ANAEROBIC TREATMENT OF DISTILLERY WASTEWATER

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ABSTRACT
The estimated global ethanol production in 2009 was about 74 mln m^3. After fermentation remains waste from bottom of distillation columns, termed stillage. This highly aqueous residue containing organic solubles is considered a troublesome and potentially polluting waste due to its extremely high BOD and COD values. Moreover, for each liter of produced ethanol 8 -15 liters of stillage are generated on average. The possibility of anaerobic treatment of distillery stillage was analyzed.

KEYWORDS: ethanol production, distillery stillage, anaerobic processes, UASB

INTRODUCTION

The estimated global ethanol production in 2009 was about 74 mln m^3. In the recent decade it has been applied by a rapidly developing energy branch as a fuel alternative to fossils. The most common raw materials for ethanol production are mainly: corn, wheat, rice, potatoes, sugar beets, sugar cane, molasses. Theoretical fermentation model assumes about 95% conversion to ethanol and carbon dioxide. The remaining sugar fraction yields yeast cellular matter (1%) and formation of alternative by-products (4%), typically glycerol, succinate, acetate and fusel oils (U.S. Grains Council, 2007). In practice the ethanol yields rarely exceed 90% of the theoretical yield (Grajek et al., 2008). The end product of fermentation is 1-12% aqueous ethanol solution. It is next transferred to distillation column and heated above its boiling point, either by means of direct steam injection or a reboiler. The vapors condensate on top of the rectifying columns reaching typically 95% ethanol concentration. The remaining stillage falls down the stripping column. If a higher ethanol concentration is desired (e.g. for biodiesels) additional dehydration or drying is required to remove the remaining 5% of water (U.S. Grains Council, 2007, Grajek et al., 2008). The residues from these processes are added to the final stillage volume (Wilkie, 2000).

Stillage characterization

Stillage, (also called: Wet Distiller's Grains with Solubles (WDGS)) is the liquid residue of ethanol distillation (Cibis et al., 2006). Its chemical composition and characteristics depend mainly on the type and specific cultivar of the raw material used for fermentation. Fresh stillage drained from the bottoms of distillation columns has a temperature of about 70-80°C and brown to dark brown colour (Sowmeyan and Swaminathan, 2008). It is of acidic nature and the pH usually varies from about 3.5 to 4.5 (Wilkie, 2000). The load of COD (Chemical Oxygen Demand) in stillage is typically in a range of 80-100 gO_2/L and results principally from the composition of feedstock (Sowmeyan and Swaminathan, 2008). High content of organic compounds is also reflected in the values of BOD (Biochemical Oxygen Demand), which typically range from 30 to 60 gO_2/L (Pant and Adholeya, 2007). The remaining organic fraction is a mixture of compounds present in trace amounts and comprises of higher-boiling or nonvolatile acids (hydroxylated, dicarboxylic, amino acids and others), polyhydric alcohols, various sugars, sugar alcohols, proteins, fats and salts (Dowd, 1993).

Variability in nitrogen and phosphorus loads is related to content of these elements in raw material. Total nitrogen content is usually 1.6-2.0 g/L, but may be as high as 6.0 gN/L. Such outstanding nitrogen content in barley stillage is due to large amount of proteins in barley grains. The content of total phosphorus is typically between 0.2 and 0.4 gP/L and deviations from this range are rare, but may reach even 3.0 gP/L. Potassium levels vary from 0.9 to 17.5 gK/L (Wilkie, 2000). Sulphates content in stillage origins principally from sulfur compounds used in the production process. In effluents from molasses fermentation this content is most notable, amounting 4.0-7.0 g/L and results from using sulphide in manufacturing of sugar. Higher sulphate concentrations can also be expected in grain stillages due to sulphuric acid pretreatment (Wilkie, 2000).

Direct disposal of untreated distillery effluents into natural waters poses a serious threat to aquatic organisms. High COD, nitrogen and phosphates content may contribute to eutrophication of lakes and rivers (Sowmeyan, Swaminathan, 2008). Colorants may intensify this effect by limiting the permeability to sunlight, which leads to inhibition of the photosynthetic activity and in turn to decreased dissolved oxygen levels (Mohana et al., 2007).

Methods of treatment and utilization of stillage

In Fig.1 the most common methods of utilization the distillery stillage is presented. The solid fraction mixed with condensed solubles can be dried and utilized as a high-value animal fodder additive, termed Dried Distiller's Grains and Solubles (DDGS) (Kim et al., 2008).

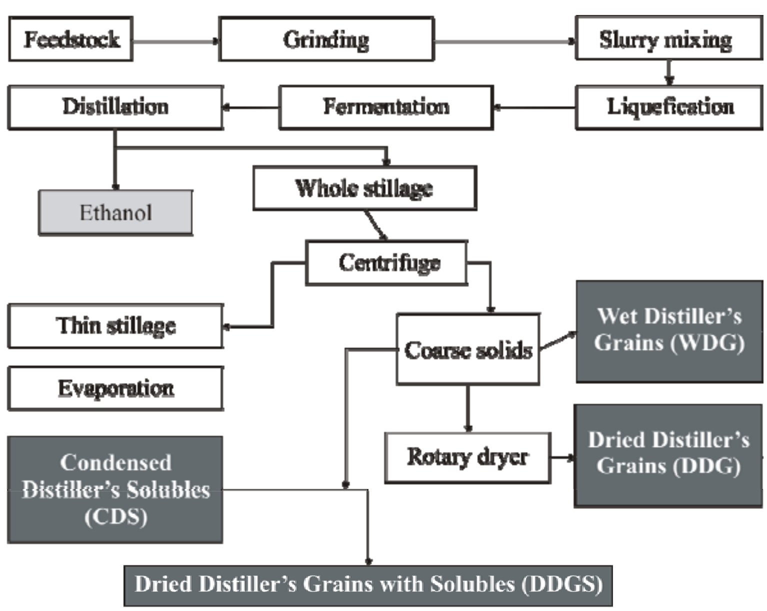

Figure 1. Dry-grind ethanol production process and co-products (U.S. Grains Council, 2007)

An idea of utilizing distillery stillage as a feedstock for methane fermentation came out as an alternative to thermal processing. In recent years anaerobic treatment has been successfully applied on both pilot and full scale. Not only it allows passing over the drying stage, but also offers an opportunity for energy recovery. Estimated biogas yield from 1 tone of stillage is 55 m^3 with methane content at least 55%. Its combustion is capable of covering significant part of thermal energy demand in ethanol production and purification stages. Depending on the choice of technology, methane combustion can cover even 75-100% of the process energy demand (Pfeffer et al. 2007).

Anaerobic treatment of distillery stillage

A typical BOD/COD ratio of 0.8-0.9 indicates suitability of distillery wastewaters for biological treatment (Mohana et al., 2007). Digestion in anaerobic conditions is most typically employed as a primary treatment for distillery effluents. Such solution is favored by the fact, that during anaerobic degradation about 50% of the COD contained in stillage can be converted to biogas at only about 10% sludge generation (Wilkie, 2000).

Anaerobic systems can operate in two modes. In a single-phase systems all stages of anaerobic digestion are performed in one vessel, while biphasic arrangements provide separate digesters for acidogenic and methanogenic stage. Such solution allows maintaining optimal conditions for both phases, thus increasing the overall process efficiency and improving the stability of a system (Mohana et al., 2007).

Continuous Stirred Tank Reactor (CSTR)

This is the simplest form of a closed digester with biogas capture. One of the most common reactors of this type is Continuous Stirred Tank Reactor (CSTR). Due to constant mixing, a uniform substrate is formed, and in consequence, SRT (Sludge Retention Time) is equal to the HRT (Hydraulic Retention Time) (Moletta, 2005). Tequila vinasse was treated in a lab-scale mesophilic CSTR by Méndez-Acosta (Méndez-Acosta, 2010). Obtained COD removal varied from 90 to 95%. Per each kg of COD removed 537 L of biogas containing over 60% of methane was produced.

Anaerobic Suspended Growth Reactor (ASGR)

Banu examined the treatment of stillage in two lab-scale Anaerobic Suspended Growth Reactors (ASGR) operating in meso- and thermophilic ranges (Banu et al., 2006; 2007). Both systems experienced souring shock after increasing the loads above these values, when the VFA concentration raised by 500%, decreasing the treatment efficiency to 52%, 40%, and 46% in terms of COD, TS and VS removal, respectively.

Upflow Anaerobic Sludge Blanket (UASB) Reactor

In UASB reactor, the anaerobic consortium appears in the form of granules, which are suspended by the produced biogas and movement of recirculating effluent. An internal settler is placed on top of the digester to hold back the granules (Moletta, 2005). A wine distillery in Wellington, South Africa, utilizes an UASB reactor for effluent pretreatment. The applied inoculum was UASB brewery sludge. The generated effluents are collected in a balancing tank and are next passed through a cooling tower to lower their temperature to 37°C. The generated biogas, after purification, is readily utilized by the plant. The applied technology accomplishes COD reduction by over 90%, allowing discharge of the treated effluents into the municipal sewer (Wolmarans and de Villiers, 2002).

Three full-scale UASB reactors treating similar effluents (anise stillage from production of cognac and raki) at three turkish distilleries were compared and evaluated by Ince et al. (Ince et al.,

2005). The digesters treating raki stillages achieved 85% of COD removal, in cognac stillage treatment it was 70-80%.
UASB was employed also in treatment of grape wine distillery stillage by Moosbrugger. Overall COD removal efficiency of the process exceeded 80% (Moosbrugger et al., 1993). Goodwin et al. (Goodwin et al., 2001) treated malt whisky stillage in a mesophilic UASB reactor. Seed sludge was taken from another UASB system treating sucrose-based materials. The COD removal efficiency accounted at least 85%.

A problem was encountered during mesophilic anaerobic treatment of grain distillation wastewater in UASB, where the ethanol was produced from corn. Distilled stillage from corn characterizes high content of fats. Problems with anaerobic treatment of wastewater containing lipids result from two phenomena: adsorption of a light lipid layer around biomass particles causing biomass flotation as well as, washout and acute toxicity of LCFA (Long Chain Fatty Acids), especially unsaturated ones, to both methanogens and acetogens, the two main trophic groups involved in LCFA degradation. The results of the research indicated, that fat can limits the applicability of UASB treatment to this type of stillage.

Anaerobic Sequencing Batch Reactor (ASBR)

Recently, Luo attempted to introduce discharge of settled sludge for enhanced treatment of cassava stillage in ASBR (Luo et al., 2009). High SS content in this type of wastewaters limits the feasibility of its treatment in high rate reactors. With COD:N:P ratio of 200:5:1 nutrient supplementation was not required. The system was maintained at 55°C by a water bath and operated as CSTR in the initial period of 140 days at HRT of 5 days, then switched to ASBR mode with 24 hour cycle, including 19 hours reacting time. Within the initial period sludge concentration was maintaned at constant level of 30g/L by daily discharging, then evaluated at increasing HRTs. COD removal efficiency was 90.8%.

Anaerobic Baffled Reactor (ABR)

Winery and distillery wastewaters were treated in ABR system. The unique structure of ABR allows to partially separate the acidogenesis and methanogenesis steps thanks to a series of baffles forcing the flow of wastewater. Elongated contact time with the microbial sludge ehnances the treatment (Moletta, 2005).

Anaerobic Fluidised Bed Reactor (AFBR)

In this type of reactor carriers for the bacterial biofilms are kept in a fluid state by drag forces exerted by the upflowing recirculating effluents (Moletta, 2005). Medium fluidisation provides large surface area for the bacterial growth and enhances contact with the wastewater. Fine-grained sand particles or activated carbon are typically used as media for the attachement of microorganisms. The distillery spent wash treatment in reactor of this type has been proposed (Mohana et al., 2007).

Upflow Sludge Blanket Filter (USBF) Reactor

An interesting configuration combining the up flow anaerobic filter (UAF) technology and an UASB reactor has been developed. Elongated biomass retention and minimized clogging are the main advantages of hybrid reactor over the conventional high-rate systems. It is particularilly favorable for effluents, which are not capable of developing granular sludge (Mohana et al., 2007).

Molina examined the treatment of stillage in USBF Reactor (Molina et al., 2007). COD removal efficiency accounted up to 96%. The methane content in generated biogas ranged from 70 to 74% at production rate of 3321 L/kg COD removed, which creates a possibility of its future utilization for energy recovery. Such outstanding performance could in this case result from a very good quality of the effluents, owing to their high volatile suspended solids (VSS) content and great granulating properties. The system was proved feasible in a long-term treatment of seasonally generated wastewaters, such as winery effluents (Molina et al., 2007).

Anaerobic Membrane Bioreactors (AMBR)

Technology of ASGR is combined with various membrane processes in Anaerobic Membrane Bioreactors (AMBR). Contrary to other anaerobic systems, this type of reactors have a relatively high energy requirements resulting from application of separation techniques. For this reason they are preferably designed for maximal energy recovery from anaerobic digestion (Melamane et al., 2007). This system was also considered for wine distillery wastewater treatment.

Kubota Submerged Anaerobic Membrane Bioreactor (KSAMBR)

Thi§s is the most recent development in methane fermentation technologies and performs the process under thermophilic conditions. It is already utilized by 15 full scale plants in Japan. In a demonstration study Kanai presented a case of distillery using barley and sweet potatoes for production of Shochu spirit, which uses full-scale KSAMBR technology (Kanai et al., 2010).

KSAMBR arrangement comprises of a separate methane fermentation tank (MF) with a sub-compartment termed submerged membrane separator (SMS). Temperature in the system is maintained by steam-fed heat exchangers. Optimal conditions, namely solid content of 3- 9% and ammonia concentration about 1.5 g/L are achieved by recirculation of effluent from SMS to MF for stillage dilution. Excellent COD removal efficiency reaching 92% was obtained in this system. The electricity consumption for heating and membrane separation is fully covered by the energy retrieved from high purity (60% of methane and 40% of carbon dioxide) biogas combustion, which production is equivalent to $12 \cdot 10^9$ J/day. It is still in a large excess to the total process requirements (Kanai et al., 2010).

MATERIALS AND METHODS

The concept of the study was based on the use of anaerobic digestion of brewery wastewater treatment in the macro-laboratory scale. The aim of this investigation was the separation of the two most important steps in the process of fermentation - acidogenesis and methanogenesis. Methanogenesis was performed in UASB-type reactor. Furthermore, the objective of the experimental work was to generate granular sludge with good sedimentation properties.

Anaerobic wastewater treatment was carried out in the system shown in Figure 1. It consisted of prefermentation chamber (2), which was fed with the raw wastewater from tank (1). The chamber (2) was equipped with a mixer and in it tank (1) the acidic fermentation took place. After acidic stage the wastewater was pumped into neutralization tank (3). The pH was set up at about 6.5. It is a necessary condition for the proper metanogenesis in the next step, methane fermentation in the UASB chamber (4).

For the experiments the mixture of synthetic wastewater (prepared according to Weinberger, Wojnowska-Baryła et al., 1993) and appropriately diluted beer were used. The synthetic wastewater was a source of minerals (Na, K, Mg, Ca), while the beer supplied mainly carbon, nitrogen and phosphorus.

Investigations on the anaerobic digestion of such prepared “brewing” wastewater in the UASB system were carried out continuously for five months. For monitoring of the process the COD was determined according to Standard Methods.

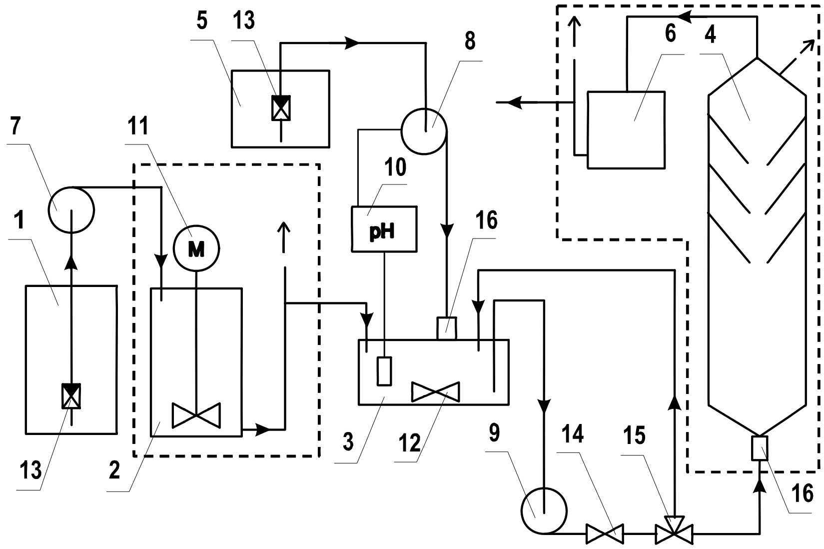

Figure 2. Anaerobic wastewater treatment system, detailed description in Table 1

Table 1. Equipment list of anaerobic wastewater treatment system (see, Fig.1)

No	Equipments
1	Raw wastewater tank
2	Prefermentation tank
3	Neutralization tank
4	UASB reactor
5	NaOH storage tank
6	Gas collector
7	Raw wastewater feed pump
8	NaOH dosing pump
9	Feed pump
10	pH - meter
11	Mechanic stirrer
12	Magnetic stirrer
13	Stop valve
14	Control valve
15	Triple valve
16	Injection valve

The UASB reactor chamber was inoculated with granular sludge, taken from anaerobic treatment plant in sugar industry. The sewage sludge had a clear granular structure, the granules were smooth, with diameter 1 - 2 mm. The sewage sludge was characterized by good sedimentation properties.

RESULTS AND DISCUSSION

The studies were carried out for 94 days. At the beginning the anaerobic sewage sludge should be adopted to synthetic brewery wastewater. Thus, the COD load during start-up was slightly lower than during the next periods and on average it was about 1800 mgO_2/dm^3. In the next phase the COD was rised to about 2550 mgO_2/dm^3, while the highest COD load (about 4000 mgO_2/dm^3) was applied during last week of the experiment. The hydraulic retention time (HRT) in the UASB reactor was 24 hours.

In the course of investigation the effectiveness of brewing wastewater treatment in the UASB system was monitored, however, the properties of anaerobic sludge were also controlled.

In the initial phase of the process with the new sewage type, the sludge has lost its granular form. New grown bacteria formed dispersed flocks instead of to aggregate into granules. The flocks small in size flowed out from the UASB reactor, what made operational problems and the process efficiency was not satisfactory in COD removal. However, after several weeks of process run the sludge began form a larger agglomerates, possessing better sedimentation properties. After 5 months we observed the new granules with smooth texture. Their shape was not identical to that of inoculated sludge (less smooth texture), also the size of granule was larger (2 - 4 mm). Thus, the newly granulated anaerobic sludge possessed better settling properties than inculating sludge.

The efficiency of wastewater treatment was monitored by the determination of COD. The obtained results of the COD of sewage after treatment are summarized in Table 2., while in Fig. 3 the COD removal versus time is presented. The efficiency of COD removal is expressed in relation to raw wastewater COD value.

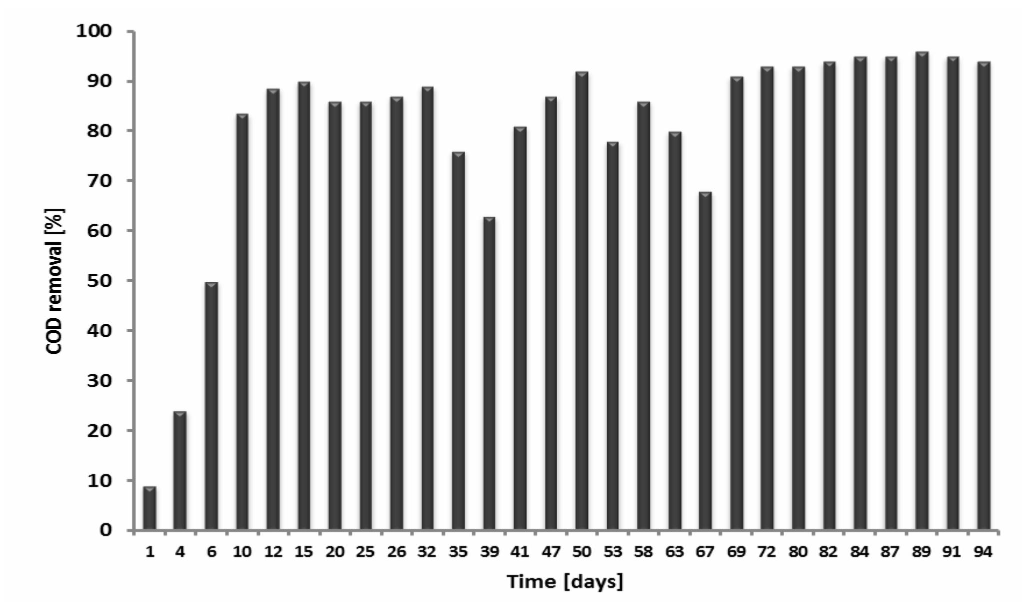

Figure 3. COD removal from wastewater

Table 2. Changes of COD during brewing wastewater treatment in UASB system

Sample	Day of treatment	COD in wastewater [mgO$_2$/dm^3]				COD removal efficiency [%]
		Raw	Prefermentation tank	Neutralization tank	Treated	
1	1	1050	1300	1650	960	8.5
2	4	1230	1670	1825	910	24.1
3	6	1540	1270	1500	770	50.0
4	10	1690	1850	1920	290	83.1
5	12	1650	1535	1450	190	88.5
6	15	2010	1790	1920	196	90.2
7	20	1500	1750	1220	209	86.1
8	25	1875	1600	1475	266	85.8
9	26	1800	1530	1415	241	86.6
10	32	2035	1835	1895	220	89.2
11	35	2440	2685	2670	270	89.0
12	39	1460	1160	1690	348	76.0
13	41	2160	2465	2095	805	62.7
14	47	2220	2541	2520	426	80.8
15	50	2115	2175	1605	270	87.0
16	53	2740	2695	1840	215	92.2
17	58	1690	1500	1400	370	78.1
18	63	3160	2920	2410	530	86.4
19	67	1750	2530	2060	310	80.0
20	69	3380	3380	3170	1050	68.0
21	72	4700	2970	2770	430	91.0
22	80	3440	2330	1920	220	93.5
23	82	5860	3000	2625	375	93.3
24	84	3375	3035	2615	180	94.1
25	87	4155	4040	3815	166	96.8
26	89	4100	3825	4740	224	95.0
27	91	3600	3535	3165	162	95.5
28	94	3145	2560	2500	230	93.9

As it is clearly visible from the presented results, the adaptation of anaerobic bacteria present in the sewage sludge in brewing wastewater was clearly visible. The initial removal of COD was below 10% (simultaneously the dispersion of the sludge granules was observed). After about two weeks of process continuing, the COD removal increased up to 90%. This level of organic matter removal was maintained till the end of the experiment.

CONCLUSIONS

Application of anaerobic digestion to distillery effluents is a preferable primary treatment option. Since aerobic processes have higher nutrient requirements and cause operational difficulties in treating high organic strength wastewaters, employing these methods in primary treatment of stillage would result in lower cost-efficiency. Conversion of COD into biogas through biomethanation, rather than into sludge in aerobic processes appears to be a reasonable solution. The generated methane can be readily utilized as a fuel covering the energy demand in ethanol production process. Contrary to the popular dryhouse processing, anaerobic digestion of stillage may significantly improve the energy balance of an ethanol plant.

Most of the anaerobic technologies applied so far in the treatment of high organic strength wastewaters - municipal and originated from other industry branches - were employed for effluents from ethanol manufacture, achieving high levels of pollutants decay.

Further development of anaerobic technologies treating ethanol stillages can be expected to tend towards processes conducted at higher temperatures. Utilization of separation techniques, particularly various membrane processes, emerge as a promising technological improvement for enhanced treatment efficiency in anaerobic digestion of distillery effluents.

Our experiments have demonstrated that anaerobic treatment of brewery wastewater in UASB system could be good method of organic, easily biodegradable wastewater utilization. The achieved efficiency of COD removal was satisfactory, it reached over 95%. During the experiment the properties of anaerobic granular sludge was also controlled. The granulated sludge used as a inoculum was characterized by good sedimentation properties. In the initial stage of treatment the newly grown bacteria had dispersed form. Besides, granules looses its solid form and diversed, what results in poor sedimentation properties. But after stabilization of the process the bacteria started to form granular shape. Their sedimentation properties ameliorated. And what is the most important – the anaerobic bacteria were able to adopt to new wastewater composition and to recover their biological and physical properties.

Successfully implemented on a full scale by over 147 facilities worldwide, anaerobic utilization of distillery effluents may already be considered as an established technology. A broad range of secondary and tertiary treatment options is available. Anaerobic digestion of stillage presents a sustainable and economically viable method allowing to mitigate the environmental impacts of ethanol industry.

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