## Kaan Dereli, MSc

# Performances Of Anaerobic Membrane Bioreactors Treating Thin Stillage from Bioethanol Plants at Different Sludge Retention Times

Ethanol production, as a renewable energy source and fuel additive, form starch based grains such as corn and wheat has increased rapidly in recent years to mitigate green-house gas emissions due to the extensive usage of fossil fuels and to regulate the instabilities in global fuel supply (Gao et al., 2011, Wilkie et al., 2000). However, bio-ethanol manufacturing is a water and energy intensive process that generates a high amount of concentrated wastewater called stillage and requires a high amount of energy input for downstream stillage management with centrifuges, evaporators and dryers. Therefore, its overall environmental benefit is still questionable. The only by-product of bio-ethanol production facilities is called dry distillers grains with solubles (DDGS) and it is produced through a series of energy intensive processes for concentrating the effluent coming from the main distillation process. DDGS, rich with proteins, carbohydrates, lipids and nutrients, has a high nutritional value and it is valorized in animal feed market to compensate the operation costs and to improve the overall feasibility of the process (Eskicioglu et al., 2011).

Thin stillage from corn to ethanol distilleries is a complex wastewater containing high concentrations of carbohydrates (glucan, xyclan and lactic acid), proteins and lipids (Kim et al., 2008) which makes it a very high strength wastewater with COD and TS values up to 100 g/L and 70 g/L, respectively. High organic matter content and biodegradability of thin stillage promotes the anaerobic reactors as the most feasible technology for the treatment of distillery wastewater.

Better stillage management alternatives instead of high energy consuming thermal processes are still under investigation. In that context, the anaerobic membrane bioreactors (AnMBRs) which combine the classical anaerobic digestion with membrane filtration offers many advantages such as biogas production, energy recovery and high effluent quality for stillage management (Dereli et al., 2012). The high particulate COD content of thin stillage limits the applicability of high rate anaerobic granular sludge bed systems for its treatment due to the problems with biomass retention. Thus, a completely mixed reactor equipped with membranes for sludge retention can provide both sufficient



Kaan Dereli TU Delft Istanbul University of Technology



### Industrial AMBR

biodegradation capacity by preventing the wash-out of slow growing anaerobic biomass and maintain a high and stable reactor performance. Apart from that, recycling of AnMBR permeate can also help to reduce the amount of fresh water necessary for hydrolysis/saccharification processes and increase the ethanol yield by supplying the necessary macro and micro nutrients for yeast growth (Zhang et al., 2009; Gao and Li, 2011).

In contrast to their many advantages, AnMBRs naturally inherit disadvantages of the membrane filtration processes such as membrane fouling (organic and inorganic), high investment and operation costs and process complexity with increased automation needs. Among these handicaps, membrane fouling seems to be the most important one that limits the wide-spread application of AnMBRs (Jeison, 2007). Cake layer formation was identified as the most important fouling mechanism for AnMBRs (Jeison and van Lier, 2007). However, inorganic fouling was also determined as another potent fouling type especially for inorganic membranes. Many operation parameters such as sludge retention time (SRT), volumetric and sludge loading rate (VLR and Food:Mass) filtration/backwash/relaxation periods, applied shear rate, etc. seem to have an influence on both membrane fouling and reactor performance. Therefore, understanding the relation of these factors with each other and optimization of them for each specific case to improve reactor performance and mitigate fouling is of crucial importance.

The sludge retention time (SRT) in AnMBRs, can be controlled much easier than other types of anaerobic reactors and it is completely independent from the hydraulic retention time. In literature, AnMBRs were reported to operate at various SRTs in the range of 30-350 days (Dereli et al., 2012). In principle, high SRTs corresponds to more biogas production due to the improved stabilization of organic matter, less sludge production and higher biomass concentrations in the reactor. However, increasing SRT also yields to a more stabilized sludge in terms of active microorganism concentration and accumulation of inert organic and inorganic matter such as decay products of bacteria and inorganic precipitates in the reactor. The effect of SRT on biological and filtration performance of AnMBRs is still a very important topic that needs further investigation. The aim of this study is to identify the effect of SRT on the treatment and filtration performance of lab-scale AnMBRs treating corn based ethanol stillage.

#### **Materials and Methods**

The lab-scale reactors consist of a feed vessel continuously mixed and kept at a temperature of 4-5 °C, a continuously mixed 10 L anaerobic digester, and a side-stream tubular cross flow microfiltration membrane with a surface area of 0.0115 m<sup>2</sup> (Figure 1). The reactors were gently stirred at 35 rpm by top-entry mechanical mixers. The membrane was supplied by Pentair X-flow and it is made of PVDF with a mean pore size of 0.03  $\mu$ m. To enable high membrane fluxes, permeate was partially recycled into the reactor, as shown in Figure 1. The biogas production, pH and the trans-membrane pressure were recorded on-line. Feed flow and permeate flow rates were manually checked daily.

Two AnMBR reactors were operated in parallel at different SRTs such as 20 and 30 days for 3 months. The SRT was then increased from 30 days to 50 days in the second reactor for another 3 months. The



Figure 1 - Lab-scale cross-flow AnMBR setup.

reactors are named after their SRTs, i.e. R-20, R-30, R-50, respectively. The reactors were inoculated with grinded and sieved (600  $\mu$ m) granular sludge from a full scale EGSB reactor and they were operated under mesophilic conditions. The membrane was operated at a cross-flow velocity (CFV) of 0.5 m/s and to limit fouling cyclic membrane operation was carried out such as 300 seconds filtration and 30 seconds backwash. Back wash was done by simply reversing the pump flow. The wastewater characterization used in the experimental study was presented in Table 1.

#### Results

During the study, the average VLR for R-20, R-30 and R-50 reactors were 8.3, 7.8, 6.1 kg COD/(m3. day), respectively. Higher loading rates could be applied to R-20 and R-30 reactors compared with R-50 reactor. Moreover, operation was interrupted several times due to VFA accumulation in R-50 reactor. The effluent COD concentrations at stable operating conditions in R-20, R-30 and R-50 reactors were 470±60, 570±60, 1070±30 mg/L, respectively. The SRT being the major operating parameter seems to have an influence on the effluent COD concentrations in the reactors and the permeate COD tends to increase at higher SRTs. The permeate COD concentrations in R-50 was always higher in comparison to the other two reactors operated at 20 and 30 days SRTs. The COD removal efficiencies of R-20 and R-30 was higher than 99% during the long term study, however, as a result of instabilities the performance of R-50 occasionally dropped down to 96% which is still a very high removal efficiency

Parameter	Unit Concentration			
COD	g/L 72.2 ± 8.6			
COD <sub>soluble</sub>	g/L	34.7 ± 6.2		
FOG	g/L	11.3 ± 0.5		
TS	g/L	41.8 ± 6.2		
VS	g/L	37.1 ± 5.6		
SS	g/L	19.2 ± 2.7		
VSS	g/L	19.2 ± 2.8		
TN	mg/L	1193 ± 263		
ТР	mg/L	909 ± 85		
PO <sub>4</sub> <sup>3-</sup> -P	mg/L	654 ± 133		
SO <sub>4</sub> <sup>2-</sup>	mg/L	948 ± 165		
Ca <sup>2+</sup>	mg/L	138 +55		
Mg <sup>2+</sup>	mg/L	307 ± 31		
K+	mg/L	1453 ± 250		
рН	-	3.89		

Table 1 - Wastewater characterization.

thanks to the membrane filtration. The average biological treatment performances of the reactors at stable operating conditions were summarized in Table 2.

The comparative filtration performances of the reactors were presented in Table 3. In general, the reactors showed very promising filtration performance considering the fact that the membranes were operated at relatively low cross-flow velocity (0.5 m/s). The filtration performance of R-20 reactor was superior compared to the others. The sludge filterability determined with capillary

Parameter	Unit	R-20	R-30	R-50			
VLR	kg COD/(m <sup>3</sup> .d)	8.3±1.3	7.8±0.9	6.1±1.4			
F/M ratio	kg COD/(kg VSS.d)	0.53±0.1	0.47±0.12	0.30±0.09			
TSS in reactor	g/L	16.5±0.8	17.2±1.8	28.3±1.1			
VSS in reactor	g/L	15.2±0.6	15.3±1.4	24.9±1.2			
Permeate COD	mg/L	470±60	570±60	1070±30			
COD removal efficiency	%	99±0.2	99±0.5	98±0.8			
Digestion efficiency	%	73±4	80±6	83±10			
Methane yield	m <sup>3</sup> CH <sub>4</sub> /kg COD <sub>removed</sub>	0.31±0.02	0.32±0.02	0.34±0.06			

Table 2 - Comparison of the steady state performance of reactors at different SRTs (average±standard deviation).

## Industrial AMBR

Parameter	Unit	R-20	R-30	R-50
Permeability (20°C)	L/(m².h.bar)	30-100	26-45	40-85
Operation flux	L/(m².h)	12	11	14
Critical flux	L/(m².h)	18	13	14.5
CST	S	951±128	1743±187	2414±145
Normalized CST	s.L/g TSS	61±5	90±12	86±4
SCR	1012 m/kg	2001±78	3137±262	2963±218
Supernatant filterability	mL/min	0.27±0.03	0.18±0.01	0.17±0.01
Mean particle size	μm	50	41	16

Table 3 - Summary of filtration performance and sludge filterability in the reactors.

suction time (CST), specific cake resistance (SCR) and supernatant filterability were quite similar for R-30 and R-50 reactors, however R-30 reactor showed worse long term membrane performance.

#### Conclusions

In this study, organic matter conversion efficiency to methane tended to increase at higher SRTs. This may be due to the better biodegradation of FOG at increasing SRTs. High and stable fluxes could be obtained considering the relatively low CFV applied in the study. The reactor operated at an SRT of 20 days showed the best membrane performance, whereas its COD conversion efficiency was the poorest. This indicates that SRT should be optimized in AnMBRs to obtain better biological and filtration performance.

#### Acknowledgements

This research was funded and supported by Biothane Systems International in collaboration with Delft University of Technology.

#### References

- Dereli, R.K., Ersahin, M.E., Ozgun, H., Ozturk, I., Jeison, D., van der Zee, F., van Lier, J.B. (2012) Potentials of anaerobic membrane bioreactors to overcome treatment limitations induced by industrial wastewaters. Bioresource Technology, 122, 160-170.
- Eskicioglu, C., Kennedy, K.J., Marin, J. and Strehler, B. (2011) Anaerobic digestion of whole stillage from dry-grind corn ethanol plant under mesophilic and thermophilic conditions. Bioresource Technology 102(2), 1079-1086.

- Gao, T. and Li, X. (2011) Using thermophilic anaerobic digestate effluent to replace freshwater for bioethanol production. Bioresource Technology 102(2), 2126-2129.
- Jeison, D. (2007). Anaerobic Membrane Bioreactors for Wastewater Treatment: Feasibility and Potential Applications. PhD Thesis, Wageningen University, Wageningen, The Netherlands.
- Jeison, D., van Lier, J.B. (2007) Cake formation and consolidation: Main factors governing the applicable flux in anaerobic submerged membrane bioreactors (AnSMBR) treating acidified wastewaters. Separation and Purification Technology 56(1): 71-78.
- Kim, Y., Mosier, N.S., Hendrickson, R., Ezeji, T., Blaschek, H., Dien, B., Cotta, M., Dale, B. and Ladisch, M.R. (2008) Composition of corn drygrind ethanol by-products: DDGS, wet cake, and thin stillage. Bioresource Technology 99(12), 5165-5176.
- Wilkie, A.C., Riedesel, K.J. and Owens, J.M. (2000) Stillage characterization and anaerobic treatment of ethanol stillage from conventional and cellulosic feedstocks. Biomass and Bioenergy 19(2), 63-102.
- Zhang, W., Xiong, R. and Wei, G. (2009) Biological flocculation treatment on distillery wastewater and recirculation of wastewater. Journal of Hazardous Materials 172(2-3), 1252-1257.