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Utilization and biodegradation of starch stillage (distillery wastewater)

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Stillage (distillery wastewater) is the main by-product originating in distilleries, and its volume is approximately 10 times that of ethanol produced. It is not surprising that the utilization of the stillage raises serious problems, and that many attempts have been made all over the world to solve them. In Poland most of the ethanol (about 90%) is produced from starch-based feedstocks, i.e. grains and potatoes. Starch feedstocks are widely used for spirit production also in other European countries, as well as outside Europe. The manuscript provides an overview of global fuel ethanol production and information on methods used for starch-based stillage biodegradation and utilization. The methods presented in this paper have been classified into two major groups. One of these includes the mode of utilizing starch stillage, the other one comprises methods, both aerobic and anaerobic, by which the stillage can be biodegraded.

Scarcely 5 per cent of world’s ethanol production comes from chemical synthesis. More than 95 per cent of the ethanol produced is obtained from agricultural or agriculture-related feedstocks. Of these, sugar-based feedstocks account for approximately 42%, and non-sugar feedstocks (mainly starch-based ones) for about 58% of the ethanol volume produced (Tolmasquim, 2007). It seems interesting to note that about 67% of the global ethanol volume (in 2006 this was a total of 39 billion litres (REN21, 2008)) is used for fuel production.

In Poland ethanol obtained from starch-based feedstock now accounts for about 90% of the overall production. Ethanol is produced from grain crops (primarily rye, triticale and wheat), root crops (mainly potatoes) and molasses (as well as other agricultural feedstocks) (Dzwonkowski et al. 2007; Lopaciuk et al. 2007). Although the use of maize grain as feedstock is now becoming increasingly frequent in Polish distilleries, it is still far from being a widely accepted practice (Lopaciuk et al. 2007). It should be noted that the structure of the agricultural feedstock made use of for ethanol production varies according to the market situation. Thus, about two decades...
ago, it was potato-based ethanol that accounted for approximately 70% of the overall production. In the year 2000 its contribution dropped to less than 8%. Potato ethanol production totalled 3.2% in 2003 and rose to 4.2% in 2004. But in 2005 it dropped again, amounting to 3.1%. In 2006 potato ethanol production decreased to 5.5 million litres (from 9.1 million litres in 2005) (Dzwonkowski et al. 2007). In general, the use of starch-based feedstocks is dominant in Poland, rye being the most popular raw material for ethanol production (approx. 90%) (Lopaciuk et al. 2007). The quite frequent use of starch-containing wastes (e.g. putrid or frozen potatoes, peelings, pulp, potato slops, waste flour or wet sprouted and mouldy grain) is to be attributed to the unfavourable proportion of the feedstock cost in the overall costs of spirit production (50 to 60%) (Dzwonkowski et al. 2007).

In Poland, 95% of the overall ethanol production comes from rural distilleries (Jarosz, 2002). In 1995 about 940 were run in this country, but their number has been falling ever since and in 2006 only 217 distilleries were operated (Kupczyk, 2007). As the number of distilleries decreased, so did the volume of the ethyl alcohol produced, which dropped from 278 million litres in 1996 to approximately 170 million litres in 1999 and 2000. But subsequently, in 2001, ethanol production increased slightly (to 181 million litres) and continued to rise in the years that followed, to reach an annual volume of 220 and 230 million litres in 2003 and 2004, respectively. In 2005 ethanol production increased by 27.56% compared to 2004, and in 2006 the volume of ethanol produced totalled 344 million litres (Dzwonkowski et al. 2007).

In 2006 approximately 62.9% of the ethanol produced by rural distilleries in Poland was used as a fuel additive (Kupczyk, 2007), and the volume of ethanol produced as a biofuel equalled 161 million litres. Compared with the volume attained in 2006, fuel ethanol production in Q1-Q3 of 2007 decreased, amounting to 68 million litres only (Licht, 2008). Polish refineries Orlen and Lotos sourced 60% of the fuel ethanol contracted from abroad, since in those days domestic producers were not competitive. But the long-term outlook for domestic biofuel production and consumption is positive (Licht, 2008). The increase in fuel ethanol demand that is expected in the context of both the national bio-fuel programme and the Biofuel Directive

Table 1. Group B vitamins [mg/kg d.m.] in potato stillage and rye stillage, and mineral compounds [g/kg d.m.] in barley and wheat stillage.

<table>
<thead>
<tr>
<th>Vitamins of group B</th>
<th>Potato stillage (Becker and Nehging, 1967)</th>
<th>Rye stillage (Becker and Nehging, 1967)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vitamin B₁</td>
<td>7.8</td>
<td>15</td>
</tr>
<tr>
<td>Vitamin B₂</td>
<td>18.6</td>
<td>14.4</td>
</tr>
<tr>
<td>Vitamin B₆</td>
<td>18.8</td>
<td>4.0</td>
</tr>
<tr>
<td>Vitamin B₁₂</td>
<td>0.0088</td>
<td>0.118</td>
</tr>
<tr>
<td>Biotin</td>
<td>0.014</td>
<td>0.56</td>
</tr>
<tr>
<td>Nicotinic acid</td>
<td>212</td>
<td>54.9</td>
</tr>
<tr>
<td>Pantothenic acid</td>
<td>71.2</td>
<td>60.0</td>
</tr>
<tr>
<td>Folic acid</td>
<td>0.78</td>
<td>2.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mineral compounds</th>
<th>Barley stillage (Mustafa et al. 1999)</th>
<th>Wheat stillage (Mustafa et al. 1999)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>5.3</td>
<td>4.2</td>
</tr>
<tr>
<td>P</td>
<td>11.3</td>
<td>12.1</td>
</tr>
<tr>
<td>Mg</td>
<td>5.4</td>
<td>5.9</td>
</tr>
<tr>
<td>K</td>
<td>0.0016</td>
<td>0.0016</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0522</td>
<td>0.1101</td>
</tr>
<tr>
<td>Na</td>
<td>0.0006</td>
<td>0.0002</td>
</tr>
<tr>
<td>Fe</td>
<td>0.4932</td>
<td>0.4191</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0054</td>
<td>0.0057</td>
</tr>
</tbody>
</table>
2003/30/EC shows great promise to distilling industries which hope to raise their production.

The United States is a global leader in the use of starch-based feedstocks for ethanol production. In 2006 the USA production accounted for 38% of world’s overall ethanol production (REN21, 2008). In the United States, maize is the principal starch feedstock. This is not surprising, as this country is the leading producer of maize crops. Besides maize, some other grains are in use as feedstocks, e.g. wheat, sorghum or rye (Tolmasquim, 2007). In the USA the distilling industry is based on large distilleries-factories. In 2005 approximately 95 of them were operated, with a total capacity of 16.4 billion litres per year. In mid-2006 there were 35 additional plants under construction, providing further capacity of 8 billion litres per year (OECD/IEA, 2007). At the beginning of 2008 there were 9 distilleries under construction and 7 undergoing expansion (Licht, 2008). In 2004 the United States ranked second in ethanol production. The leader was then Brazil with an annual ethyl alcohol volume of 14.66 billion litres produced (RFA, 2008). It is essential to note, however, that this country almost invariably uses sugar cane as feedstock. In 2005 the USA became world’s largest fuel ethanol producer, and thus outdistanced Brazil. In 2006 fuel ethanol production in the USA and Brazil amounted to 18.3 billion litres and 17.5 billion litres, respectively (REN21, 2008). In the USA over 99% of the ethanol produced is utilized for fuel production (Ribando Seelke and Yacobucci, 2007); in Brazil the proportion amounts to 90%. Canada (with an annual ethanol volume of 550 million litres produced in 2006 (OECD/FAO, 2007) and fuel ethanol production of 200 million litres (REN21, 2008)) uses starch feedstocks (mainly maize grains) for ethanol production (Berg, 2004). Other widely accepted feedstocks include wheat, barley, triticale and rye (Klein et al. 2008).

In 2006 the EU produced close to 1.6 billion litres of ethanol for fuel (EUBIA, 2008). The major part of this was distilled out of cereals, which accounts for 976 million litres or roughly 61% of total ethanol feedstock. Among the different grains used for the ethanol production, wheat is the most important cereal with a market share of 36%, followed by rye (15%), barley (7%), maize (only 2%) and triticale (marginal) (Biofuels International, 2007). In 2006 the largest starch-based bioethanol fuel producer in the EU was Germany with an overall output of 430 million litres (Biofuels International, 2008). The main feedstock used for the German ethanol production was rye (49.5%) followed by wheat (41.3%), barley (8%) and triticale (no precise numbers). Spain, as the second largest producer of ethanol in the EU (396 million litres in 2006), mainly processed wheat (57%) followed by barley (21%). The rest of the Spanish production came from wine alcohol. In 2007 the greatest production was achieved in France (578 million litres), where the production almost doubled (Biofuels International, 2008), but France was the only large scale producer of bioethanol coming from sugar beet (around 81%) (Biofuels International, 2007). In 2007 the next largest producers were Germany (394 million litres) and Spain (348 million litres). In that year fuel ethanol production decreased compared to 2006 with the most significant decline in Sweden, which halved its production to 70 million litres due in part to high cereal prices. As a result the costs of bioethanol production rose to a level that made its manufacture no longer profitable (Biofuels International, 2008).

As is the case with the United States, Europe invests a great deal in large distillery plants, whose overall ethanol production capacity is likely to approach 3 billion litres per annum by the end of 2008 (Kupczyk, 2007). As for Asia, the leadership in utilizing starch-based feedstocks for ethanol production belongs to China, which ranks third as a global ethanol producer with a yearly volume of approximately 4.1 billion litres in 2006 (Tolmasquim, 2007). Fuel ethanol production in that country in 2006 amounted to 1.5 billion litres (OECD/FAO, 2007).

The choice of the feedstock for the production of fuel ethanol is determined by economic calculation, and this includes all the protective measures taken by the governments of some countries that want to pursue their social policy also in this way. But if spirits are produced for human consumption, this is the recipe for the alcoholic drink that determines the choice of the feedstock. For example, the production of whisky, of some flavoured vodkas, or of the majority of the Japanese shochu types requires starch-based feedstock. And that is why in many countries local distillers specialise in the production of regional alcoholic drinks. The diversity of the feedstocks used for ethanol production and the fact that distillery plants widely differ in size (production capacity) are the contributory factors in the use of different methods for distillery wastewater utilization and biodegradation.

The purpose of the paper was to provide an overview of the growing scale of ethanol production worldwide, as well as to give an account of methods that are used for starch stillage biodegradation and utilization. The methods presented in the paper have been classified into two major groups. One of these includes the mode of utilizing starch stillage, the other one comprises methods, both aerobic and anaerobic, by which the stillage can be biodegraded.

**Methods of stillage utilization**

Distillery stillage from the fermentation of starch-based feedstock by the yeasts contains not only some feedstock components (Sweeten et al. 1981-1982; Davis et al. 2005), but also degraded yeast cells (Sanchez et al. 1985). Many of those substances are characterised by a high nutritive value. They contain vitamins (with large amounts of those classified as group B) (Table 1), proteins rich in exogenous aminoacids (Mustafa et al. 1999), and mineral components (Table 1). Upon comparing the proportions of particular mineral compounds in barley and wheat stillage it can bee seen that barley stillage contains more calcium, iron and...
sodium than wheat-based stillage (Mustafa et al. 1999). Owing to the chemical composition of the dry matter basis (Table 2) (but primarily because of the beneficial proportion of the total protein content to the contents of the other nutrients) potato stillage has been regarded as valuable fodder (despite high water content, 90 to 95.3%) (Maiorella et al. 1983; Larson et al. 1993; Ham et al. 1994; Fisher et al. 1999; Mustafa et al. 2000). It should, however, be noted that the feeding value of the potato stillage (determined as protein and vitamin content) is lower than that of the grain stillage (Maiorella et al. 1983). As far as the stillage derived from wheat, rye, triticale and barley is concerned, the lowest nutritive value (measured as crude protein and neutral detergent fibre fraction) is that of the barley-derived stillage, both in its liquid and solid fraction (Mustafa et al. 2000).

Unprocessed warm stillage has the highest feeding value, but also a serious drawback: it cannot be stored over a longer period because of its proneness to souring and mould growth. This means that the animals should be fed shortly after the stillage has been produced, which makes this method of stillage utilization really troublesome. Feeding farm animals with “raw” stillage is cost-effective only if the users live in the close proximity of the distillery. Because of the high water content, the transport of the stillage over long distances is unprofitable (The Mother Earth News, 1980; Ganesh and Mowat, 1985; Aines et al. 1986). The best solution to this problem seems to be the integration of a small rural distillery with a large animal farm that would be able to consume the whole volume of the stillage produced (Carioca et al. 1981; Ganesh and Mowat, 1985). But in Poland an opposite trend is being observed. Rural distilleries are becoming independent economic units interested in their own development. On the other hand, large animal farms are lacking. Under such conditions the problem of utilizing the stillage volume produced entirely as animal fodder remains unsolved.

Since “raw” stillage cannot be stored over a long period, it must be processed as otherwise its nutritive value is lost. One of the methods for extending the storage life of starch-based stillage is souring by the addition of corn or hay for example. The fodder obtained in this way can be stored for several months but the nutritive value may decrease (McCullough et al. 1963; Hunt et al. 1983; Muntifering et al. 1983). Another drawback inherent in stillage is the remarkably high content of crude fibres, which limits its application as fodder, especially for nonruminant farm animals (Kienholz et al. 1979). Recent research has shown that lactic bacterial inoculants improve feed preservation (Garcia and Kalscheur, 2004).

Another method of utilizing starch stillage is yeast cultivation, where the yeast biomass is used as fodder (Murray and Marchant, 1986; Jamuna and Ramakrishna, 1989). However, the investigations reported on in the literature involved predominantly vinasse (Taufk, 1982; Malnou et al. 1987; Moriya et al. 1990; Cibis et al. 1992), while yeast was cultivated on an industrial scale. Unfortunately, the COD level in the effluent from cultivation was so high that the reduction in this pollutant approached 70% at the most. That is why this method of utilizing vinasse has been abandoned and investigations into yeast cultivation on distillery stillage have been practically discontinued.

### Table 2. Chemical composition of dry matter content for starch stillage of choice [%].

<table>
<thead>
<tr>
<th>Stillage</th>
<th>Dry matter</th>
<th>Crude protein</th>
<th>Fat</th>
<th>Crude fibre</th>
<th>Sugars</th>
<th>Starch</th>
<th>Ash</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain sorghum</td>
<td>5.8</td>
<td>1.7</td>
<td>nd</td>
<td>1.51</td>
<td>2.6</td>
<td>1.01</td>
<td>3.77</td>
<td>(Sweeten et al. 1981-1982)</td>
</tr>
<tr>
<td>Barley</td>
<td>5.97</td>
<td>2.21</td>
<td>0.76</td>
<td>2.35</td>
<td>2.14</td>
<td>0.04</td>
<td>0.58</td>
<td>(Mustafa et al. 1999)</td>
</tr>
<tr>
<td>Maize</td>
<td>6.2</td>
<td>1.3</td>
<td>1.3</td>
<td>0.1*</td>
<td>2.8</td>
<td>0.5</td>
<td>0.8</td>
<td>(Kim et al. 1999)</td>
</tr>
<tr>
<td>Maize</td>
<td>3.7</td>
<td>1.44</td>
<td>nd</td>
<td>1.81</td>
<td>0.97</td>
<td>0.56</td>
<td>0.27</td>
<td>(Sweeten et al. 1981-1982)</td>
</tr>
<tr>
<td>Maize</td>
<td>7.5</td>
<td>2.3</td>
<td>nd</td>
<td>nd</td>
<td>0.5</td>
<td>nd</td>
<td>2.1</td>
<td>(Maiorella et al. 1983)</td>
</tr>
<tr>
<td>Potato</td>
<td>6.0</td>
<td>1.45</td>
<td>0.05</td>
<td>0.7</td>
<td>3.1</td>
<td>nd</td>
<td>0.7</td>
<td>(Czupryński et al. 2000)</td>
</tr>
<tr>
<td>Wheat</td>
<td>8.4</td>
<td>3.8</td>
<td>1.14</td>
<td>2.86</td>
<td>2.67</td>
<td>0.185</td>
<td>0.7</td>
<td>(Mustafa et al. 1999)</td>
</tr>
<tr>
<td>Wheat</td>
<td>12.0</td>
<td>3.8</td>
<td>2.3</td>
<td>0.12</td>
<td>6</td>
<td>nd</td>
<td>0.156</td>
<td>(Davis et al. 2005)</td>
</tr>
</tbody>
</table>

Note: nd = no data available. *Acid detergent fibre.
Utilisation and biodegradation of starch stillage (distillery wastewater)

Table 3. Chemical composition of liquid phase in starch stillage [g/L] (except pH [-], density [°Brix], COD and BOD₅ [g O₂/L]).

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>-</td>
<td>3.70</td>
<td>3.8-4.0</td>
<td>4.6</td>
<td>3.35</td>
<td>3.7</td>
<td>3.7-4.1</td>
<td>5.1</td>
<td>3.94</td>
<td>4.0-4.5</td>
<td>3.65</td>
<td>3.6</td>
<td>2.9</td>
<td>3.88</td>
<td>3.69</td>
<td>3.62</td>
<td>3.88</td>
<td>3.9-4.9</td>
<td>4.5</td>
</tr>
<tr>
<td>Density</td>
<td>-</td>
<td>2.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>12.2</td>
<td>4.6</td>
<td>4.7</td>
<td>7.9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>-</td>
<td>-</td>
<td>40-65</td>
<td>18.4-23.0</td>
<td>38.6</td>
<td>70.34</td>
<td>15.3</td>
<td>1.0**</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>20-50</td>
</tr>
<tr>
<td>COD (BOD₅)</td>
<td>59.4</td>
<td>(43.1)</td>
<td>21.64</td>
<td>40-55</td>
<td>17.5-20.8</td>
<td>(12.5-13.6)</td>
<td>90.75</td>
<td>107.0</td>
<td>97 (83)</td>
<td>17.6</td>
<td>28.98</td>
<td>20-30</td>
<td>56 (50)</td>
<td>10.8</td>
<td>35</td>
<td>122.33</td>
<td>48.95</td>
<td>51.75</td>
<td>103.76</td>
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<tr>
<td>TOC</td>
<td>-</td>
<td>9.15</td>
<td>-</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>10.70</td>
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<td>28.33</td>
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<td>-</td>
<td>45.60</td>
<td>-</td>
<td>-</td>
<td>35.15</td>
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<tr>
<td>Reducing substances</td>
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<td>4.05</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.81</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>2</td>
<td>37.06</td>
<td>10.47</td>
<td>10.6</td>
<td>37.44</td>
<td>-</td>
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<tr>
<td>Glycolic acid</td>
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<td>3.22</td>
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<td>-</td>
<td>3.81</td>
<td>3.04</td>
<td>3.25</td>
<td>5.96</td>
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<td>Lactic acid</td>
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<td>6.63</td>
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<td>-</td>
<td>3.51</td>
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<td>1.4</td>
<td>-</td>
<td>61.14</td>
<td>-</td>
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<td>17.53</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>Propionic acid</td>
<td>-</td>
<td>0.21</td>
<td>-</td>
<td>0.8-1.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.12</td>
<td>-</td>
<td>0.623</td>
<td>-</td>
<td>-</td>
<td>2.77</td>
<td>-</td>
<td>2.64</td>
<td>-</td>
<td>0.80</td>
<td>-</td>
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</tr>
<tr>
<td>Succinic acid</td>
<td>-</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.31</td>
<td>-</td>
<td>1.059</td>
<td>-</td>
<td>0.23</td>
<td>-</td>
<td>-</td>
<td>0.430</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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<tr>
<td>Acetic acid</td>
<td>-</td>
<td>0.44</td>
<td>-</td>
<td>2.1-6.6</td>
<td>-</td>
<td>-</td>
<td>0.27</td>
<td>-</td>
<td>0.132</td>
<td>-</td>
<td>4.14</td>
<td>-</td>
<td>2.10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Sum of organic acids</td>
<td>-</td>
<td>9.67</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.29</td>
<td>-</td>
<td>10.795**</td>
<td>0.65***</td>
<td>1.46***</td>
<td>75.11</td>
<td>-</td>
<td>24.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total nitrogen</td>
<td>0.546</td>
<td>0.67</td>
<td>1.5-1.6</td>
<td>4.0*</td>
<td>8.8*</td>
<td>6.0</td>
<td>0.83</td>
<td>0.17-0.18*</td>
<td>2.18*</td>
<td>0.126</td>
<td>0.140</td>
<td>2.57</td>
<td>0.52</td>
<td>0.81</td>
<td>1.05</td>
<td>-</td>
<td>1.20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>-</td>
<td>0.096</td>
<td>0.5-0.6</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.01</td>
<td>0.19</td>
<td>0.052</td>
<td>-</td>
<td>-</td>
<td>0.361</td>
<td>0.235</td>
<td>0.07</td>
<td>0.308</td>
<td>-</td>
<td>-</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>Total phosphorus</td>
<td>0.228</td>
<td>0.441</td>
<td>0.17-0.18</td>
<td>0.40</td>
<td>0.218</td>
<td>-</td>
<td>0.47</td>
<td>0.27-0.30</td>
<td>-</td>
<td>-</td>
<td>0.816</td>
<td>0.259</td>
<td>0.327</td>
<td>0.277</td>
<td>-</td>
<td>0.140</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phosphate phosphorus</td>
<td>-</td>
<td>0.363</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.039</td>
<td>0.28</td>
<td>0.004</td>
<td>0.0642</td>
<td>0.0416</td>
<td>0.588</td>
<td>0.167</td>
<td>0.260</td>
<td>0.165</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Note: * TKN = Total Kjeldahl Nitrogen. ** TSS = Total Suspended Solids. ***VFA = Volatile Fatty Acids.
Attempts have been reported of recirculation of liquid part the stillage after solids separation (thin stillage) to the steamer or mash tub. It has been found that when approximately 75% of the water entering the steamer was replaced with grain sorghum-based thin stillage, a large increase was observed in the solids content and COD in the stillage (Egg et al. 1985). It should, however, be noted that the recirculation of the thin stillage to the mash tub is effective only if no more than 40-50% of thin stillage is recycled (Sheehan and Greenfield, 1980; Wilkie et al. 2000; Yeoh et al. 2001). Once these values have been exceeded, alcohol yield decreases, which might be attributed to the accumulation of such substances that inhibit the activity of the yeast cells (Egg et al. 1985; Kim et al. 1999; Wilkie et al. 2000). Although the recirculation of thin stillage brings about a 25% reduction in the final volume of the distillery wastewater, this is concomitant with a rise in the COD level (Wilkie et al. 2000).

Other methods of utilizing starch-based stillage include concentration and drying. Both are characterised by a high energy demand, which makes them apply to very large distilleries only (Murphy and Power, 2008). Such are in Poland the distilleries under construction with an expected production volume much greater than that of the existing ones (Reuters, 2008). The concentration and drying of starch stillage that is to be used as fodder have found wide acceptance in the United States and in Canada, where the processes are carried out in several variants (The Mother Earth News, 1980; Aines et al. 1986; Wu, 1988; Akayezu et al. 1998). One of these involves the separation of the solid fraction from the liquid fraction, using sieves, centrifuges or pressing devices (the product obtained in this way is referred to as Wet Distiller’s Grain). The solid phase is then dried (Distiller’s Dried Grain), while the liquid phase is concentrated until a 30-40% suspended solids content has been obtained (Condensed Distiller’s Solubles). In some distilleries the concentrated liquid fraction is dried (Distiller’s Dried Solubles) or mixed with the previously separated solid fraction, and the mixture obtained is dried (Distiller’s Dried Grains with Solubles).

Investigations into less energy-consuming methods that would increase the suspended solids content of the stillage have also been reported. Promising results have been obtained with ultrafiltration and high-pressure reverse osmosis. The solids and ash concentrations in the permeate after reverse osmosis (measured indirectly as conductivity) are lower than those of tap water (Wu, 1988), and that is why the permeate can be used as substitute for technological water in the process of ethanol production. It is worth noting that the fermentation yield does not change even after 8-fold recirculation of the permeate (Kim et al. 1999). The concentrated fraction can be used as fodder in unprocessed or dried form (Nguyen, 2003). A major drawback of this method is the occurrence of fouling and scaling phenomena, which account for membrane clogging (Gryta, 2005).

Another method for increasing the suspended solids content includes drying stillage together with a carrier, e.g. soy hulls or dry beet pulp. In this way pellets are obtained (Garcia and Kalscheur, 2004).

Consideration has also been given to the problem of utilizing starch-based feedstock as fertilisers (Jenkins et al. 1987), the more so as vinasse has been used for this purpose (Monteiro, 1975; Maiorella et al. 1983). It has been suggested that starch based stillage should be used for direct soil fertilization or for the production of organic fertilisers, after being mixed and composted, for example, with cow feces (Tanaka et al. 1995). However, direct fertilization must be carried out when the time is right for doing this, so as not to damage the crops (Sheehan and Greenfield, 1980; Milewski et al. 2001; Czuprynski et al. 2002), but this requires storage of the stillage. It is not recommended to pour the stillage direct onto the soil, which is hollow in places, because the stillage may accumulate there and produce contamination. One of the weaknesses inherent in such application is the unpleasant odour. It is also possible to fertilise soil with the product of starch stillage incineration (Yamauchi et al. 1999), as in the case of vinasse (Maiorella et al. 1983).

The literature also includes references to other methods of utilizing starch stillage. One of these publications pertains to the use of this waste effluent for the production of rigid polyurethane-polyisocyanurate foams (Czuprynski et al. 2000). The product obtained displayed properties identical to those of standard foam, besides brittleness. There are also reports on the utilization of concentrated liquid maize stillage fractions as the feedstock for the production of some cosmetics, e.g. alternan (Leathers, 1998) and pullulan (West and Strohfuß, 1996). Furthermore, maize stillage was made use of as the feedstock for the synthesis of astaxanthin carotenoid by Phaffia rhodozyma (Leathers, 2003). Other starch stillage has been used for the synthesis of protease (Morimura et al. 1994; Yang and Lin, 1998), chitosan (Yokos et al. 1998) and biodegradable plastics, e.g. poly β-hydroxybutyrate (Khardenavis et al. 2007).

**Biodegradation of starch stillage**

The methods considered in the foregoing section do not enable utilization of the whole starch stillage volume produced. As a result distilleries are facing a serious problem. The stillage is a high-strength effluent which - because of a considerable organic matter content (Table 3) - can neither be sent to the sewer system nor be discharged into a watercourse or soil; at least a certain portion of the COD load must be removed at the source origin.

The COD load of the liquid phase varies from 12.1 g O₂/l for the sweet potato stillage (Nagano et al. 1992) to 122.33 g O₂/l for the stillage from waste feedstocks containing wheat starch (80%) and potato starch (20%) (Cibis, 2004). The comparison of the chemical composition (Table 3) shows that even if the stillage comes from the same
feeds stills, it differs considerably in its chemical properties. This finding should be attributed to the fact that the COD content is influenced not only by the feedstock but by the technology of spirit production and the method of feedstock and stillage storage as well.

Distiller’s stillage shows a proneness to sour fermentation. This is due to the formation (within a comparatively short period) of organic acids, mainly lactic acid, which usually dominates in that type of stillage (Table 3). As for the other carbon sources, reducing substances and glycerol are found to occur in large amounts (Table 3). The presence of total and phosphate phosphorus, as well the large amounts of total nitrogen (Table 3), can be explained as being associated with the high protein proportion in the feedstock from which the stillage comes (Wilkie et al. 2000).

Such chemical composition suggests that starch stillage is biodegradable to a great extent. Aerobic and anaerobic fermentation of thin stillage was first reported four decades ago (Fargey and Smith, 1965; Smith and Fargey, 1965). The problem, however, has not attracted much attention until recently. In the past 15 years, a number of publications have dealt with the biodegradation of starch stillage, but they have described anaerobic processes only (Weiland and Thomsen, 1990; Nagano et al. 1992; Goodwin and Stuart, 1994; Laubscher et al. 2001; Gao et al. 2007; Tang et al. 2007). Laboratory investigations into the anaerobic treatment of wheat stillage of an initial COD ranging from 91 to 107 g O₂/l (Hutnan et al. 2003) and of malt whisky distillery wastewater with an initial COD between 30.5 and 47.9 g O₂/l (Goodwin and Stuart, 1994) have revealed an approximately 90% reduction of this pollutant. The treatment of grain distillation wastewater whose initial COD level ranged from 20 to 30 g O₂/l with the aid of an upflow anaerobic sludge bed (UASB) system has yielded an approximately 80% COD removal efficiency (Laubscher et al. 2001). When barley stillage and sweet potato stillage of an initial organic matter content of 29.5 g O₂/l were treated in a continuous process, COD reduction amounted to 80% (Shin et al. 1992). A 98% reduction in COD was attained with wheat stillage and sweet potato stillage of an initial pollution load of 40 g O₂/L (Nagano et al. 1992). When potato stillage with an initial content of organics ranging between 20 and 55 g O₂/l was treated, the extent of COD reduction varied from 80 to 95% (Weiland and Thomsen, 1990). With a potato and sugar beet stillage of an initial organic pollution load of 40 g O₂/l, the reduction in COD amounted to 90% (Wilkie et al. 2000).

Anaerobic biodegradation of stillage is being carried out on an industrial scale. At least 135 anaerobic bioreactors are operated all over the world; nine of these (with four operating in Germany) are used for the treatment of starch stillage, the other bioreactors being made use of for treating primarily vinasse (Wilkie et al. 2000).

Starch stillage can be treated with an equal efficiency by aerobic methods. One of the first publications dealing with this problem comes from 1965 (Smith and Fargey, 1965). The investigations reported there have shown that if maize stillage is treated in a stirred tank reactor (STR) at room temperature, COD can be reduced by 60.7%. The same investigators have obtained a much higher (98%) reduction in COD, using a bioreactor with a fixed bed and recirculation of the stillage being treated.

Over the 35-year period that followed no research on aerobic biodegradation of starch stillage was reported. It was only a few years ago that such problems became, again, the focus of attention (Cibis et al. 2002; Krzywonos et al. 2002; Cibis, 2004; Cibis et al. 2004; Ferzik et al. 2004; Cibis et al. 2006; Krzywonos et al. 2008). Some of the investigations dealt with the treatment of potato stillage, and were conducted batchwise in an STR with a mixed culture of thermo- and mesophilic bacteria of the genus *Bacillus*. The extent of COD reduction obtained in this way totalled up to 89.8%. The efficiency of biodegradation depended on the following factors: temperature, pH, initial COD, and addition of nutrients (ammonia nitrogen and phosphate phosphorus) (Cibis et al. 2002, Krzywonos et al. 2002; Cibis, 2004; Cibis et al. 2004; Cibis et al. 2006; Krzywonos et al. 2008). The same bacterial culture was used for the biodegradation of the stillage coming from maize and rye. With the maize stillage, the reduction in COD amounted to 82.6%; with rye stillage, COD reduction totalled 84.6% (Cibis, 2004). When the stillage under treatment came from the waste feedstock for the production of glucose syrup and chips (about 80% of wheat starch and about 20% of potato starch), the extent of COD reduction approached 94% (Cibis, 2004). Similar treatment effects for this stillage were obtained with the continuous biodegradation process (Cibis, 2004). Reports are also available on the aerobic degradation of distiller’s stillage (wheat grain) with bacterial cultures (Ferzik et al. 2004). A batch biodegradation system yielded a 64% COD reduction at 45°C, whereas a continuous process brought about an approximately 90% reduction in COD at 55°C.

In contrast to anaerobic methods, aerobic biodegradation of starch stillage with thermo- and mesophilic bacteria has not yet been conducted on an industrial scale. The results obtained during laboratory-scale aerobic thermo- and mesophilic biodegradation of distillery wastewater indicate that the effectiveness of this method the same as for another microorganisms (Anastassiadis and Rehm, 2006; Battestin and Macedo, 2007; Choorit and Wisanwan, 2007) is influenced by the aerobic conditions, pH and temperature (Cibis et al. 2002; Krzywonos et al. 2002; Krzywonos et al. 2008). The results of laboratory investigations seem to encourage the upgrading of the research scale.

**CONCLUDING REMARKS**

In principle, only distilleries integrated with stock farms and large distilleries-factories rarely have trouble with the utilization of starch-based stillage. Any other distillery has to tackle the problem more or less successfully (Wilkie et
al. 2000; Nguyen, 2003). It is essential to note, however, that in Germany the integration of distilleries with stock farms permits them to avoid troubles. This is not so in the USA, where ethanol plants have difficulties with the profitability of stillage marketing or disposal. Most of the stillage produced is sold in the form of Distiller’s Dried Grains with Solubles. As for Poland’s distilleries, the majority of them are not able either to utilize their stillage in ruminant diets or treat it efficiently. Only four have constructed mechanical-biological wastewater treatment plants, and some distilleries treat their effluents with mechanical methods (Cavey et al. 1998). Regrettfully, 20% of distilleries discharge their wastewater directly into a watercourse or into soil without recultivation (Milewski et al. 2001). This indicates that the poor utilization of the stillage produced must raise serious concern. Considering the environmental rules and regulations recently enforced in Poland immediate measures have to be taken to solve the problem, which has taken on a sense of urgency.

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