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### **► To cite this version:**

Luc Fillaudeau, Andre Bories, Martine Decloux. Brewing, winemaking and distilling: an overview of wastewater treatment and utilization schemes (Part IV - Chapter 35). Improving Water and Energy Management in Food Industry, Woodhead Publishing Limited, 2008. <hal-02310087>

**HAL Id: hal-02310087**

**<https://hal.science/hal-02310087v1>**

Submitted on 9 Oct 2019

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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  $159.8 \cdot 10^9$  L beer,  $26.7 \cdot 10^9$  L wine and  $7.0 \cdot 10^9$  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

**Table 35.1** World production of beer (10<sup>9</sup> L), wine (10<sup>9</sup> L), spirits (10<sup>9</sup> L pure alcohol) in 2004

Area	Beer	Wine	Spirits
America	50.29	4.6	na
Europe	54.33	18.7	na
Asia	45.65	1.3	na
Africa	7.42	1.01	na
Oceania	2.11	1.07	na
World	159.8	26.7	7.0

na = not available

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 10<sup>9</sup> L/y<sup>-1</sup>), while a microbrewery may start its activity with an annual production of around 1000 hL (Verstl, 1999).

World-wide wine production is 26.7 10<sup>9</sup> 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 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 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 10<sup>9</sup> LPA/y in 2004. These tendencies and figures are unlikely to change in the near future. According to the European

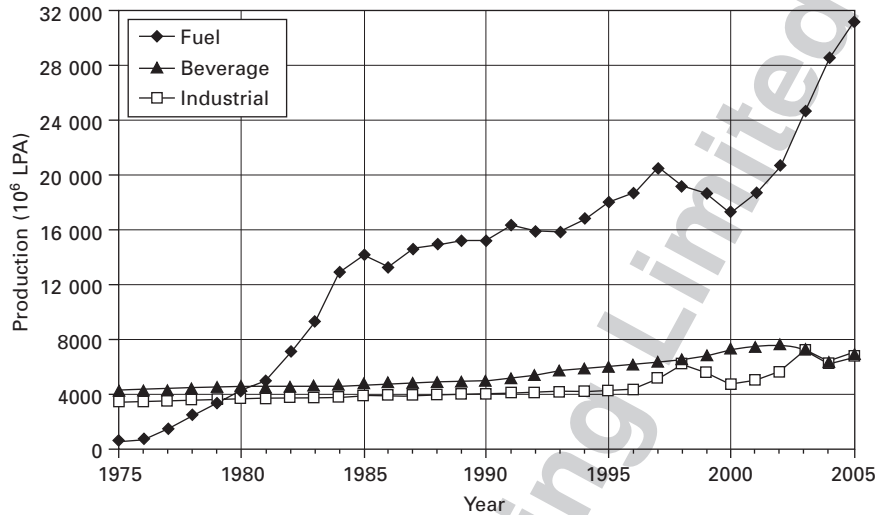


Fig. 35.1 World alcohol production in million litres of pure alcohol (Berg, 2006).

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 ( $\approx 6.5 \cdot 10^9$  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  $18 \cdot 10^9$  L/y in 2000,  $28 \cdot 10^9$  L/y in 2004 and is projected to reach  $60 \cdot 10^9$  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).

1 The role of environmental technology for industry has greatly evolved  
2 over the past decades. Since the mid-seventies, the general trend is to consider  
3 that pollution from industrial processes should be cleaned up. 'The polluters  
4 pay' remains the basis of regulations. During beer, wine or alcohol production,  
5 the product goes through a whole series of chemical and biochemical reactions  
6 (mashing, boiling, fermentation, distillation, evaporation) which require solid-  
7 liquid separations, cleaning, other water processes and energy. The brewing,  
8 wine and alcohol industries have grown from ancient tradition but stand as  
9 a dynamic sector open to new technological and scientific developments.  
10 These agro-industries recognise that business success should depend upon  
11 consumer perception of company reliability. To be considered reliable by  
12 consumers, they are making efforts to establish compliance statements, to  
13 guarantee the quality of their product, to build consumer satisfaction and  
14 confidence, and to actually practice ecoship and sustainability management.  
15 Ecoship management can be defined as an attitude and policy towards  
16 environmental issues. The aim is to take advantage of natural energy sources,  
17 to promote reuse of packaging and recycling waste, to reduce waste and to  
18 promote diversification (Kawasaki and Kondo, 2005).

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

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

## 38 39 40 41 **35.2 Water use: the Origin and nature of effluents** 42 **in the brewing, wine and distilling industries**

### 43 **35.2.1 Brewing industry**

44 The main ingredients for the production of beer are barley malt, adjuncts,  
45 hops and water. The brewing process includes wort production, fermentation,

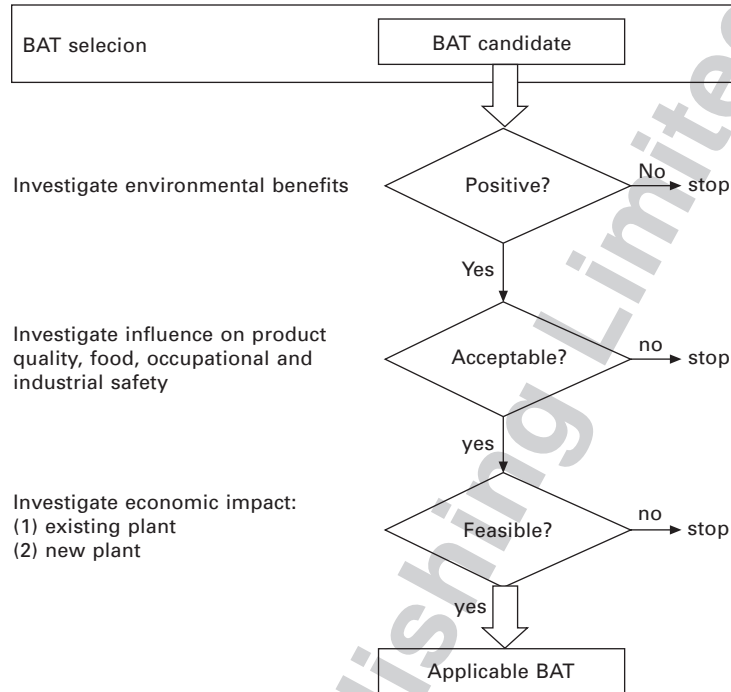


Fig. 35.2 Best available techniques (BAT) applicability scheme.

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, CO<sub>2</sub> recovery, N<sub>2</sub> 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 worldwide benchmark study on specific energy consumption (SEC) in the brewing industry in 2003. 158 breweries (production capacity: 0.05–1.2 10<sup>9</sup> 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

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

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

COD = chemical oxygen demand

PVPP = polyvinyl polypyrrolidone

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.

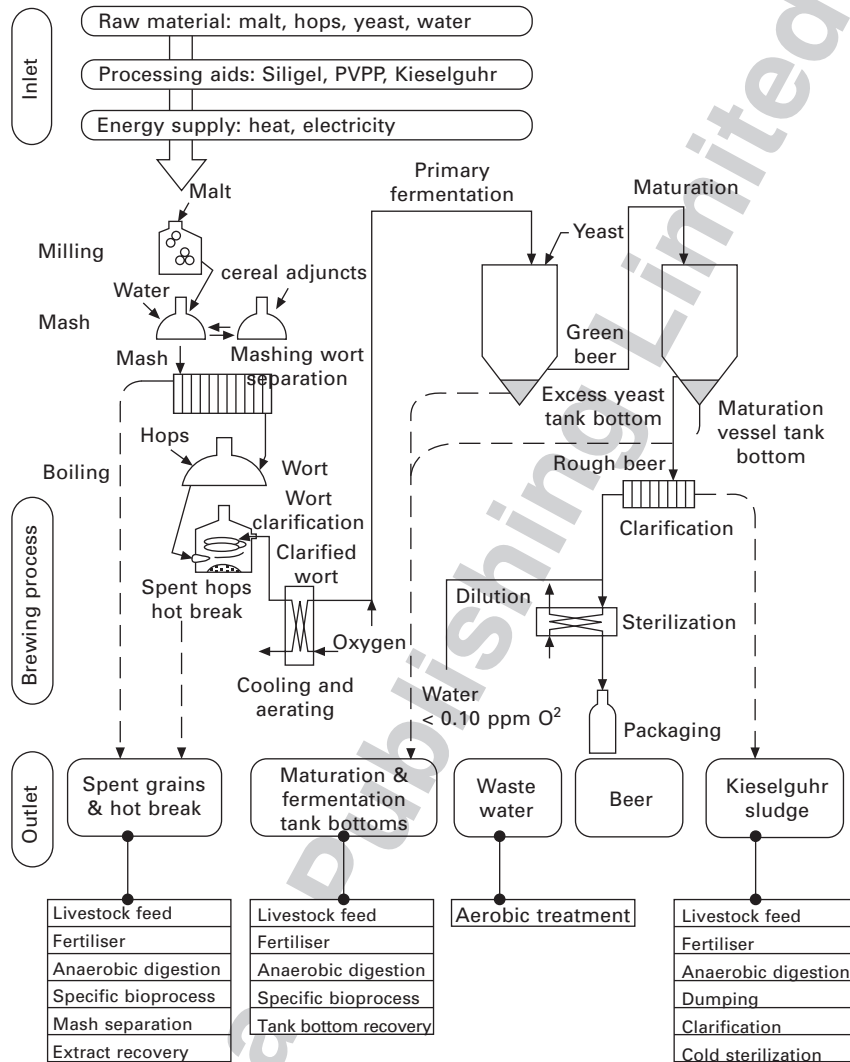


Fig. 35.3 Brewing process and effluent treatment.

- 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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1 water is used as rinsing water in the brewing house (during the production)  
 2 and in the bottling plant. In addition to the hot water required for the brewing  
 3 process (depending on the mashing programme and mash water cycles 0.9–  
 4 1.1 L/L including false bottom rinsing, product displacement and vessel  
 5 cleaning), additional quantities of hot water are needed in the plant for  
 6 cleaning and sterilisation operations. Specific hot process water requirements  
 7 fluctuate widely between 0.2 and 1.5 L/L of cast wort (Schu and Stolz,  
 8 2005). Cooling and brewing water only comprise a small part of the water  
 9 consumption: cooling water is usually only needed as supplementation water  
 10 in a closed circuit; the brewing water is essentially the basis of the end-  
 11 product (Braeken *et al.*, 2004).

12 In brewing, the average water consumption is correlated to beer production  
 13 for industrial breweries (Perry and De Villiers, 2003). Water consumption is  
 14 divided into 2/3 used in the process and 1/3 in the cleaning operations (Moll,  
 15 1991). In the same way, the effluent to beer ratio is correlated to beer production.  
 16 It has been shown that the effluent load is very similar to the water load since  
 17 none of this water is used to brew beer and most of it ends up as effluent  
 18 (Perry and De Villiers, 2003). The wastewater discharge will be equal to the  
 19 water supply minus the beer produced, water evaporated in brew house and  
 20 utility plants, and the water present in the by-products and solid-wastes  
 21 (spent Kieselguhr, surplus yeast and spent grains). Water loss along the  
 22 process is estimated to be 1.3–1.8 L water/L beer.

$$23 \quad (Water)_{Beer} = 2.89 + 8731200/Beer \quad \text{For } 30 < \text{Beer} < 60 \text{ } 10^6 \text{ L/month}$$

$$24 \quad (Effluent)_{Beer} = 2.21 + 54589200/Beer \quad \text{Beer [L/month] with}$$

25  
 26 Effluent/Beer and Water/Beer, [L/L beer]

27  
 28 The brewing process generates a unique, high-strength wastewater as a  
 29 by-product. The wastewater typically has a high biochemical oxygen demand  
 30 (BOD) from the carbohydrates and protein used in brewing beer. The  
 31 wastewater from the brewery is usually quite warm (over 38 °C). Both these  
 32 specificities make brewery wastewater an ideal substrate for anaerobic  
 33 treatment. Anaerobic digestion of brewery wastewater is a proven process  
 34 with more than 250 full-scale systems in operation (Totzke, 2005).

### 35 *Spent grain*

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

**Table 35.3** Composition of spent grains and their ability to degrade (Voigt and Sommer, 2005)

Ingredient	Barley malt	Wheat malt	Degradation
Protein	20–22	20–18	Easy
Fat	16–18	15–18	Easy
Starch	0.8–1.0	0.6–1.0	Easy
Hemicellulose	25–30	35–40	Difficult
Cellulose	18–20	14–16	Difficult
Lignin	8–10	4–7	Difficult
Ash	3–4	3–4	Difficult

*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

1 due to its polluting effect and the increasing cost of disposal. From a health  
2 perspective, the diatomaceous earth is classified as 'hazardous waste' before  
3 and after filtration (The World Health Organization defines the crystalline  
4 silica as a cause of lung disease) and its use requires safe working conditions.  
5 From an economic standpoint, the diatomaceous earth consumption and sludge  
6 disposal generate the main cost of the filtration process ranging between  
7 0.0025 and 0.007 €/L. In Europe, the economic aspect is strengthened because  
8 its consumption is higher (around 1.7 g/L of clarified beer). The disposal  
9 routes of Kieselguhr sludge are into agriculture and recycling with an average  
10 cost of 170 €/t. Disposal costs vary widely from one brewery to another  
11 with a positive income of 7.5 €/t up to a maximum charge of 1100 €/t of  
12 Kieselguhr purchased (Knirsch *et al.*, 1999).

### 15 35.2.2 Wine industry

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

- 17 • wine production (winemaking) within the wineries that creates winery  
18 effluents and co-products: pomace, lees;
- 19 • transformation/recycling of winery co-products within wine distilleries  
20 (alcohol distillation, extraction of components, etc.), whose wastewaters  
21 consist mainly of stillage.  
22

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

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

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

#### 39 *Winery wastewater*

##### 40 Water use and wastewater

41 Winery wastewater mainly consists of the water used to wash and clean  
42 winery equipment and facilities used for destalking, pressing, racking, alcoholic  
43 and malolactic fermentation, clarifying, tartaric stabilisation, filtering and  
44 bottling operations. The organic pollution of the effluent is due to the  
45 contribution of matter from wash water and product loss.

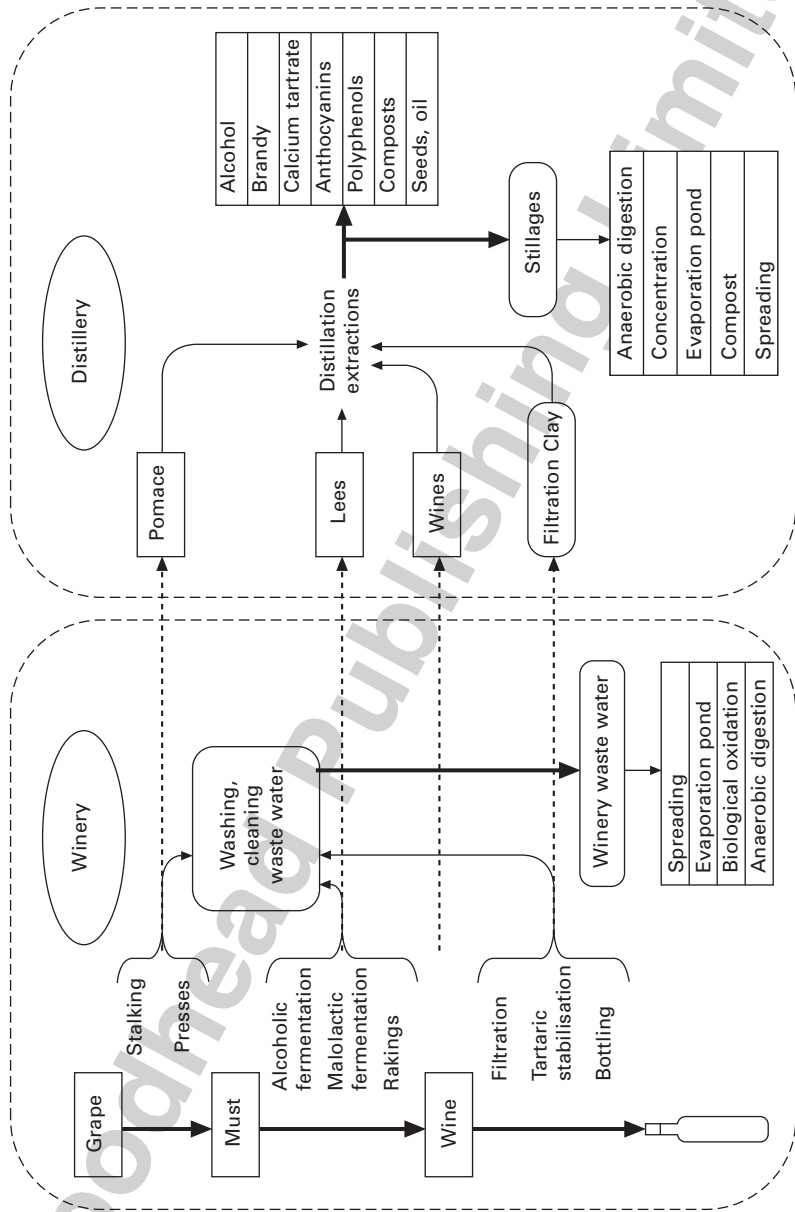


Fig. 35.4 Overview of wine industry processes and waste water production.

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1 Wineries vary considerably, in production capacity – from several tens of  
2 thousands to several tens of millions of litres of wine – and as a result of the  
3 extremely varied vinification methods and techniques used. They also vary  
4 as to their water resources – underground and/or drinking water systems – as  
5 well as to the wastewater treatment methods that they use and to the level of  
6 awareness of the operators responsible for water management. All these  
7 differences lead to water consumption levels that vary considerably from  
8 one establishment to another: from 0.3–10 L of water per litre of wine  
9 produced (Duarte *et al.*, 1998; Picot and Cabanis, 1998; ITV, 2000). The  
10 establishment of regulations and the levying of taxes on winery effluents, the  
11 implementation of water purification treatments and the improved awareness  
12 of operators in relation to water management have contributed to the reduction  
13 of water consumption to approximately 0.8 L/L (Rochard *et al.*, 1996; ITV,  
14 2000; Rochard, 2005). The amount of taxes levied on waste depends on the  
15 country; the French and Italian wine industries generate six times less effluents  
16 than those of Spain where taxes are lower (Prodanov and Cobo Reuters,  
17 2003; Bustamante *et al.*, 2005). The seasonality of wine production activity  
18 is an important factor to be taken into consideration in the management of  
19 wastewater treatment. Of the annual volume of effluents 60 % is produced  
20 over a period of approximately two months (harvest/vinification) and waste  
21 production is maximal from the start.

#### 22 23 Water management

24 After separating rain water from uncontaminated process water (cooling  
25 water), efforts to reduce water consumption focused on washing and cleaning  
26 operations, the choice of materials and the intrinsic consumption of the  
27 various operations involved. Since the washing of facilities (tanks, equipment,  
28 floors) is a major source of water consumption in wineries, the use of high-  
29 pressure blowers (> 50 bars) or medium-pressure blowers (20–40 bars) that  
30 are just as efficient but without the disadvantages (less splattering, aerosols  
31 and abrasion), makes it possible to reduce water consumption (Seegers,  
32 2006). The nature and the quality of tank construction materials are also  
33 considered in terms of water management. For example, the use of  
34 electropolished-type stainless steel for tanks not only reduces the quantity of  
35 water required for washing but the pollution load discharged into the water  
36 as well, as a result of decreased adherence and retention of matter on the tank  
37 surface. Concerning cleaning (disinfecting) of equipment, the application of  
38 chemicals (biocides) in the form of foams is recommended to limit product  
39 consumption and to increase efficiency.

40 Among the different vinification operations, the filtering of musts and  
41 wines is an important step in the management of water and waste. Membrane  
42 filtering processes (tangential microfiltration) applied to wine production  
43 are a considerable improvement in terms of the environmental impact of  
44 vinification processes (Moutounet and Vernet, 1998). Some of the advantages  
45 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 ( $-4^{\circ}\text{C}$ ) for around eight days, and then filtering it to eliminate potassium acid tartrate precipitates. This process consumes a great deal of electrical energy ( $5\text{ kWh/m}^3$  wine) and produces considerable quantities of waste (filtration clay:  $2\text{ kg/m}^3$  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 ( $0.5\text{--}1\text{ kWh/m}^3$ ) and filtration wastes are eliminated. Water consumption in the electrodialysis brine circuit ( $0.1\text{ L/L}$  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  $15\text{ g O}_2/\text{L}$ , and this organic load is easily biodegradable ( $\text{COD/BOD} < 1.5$ ). 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 –  $200\text{--}250\text{ g/L}$  – and ethanol in wines –  $100\text{--}120\text{ g/L}$  – that present a similar COD ( $\approx 250\text{ g O}_2/\text{L}$ ), 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 ( $\text{pH} > 10$ ) that are generally acidic ( $\text{pH} 3.5\text{--}5$ ).

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.

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

	Concentration (g/L) <sup>1</sup>	% COD/d
pH	5.0	
Suspended solids (g /L)	3.3	
COD raw (g O <sub>2</sub> /L)	14.6	
COD dissolved (g O <sub>2</sub> /L)	12.7	100
Ethanol (g/L)	4.9	80.3
Glucose + fructose (g/L)	0.87	7.3
Glycerol (g/L)	0.32	3.1
Tartaric acid (g/L)	1.26	5.3
Malic acid (g/L)	0.07	0.4
Lactic acid (g/L)	0.16	1.2
Acetic acid (g/L)	0.30	2.6

<sup>1</sup>except pH

COD = chemical oxygen demand

### Winery stillage

#### Water use and wastewater

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.

#### Load and composition of distillery stillage

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 O<sub>2</sub>/L). Of the dissolved organic matter in detartated lees stillage (COD d # 30 g O<sub>2</sub>/L) 45 % is due to simple compounds (glycerol,

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

	Pomace stillage		Lee stillage		Wine stillage (White wine)
	Not recycled	Recycled	Without tartrate recovery	After tartrate recovery	
pH	3.8	3.7	4.9	4.9	3.2
Suspended solids (g/L)	0.69	2.4	86.9	64	3.25
COD raw (g O <sub>2</sub> /L)	17.3	46.8	100	76	29.8
COD dissolved (g O <sub>2</sub> /L)	15.2	44.9	36.1	27.2	26.2
Ethanol (g/L)	0	0.13	0	0.07	0
Glucose + Fructose (g/L)	0	6.8	0	4.8	0
Glycerol (g/L)	3.69	4.28	2.58	2.22	7.5
Tartaric acid (g/L)	4.64	5.66	30.0	2.46	2.7
Malic acid (g/L)	0	0	0.447	0.10	–
Lactic acid (g/L)	1.13	13.0	4.58	3.53	5.6
Acetic acid (g/L)	0.58	2.64	2.87	2.71	–
Sulfate (SO <sub>4</sub> ) (g/L)	0.264	0.62	0.885	8.09	–

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 O<sub>2</sub>/L, whereas recycled pomace wine stillage is characterised by a high organic load (COD: 30–50 g O<sub>2</sub>/L).

Almost 70 % of the organic load of wine stillage (COD: 20–30 g O<sub>2</sub>/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 SO<sub>4</sub>/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

1 listed by the Central Pollution Control Board (Nataraj *et al.* 2006). For each  
2 litre of alcohol produced, the molasses-based distilleries would usually have  
3 water consumption per litre of alcohol produced of 14–22 L in process  
4 applications (yeast propagation, molasses preparation, steam generation) and  
5 100–240 L in non-process applications (cooling water, steam generation).  
6 They generate about 8–15 L of wastewater.

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

- 8 • wastewater with high solids concentrations as spent wash (named also  
9 stillage or vinasse) removed from the bottom of the column receiving  
10 the fermented broth,
- 11 • wastewater with very low solids concentration as cooling water used to  
12 evacuate the heat from the fermentation and distillation steps and the  
13 condensates from the stillage concentration plants.  
14

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

#### 18 *Spent wash from the distillation column*

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

23 The distilleries that ferment cane juice produce spent wash with a low  
24 concentration of solids (2–4 % solids) but high COD level (14–34 g/L)  
25 (Table 35.6) (Decloux and Bories, 2001). Their biodegradability is high  
26 (BOD/COD > 0.6) as 87 % of the COD of the cane juice stillage is represented  
27 by simple compounds: glycerol, organic acids. The glycerol alone represents  
28 38 %. Direct land application, anaerobic biodigestion, aerobic treatment and  
29 discharge in aquatic environments are the main post-treatments.  
30

31 Fermentation units working with cane molasses or green cane syrup need  
32 dilution water to decrease the sugar concentration to 16 % before fermentation.  
33 They produce stillage (8–10 % solids) of variable chemical composition  
34 with high mineral and organic matter content. Its COD is between 60 and  
35 120 g/L. The BOD/COD ratio (0.3–0.35) demonstrates the limited  
36 biodegradability of the organic load. Substances which are not easily  
37 biodegradable represent a large proportion of the COD. It is made up of  
38 complex compounds (hetero-polymers) responsible for the dark brown colour  
39 of molasses stillage (phenolic compounds, mixtures of caramels, melanoidins  
40 and products of the alkaline degradation of hexoses). The mineral load is  
41 mainly made up of potassium (4–12 g/L), magnesium (2–3 g/L), calcium  
42 (2–3 g/L) sulphate (4–8 g/L) and chloride (5–6 g/L). Cane molasses stillage  
43 is rich in glycerol. Direct land application, anaerobic digestion, aerobic  
44 treatment, livestock feed production and other forms of recycling are the  
45 main post-treatments.

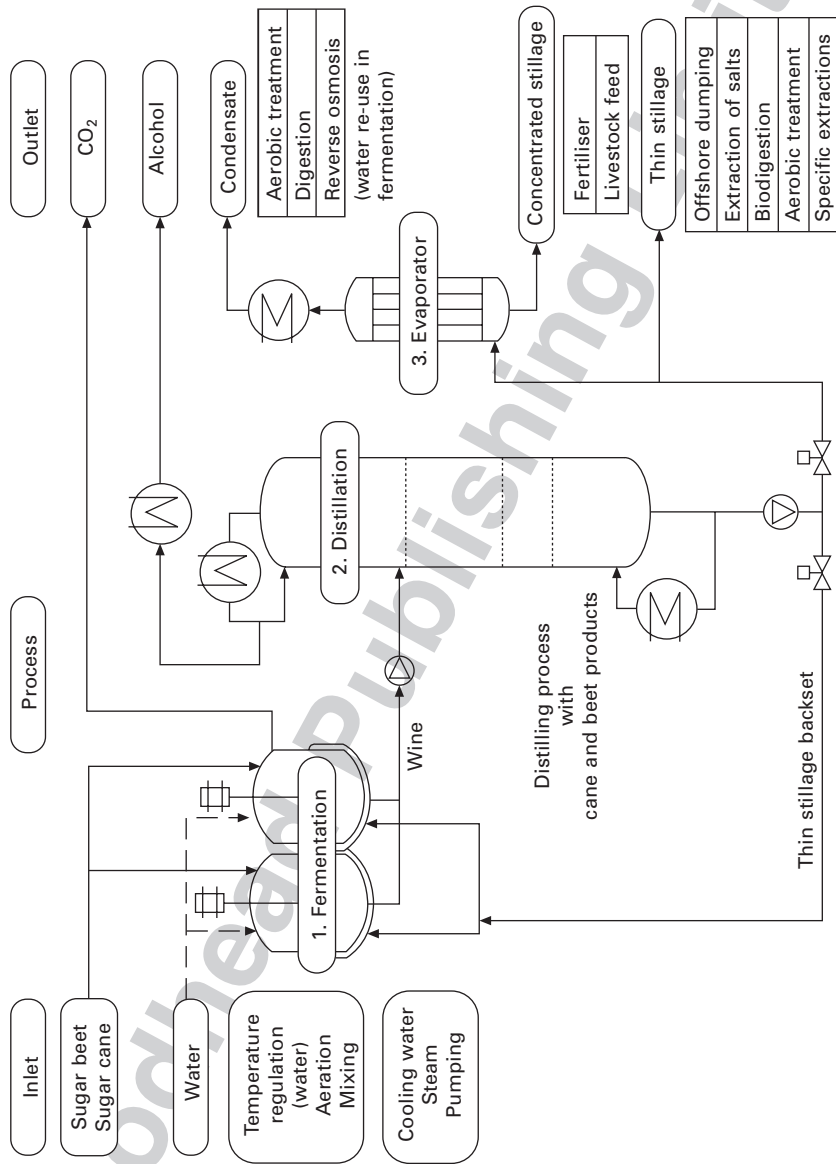


Fig. 35.5 Typical distilling process with cane and beet products.

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**Table 35.6** Characteristics of stillage from sugar cane products (juice, molasses and mixed) (from Cortez *et al.*, 1999)

Parameter		Juice	Molasses	Mixed
pH		3.7–4.6	4.2–5.0	4.4–4.6
BOD	(g/L)	6–16.5	25	19.8
COD	(g/L)	15–33	65	45
Total solids	(g/L)	23.7	81.5	52.7
Organic matter	(g/L)	19.5	63.4	38.0
Reducing substances	(g/L)	7.9	9.5	8.3
Volatile matter	(g/L)	20.0	60.0	40.0
Fixed matter	(g/L)	3.7	21.5	12.7
Nitrogen (N)	(g/L)	0.15–0.70	0.45–5.18	0.48–0.70
Phosphorus (P <sub>2</sub> O <sub>5</sub> )	(g/L)	0.01–0.21	0.10–0.29	0.09–0.20
Potassium (K <sub>2</sub> O)	(g/L)	1.2–2.1	3.74–7.83	3.34–4.60
Calcium (CaO)	(g/L)	0.13–1.54	0.45–5.18	1.33–4.57
Magnesium (MgO)	(g/L)	0.2–0.49	0.42–1.52	0.58–0.70
Sulfate (SO <sub>4</sub> )	(g/L)	0.60–0.76	6.4	3.7
Carbon (C)	(g/L)	5.7–13.4	11.2–22.9	8.7–12.1
C/N ratio		19.7–21.07	16–16.27	16.4

BOD = biological oxygen demand

COD = chemical oxygen demand

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 (K<sub>2</sub>O) 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  $\alpha$ -amylase to hydrolyse the cereal to dextrins, which are a mix of oligosaccharides. The hydrolysis is done above the

**Table 35.7** Composition of concentrated beet molasses stillage (g/100 g solids) from three different French sugar plants (Decloux and Bories, 2002a)

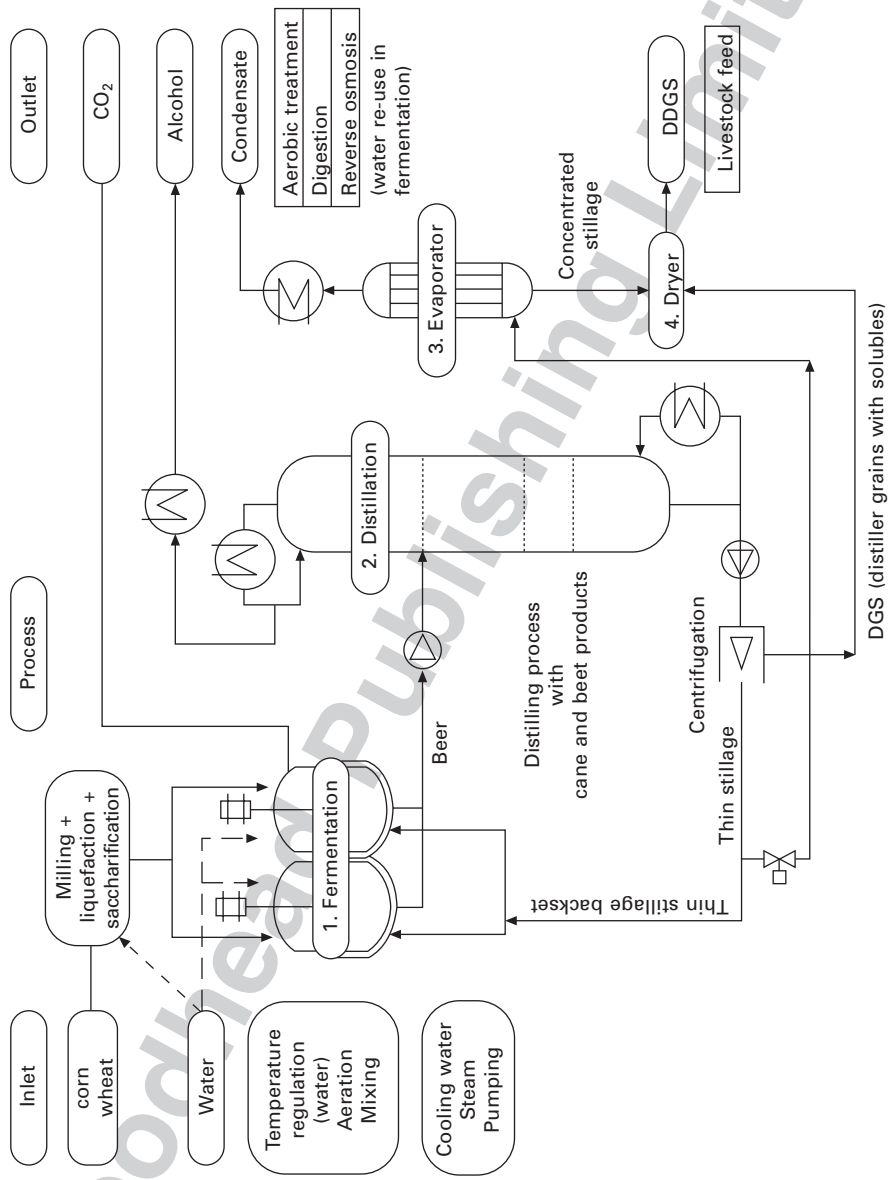
Plant	1	2	3
Mineral solids	30.5	27.6	21.1
Organic solids	69.5	72.4	78.9
Glycerine	9.0	13.6	26.0
Betaine	14.4	14.2	12.8
Sodium	2.0	2.4	0.9
Potassium (K <sub>2</sub> O)	7.7	10.7	8.8
Sulfate	1.2	1.0	1.5
Chloride	1.0	4.5	3.8
Calcium	0.08	0.3	0.2
Magnesium	0.03	0.02	0.03
Nitrogen (N)	4.2	4.04	2.9
TOC	37.0	36.88	42.4

TOC = total organic compounds

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 m<sup>3</sup>/

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**Fig. 35.6** Typical distilling process with cereal products.

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 dehydration 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)

Property		Reported values
Dry matter	%	86.2–93.0
Protein	% solids	26.8–33.7
Fat	% solids	3.5–12.8
Nitrogen free extract	% solids	33.8–54.0
Starch	% solids	4.7–5.9
Total dietary fiber	% solids	25.0–39.8
Ash	% solids	2.0–9.8

1 and from the top of the distillation columns. To prevent any decrease in  
2 fermentation kinetics, water cooler than 30 °C is necessary. In the condensers  
3 of the distillation columns, the cooling water temperature must be lowered  
4 as the distillation pressure is lowered, but generally not lower than 45 °C.  
5 The dehydration step also needs cooling water at about 50 °C.

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

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

### 31 **35.3 Most widely used treatment methods: Livestock feed,** 32 **discharge, anaerobic and aerobic treatments, incineration**

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

- 41 • knowledge of process and product specificities;
- 42 • characterisation of the effluent (nature, composition, concentration,  
43 flowrate);
- 44 • historical, economical and environmental constraints;
- 45 • efficiency of the technique in agreement with BAT selection.

**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)

	Brewing industry			Wine industry		Distilling industry		
	Spent grain (mash)	Yeast surplus (tank bottoms)	Kieselguhr sludge	Winery effluent	Stillage	Sugar beet	Sugar cane	Wheat maize
Livestock feed	I-CP	I-CP	I-CP			I-CP	I-CP	I-CP
Direct land application	I-CP	I-CP	I-CP	I-CP		I-CP	I-CP	I-CP
Fertiliser	I-CP	I-CP	I-CP	I-CP	I-CP	I-CP	I-CP	I-CP
Composting	A-PP	A-PP			I-CP	A-PP	A-PP	
Dumping/offshore dumping			I-CP				I-CP	
Evaporation in pond	I-CP	I-CP	I-CP	I-CP	I-CP	A-PP/I-ND	A-PP/I-ND	
Anaerobic digestion	I-CP	I-CP	I-CP	I-CP	I-CP	I-CP	I-CP	I-CP
Aerobic treatment								
Incineration	A-PP/I-ND				I-CP	A-PP	I-ND	

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1 In the brewing and distilling industries, the most common treatment is  
2 livestock feed, discharge in soil and biological treatment. In wine production,  
3 the choice of wastewater treatment techniques is based on the seasonal nature  
4 and dependent on winery production capacities. Spreading and natural  
5 evaporation were among the first treatments to be implemented since they  
6 suit the variability of the pollution load and the technical and economic  
7 context of the sector (limited operating costs and investment). With the  
8 development of biological wastewater treatment technologies, companies  
9 with large production capacities (distilleries, wineries) began using aerobic  
10 and anaerobic biological processes. The specificities of the composition of  
11 winery effluents were also a determinant factor in the study and development  
12 of new treatment methods (fractionation, membrane separation) and valorisation  
13 (molecule production/extraction).  
14

### 15 16 **35.3.1 Livestock feed**

17 In breweries, the livestock feed is limited by several economical, technological  
18 and biological constraints. The fibre content of spent grain is 150–160 g/  
19 kg DM (dry matter) making them unsuitable as a feed for non-ruminant  
20 animals (pork, poultry). Spent grain is bulky, due to its high water content  
21 (70–80 % w/w) making handling and transport inefficient. In wet form the  
22 spent grain is not stable and must be consumed within two or three days  
23 otherwise a biological degradation takes place. The production of spent grain  
24 is high in summer when the demand for cattle feed is low, and in certain  
25 areas (Africa, Singapore) the cattle feed market does not exist.

26 Heineken Technical Service and 2B Biorefineries (Bruijn *et al.*, 2001;  
27 Schwencke, 2006) adapted a grass separation method for use with spent  
28 grains, which is environmentally sustainable, applicable world-wide and  
29 economically viable. The process separates spent grains into two useful  
30 fractions, a 'protein concentrate' and a 'fibre concentrate' and produces a  
31 wastewater stream. Wet spent grains (0.18–0.2 kg/L beer with 20–25 % w/  
32 w DM) are collected in a tank from which it is measured into an impeller  
33 mixed tank. Water (0.54–0.80 kg/L beer) at 80 °C is added to obtain a  
34 suspension of 5 % w/w DM. This suspension is pumped through a vibrating  
35 screen, which separates water and small particles (70 % vol/vol with 1.5–  
36 2 % w/w DM) and the coarse material (30 % vol/vol with 16–18 % w/w DM).  
37 After separation, the fibre material is fed into a screw press for water removal  
38 to reach 40 % w/w DM (0.095–0.140 kg/L beer), and the protein fraction is  
39 fed into a scroll-type decanter, where it can be dehydrated to 30 % w/w DM  
40 (0.030–0.050 kg/L beer). The liquid stream coming from the screw press  
41 and the decanter is recirculated to the mixing tank and extracted as drain  
42 (0.60–0.85 L/L beer with an estimated COD 0.02 kg/L). In 2001, the protein  
43 concentrate fetched 170 €/t (88 % w/w DM) and the fibre concentrate, 20 €/  
44 t (45 % w/w). The value of the protein product is the most important factor  
45 and determines the success and applicability of a spent grain separation

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, combust 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 phosphorus 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)

1 ratio; this is generally very high and can result at any given moment in a  
2 considerable mobilisation of nitrogen in the soil, with a heavy organic load  
3 that can precipitate aerobic and anaerobic phenomena capable of leading to  
4 the release of calcium, magnesium, iron and manganese, as well as to a  
5 concentration in heavy metals (Debroux *et al.*, 2004; Perès *et al.*, 2004;  
6 Bustamante *et al.*, 2005).

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

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

### 32 *Concentration and land application as fertiliser*

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

44 In Turkey, Kütük *et al.* (2003) investigated the effects of beer factory  
45

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<sup>-1</sup> considering root growth, this being the economic part of the sugar plant. Application above 10 t ha<sup>-1</sup> negatively affected the root quality, possibly due to high levels of organic acids, NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub>-N, all released during mineralisation. BSF 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<sup>2</sup> 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 (N + P<sub>2</sub>O<sub>5</sub> + K<sub>2</sub>O) with a minimum of 3 % nitrogen and 6 % potash (K<sub>2</sub>O) and 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

1 in lagooning or in aeration ponds. Research is being conducted on their  
2 treatment to enable their recycling in fermentation (see later).

3 As explained by Decloux and Bories (2002) during the concentration of  
4 beet molasses stillage, large quantities of potassium tend to crystallise and  
5 clog up the evaporators. To limit this spontaneous formation of potassium  
6 sulphate crystals during the concentration stage or during the storage of the  
7 concentrated stillage, many distilleries acidify the fermentation must with  
8 hydrochloric acid instead of sulphuric acid, potassium chloride being much  
9 more soluble than potassium sulphate. It is, however, possible to promote  
10 and control the crystallisation of potassium sulphate that is then used as  
11 fertiliser. Moreover, potassium sulphate crystallisation is a legal requirement  
12 when using stillage for cattle feed. It must in this case contain less than 2–  
13 3 % of potassium per unit dry matter and have a total nitrogen content  
14 (measured by mineralisation and multiplied by 6.25) at least equal to 39 %.  
15 To obtain complete precipitation of potassium and be within the acceptable  
16 limits for using stillage in cattle feed, it is necessary to add sulphate ions,  
17 most of time ammonium sulphate (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> that increase the total nitrogen  
18 content of the concentrated stillage. The cost of the ammonium sulphate is  
19 thus in part compensated by a better utilisation of the stillage. Few beet  
20 molasses distilleries go as far as to crystallise out the potassium sulphate. On  
21 the other hand, several distilleries do extract crystals from concentrated  
22 stillage, but only to avoid deposits in the storage reservoir.

### 23 24 *Composting*

25 To integrate stillage into compost it is necessary to have solid matter available.  
26 In the case of wine distilleries, the stillage can be mixed with the grape. In  
27 the case of cane alcohol industry, Liu *et al.* (1995) have shown the utility of  
28 compost composed of stillage and bagasse. A technique of inoculating the  
29 stillage has been developed by Alfa-Laval. The sugar-distillery Yestwant in  
30 the Maharashtra in India mixes the cooled stillage with a foam (floculate  
31 resulting from the purification by sulphitation and filtration in the presence  
32 of bacilli) then inoculates the mixture with bacteria and fungi. It is then  
33 spread over a large surface in the sun to dry. The compost is regularly (once  
34 a week) turned over for aeration with a specially designed machine with a  
35 large capacity (> 1000 m<sup>3</sup>/h). The total duration of composting is 11 weeks.  
36 All the stillage is treated before the rainy season. The compost is a much  
37 sought fertiliser. More often, press mud generated from the sugar mill is  
38 simply mixed with distillery effluent (Nagaraj and Kumar, 2006).

39 In the beet industry, according to Madejon *et al.* (2001), direct application  
40 of concentrated stillage on agricultural land may lead to economical and  
41 environmental problems due to high salinity, low P content and high density.  
42 Then composting of stillage with other solid agricultural residues would be  
43 used to overcome these disadvantages by producing compost that is easily  
44 handed, 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 10<sup>9</sup> 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

1 treatment systems produce biological sludge at a low rate is a key factor, in  
 2 addition to their ability to reduce chemical and biological oxygen demand  
 3 (COD, BOD) without energy consumption. The biological treatment of brewery  
 4 effluents is not really complex and the anaerobic processes used and related  
 5 performance aspects are well understood and described in the literature.  
 6 Compact wastewater treatment systems able to produce high-quality effluents  
 7 and to handle nutrient removal are of major industrial interest. However,  
 8 wastewater from breweries is highly variable (Table 35.10); depending on  
 9 the step of the brewing process, pH, temperature, quantity, organic load,  
 10 solids contents, cleaning and disinfecting agents can all change. Volumetric  
 11 conversion capacities of the biological reactor are defined by (i) the biomass  
 12 conversion capacity (bacterial kinetic parameters, physicochemical  
 13 environment), (ii) mass transport (hydrodynamics, reactor geometry) and  
 14 (iii) biomass concentration (retention of biomass, settler system, viscosity).

15 Considering the heavy organic load of distillery wastewater, anaerobic  
 16 digestion has long been considered to be ideal technique, combining the  
 17 advantages of being both a primary treatment for depolluting the organic  
 18 load and energy-producing due to the large production of biogas reusable for  
 19 distillation (Bories and Maugenet, 1978; Chabas *et al.*, 1990). Now used  
 20 principally for the treatment of industrial liquid effluents, it has been the  
 21 subject of numerous studies in France since the 1980s. Its efficiency for  
 22 treating carbon pollution has aroused particular interest in the agrifood and  
 23 pulp industries (Perillat and Boulenger, 2000). Approximately 50 units operate  
 24 in France in the agrifood industry at this time; they are most prevalent in  
 25 brewing and malting industries, wine distilleries and wineries. However, the  
 26  
 27

28 **Table 35.10** Effluent properties in the brewing industry  
 29 (Pesta and Meyer-Pittroff, 2005; Totzke, 2005)

30	Flow	1.5–7.5 L/L beer
31	Total BOD	3–6 g/L beer
32		0.7–2 (max 3.3) g/L
33	Total COD	3.7–22.4 g/L beer
34		0.9–4 (max 5.5) g/L
35	COD/BOD	1.5–1.8
36	Total nitrogen	25–85 mg/L
37	Total phosphate	5–35 mg/L
38	Soluble COD	4.7 g/L
39	Soluble BOD	3.0 g/L
40	Total SS	0.74–2.92 g/L beer
41		0.6 g/L
42	FOG	0.05 g/L
43	Settling sediment	0.15–1.5 g/L

44 BOD = biological oxygen demand  
 45 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 microorganisms 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, (iii) a phase of conversion of fatty acids or alcohols into acetic and hydrogen (acetogenesis) using acetogenic bacteria (syntrophic bacteria or OHPA – obligate hydrogen-producing acetogenic – bacteria, homoacetogenic bacteria, sulphate-reducing bacteria), (iii) a final stage of methane production exclusively from acetate, formate, H<sub>2</sub> and CO<sub>2</sub> 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 (CH<sub>4</sub>, CO<sub>2</sub>). Fermentation residues (1–5 % of carbon) require an advanced effluent treatment by aeration. The aerobic step generates 1–3 % of CO<sub>2</sub>, 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 (CH<sub>4</sub>, 50–85 % v/v), carbon dioxide (CO<sub>2</sub>, 15–50 % v/v) and trace gases (H<sub>2</sub>O, H<sub>2</sub>S or H<sub>2</sub>). Before utilisation, water and hydrogen sulphide need to be removed. The calorific value of biogas depends on its CH<sub>4</sub> content and varies between 4 and 7.5 kWh/m<sup>3</sup>.

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

1 concentration (Bories, 1981). Glycerol, a major compound of stillage, is  
2 easily fermented into propionic acid by propionic bacteria or butyric acid  
3 and 1,3-propanediol by clostridia (Claret, 1992; Barbirato *et al.*, 1997; Colin  
4 *et al.*, 2001). Since methanogenesis is the limiting stage of the anaerobic  
5 digestion of stillage, the equilibrium of the fermentation must be controlled  
6 to avoid the accumulation of VFA and the acidification of the digester, which  
7 would inhibit methanogenesis. The separation of the acidogenic and  
8 methanogenic phases in two distinct digesters is a practice proposed to control  
9 these phenomena (Ghosh and Klass, 1978; Massey and Pohland, 1978; Bories,  
10 1980). The high sulphate contents (the case for molasses stillage and wine  
11 stillage treated with calcium sulphate) pose a problem (Karhadkar *et al.*,  
12 1987). The sulphate-reducing bacteria form sulphide with a high concentration  
13 both in the biogas (3–6 % in H<sub>2</sub>S) and in the liquid phase where the free,  
14 non-dissociated (H<sub>2</sub>S) form inhibits anaerobic bacteria at concentrations of  
15 about 200 mg S<sup>-2</sup>/L. The cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, NH<sub>4</sub><sup>+</sup>) are inhibitors  
16 at high concentrations as is sometimes the case in molasses stillage. Often  
17 considered as difficult to biodegrade, and even reported to act as inhibitors  
18 in biodegradation processes, phenolic compounds, in their monomeric forms,  
19 can be degraded by the microflora of anaerobic digestion (Bories and Allaux,  
20 1989a,b). For the complex polyphenolic forms, adsorption by the micro-  
21 organisms in the purification systems leads to a partial elimination. Wine  
22 stillage has a high degradation rate (% of eliminated COD) by anaerobic  
23 treatment (85–90 %), as does cane juice stillage (90–98 %), which is not the  
24 case for molasses stillage that is being studied in many countries in order to  
25 optimise fermentation conditions (Decloux and Bories, 2002a).

### 27 *Biodigestion technology*

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

### 33 Treatment in anaerobic lagoons

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

### 39 Treatment in mixed digesters

40 Treatment in mixed digesters at a controlled temperature was developed in  
41 wine distilleries in Italy in the 1970s and is particularly well adapted to  
42 treating stillage with high suspended matter content (lees stillage). The  
43 residence times vary from 15 to 25 days and the volume load is from 1–2 kg  
44 COD m<sup>-3</sup>d<sup>-1</sup>.

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<sup>-3</sup>d<sup>-1</sup>, 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

Plant	REVICO (Cognac)	UCVA (Coutras)	ECLIPSE (Limoux)
Waste water	White wine stillage (pre-concentrated and detartrated) and lee stillage	Lee, pomace and wine stillages	Winery effluents/ stillages
Flow (m <sup>3</sup> /d)	2000	500	500
Organic load (kg COD/d)	80 000	35 000	
Digester process	Mixed tanks: 19 500 m <sup>3</sup> (6000 + 5500 + 4500 + 3500 m <sup>3</sup> )	Mixed tanks (3000 + 6000 m <sup>3</sup> )	UASB (700 m <sup>3</sup> )
Secondary treatment	Aerated lagoon (10 000 m <sup>3</sup> )	Thermal evaporation (evaporator 15 T/h)	Activated sludges (1600 m <sup>3</sup> )
Biogas production (m <sup>3</sup> /d)	24 000	12 000	
Biogas use	Steam production for distillation and preconcentration of stillage Heat water (1.2 MW) for temperature control of digester and greenhouse	Steam production (30 % of distillery and treatments needs) Mixed boiler biogas/natural gas	Boiler, heating effluent/digester

COD = chemical oxygen demand  
 UASB = upflow anaerobic sludge blanket

(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 m<sup>3</sup> 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 m<sup>3</sup>) at the current time and its capacity is 300 000 m<sup>3</sup> of wine stillage/year (2000 m<sup>3</sup>/d) (Table 35.12). The biogas (800 m<sup>3</sup>/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 Sucrierie) distillery in Guadeloupe, with a fixed biomass (PVC rings) and a volume of 1700 m<sup>3</sup> was the first French plant to use anaerobic treatment of cane molasses stillage in 1986. A second anaerobic filter (6000 m<sup>3</sup>) 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<sup>-3</sup> d<sup>-1</sup>. 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 35.12** World-wide installations of anaerobic system in the brewing industry.

Technology	Number	Area	Number
Lagoon	3	Africa	18
Contact	3	Asia	137
Filter	6	Europe	108
Hybrid	5	America	142
UASB	265		
EFB	123		
Total	405	Total	405

EFB = expanded fluidised bed

UASB = upflow anaerobic sludge bed

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 (Ettheridge and Leroff, 1994; Kormelinck, 2003; Nordenskjold 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 CH<sub>4</sub>/kg degraded COD. The biogas produced has a CH<sub>4</sub> content of 60–65 %. This gas (65 % methane) has a net heating value of 1450 kJ/m<sup>3</sup> 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 m<sup>3</sup> CH<sub>4</sub>/m<sup>3</sup> 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

1 irrigation of agricultural crops, can provide 245 000 t of potassium, 12 500 t  
2 of nitrogen and 2100 t of phosphorus annually. However, technical,  
3 environmental and economic problems still arise when stillage is treated by  
4 anaerobic digestion (Cortez *et al.*, 1999) and it requires further treatment in  
5 order for the effluent produced, particularly in the case of molasses stillage,  
6 to comply with discharge standards.

### 9 **35.3.4 Aerobic treatment**

10 In the cases of breweries, aerobic treatment combined with anaerobic sludge  
11 stabilisation could be considered for dilute effluents. Biological wastewater  
12 treatment in municipal sewage plants is usually an aerobic process, then the  
13 sludge surplus can be stabilised by anaerobic digestion. The carbon mass  
14 balance indicates that 100 % of organic carbon in the wastewater influent is  
15 lost: 50 % through CO<sub>2</sub> production in the aerobic step and 50 % through  
16 biomass and sewage production. Sludge is stabilised by anaerobic digestion  
17 and generates 28–36 % of biogas (CH<sub>4</sub>, CO<sub>2</sub>) and 13–21 % of residual  
18 sludge (Pesta and Meyer-Pittroff, 2005). Only 1 % of organic carbon ends up  
19 in the effluent.

20 Sludge production and energy costs are the limiting factors in relation to  
21 the aerobic treatment of concentrated wastewaters, such as those produced  
22 by distilleries. The aerobic biological purification parameters of stillage from  
23 wine distilleries were studied by Bories and Maugenet (1978), who also  
24 studied the performance and cost of treatment on an industrial scale. As a  
25 result of the heavy organic load, the deficiency in nutrients, the seasonal  
26 nature and the variability of winery wastewater production, the design of  
27 aerobic wastewater treatment processes has either tended towards extensive  
28 approaches such as one- or two-stage aerated lagooning (Canler *et al.*, 1998;  
29 Racault *et al.*, 1998), aerated storage (Rochard *et al.*, 1998) with different  
30 levels of discharge, and mixed treatment with domestic waste (Badie, 1998),  
31 and activated sludge (Bolzonella *et al.*, 2006) or towards intensive systems  
32 such as two-stage activated sludge (Racault *et al.*, 1998), two-stage bacterial  
33 filters (Andreottola *et al.*, 2005), or very heavy-load mono-stage pre-treatment  
34 (Ehlinger *et al.*, 1994). The study of microbial population dynamics during  
35 treatment of synthetic winery wastewater with a rotating biological contactor  
36 illustrates the involvement of yeasts and bacteria in the biofilm and the role  
37 of yeasts in the degradation of the COD (Malandra *et al.*, 2003) that had also  
38 been observed by Ehlinger *et al.* (1994) and Lefebvre (1998). Lalane *et al.*  
39 (1996) and Rols (1996) studied the biological treatment of rum distillery  
40 stillage by aerobic digestion, in particular with the system of aeration by  
41 hydro-ejectors. It is possible to reduce 90 % of the soluble COD and more  
42 than 95 % of the BOD in only one stage, provided that the pH of the stillage  
43 is neutralised, that it is cooled to 30 °C, and that the nutritive balance (nitrogen  
44 and phosphorus) is guaranteed, followed by a second stage to reduce the  
45 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 O<sub>2</sub>/L) obtained a high output (97 % COD) and a low residual COD (< 100 mg O<sub>2</sub>/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 caustic (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<sup>-3</sup> h<sup>-1</sup>.

### 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).

#### *Degrading 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 micro-organisms (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; Sirianuntapiboon *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

1 anaerobic treatment, in order to reduce the phenol concentration from 60 to  
2 70 %. Research on the selection of strains capable of destroying these pigments  
3 continues (Fitz-Gibbon *et al.*, 1998; Nakajima-Kambe *et al.*, 1999; Patil *et*  
4 *al.*, 2001) as well as studies aimed at understanding the degradation mechanism  
5 (Miyata *et al.*, 1998). The aerobic degradation of beet molasses stillage with  
6 *Penicillium* sp strains and *Aspergillus niger*, before anaerobic digestion,  
7 resulted in a degree of higher COD removal and increased the decolourisation  
8 of the wastewater (Jiménez *et al.*, 2003). Finally, Shibu *et al.* (1999) showed  
9 that the bacteria *Lactobacillus casei* reduces the colouring by 54–57 % and  
10 results in a simultaneous production of lactic acid in batch fermentation over  
11 five days at a rate of 113 mg/L of lactic acid with immobilised cells. Lactic  
12 acid has a market in India, since 70 % is imported from other countries such  
13 as Japan.

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

#### 27 *Decolouration by ozonation and/or oxidative treatment*

28 Dhamankar *et al.* (1993) studied ozonation and showed that it is more effective  
29 when sodium hydroxide is added to modify the pH (decolourising of 26 %, 68 %  
30 and 92 % at a pH of 4.3, 7 and 10, respectively) in the presence of  
31 1.2 % H<sub>2</sub>O<sub>2</sub>. Gehringer *et al.* (1997) studied different modes of ozonation  
32 (alone or combined with  $\gamma$  rays). Beltrán *et al.* (1999) also showed that  
33 ozonation of wine stillage improves its biodegradability and makes its  
34 subsequent decolouration more complete. However, degradation levels are  
35 highly dependent on the pH of the wastewater because pH affects the double  
36 action of ozone on the organic matter, that may be a direct or an indirect (free  
37 radical) oxidation pathway (Beltrán *et al.*, 2001). The degradation of phenolic  
38 compounds is not necessarily complete, but it contributes to the bleaching of  
39 the effluents and improves the biodegradability of the degradation products  
40 (Bijan and Mosheni, 2005). The inclusion of an ozonation step prior to  
41 treatment in an anaerobic sequencing batch reactor was found to be useful  
42 for the treatment of cherry stillage, since more than 75 % of the polyphenols  
43 could be removed by ozone and an improvement in the parameters of the  
44 anaerobic treatment (COD removal rate, higher organic load rate (OLR),  
45

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 ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) and ferric chloride ( $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ) 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  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ ) 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:  $\text{H}_2\text{O}_2$  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/m<sup>3</sup>.

#### *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

1 recommended level for discharge into a river. Coupling the anaerobic digestion  
2 of stillage with a secondary treatment by thermal evaporation of digested  
3 stillage provides an interesting solution to this problem. The SIS distillery in  
4 Guadeloupe initiated treatment by thermal evaporation of cane molasses  
5 stillage produced by anaerobic digestion in 2004. The condensate resulting  
6 from the evaporation presents a very high level of purification in terms of  
7 COD, colour, mineral content and suspended matter. The concentrate from  
8 digested stillage can be highly concentrated because of its low organic load,  
9 and is used for agronomic purposes (spreading, composting). The thermal  
10 concentration of effluent from anaerobic digestion of wine stillage has been  
11 recently achieved at the UCVA distillery (Coutras, France) for secondary  
12 treatment in order to obtain high-quality final wastewater for discharge into  
13 a river. The condensate from the evaporator (15 t/h, multiple effects) that  
14 treats digested stillage (pomace, wine, lees) has a low COD (< 300 mg/L)  
15 and is colourless, demineralised and has no suspended matter or micro-  
16 organisms. The energy for the thermal evaporation is provided by steam  
17 generators using biogas produced at the anaerobic stage.

### 20 35.3.6 Incineration

21 In the brewing process, spent grain is a by-product (0.18–0.20 kg/L beer)  
22 with a high water content (70–80 % w/w). The constraints involved in using  
23 it as ruminant cattle feed or landfill material were described on pp. 000–000  
24 Brau Union Atria and Loeben university (Kepplinger and Zanker, 2001)  
25 developed a process associating the combination of mechanical pre-drying  
26 and combustion in a biomass vessel. The wet spent grains (20–30 % w/w  
27 DM) are stored in a butter vessel to compensate for fluctuating production  
28 and then press-filtered up to 42 % w/w DM. The dried matter is stable and  
29 can be stored in a tank before combustion in a biomass vessel. The wastewater  
30 could be processed by anaerobic treatment. In the process proposed by Heineken  
31 Technical Service and 2B Biorefineries (Bruijn *et al.*, 2001; Schwencke,  
32 2006), the fibres extracted from spent grain could be sent to a furnace, where  
33 the heat of combustion from the fibre product is used to generate steam. In  
34 both processes, the heat of combustion of the spent grains is similar to that  
35 of lignite coal or dry wood, i.e. approximately 21 MJ/kg. The exact heat of  
36 combustion depends on the water content because of the relatively high  
37 vaporisation energy of water:  $H = 21\,000 \cdot (1 - w) - 2250 \cdot w$ . Above 40 %  
38 w/w DM, the combustion properties improve considerably. Combustion also  
39 produces ash, which is another valuable product. Its high phosphorus pentoxide  
40 ( $P_2O_5$ ) content is of great value as a fertiliser additive and can be added to  
41 standard NPK-fertilisers. Wet cleaning of the flue gas is normally not necessary,  
42 the discharge of exhaust gases ( $NO_x$ ,  $SO_2$ ,  $CO_2$ ) that are emitted from the  
43 combustion of spent grains or fibres is below the standards set by the European  
44 governments.

45 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 liquors 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 ( $K_2O$ ) and 2–3 % phosphate ( $P_2O_5$ ), 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

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**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)

	Brewing industry			Wine industry		Distilling industry		
	Spent grain (mash)	Yeast surplus (tank bottoms)	Kieselguhr sludge	Winery effluent	Stillage	Sugar beet	Sugar cane	Wheat corn
<b>Treatment of effluent:</b>				A-PP		A-PP	A-PP	
<b>alcohol/sugar</b>								
<b>Specific molecule extraction:</b>								
Glycerol, betaine, organic acids						A-PP/I-ND	A-PP/I-ND	
Tartaric acid				A-L / A-PP	I-CP			
Colouring and phenolic compounds				A-L	I-CP			
Heavy metals		A-L						
<b>Bioproduction of molecules</b>								
Yeast, enzyme, fungi, algae	A-L	A-L			A-L	A-L/A-PP	A-L/A-PP	
Organic acids	A-L			A-L	A-L	A-L		
Complex organic compounds	A-L				A-L/I-ND			A-L
<b>Regenerable filter-aids</b>								
<b>Membrane process:</b>			A-L					
ED: Salt extraction						A-PP	A-PP	
OI: Water condensate re-use				A-L / A-PP	A-PP	A-PP and I-ND	A-PP and I-ND	
UF/MF: Loss reduction	A-L	I-CP				A-PP	A-PP	
UF/MF: Technical alternative	A-L		I-CP	A-L				

ED =  
OI =  
mF = micro filtration  
UF = ultra filtration

and taken into consideration when assessing any of these alternative technologies.

### 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/m<sup>3</sup>). 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 electro dialysis after a prefiltration on a 0.2 µm ceramic

1 membrane. However, it is chromatography techniques which have been  
2 developed on the industrial scale, particularly with regard to molasses.  
3 Numerous authors have published on the subject with patents pending (Kampen,  
4 1990; Kampen and Saska, 1999a, b) for the University of Louisiana. Most of  
5 the patents involve stillage concentration phases, potassium removal by  
6 crystallisation, clarification and one or several chromatography techniques  
7 depending on the number of compounds to separate.

#### 8 9 Extraction of tartaric acid

10 Tartaric acid is present in all wine distillery effluents (Mourgues *et al.*, 1996)  
11 and represents from 4–30 % of the pollutant load. Extracting tartaric acid  
12 from lees stillage by precipitation in the form of calcium tartrate salt is a  
13 widespread practice in wine distilleries (Mourgues and Maugenet, 1975;  
14 Mourgues *et al.*, 1993). Moreover, the recovery of tartaric acid is essential  
15 before concentrating stillage. To precipitate tartaric calcium salt, the stillage  
16 is first made neutral with calcium carbonate milk or quick lime to pH 4.5–  
17 5, then calcium sulphate ( $\text{CaSO}_4$ ) is added to have a full precipitation and to  
18 avoid the potassium tartrate ( $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ ) formed during the neutralisation  
19 process from remaining in solution. There are two main types of procedure,  
20 which have been described by Mourgues (1986). Distilleries recover 4–6 kg  
21 of tartaric calcium salt per hL of lees received. The products obtained contain  
22 48–53 % of tartaric acid. Particular attention must be paid to the impact of  
23 tartaric acid extraction on subsequent treatments, in particular biodigestion  
24 where the sulphate can indirectly inhibit fermentation. It is therefore preferable  
25 to reduce the tartaric acid extraction rate but to avoid adding sulphate ions if  
26 biodigestion takes place. However, in order to maintain optimal recovery of  
27 tartaric calcium salt and to prevent the formation of soluble tartaric potassium  
28 salt, the sulphate (a mixture of lime and calcium sulphate) is replaced by  
29 nitrate (lime and nitric acid). Moreover, this process change is advantageous  
30 for the treatment of lees stillage by natural evaporation, since nitrate reduces  
31 the production of odorous compounds (Bories, 2006). Other procedures for  
32 extracting tartaric acid have been studied, as explained below.

33 Liquid–liquid extraction has been envisaged in the laboratory using wine  
34 effluent and synthetic solutions of tartaric, malic or lactic acids with the  
35 solvents tributyl-phosphate-n-dodecane and triisocytamine-octanol-1  
36 (Smagghe, 1991; Malmay *et al.*, 1994; Marinova *et al.*, 2004). It has the  
37 advantage of eliminating the intermediate precipitation in the form of tartaric  
38 calcium salt.

#### 39 40 Extraction of colouring anthocyanic matter and 41 phenolic compounds

42 Mourgues *et al.* (1996) mentioned the separation of colouring matter from  
43 grape pomace before distillation, either by extraction by diffusion in the  
44 presence of  $\text{SO}_2$  or by adsorbing resins. The industrial production of  
45 concentrated anthocyanic extracts (E163) has rapidly expanded these past

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; Fillaudeau *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

1 to be reduced. Various systems are in use and it has been shown that ceramic  
2 (0.4–0.8  $\mu\text{m}$ , Schlenker, 1998) or polysulfone (0.6  $\mu\text{m}$ , Wenten *et al.*, 1994)  
3 membranes concentrate solids from 12–15 % to 20–22 %. The payback is  
4 less than two years regarding the recovery of sterile beer from yeast beer  
5 with 0.4–0.8  $\mu\text{m}$  pore diameter multichannel ceramic membranes installed  
6 in 1 MHL capacity breweries. Bock and Oechsle (1999) explained that brewing  
7 plants are running with ceramic membranes made of  $\alpha$ -aluminium oxide  
8 (multichannel membrane: 19 channels, length: 1020 mm, mean pore diameter:  
9 0.80  $\mu\text{m}$ ). Surplus yeast can be processed with about 17–20  $\text{L h}^{-1} \text{m}^{-2}$ , up to  
10 a concentration of 20 % w/w (transmembrane pressure up to 3 bar) and three  
11 process options exist: batch, semi-batch and continuous. This material can  
12 be cleaned in place since it is resistant to caustic, acid and oxidising sterilants  
13 even at high temperature (above 90° C).

14 Snyder and Haughney (1999) and Methner *et al.* (2004) described a new  
15 system called VMF (vibrating membrane filtration) produced by PallSep™  
16 (Pall Corporation, USA). The system differs from traditional cross-flow  
17 filtration systems in that the shear at the membrane surface is generated  
18 mechanically by vibrational energy and not from high cross-flow rates. VMF  
19 enables uncoupling of pressure differential from cross-flow velocity, with a  
20 reduced installed pump capacity, a minimum energy input, reduced mechanical  
21 and thermal stressing of yeast cells and a compact design of filter module  
22 operating without backwashing. The system operates with a transmembrane  
23 pressure (TMP) of 500–800 mbar, with 0.45  $\mu\text{m}$  polytetrafluoroethylene (PTFE)  
24 membranes, under an oscillation of around 50 Hz and amplitude of 20 mm  
25 at the outer rim (diameter 800 mm). Recovery of beer from surplus yeast can  
26 achieve an average flux of 18–22  $\text{L h}^{-1} \text{m}^{-2}$  with an industrial module of  
27 40  $\text{m}^2$  (energy input: 6 Wh/L) with solids concentration of 10.5–18 % w/w.  
28

### 29 *Process modification with ultra and microfiltration*

30 In breweries, MF can be utilised as a technological alternative in three  
31 applications: mash separation, clarification of rough beer, cold-sterilisation  
32 of clarified beer before conditioning. Scientific studies and industrial  
33 applications essentially concern the clarification of rough beer and sterile  
34 filtration of clarified beer. Modrok *et al.* (2006) reported that the filtration  
35 technologies in breweries use diatomaceous earth (91 %), trap filters (68 %),  
36 sheet and fine filters to reduce the level of micro-organisms (32 %) and  
37 sterile filtration with membranes (8 %).  
38

### 39 *Cold-sterilisation of clarified beer*

40 The clarification of rough beer is usually followed by heat treatment so as to  
41 ensure its microbiological stability and conservation. Currently, heat treatment  
42 is mainly performed by flash pasteurisation (72–74 °C during 15–30 s with  
43 a plate heat exchanger or at 60 °C in a tunnel pasteuriser) before conditioning.  
44 Conventional heat treatment requires water loops to heat and cool the product  
45 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 m<sup>2</sup> 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–

1 500 L h<sup>-1</sup> m<sup>-2</sup>). Since 1995, a lot of reports have mentioned the economic  
2 and scientific stakes of the clarification of rough beer. Recent scientific and  
3 industrial studies (e.g. Fillaudeau *et al.*, 2007) have dealt with (i) fouling  
4 mechanisms, (ii) the relationship between quantitative and qualitative  
5 performance, (iii) the development of alternative membrane filtration such  
6 as membrane structure and dynamic filtration and (iv) industrial applications.

7 Since 2000, the first industrial plants have started to run with three membrane  
8 systems proposed by Norit Membrane Technology/Heineken Technical Service  
9 (Schuurman *et al.*, 2005a,b), Alfa-Laval AB/Sartorius AG (Modrok *et al.*,  
10 2004, 2006), and Pall Food & Beverage/Westfalia Food Tech (Denniger and  
11 Gaub, 2004; Höflinger and Graf, 2006; Rasmussen *et al.*, 2006). Norit/  
12 Heineken (Schuurman *et al.*, 2005a,b) reported several industrial processes  
13 running with a MF unit for rough beer clarification with a capacity above 10  
14 000 L/h. The filtration unit contains between 10 and 24 hollow fibre modules  
15 X-Flow R-100 (pore size: max 0.50 µm, length: 1 m, inner diameter: 1.5 mm,  
16 filter area: 9.3 m<sup>2</sup>, material: polyethersulfone, PES). The key to the process  
17 is based on a specific cleaning procedure patented by Heineken and Norit  
18 Membrane Technology. It combines a caustic step, an acidic step and a  
19 strong oxidative step (two hours in duration), which is successful in achieving  
20 a run time between seven and 20 hours for about 120 runs. Filtration is  
21 accomplished at 0 °C, 1.5–2 m/s flow velocity and up to 1.6 bar transmembrane  
22 pressure. During filtration, 10 minute periods of back-flushing are applied  
23 every two hours to remove the reversible fouling that has built up. The flux  
24 is maintained at 100 L h<sup>-1</sup> m<sup>-2</sup> and clarified beer fulfils the European Brewery  
25 Convention (EBC) standard in terms of turbidity (close to 0.6 EBC units),  
26 bitterness, total extract, colour, and protein content. In 2005, the cost of  
27 membrane filtration for bright beer was estimated to be between 0.20 and  
28 0.40 €/hL, i.e. identical to Kieselguhr filtration 0.20–0.40 €/hL. By 2007,  
29 the total cost of membrane filtration is expected to be 20–30 % cheaper than  
30 Kieselguhr filtration (Schuurman *et al.*, 2003).

31 In the Alfa-Laval/Sartorius cross-flow filtration process (Modrok *et al.*,  
32 2004, 2006), the rough beer goes from the maturation tank to a high-  
33 performance centrifuge, which is directly followed by the cross-flow system.  
34 From there the beer goes to a bright beer tank and then on to sterile cartridge  
35 filtration before conditioning. The filtration unit contains up to six holding  
36 devices with up to 72 filter Sartocon<sup>®</sup> cassettes (20 membranes, dimension:  
37 175 × 210 mm, small channel spacers: 120 µm, filter area: 0.7 m<sup>2</sup>, material:  
38 PES). Filtration steps are accomplished with a combination of normal filtration,  
39 feed reverse to loosen the clogging and back-flushing with the product. An  
40 intermediate cleaning (duration: 15 min) is done every three to five hours  
41 and maintains high and constant flux rates (80–120 L m<sup>-2</sup> h<sup>-1</sup>). The costs are  
42 estimated at 0.46 €/hL and can roughly be divided into 22 % for the running  
43 costs, 48 % for the membranes, and 30 % for the system.

44 PROFi<sup>®</sup> technology is a joint project of Westfalia Food Tec and Pall Food  
45 & Beverage (Denniger and Gaub, 2004; Höflinger and Graf, 2006; Rasmussen

*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/hL.

#### 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

1 of a mixture of synthetic polymer or special cellulose fibres and 44–88 µm  
2 microbeads coated with a polymer which improves surface properties. The  
3 mixture combines the mechanical properties of the microbeads  
4 (incompressibility, low porosity) with the qualities of the fibres. Filtration  
5 performance is reported to be similar to conventional Kieselguhr filters.  
6

#### 7 *Bioproduction of added-value molecules*

8 Industrial and agricultural by-products and waste can often be used as substrates  
9 in fermentation processes. Their complex composition, containing carbon,  
10 nitrogen and mineral supplies, is accurate for the growth of micro-organisms.  
11 The aim of the bioprocess may be the production of biomass, or its metabolic  
12 products (i.e. organic acids), flavour and aroma compounds or enzymes. The  
13 carbon components of stillage can be considered as substrates for the production  
14 of molecules of interest to industry via biotechnological pathways. Tibelius  
15 and Trenholm (1996) have published a whole report on recycling the co-  
16 products from cereal fermentation and Decloux and Bories (2001) a literature  
17 survey on uses for stillage from molasses fermentation. They mentioned  
18 several examples of bioproduction of added value molecules that may be  
19 grouped in three categories  
20

#### 21 *Yeast, enzymes and algae*

22 The production of yeast in aerated medium is an efficient means for reducing  
23 the pollutant load of stillage originating from alcohol production either from  
24 cane or beet. This technique, developed on an industrial scale, however,  
25 consumes a lot of energy to ensure the oxygen supply and the cooling of the  
26 fermenter. It is possible to produce 16 kg of Torula yeast (*Candida utilis*) per  
27 tonne of stillage and to consume non-fermentable sugars, hence increasing  
28 the ratio which can be recycled to fermentation and, similarly, to decrease  
29 the quantity of water to be evaporated during concentration. The residual  
30 BOD is reduced to 10–15 g/kg (Maiorella *et al.*, 1983). According to Lee and  
31 Lee (1996), *Candida utilis* yeasts, generally used for producing SCP (single  
32 cell proteins) are not very well adapted to stillage. After screening tests, they  
33 selected a thermoresistant strain *Candida rugosa*. Shojaosadati *et al.* (1999)  
34 studied the culture of the *Hansenula* yeast strain in continuous culture on  
35 beet stillage and showed that it is possible to reduce the COD by 31 % and  
36 to produce 3–5 g/L of biomass with a protein content of 39.6 % without any  
37 addition to the culture medium. Other compounds such as glycerol, acetic  
38 acid and the rest of the ethanol can also be consumed (Maiorella *et al.*,  
39 1983).

40 The production of enzymes is also under study. In breweries, Zvauya and  
41 Zvidzai (1996) found that an aerobic and spore forming *Bacillus* sp. produces  
42 hydrolytic extracellular enzymes when cultured on opaque brewery wastewater  
43 supplemented with defatted soya, spent yeast and malt flour. The strain  
44 produced endo-1-4- $\alpha$ -glucanase, amylase, polygalacturonase, xylanase and  
45 protease. Hatvani and Mecs (2001) investigated the mycelial growth (biomass

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 1970 s 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/cm<sup>2</sup>, 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<sup>-1</sup> h<sup>-1</sup> and a DHA

1 concentration from 34–45 g/L (Bories *et al.*, 1991; Bories and Claret, 1992;  
2 Claret, 1992; Claret *et al.*, 1993).

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

7 The Revico company has applied for a patent to produce aromatic  
8 compounds (Ambid *et al.*, 1998; de Billerbeck *et al.*, 1999). It involves  
9 aerobic cultivation of a *Sporobolomyces odorus* type bacterium capable of  
10 producing  $\gamma$ -decalactone. The medium is constituted of wine stillage  
11 supplemented with a ricinoleic-type precursor. The aromatic compound is  
12 separated from the aqueous fermentation medium by adding a coconut oil  
13 type lipid phase which is solid at room temperature and which absorbs the  
14 aroma. After separation, the lipid phase is dissolved in 96 % ethanol (1v/  
15 10v) then separated out by crystallisation on cooling the alcohol mixture to  
16  $-20^{\circ}\text{C}$ . Simple filtration then makes it possible to recover the alcohol phase  
17 containing the aromatic compound.

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

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

31 Bioplastic production by micro-organisms was investigated by Yu *et al.*  
32 (1998) with malt waste from a brewery. Specific polymer production yield  
33 by *Alcaligenes latus* DSM1124 increased up to 70.1 % w polymer/w cell  
34 with a final biomass and polymer concentration of 32.36 g/L cell dry wt and  
35 22.68 g/L cell dry wt. In this fermentation, biopolymer accumulation is  
36 controlled by nitrogen limitation.

### 37 *Extraction of specific compounds*

#### 38 Recovery of dissolved molecules and water

39 As the cost of wastewater disposal increases, more emphasis is being placed  
40 upon the recovery and recycling of valuable chemicals contained within the  
41 effluent. As mentioned by Decloux and Bories (2001), a lot of research has  
42 been carried out into the recovery of molecules using MF to NF and reverse  
43 osmosis membranes (Wu *et al.*, 1989; Kim *et al.*, 1997; Nataraj *et al.*, 2006).  
44 Kim *et al.* (1997) proposed a new process for producing alcohol from wheat,  
45

associating a centrifuge separation and a stillage ultrafiltration (UF) 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 contaminant 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).

1 Then concentration up to 70 % solids should be possible without potassium  
2 sulphate crystallisation. Nevertheless, considering the sale cost of concentrated  
3 vinasses as fertiliser, the investment costs still do not allow industrial  
4 application.

#### 5 6 Elimination of heavy metals

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

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

### 37 38 39 40 **35.5 Acknowledgements**

41 Authors gratefully acknowledge Dr Peter Winterton (Université Paul Sabatier,  
42 Toulouse, France) for advice, corrections and improvements to the final  
43 English version of the chapter.  
44  
45

<b>35.6 Nomenclature</b>	1
<i>BAT</i> Best available techniques	2
<i>BFS</i> Beer factory sludge	3
<i>BOD</i> Biochemical oxygen demand	4
<i>CIP</i> Cleaning in place	5
<i>COD</i> Chemical oxygen demand	6
<i>DDGS</i> Dried distillers grains solubles	7
<i>DGS</i> Condensed distillers solubles	8
<i>DM</i> Dry matter	9
<i>EFB</i> Expanded fluidized beds	10
<i>HRT</i> Hydraulic residence time	11
<i>LPA</i> Litres of pure alcohol	12
<i>MBR</i> Membrane bioreactor	13
<i>MF</i> Microfiltration	14
<i>SEC</i> Specific energy consumption	15
<i>NF</i> Nanofiltration	16
<i>RO</i> Reverse osmosis	17
<i>UASB</i> Upflow Anaerobic Sludge Blankets	18
<i>TEP</i> Tonnes equivalent petroleum	19
<i>TDS</i> Total dissolved solid	20
<i>TS</i> Total solid	21
<i>UF</i> Ultrafiltration	22
<i>UV</i> Ultra violet	23
<i>VFA</i> Volatile fatty acids	24
	25
	26
	27
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