionic acid concentration (Barbirato *et al.*, 1997; Bories *et al.*, 1997a 2001; Himmi *et al.*, 2000). Volatile fatty acids (acetic, propionic, butyric acids) can be produced by acidogenic fermentation in distillery stillage recycling (Goma *et al.*, 1980).

**Complex organic compounds**

Dihydroacetone (DHA) is used in cosmetics. It can be produced with *Gluconobacter oxydans* from distillery wastewater (pre-concentrated) with a yield of 0.78 g DHA/g glycerol, a productivity of 0.96 L⁻¹ h⁻¹ and a DHA
concentration from 34–45 g/L (Bories et al., 1991; Bories and Claret, 1992; Claret, 1992; Claret et al., 1993).

The precursor 1,3-propanediol is interesting for polymer synthesis. Its production by fermentation of glycerol by anaerobic bacteria (Clostridium butyricum and Enterobacter agglomerans) has been examined using wine distillery stillage (Bories and Claret, 1992; Barbirato et al., 1998).

The Revico company has applied for a patent to produce aromatic compounds (Ambid et al., 1998; de Billerbeck et al., 1999). It involves aerobic cultivation of a Sporobolomyces odoratus type bacterium capable of producing γ-decalactone. The medium is constituted of wine stillage supplemented with a ricinoleic-type precursor. The aromatic compound is separated from the aqueous fermentation medium by adding a coconut oil type lipid phase which is solid at room temperature and which absorbs the aroma. After separation, the lipid phase is dissolved in 96% ethanol (1v/10v) then separated out by crystallisation on cooling the alcohol mixture to −20 °C. Simple filtration then makes it possible to recover the alcohol phase containing the aromatic compound.

Carotenoids, in particular astaxanthin, can be produced by fermentation of the yeast Phaffia rhodozyma on different residues of the wheat industry (Hayman et al., 1995). Certain co-products such as soluble stillage can be interesting media. Cell growth and polysaccharide production by a local strain of Ganoderma lucidum was studied using thin stillage with an added carbon source (Yang et al., 2003; Hsieh et al., 2005).

Biosurfactants are beginning to be accepted as potential performance-effective molecules that are ecofriendly alternatives to synthetic surfactants. Economic strategies, which emphasise the utilisation of waste streams as no-cost substrates are essential for developing large-scale biosurfactant production technology. It has been reported that biosurfactant production from distillery and whey wastewaters and synthetic medium was comparable using Pseudomonas aeruginosa strain BS2 (Dubey et al., 2005).

Bioplastic production by micro-organisms was investigated by Yu et al. (1998) with malt waste from a brewery. Specific polymer production yield by Alcaligenes latus DSM1124 increased up to 70.1% w polymer/w cell with a final biomass and polymer concentration of 32.36 g/L cell dry wt and 22.68 g/L cell dry wt. In this fermentation, biopolymer accumulation is controlled by nitrogen limitation.

**Extraction of specific compounds**

Recovery of dissolved molecules and water

As the cost of wastewater disposal increases, more emphasis is being placed upon the recovery and recycling of valuable chemicals contained within the effluent. As mentioned by Decloux and Bories (2001), a lot of research has been carried out into the recovery of molecules using MF to NF and reverse osmosis membranes (Wu et al., 1989; Kim et al., 1997; Nataraj et al., 2006). Kim et al. (1997) proposed a new process for producing alcohol from wheat,
associating a centrifuge separation and a stillage ultrafiltration (UP) stage. Permeate is recycled for the preparation of the fermentation must. The retentate is recycled to the head of the centrifuge separator. The only output is the cake, which comes out of the centrifuge separator and which, after drying, can be used in animal feed.

Numerous articles were published between 1985 and 1990 by Wu (research centre in Illinois, USA) on the recovery of dissolved and nitrogenous matter from pre-filtered and centrifuged stillage originating from the fermentation of different raw materials including beet (Wu et al., 1989). Treatment on an UF membrane then RO makes it possible to concentrate the dissolved matter and the nitrogenous matter in a small volume (final volumetric reduction ratio, VRR between eight and four) and obtain water with a lower conductivity than tap water. Nataraj et al. (2006) tested a hybrid NF and RO pilot plant to remove the colour and the contaminants of spent molasses distillery wash. Colour removal by NF and rejection of 99.8% TDS, 99.9% of COD and 99.99% of potassium was achieved from the RO runs, by retaining a significant flux as compared to the pure water flux, which shows that membranes were not affected by fouling during the wastewater run. The pollutant levels in permeates were below the maximum contamnial levels as per the guidelines of the World Health Organization and the central pollution board specifications for effluent discharge (less than 1000 ppm of TDS and 500 ppm of COD). The paper does not indicate the composition of the final retentate (mixture of NF retentate and RO retentate) or the applicability on a large scale.

Other studies were carried out on the recovery of water from condensates generated during stillage concentration. The condensates were used to dilute the molasses. It was quickly observed that the kinetics of the fermentation was decreased and even completely stopped. Analysis of the condensates demonstrated the concentration of molecules that inhibit fermentation was high. Morin et al. (2003) demonstrated that the molecules responsible were mainly aliphatic acids (formic, acetic, propionic, butyric, valeric and hexanoic), alcohols (2,3 butanediol), aromatic compounds (phenyl-2-ethyl-alcohol) and furane derivatives (furfural). These are small molecules present at low concentrations in the system. Anaerobic digestion experiments and RO experiments were carried out to choose an appropriate treatment for the condensates. Preliminary results showed that most of the organic compounds were degraded by anaerobic treatment, but not completely, and a subsequent filtration by RO was necessary. Direct RO experiments with the condensates showed good but not total rejection of the molecules (Morin-Couallier et al., 2007). Increasing the pH of the condensates nearly achieved total retention. Research continues on both treatments.

**Extraction of salts by electrodialysis**

Electrodialysis tests in the laboratory showed that it is possible to reduce the potassium concentration of beet stillage by 92% (Decloux et al., 2002).
Then concentration up to 70% solids should be possible without potassium sulphate crystallisation. Nevertheless, considering the sale cost of concentrated vinasses as fertiliser, the investment costs still do not allow industrial application.

Elimination of heavy metals

Plant-derived materials may be used to adsorb heavy metals, but many reviews report the efficiency of micro-organisms (fungi, algae, bacteria). The ability of micro-organisms to remove metals from solutions is well known, and both living and dead biomass is capable of metal accumulation. Effluents from many industries contain metals in excess of permitted levels. Biomass use may be economically feasible. Wang and Chen (2006) report that biosorption may constitute a cost-effective biotechnology for the treatment of high-volume and low-concentration complex wastewaters containing heavy metal(s) in the order of 1–100 mg/L. Among the promising biosorbents for heavy metal removal which have been researched during the past decades, *Saccharomyces cerevisiae* has received increasing attention due to the unique nature in spite of its mediocre capacity for metal uptake compared with other fungi. *S. cerevisiae* is widely used in food and beverage production, is easily cultivated using cheap media, is also a by-product in large quantity as a waste of the fermentation industry, and is easily manipulated at molecular level. Dostalek *et al.* (2004) report the sorption of cadmium, Cd$^{2+}$, copper, Cu$^{2+}$ and silver ions, Ag$^{+}$. Marques *et al.* (1999) found that waste brewery biomass of non-flocculent and flocculent types are promising biosorbents for the removal of Cu$^{2+}$, Cd$^{2+}$ and Pb$^{2+}$ at concentrations of up to 1.0 mM from non-buffered aqueous solutions. Runping *et al.* (2006) studied the influence of the uptake of Cu$^{2+}$ and Pb$^{2+}$ by waste beer yeast in different adsorptive conditions (pH, contact time, yeast concentration, temperature, ion concentrations) to compare the biosorption behaviour of a single-metal system and a two-system in batch mode. The process of biosorption nearly reached equilibrium in 30 min and the optimum pH was near 5.0. Beer yeast absorbed 0.0228 mmol g$^{-1}$ for Cu$^{2+}$ and 0.276 mmol g$^{-1}$ for Pb$^{2+}$.

Extraction studies on laboratory and pilot scales from wine and by-products (pomace) have focused on novel molecules such as RG-II (rhamnogalacturonan II), which have metal complexing properties (Vidal *et al.*, 1999).

35.5 Acknowledgements

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35.6 Nomenclature

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>BAT</td>
<td>Best available techniques</td>
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<tr>
<td>BFS</td>
<td>Beer factory sludge</td>
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<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
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<tr>
<td>CIP</td>
<td>Cleaning in place</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
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<tr>
<td>DDGS</td>
<td>Dried distillers grains solubles</td>
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<tr>
<td>DGS</td>
<td>Condensed distillers solubles</td>
</tr>
<tr>
<td>DM</td>
<td>Dry matter</td>
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<tr>
<td>EFB</td>
<td>Expanded fluidized beds</td>
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<tr>
<td>HRT</td>
<td>Hydraulic residence time</td>
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<tr>
<td>LPA</td>
<td>Litres of pure alcohol</td>
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<tr>
<td>MBR</td>
<td>Membrane bioreactor</td>
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<tr>
<td>MF</td>
<td>Microfiltration</td>
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<td>SEC</td>
<td>Specific energy consumption</td>
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<td>NF</td>
<td>Nanofiltration</td>
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<td>RO</td>
<td>Reverse osmosis</td>
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<tr>
<td>UASP</td>
<td>Upflow Anaerobic Sludge Blankets</td>
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<tr>
<td>TEP</td>
<td>Tonnes equivalent petroleum</td>
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<tr>
<td>TDS</td>
<td>Total dissolved solid</td>
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<tr>
<td>TS</td>
<td>Total solid</td>
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<tr>
<td>UF</td>
<td>Ultrafiltration</td>
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<td>UV</td>
<td>Ultra violet</td>
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<td>VFA</td>
<td>Volatile fatty acids</td>
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35.7 References


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