



# Anaerobic Methods of Distillery Waste and Wastewater Treatment

Naturgerechte Technologien, Bau- und Wirtschaftsberatung (TBW) GmbH Frankfurt, Germany June 2000

**During** alcohol production, amounts of waste and wastewater are produced. These mav have considerable environmental impact by polluting both water bodies and soil, by causing an adverse climatic effect and odour nuisance. Due to the high concentration of organic matter, both distillery waste and wastewater at the same time do have a great nutrient and energy potential that can be utilised for fertilising or power generating purposes. The water can principally be reused for irrigation purposes.

#### 1 Introduction

Alcohol production through the process of fermentation is an industrial activity implemented almost world-wide. Due to the agricultural origin of the primary matter used, distilleries are usually located in rural areas. Agricultural products like sugar cane, sugar beet, different cereals, grapes etc. are either fermented directly or in the form of sub-products, after being processed in order to condition the sugar contained in the plants for the alcoholic fermentation with yeast.

The distillation (i.e. the separation process) with 2 or 3 columns – the number depending on the required concentration of ethanol – produces a highly polluting residue. For the production of every litre of alcohol, 10 to 30 litres of industrial wastewater, called vinasse, stillage or slops, are generated. Its organic load is high, varying from 20 to 120 g COD (or 2,000-12,000 mg) per litre, the effluent temperature is high (around 90 C), the

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average pH-value is low (3,5 to 6). Table 1 represents a summary of research results on cane molasses, confirming these average values. The named characteristics make the distillery wastewater one of the industrial residues most difficult to treat and dispose off properly.

Table 1: Average values for stillage from cane molasses (Source: [2])

Parameter	Range of Values for Cane Molasses
pН	3.5 – 5.7
Temperature	80 – 105 °C
COD	15 – 176 g/l

The high organic loading is the cause for a great potential for negative climatic impacts and heavy pollution of water and soil if the residues are being disposed of untreated. The large production of fuel ethanol in Brazil for example, has generated severe problems of water pollution. Brazil is producing more than 13 x 10<sup>6</sup> litres of ethanol per year (a typical distillery in Brazil producing about 120,000 l/d), utilising sugar cane juice, molasses or mixtures from both as substrate for the ethanol production.

Different forms of utilisation, treatment and final disposal have been developed to avoid environmentally negative impacts of stillage. Physical and chemical treatment options of the residue have not been very successful until now, whereas the high organic content of the residue make it well suitable for biological treatment, especially for anaerobic fermentation. Therefore, the treatment of distillery wastewater with





anaerobic systems is broadly applied and accepted and more than 40 industrial treatment plants in distilleries are in operation world-wide. Mostly, the so-called UASB (Upflow Anaerobic Sludge Blanket) and the anaerobic filter, in some cases anaerobic contact systems, are applied.

The high organic concentration in the stillage can make anaerobic treatment profitable, particularly due to the primary energy yield in form of methane, combining environmental soundness with economical usefulness due to possible savings in the fuel needs of the distillery.

#### 2 Social aspects

Social impacts associated with the production of alcohol can be considered from two main points of view: a positive one in terms of job creation and a potentially negative one due to the environmental pollution caused by the industrial production process.

The disposal of the high-strength stillage (vinasse) into rivers and streams poses particularly serious risks to the neighbouring population since the sugargrowing regions are usually rural areas with a considerably high population density, in Cuba even the highest in the whole country. This is the result of sugar cane cultivation being labour intensive, especially during the harvest season, which extends during six to eight month a year. Many seasonal workers come from neighbouring regions or countries, other provinces or from suburban sectors and settle down temporarily in villages and camps, in addition to people permanently living downstream in villages and cities close to the rivers. As these foul up with continuous discharge of highly polluted, untreated wastewater. water-quality related illnesses like diarrhoea or viral hepatitis become an ever recurring problem.

Fish, representing a valuable source of protein within the diet of the local and the

temporary population, is being wiped out by the discharge of stillage into surface waterbodies, causing eutrophication and, as a result, lack of oxygen. Foul smells are commonplace near a distillery and downstream of alcohol production sites.

#### 3 Distillery process

The distillation process has three main steps:

**Step 1:** The fermentation of the carbon (sugar) source:

The substrate – e.g. molasses from sugar cane (molasse is the residual syrup from sugar production from which no crystalline sucrose can be obtained by simple means) – is brought into contact with yeast cultures. Under appropriate conditions (pH 4-4.5, 10-20% sugar in the substrate, balanced nutrient content), the enzymes transform the glucose into ethanol within a time span of 20-26 hours. Nutrients and inoculum are added for optimum conditions, sulphuric acid in order to reach the optimum pH. If molasse is used as raw material, it has to be diluted with water or sugar cane juice before fermentation.

**Step 2:** The separation of yeast and alcoholic solution:

After the fermentation process ends by reaching the inhibitory alcohol concentration or the temperature limit (around 40 C), the substrate is usually separated into alcoholic solution and yeast sludge by centrifugation. The recuperation of yeast is important in order to reduce the organic load of the wastewater. The dried yeast can be utilised as animal feed with high protein content.

**Step 3:** The extraction of alcohol by distillation:

The produced alcohol is distilled utilising a counter current of steam. A first distillation column removes the biggest part of the water (and yeast if it was not removed





before) which represents the principal residue of the distillery. A second column concentrates and purifies the ethanol to a content of 60%, a third column (rectification column) – if installed – is designated for the production of ethanol of more than 95%.

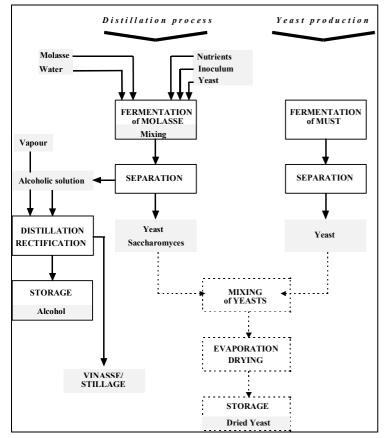


Fig. 1: Fermentation process for alcohol and yeast production

# 4 Origin and composition of distillery waste and wastewater

The liquid wastes from alcohol production can mainly be divided into (see Fig. 2)

- stillage from the
  - separation (centrifuge) and
  - distillation process;
- **cleaning water** from the different plant components, i.e.
  - fermenters.
  - > distillation columns,
  - > floors
- refrigeration water from cooling after distillation.

The **stillage** from the **separation** process contains a large amount of yeast which, as mentioned above, should be dried and utilised as animal feed. This yeast sludge is therefore usually not being treated within a wastewater treatment system.

Speaking of wastewater treatment, the **stillage** from the **distillation** process is the major stream of liquid waste with the highest organic loading. Its composition depends significantly on the raw material used for the fermentation process. All stillages do however contain sugar compounds (glucose, polysaccharides) and alcohol (ethanol, glycerol). Yeast residues will lead to the presence of amino acids and proteins in the wastewater.

Speaking of molasse as substrate for alcohol fermentation, only about 10% of the substrate are retained in the process, 90% will be contained in the wastewater, including caramels developed during sugar production that are causing a darker colour of the wastewater. Because molasse already is a more concentrated liquid, its stillage will also have higher concentrations of salts and organic matter as well as sulphate. Stillage from sugar cane molasse in average contains 93% of water, 5% dry matter and 2% minerals.

Table 2 shows average values for different wastewater parameters in the alcohol industry in Cuba.

Table 2: Average values for composition of stillage from alcohol production from sugar cane molasse in Cuba

Unit	Value
I/I alcohol	17 – 25
mgO <sub>2</sub> /l	70,000
mgO <sub>2</sub> /l	34,000
(none)	4.2 - 4.4
g/l	70 – 95
g/l	2.8 - 3.4
g/l	65 – 75
g/l	7 – 37
mgN/l	800
mgP <sub>2</sub> O <sub>5</sub> /I	200
mgK <sub>2</sub> O/l	3,200
mgSO <sub>2</sub> /l	2,670
mgNa/l	310
	$\begin{tabular}{ll}   I/I & alcohol \\ & mgO_2/I \\ & mgO_2/I \\ & (none) \\ & g/I \\ & g/I \\ & g/I \\ & g/I \\ & mgN/I \\ & mgP_2O_5/I \\ & mgK_2O/I \\ & mgSO_2/I \\ \end{tabular}$

Source: [3]





The **cleaning water** has a comparably low organic loading and can be used to dilute the heavily polluted stillage in order to condition it for anaerobic treatment.

The **refrigeration water** is only exposed to "heat pollution", i.e. a rise in temperature, and is usually not contaminated additionally during the process, as it is led in a closed cycle within the heat exchange system. Therefore, it generally will not be subject to wastewater treatment.

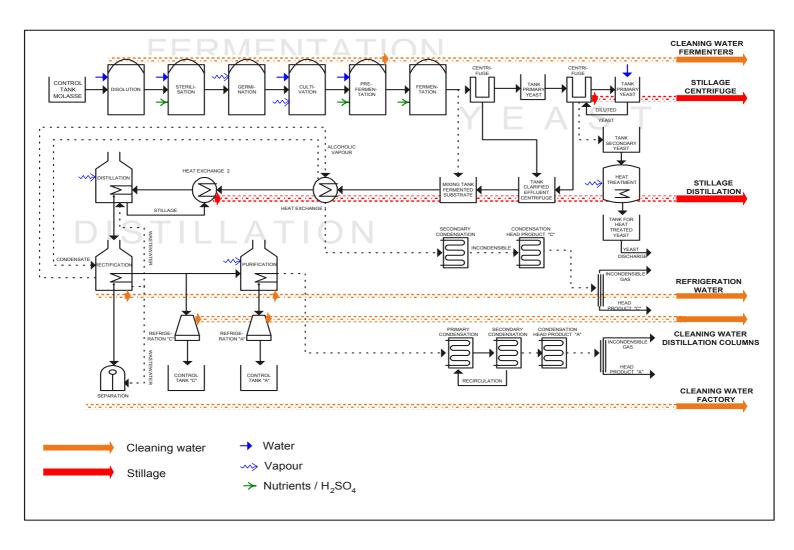


Fig. 2: Alcohol production and wastewater streams (Source: TBW, [3])





# 5 Suitability of distillery wastewater for anaerobic treatment

Due to its high energy content in the form of contained organic material, distillery stillage is generally very well suitable for anaerobic treatment. Owing to its characteristics, a possible COD-removal of 65–75% can be assumed.

Prior to the actual treatment steps, some conditioning measures for the stillage do however have to be taken:

# 5.1 Necessary conditioning of stillage Cooling

The high temperature of the stillage from the distillation process have to be adjusted at least to the maximum values tolerable for the biologic degradation.

#### Flow regulation, mixing

Strong variations in the volumetric flow of the wastewater have to be compensated by storage/equalisation capacities and appropriate dosage/mixing device. The stillage should be kept separately from other wastewater streams (cleaning water) in order to ensure maximum control of its concentration.

#### Conditioning of pH-Value

The usually low pH-value has to be corrected by neutralisation. Further to the addition of alkaline solution, treated substrate, having a pH-value of about 7, can be recirculated for this purpose.

#### Nutrients, alcalinity, suspended solids

The content of macro-/micro-nutrients and suspended solids as well as the alcalinity of the substrate usually range within the tolerable limits for anaerobic bacterial activity. Should the values exceed the limits in individual cases, these need to be adjusted.

#### 5.2 Suitable anaerobic processes

Among a number of different treatment alternatives generally applicable, the following processes are considered to be the most suitable ones for the anaerobic treatment of distillery wastes.

# UASB (Upflow Anaerobic Sludge Blanket) – Reactor

Anaerobic reactor with up-flow regime of the treated wastewater, sludge retention and 3-phase separation for the separation of methane, sludge and treated wastewater. The EGSB – Expanded Granular Sludge Bed Reactor – may be used as alternative: this is in principle a high, lean UASB with high upflow velocity.

#### **Anaerobic Filter (Fixed Bed Reactor)**

Reactor with an inert filter medium with a high specific surface for on-growth of biomass (today mostly plastic material), mostly with external separation and recirculation of sludge.

#### **Anaerobic Contact Process**

Totally mixed reactor with separation and recirculation of sludge to the methanogenic reactor. The realisation of sludge-degassing improves the sludge consistency for separation.

#### 6 Advantages of anaerobic treatment of distillery wastewater

#### 6.1 Environmental aspects

The implementation of anaerobic technology for the treatment of distillery wastewater has several environmental benefits as a considerable contribution to a sustainable development:

### Prevention of pollution of water and soil:

Anaerobic treatment of the wastewater avoids – as any other installed treatment technology would – the discharge of highly polluted wastewater into water, onto surface land and its possible infiltration into the groundwater level.





#### Mitigation of greenhouse gases

- Reduction of methane emissions:
   The emission of large amounts of methane to the atmosphere from uncontrolled disposal and discharge of wastewater are prevented by controlled anaerobic digestion of the organic matter in the wastewater. The methane produced within the digestion process has to be collected and must not be released to the atmosphere.
- Reduction of fossil fuel demand:
   If the methane produced is utilised as a renewable source of energy for power and heat production, the fossil fuel demand of the distillery can be reduced considerably. In contrast to fossil fuels, methane represents a CO<sub>2</sub>-neutral source of energy, i.e. no additional CO<sub>2</sub>-equivalents adding to the greenhouse effect are emitted by its use.

For an exemplary distillery producing an average of 800-1,000 litres of stillage per day (50,000 l/d of alcohol), the reduction of  $CO_2$ -emissions by collection and utilisation of methane is in the order of 10,000 t/a of  $CO_2$ -equivalents, the reduction by substitution of fossil fuels is in the order of 10,000 t/a of  $CO_2$ -equivalents.

An examplary distillery ([3]; plant concept: stillage treatment in ponds transformed into modular anaerobic reactors (digester volume: 10,000 m³) with upflow-regime (UASB) and gas collection) may clarify both above named aspects:

- generation of 12 m³ to 14 m³ of biogas per m³ of stillage;
- avoidance of methane emissions with a CO<sub>2</sub>-equivalent of 60,000 t/a by gas collection and combustion;
- avoidance of further 10,000 t/a of CO<sub>2</sub> emission by substitution of fossil fuels in the production process.

#### 6.2 Socio-economic aspects

#### Hygiene aspects

The hygiene conditions for the population in the neighbourhood of distilleries will be significantly improved, reducing health risks by waterborne diseases and ensuring a better water quality of potential sources for drinking water.

#### **Nutritional aspects**

The necessary ambient conditions for fish can be restored to a certain extent, thus again making available an important source of food for the people.

#### 6.3 Economic aspects

#### Fuel savings

Significant amounts of fossil fuel can be saved in the distillery by generating power and heat from the methane produced during wastewater treatment in cogeneration units and using the generated form of energy within the alcohol production process. One of the most important process steps in this respect is the production of vapour for the distillation process. Produced electric power can also be utilised for process control, steering devices or other electric appliances within the industrial plant.

#### Revenues from energy sales

If the methane is utilised in co-generation units, the high energy content of the wastewater will often lead to a production of surplus energy which can be fed to regional or national power grids. Given appropriate legislation that guarantees the remuneration of power feeding to the grid, this will contribute to the economy of the wastewater treatment plant and may even lead to an economic benefit.

In the above named distillery (chapter 6.1), only 10 % of the total electricity produced by biogas utilisation are used in the alcohol production process, so that in theory the entire energy demand could be substituted – in order to be independent of possible irregularities of biogas and electricity production, 10 % of the energy





demand are still calculated to be provided by fossil fuels.

If the produced energy surplus of more than 15 Mio kWh/a is fed to the public grid at a rate of for example 0.067 US\$/kWh, revenues from energy sales will amount to about 1 Mio US\$.

# 7 Alternative treatment and disposal options for stillage

Further to the anaerobic treatment option, there are several other possibilities for treatment and/or reuse of waste streams from alcohol production. Some examples are listed below.

#### **Incineration after evaporation**

The water content of the stillage is significantly decreased by evaporation, so that the dried substrate – that may also be used as animal feed – is suitable for incineration. The ashes can be utilised as fertiliser or, with the addition of chemicals, for the recuperation of  $K_2SO_4$  and  $CaSO_4$ . The adverse environmental effects of disposal of untreated stillage are avoided, but the high energy demand of the evaporation process that will in most cases be met by using fossil sources of energy should be taken into consideration.

#### **Spray-irrigation**

The stillage is applied directly to agricultural land for fertilising purposes. Due to the high organic loading, this can however lead to undesired accumulation of nutrients in the soil and to infiltration of soluble components to groundwater. In Brazil, where spray irrigation is very popular, high concentrations of nitrate and chlorine were found in the groundwater.

#### Growing of algae and fungus

Owing to its high protein content and nutritional value, the stillage can be used as nutritional substrate for the growing of algae and fungus.

# 8 Example: Coconut Toddy Distillery

The distillery produces alcohol through distillation of coconut toddy. Bottling is carried out at a different section on the same site. The distillery is situated close to a river. It operates during the daytime from 8 a.m. to 5 p.m.

#### 8.1 Industrial process

distillery Coconut toddy has two continuous and three pot distillation columns out of which 3-4 columns normally operate. Two pot distillation columns have a daily capacity of 6,750l/ batch each, the third of 4,050l/ batch. Distillation rates of the two continuous columns are 4,500 l/h and 1,000 l/h. Toddy is received from 1 p.m. to 9 p.m. and stored in the two receiving tanks from which it is transferred to wash backs (collection tanks). There are 27 wash backs of 1,700-2,000 I capacity each. After pumping the toddy into the pot distillation columns and the overhead tank to feed the continuous distillation columns, the wash backs and collection tanks are washed using a hose connected to a pipe. This wash water is pumped to the overhead tank to be fed to the continuous distillation columns. Similarly, the overhead tank wash water is fed to a continuous column. After washing the wash backs, a lime solution is applied on the tank surfaces with a brush. Floor washings in the toddy collection area go to the river through a drain. The amount of toddy distilled per day is in the range of 40 m<sup>3</sup> -60 m<sup>3</sup>. Since the alcohol present in the toddy is about 5-8%, the maximum volume of effluent generated in the distillery per day can be assumed to be 60 m<sup>3</sup>. Bottle washing is also carried out using a bottle washer with a capacity of 6,000 bottles per hour and the continuous flow of effluent ends up in the river along with wash water from manual washings. The washing starts with a fresh water bath which is discharged daily followed by two caustic baths, two water baths and three more water baths





used counter currently. The caustic baths of capacity of 9,000 I and 6,600 I are replenished daily and discharged twice a week and once a week respectively. 500 kg -700 kg of NaOH is applied per month. The labels removed from the bottles are extracted from the machine adhering to a screen and are detached with fresh water.

# 8.2 Effluent generation (Quantity and quality)

The two sources of effluent identified in this distillery are:

- 1. Stillage from distillation process and wash water from distillation columns
- 2. Waste water from bottling plant
  - Distillery effluent

flow: 90 m³/d (estimated amount including washing effluent), effluent quality:

pH: 3.2

BOD: 15,000 mg/l COD: 30,000 mg/l SS: 750 mg/l TS: 21,150 mg/l Temp.: 95°C

> Bottle washer effluent

flow: 69m³/d, effluent quality:

pH: 12 – 14 COD: 385 mg/l NaOH: 0.003 %

# 8.3 Recommended waste minimisation options

- Good house keeping should be maintained at all times in the wash back area. Frequent washing and cleaning is therefore necessary.
- 2. Stillage is discharged at a temperature above 90°C. A waste heat exchanger could be designed to lower the temperature from 90°C to 65°C. The discharge rate is 5,500 l/h. The cooling water temperature will be elevated from 30°C to 55°C, recovering 574 MJ of heat at the same rate per hour. If the energy content of the hot water from this system is used for the boiler, approximately 15 l of fuel oil can be

- substituted. In this, capital investment is needed for the counter current heat exchanger and for the cooling water pumps. Further, this will eliminate the necessity of including a cooling tower in the effluent treatment system.
- 3. Spillage of furnace and other oil should not be discharged to the effluent drain. The oil can be separated and collected by installing suitable oil interceptors.
- 4. In the anaerobic digester system suggested for the treatment of distillery effluent, a reduction of 96% BOD is expected. The daily total BOD removal of 864 kg will generate about 260 m³ of biogas (based on 0.3 m³ biogas generation per kg of BOD removed). This is equivalent to 170 I of fuel oil. In this, capital investment is needed for the gas holder, gas burner and distribution line.
- 5. Collection of concentrated alkaline effluent separately and using it for the neutralisation of distillery stillage. By this, consumption of alkaline solution for neutralisation purposes could be minimised. Capital investment is requested for the construction of a separate drain for alkaline effluent, collection tank, filter unit and the dosing pump.
- Recycling of wastewater generated in the screen-washing unit of bottle washer after filtration. This source is measured as 2.7 m³/h. This option reduces daily effluent flow from 69 m³ to 47 m³. This option necessitates investments in a filter unit and feed pump.

#### 8.4 Motivation for investment

- Waste heat recovery from stillage
- Recovery of biogas from anaerobic digesters
- Use of alkaline effluent for neutralisation of stillage
- ➤ Recycling of screen wastewater
- > Cleaner Production options given





#### 8.5 Benefits from investment

- Use as fuel oil for boiler to heat boiler feed water
- > Reduction in NaOH consumption.
- Reduce total effluent volume.

#### 9 References and further information

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- [2] Noyola, A. 1996: Tratamiento de Aguas Residuales de Destilerías. Memorias IV Seminario-Taller Latinoamericano sobre Tratamiento de Aguas Residuales, Bucaramanga (Colombia).
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- [4] TBW GmbH Frankfurt 1998: Endbericht zur Förderung der Anaerobtechnologie zur Behandlung kommunaler und industrieller Abwässer und Abfälle. GTZ-TBW-BMZ, Frankfurt (Germany).
- [5] Tilche A. and Rozzi A. 1988: Poster Papers of the Fifth International Symposium on Anaerobic Digestion. Monduzzi Editore, Bologna (Italy).
- [6] Verink J. 1994: Anaerobic Wastewater Treatment at the Distillery in Cardenas. TBW, Frankfurt (Germany).

#### 9.1 Useful Links

http://www.sunbeam.net/vsi/

(Vasantdada Sugar Institute, India)

http://www.gtz.de/anaerob/index.html

(GTZ Sectoral Project "Promotion of anaerobic treatment for municipal and industrial sewage and waste")

http://www.execpc.com/~drer/anadoc.htm (Bioenergy from anaerobically treated wastewater)

http://www.distill.com/spanish.html

(Distillery terminology in English and Spanish)

#### 9.2 Institutions and Organisations

Deutsche Gesellschaft für Technische Zusammenarbeit (GTZ) GmbH, German Appropriate Technology Exchange GATE Information Service

P.O. Box 5180, 65726 Eschborn,

Germany

Phone: ++49 (0)6196 / 79-3094, Fax: ++49 (0)6196 / 79-7352,

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