

Ethanol purification with ozonation, activated carbon adsorption, and gas stripping

**Shinnosuke Onuki,^a Jacek A. Koziel,^{a,b,d,*} William S. Jenks,^c Lingshuang Cai,^a
Somchai Rice^{a,e} and J.(Hans) van Leeuwen^{a,b,d}**

^aDepartment of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA, 50011, USA

^bDepartment of Civil, Construction, and Environmental Engineering, Iowa State University, Ames, IA, 50011, USA

^cDepartment of Chemistry, Iowa State University, Ames, IA, 50011, USA

^dDepartment of Food Science and Human Nutrition, Iowa State University, Ames, IA, 50011, USA

^eInterdepartmental Toxicology Program, Iowa State University, Ames, IA, 50011, USA

*corresponding author: koziel@iastate.edu, phone: 515-294-4206, fax: 515-294-4250

Abstract

Fermentation of sugar to produce ethanol also produces volatile byproducts. This study was aimed at purifying corn-based ethanol for industrial and pharmaceutical use. The research was on treatment for 10 impurities removal after distillation. The ethanol headspace was sampled with solid-phase microextraction and analyzed with gas chromatography-mass spectrometry. A 40 mg/L ozone treatment resulted in >56 % and >36 % removal of styrene and 2-pentylfuran, respectively, without significant generation of byproducts. A 60 g/L activated carbon (AC) treatment with 270 min adsorption time

resulted in 84 %, >72 %, and >78 % removal of ethyl hexanoate, ethyl octanoate, and ethyl decanoate respectively. CO₂-based stripping, at 675 L_{Stripping gas}/L_{Sample}, removed 65%, >82%, and >83 % acetaldehyde, ethyl vinyl ether, and 1,1-diethoxyethane respectively. A combination of three approaches effectively removes these 8 impurities.

Keywords

Activated carbon adsorption; Ethanol; Gas stripping; Ozonation; Volatile byproducts

1. Introduction

The total ethanol (EtOH) production in the United States approaches 53 million m³ (14 billion gal/year [16]. The value of EtOH as a fuel additive is tied to the price of oil and is lower than other EtOH products used in industry, so conversion of some of the EtOH to industrial or pharmaceutical alcohol creates a higher-value product.

The dry-grind EtOH production process includes corn milling, cooking, saccharification, fermentation, and separation by distillation. The volatile byproducts from fermentation are the most significant impurities in fermentation of EtOH, since these impurities are not efficiently removed by distillation and this is not required for fuel production. The remaining impurities in EtOH would need to be removed to acceptable levels as these could threaten human health and cause unpleasant flavors [7], [6], [14]. Higher alcohols, acetaldehyde, esters, fatty acids, and ketones are all present in commercial EtOH and derive from starch [25]; cyclic compounds are produced from lignin [8], [18]. Congeners of ethanol make a contribution to the unease and weakness following excessive

drinking known as hangover [19], [32] and this provides an additional reason to purify alcohol for human consumption.

There are various kinds of purification techniques for the removal of low-level organic compounds used in the water treatment industry, while distillation has been the only practical purification technique for EtOH in industry. These treatment techniques include air stripping [22], [26], adsorption to activated carbon (AC) [30], [11] and ozonation [28], [29].

Among these water and wastewater treatment techniques, ozonation would be an interesting treatment for EtOH purification. Ozone, O₃, is an allotrope of oxygen that is much less stable than the diatomic species, O₂. The strong oxidation potential of O₃ makes it very reactive towards organic compounds [20]. Since O₃ reacts only very slowly with EtOH, if at all, it would be possible to selectively oxidize certain impurities if their reaction rate with O₃ is much higher than with EtOH. Although, in many cases, O₃ does not achieve complete oxidation of organic compounds, the organic compounds are altered, resulting in changes in the properties of the compounds such as increased volatility, biodegradability, and lowered toxicity [3], [9], [24], [33]. These byproducts would require subsequent post-ozonation treatment for their removal.

AC adsorption is a very common post-ozonation treatment [17], [21]. AC has a large surface area, between 300 and 2000 m²/g [4]. The internal structure of AC consists of macropores (>25 nm), mesopores (1 nm < D < 25 nm), and micropores (<1 nm) [27]. It can adsorb various size molecules on its surface due to its large surface area and wide pore distribution. Most volatile byproducts of fermentation, such as higher alcohols, cyclic

compounds, and ethers, have higher adsorbability on AC than EtOH [1]. Thus, AC could selectively adsorb volatile byproducts from EtOH. Acetaldehyde, however, the most significant volatile byproduct of EtOH fermentation is not expected to be effectively removed by adsorption.

Gas stripping can be used to remove volatile compounds from solution. Gas stripping is a transfer of contaminants from liquid to gas phase. It is common in water and wastewater treatment [23], [12]. Gas stripping efficiency is determined by the transfer ratio of compounds from liquid to gas phase. The equilibrium condition between liquid and gas phases are expressed by Henry's law [2]:

$$H = \frac{P_{vap}}{C_{sat}}$$

Where H = Henry's law constant (L•atm/mol)

P_{vap} = the partial pressure of a pure compound (atm), and

C_{sat} = the saturation concentration of the pure compound in the liquid phase (mol/ or mg/L)

or,
$$H = \frac{C_G}{C_L}$$

Where H = Henry's law constant (dimensionless)

C_G = gas phase concentration (identical concentration units), and

C_L = liquid phase concentration (identical concentration units)

Henry's law constant, H , varies depending on the components involved. Although there is not much data on H between EtOH and different gases, high H , and thus high gas stripping capability, is expected from compounds with low $b.p.$ such as acetaldehyde.

The purpose of this study was to investigate the potential usefulness of ozonation and post-ozonation treatments, AC adsorption and gas stripping, as advanced purification techniques of EtOH (Figure S1). All chemical analyses used solid-phase microextraction - gas chromatography - mass spectrometry (SPME-GC-MS) [13] (Figure S2). The required O₃ dose, the effect of activated C adsorption time, the effect of activated C dose, the effect of gas stripping ratio, and the effect of different stripping gases were examined on a small batch basis.

2. Materials and methods

2.1 Ethanol sample

Seventy-nine %, v/v, industrial EtOH sample used in this study was provided by Grain Processing Corporation (Muscatine, IA). The sample was transferred to one gallon amber glass bottles (Iowa State University Chemistry Store, Ames, IA) from one gallon metal containers after shipping. All amber glass bottles were stored in the flammable-material storage at room temperature.

2.2 Reagents

Standard chemicals of acetaldehyde, 1,1-diethoxyethane, ethyl vinyl ether, isoamyl alcohol, isoamyl acetate, styrene, 2-pentylfuran, ethyl hexanoate, ethyl octanoate, and ethyl decanoate were purchased from Sigma-Aldrich (Milwaukee, WI). Two hundred proof ACS grade pure EtOH (from Sigma-Aldrich, St. Louis, MO) was used as a standard.

2.3 Multidimensional GC-MS

Multidimensional GC-MS (Microanalytics, Round Rock, TX) was used for all the analyses (Figure S2). The system was equipped with a non-polar precolumn and a polar analytical column in series as well as system automation and data acquisition software (MultiTrax™ V. 6.00, Microanalytics and ChemStation™, Agilent). An auto injection system, CTC PAL system Autosampler (LEAP Technologies, Carrboro, NC), was used for automatic sample injection. The general run parameters used were as follows: injector, 260 °C; column, 40 °C initial, 6 min hold, 10 °C /min, 220 °C final, 4 min hold; carrier gas, He. Mass to charge ratio (m/z) range was set between 29 and 280. Spectra were collected at 6 scans/s and electron multiplier voltage was set to 1500 V. The MS detector was auto-tuned weekly.

The identity of compounds was verified using (a) reference standards (Sigma-Aldrich, Fisher, Fluka) and matching their retention time on multidimensional GC capillary column and mass spectrums; (b) matching mass spectrums of unknown compounds with BenchTop/PBM (Palisade Mass Spectrometry, Ithaca, NY, USA) MS library search system and spectrums of pure compounds.

2.4 SPME conditions

SPME conditions were determined based on the previous study for the analysis of industrial EtOH [13] (Figure S2). Carboxen/PDMS 85 µm fiber (Supelco, Bellefonte, PA) was used for extraction of volatile compounds. Ten mL of 10% diluted EtOH samples were transferred to 25 mL screw-capped amber vials with polytetrafluoroethylene (PTFE)-lined silicon septa. The vial was agitated for 10 min at 750 rpm and 40 °C before SPME

extraction. The SPME fiber was inserted into the headspace of the vial through the septum on the screw cap and exposed in the headspace of the vial for 20 s. With each extraction, the SPME fiber was removed immediately from the vial and inserted into the GC injection port for the analysis.

2.5 Ozone generation setup and ozone dose calibration

A purer feed gas providing setup was designed to avoid contamination from the room air. An O₃ generator (TOG C2B, Triogen, Glasgow, Scotland) was connected to an air cylinder. Moisture and hydrocarbon were removed through a moisture trap (Restek, State College, PA) and a hydrocarbon trap (Restek, State College, PA). Gas flow was controlled by a mass flow controller (GLC17, Aalborg, Orangeburg, NY) (Figure 1). The quality of feed gas was evaluated by GC-MS. Details of the standard method [15], [31] used for ozone dose calibration by titration is presented in the Supplemental Material.

2.6 Ozonation

The same ozonation condition as ozone generator calibration was used. Ozone gas was passed through 79%, v/v, 200 mL industrial EtOH samples at a flow rate of 500 mL/min. The output setup of O₃ generator was kept constant, and the O₃ dose was controlled by ozonation time. Ozone doses between 2 to 160 mg/L were examined. The ozonated samples were diluted to 10%, v/v, EtOH content. Ten mL of ozonated samples were transferred to 25 mL screw-capped amber vials with polytetrafluoroethylene (PTFE)-lined silicon septa for SPME headspace sampling before the analysis with GC-MS.

2.7 Activated carbon adsorption (post-ozonation treatment)

Post-ozonation treatment with granular AC (GAC) (F-400, Calgon Carbon, Pittsburgh, PA) was examined. Fifty mL ozonated EtOH sample (40 mg/L O₃ dose) was transferred to each of 250 mL Erlenmeyer flask. Specific amounts of GAC between 0.1 to 3 g were added to the EtOH samples. The samples were agitated at 220 rpm for a specific time between 10 to 270 min. The treated sample was diluted with water to 10%, v/v EtOH concentration. Ten mL of treated samples were transferred to 25 mL screw-capped amber vials with PTFE-lined silicon septa for the extraction with SPME and analysis with GC-MS.

2.8 Gas stripping (post-ozonation treatment)

Post-ozonation treatment with gas stripping was examined. Air, N₂, or CO₂ was passed through 79%, v/v, 200 mL ozonated EtOH samples (40 mg/L O₃ dose) with the flow rate of 500 mL/min for specific time between 10 to 270 min (stripping ratio between 25 to 675 L_{Stripping gas}/L_{Sample}). Then, the treated sample was diluted with water to be 10%, v/v EtOH concentration. Ten mL of treated samples were transferred to 25 mL screw-capped amber vials with PTFE-lined silicon for the extraction with SPME and analysis with GC-MS.

2.9 Data Analysis

The relative % reduction/generation was used to evaluate the effectiveness of each treatment. Treatment effectiveness for target VOCs was expressed as % reduction, i.e., as the ratio of the difference between the control and treatment to the control, of the form:

$$\% \text{Reduction} = \frac{C - T}{C} \times 100\%$$

where:

C = gas chromatographic peak area counts or concentrations of VOCs, and

T = gas chromatographic peak area counts or concentrations of VOCs

The VOC concentrations were estimated by using the method and calibration curves developed in a previous study [13].

3. Results and discussion

3.1 Ozonation

Industrial EtOH samples after O₃ doses between 2 to 160 mg/L were examined.

Figure 2 and Table S2 represent the effect of O₃ dose on the removal of volatile byproducts in the industrial EtOH sample. Styrene and 2-pentylfuran were removed with a 40 mg/L of O₃ dose to below the MDLs. The concentrations of styrene and 2-pentylfuran were lowered to 1.49×10^{-6} and 1.30×10^{-6} mol/L respectively after 40 mg/L of O₃ dose. There was no significant effect on all the other volatile byproducts by ozonation with an increase in the O₃ dose to 160 mg/L. The generation of ozonolysis byproducts was not observed.

Although trace level generation of acetaldehyde by oxidation of EtOH and generation of ethyl vinyl ether and 1,1-diethoxyethane by condensation of acetaldehyde and EtOH were expected, no significant changes in the concentrations of these three byproducts by ozonation were observed. Higher alcohol, acetaldehyde, and esters were not removed by

ozonation; none of these compounds are classically expected to be especially reactive with ozone, compared to furans and alkenes.

Styrene and 2-pentylfuran were effectively removed by ozonation at 40 mg/L. While removal of styrene and 2-pentylfuran by ozonation was observed, the generation of ozonolysis byproducts was not observed. This indicates that cyclic and heterocyclic volatile byproducts, lignin-derived compounds from EtOH fermentation could be removed effectively by ozonation from EtOH without any detrimental changes to the quality of EtOH. Thus, 40 mg/L O₃ dose was selected for the subsequent experiments. Other volatile fermentation byproducts, such as aldehydes, condensation products of acetaldehyde and EtOH, higher alcohols, acetate, and ethers, were not removed by ozonation only.

3.2 Activated carbon adsorption (post-ozonation treatment)

3.2.1 Adsorption time (post-ozonation treatment)

Post-ozonation treatment with granular AC (GAC) was examined. Fifty mL ozonated EtOH samples (40 mg/L O₃ dose) were transferred to 250 mL Erlenmeyer flasks. One g GAC was added to the EtOH samples, i.e. 20 g/L. The samples were agitated at 220 rpm for specific time between 10 to 270 min. Figure 3 (Part A) and Table S3 represent the effect of activated C adsorption time on the removal of volatile byproducts in the industrial EtOH sample after ozonation.

Ethyl hexanoate, ethyl octanoate, and ethyl decanoate were effectively removed by high dosages of GAC. Within 270 min contact time, the concentrations of ethyl hexanoate, ethyl octanoate, and ethyl decanoate were lowered by 33%, 70% and >78% respectively.

The removability increased with an increase in the adsorption time and molecular size. Also, apparent decreases in the % removals after initial increases in the % removals were observed on ethyl vinyl ether and 1,1-diethoxyethane. This could be explained by competitive adsorption and displacement. Firstly, small molecules, which are ethyl vinyl ether and 1,1-diethoxyethane here, were adsorbed on the surface of AC due to their high diffusivities. After that, these small molecules were displaced by larger ones, such as ethyl hexanoate here. As a result, ethyl vinyl ether and 1,1-diethoxyethane were returned to the solution resulting in the decreases in the % removals. Therefore, the determination of adsorption time is important for the selective removal of target compounds. The longer adsorption time is required to remove the larger molecules such as ethyl hexanoate, ethyl octanoate, and ethyl decanoate here. The determination of optimum adsorption time, the longest adsorption time without the occurrence of displacement, is required to remove smaller molecule compounds, such as ethyl vinyl ether and 1,1-diethoxyethane here. The adsorption of acetaldehyde and isoamyl alcohol was not observed. GAC is clearly more effective in removing larger, less polar molecules.

3.2.2 Activated carbon dose (post-ozonation treatment)

Post-ozonation treatment with GAC was examined. Fifty mL ozonated EtOH samples (40 mg/L O₃ dose) were transferred to each 250 mL Erlenmeyer flask. Specific amounts of GAC between 0.1 to 3.0 g were added to the EtOH samples resulting in 2 to 60 g/L GAC dose. The samples were agitated at 220 rpm for 270 min. Figure 3 (Part B) and

Table S4 represent the effect of AC adsorption with different GAC doses on the removal of volatile byproducts in the industrial EtOH sample after ozonation.

Three ethyl esters, ethyl hexanoate, ethyl octanoate, and ethyl decanoate, were removed by AC. A dosage of 60 g/L AC lowered the ethyl hexanoate, ethyl octanoate, and ethyl decanoate by 84%, >72%, and >78 %, respectively. An increase in the AC dose resulted in a corresponding increase in the percent removal. Ethyl vinyl ether, 1,1-diethoxyethane, and isoamyl acetate were also removed with 60 g/L AC dose by >52 %, 35%, and >89%, respectively. The compounds with high polarities, acetaldehyde and isoamyl alcohol, were not removed even with 3 g (60 g/L) AC dose.

Based on the % removal of volatile byproducts in the industrial EtOH sample by AC with different doses, all compounds except highly polar compounds, acetaldehyde and isoamyl alcohol, were removed with 3 g (60 g/L) AC dose. Although the compounds that could be displaced by ethyl esters, including ethyl vinyl ether and 1,1diethoxyethane, were also removed with 3 g (60 g/L) AC dose, it is still recommended to optimize the adsorption time for the removal of the target compounds. It is also to be expected that full-scale application would make use of columns with granular AC, where a longer path length will ensure more effective utilization of the AC, Another treatment, such as gas stripping, could be tested to remove the more tenacious polar compounds from EtOH.

3.3 Gas stripping (post-ozonation treatment)

3.3.1 Air Stripping

Post-ozonation treatment with air stripping was examined. Air was passed through 79 % v/v, 200 mL ozonated EtOH samples (40 mg/L ozone dose) with a flow rate of 500 mL/min for specific time between 10 to 270 min (stripping ratio between 25 to 675 mL_{Stripping gas}/mL_{Sample}). Figure 4 and Table S5 summarize the effect of air stripping with different stripping ratios on the removal of volatile byproducts in the industrial EtOH sample after ozonation.

The removals of acetaldehyde, ethyl vinyl ether, and 1,1-diethoxyethane, were observed with air stripping. The concentrations of acetaldehyde, ethyl vinyl ether, and 1,1-diethoxyethane were lowered by 35%, >67%, and 59% respectively with 675 L_{Stripping gas}/L_{Sample} air stripping ratio. The boiling points (*b.p.*) of these three compounds are relatively low compared to the other compounds in the EtOH sample: the *b.p.* of acetaldehyde is 21 °C; the *b.p.* of ethyl vinyl ether is 35 °C; the *b.p.* of 1,1-diethoxyethane is 103 °C. The high volatilities is reflected in good removal of these compounds by air stripping. Acetaldehyde has the lowest *b.p.* among the volatile byproducts in the EtOH and was expected to be easily removed by air stripping.

Ethyl vinyl ether and 1,1-diethoxyethane are condensation products of acetaldehyde and EtOH. Thus, removal of acetaldehyde may cause the decrease in the concentrations of ethyl vinyl ether and 1,1-diethoxyethane by reversing the condensation by simple mass-action, i.e., by hydrolysis to return the acetaldehyde to equilibrium with the ethyl vinyl ether and 1,1-diethoxyethane. Figure 4 shows that acetaldehyde stripping is linear over the

range tested. This indicates that acetaldehyde was simply volatilized by air passing through the EtOH sample. The percent removals of ethyl vinyl ether and 1,1-diethoxyethane increased sharply until $25 \text{ L}_{\text{Stripping gas}}/\text{L}_{\text{Sample}}$ and after $25 \text{ L}_{\text{Stripping gas}}/\text{L}_{\text{Sample}}$ the increases in the % removals increased gradually showing high linearity. Thus, it is expected that for the first $25 \text{ L}_{\text{Stripping gas}}/\text{L}_{\text{Sample}}$, some fraction of the ethyl vinyl ether and 1,1-diethoxyethane was removed by air passing through an EtOH sample. After $25 \text{ L}_{\text{Stripping gas}}/\text{L}_{\text{Sample}}$, the removal came from the change in the equilibrium condition between acetaldehyde and its condensation products due to decrease in the concentration of acetaldehyde.

3.3.2 Nitrogen stripping

Post-ozonation treatment with N_2 -based stripping was examined. Experimental conditions were the same as those used for air. It is expected that the introduction of O_2 through air stripping could cause a small amount oxidation of EtOH, resulting in the generation of acetaldehyde and its condensation products, counterproductive to the removal of these compounds. Figure 5 and Table S6 represent the effect of N_2 stripping with different stripping ratios on the removal of volatile byproducts in the industrial EtOH sample after ozonation.

The concentrations of acetaldehyde, ethyl vinyl ether, and 1,1-diethoxyethane were lowered by 38%, >67%, and 63% respectively with $675 \text{ L}_{\text{Stripping gas}}/\text{L}_{\text{Sample}}$ N_2 stripping ratio. There was no significant difference between air stripping and N_2 stripping. Oxygen in air did not cause the generation of acetaldehyde through EtOH oxidation. Thus, there is no benefit to the use N_2 for stripping from the standpoint of treatment cost.

3.3.3 Carbon dioxide stripping

Post-ozonation treatment with CO₂-based stripping was examined. Experimental conditions were the same as those used for air- and N₂-based stripping. Carbon dioxide is one of the main byproduct of EtOH fermentation and thus readily available at EtOH plants. Figure 6 and Table S7 represent the effect of CO₂ stripping with different stripping ratios on the removal of volatile byproducts in the industrial EtOH sample after ozonation.

The removal of acetaldehyde, ethyl vinyl ether, and 1,1-diethoxyethane, was observed by CO₂ stripping by 65%, >82 % and >83 % removal, respectively with 675 L_{Stripping gas}/L_{Sample} CO₂. While the tendencies of removability of volatile byproducts were similar to air or N₂ stripping, CO₂ stripping removed acetaldehyde, ethyl vinyl ether, and 1,1-diethoxyethane more effectively than air and N₂ stripping. This could possibly be because (a) CO₂ worked as a salting-out agent in the EtOH. In aqueous solution, CO₂ is ionized to produce bicarbonate and carbonate ions or (b) higher solubility in CO₂. Since CO₂ is readily available as a waste product on EtOH plants, there are benefits for its use in stripping acetaldehyde, ethyl vinyl ether, and 1,1-diethoxyethane over simply using air.

3.3.4 Off-gas

Ozone concentrations in the off-gas could be maintained at less than 0.1 ppm. Other off-gas concentrations have not been measured specifically, but a simple mass balance will show that the high gas-flow rates, along with quite small concentrations of the

compounds in the ethanol, would have produced very low levels of volatile organic compounds in the off-gas.

3.4 Commercial considerations

The cost of treatment is an important factor in commercialization. Distillation is a cost-intensive purification technique since it is a repetition of heating and cooling. McAllon et al. [10] estimated the distillation cost in EtOH production at ~\$0.10 to \$0.20 per gal (\$0.025 to \$0.05/L). The treatment of fuel-grade alcohol with ozonation and gas stripping can be effected at a relatively low cost. The high dosages of AC required should be investigated further as the high dosages required would be uneconomical. More prior distillation/rectification should be required to remove the higher esters at lower cost. In reality, making food-grade alcohol from fuel-grade ethanol is not quite economical without also additional distillation stages. However, combining more distillation with the three physical–chemical unit processes is able to produce a superior alcoholic product [5] and is being commercialized by Oz Spirits, LLC in making a vodka that contains no detectable impurities.

The largest component of the sales price of the vodka produced involving this process is the sum of the federal and state taxes on sales (30%). The second largest component is the mark-up by retailers (on average 27%). The bottling, labeling and physical-chemical treatment contribute 6% to the cost as a fraction of the retail sales cost. The cost of the processing is actually minimal as compared to the cost of bottling, labeling and marketing.

4. Conclusions

Ozonation, AC adsorption and gas stripping were investigated for EtOH purification of ten volatile byproducts. Ozone removed styrene and 2-pentylfuran without significant generation of byproducts. This demonstrated that it is possible to oxidize some impurities in alcohol at a higher rate than the ethanol itself. AC adsorbed ester compounds (ethyl hexanoate, ethyl octanoate, ethyl decanoate). Longer/greater adsorption time/dose caused greater removals, albeit at very high dosages. All three gases (air, N₂, CO₂) effectively stripped acetaldehyde and condensation products of acetaldehyde and EtOH, ethyl vinyl ether and 1,1-diethoxyethane. CO₂ stripping showed the most potentially useful results. Eight out of ten impurities were effectively removed by the combination of ozonation, adsorption and gas stripping.

5. Acknowledgment

The authors gratefully acknowledge Grow Iowa Values Fund (GIVF) for the financial support. Oz Spirits, LLC, Iowa contributed funding to the research and are now applying some of the findings in producing IngeniOz, the 'purest vodka on Earth'.

6. References

- [1] Abe, I., Hayashi, K., Kitagawa, M., Hirashima, T. 1983. Prediction of adsorbability of organic compounds from aqueous solution on activated carbon by means of the linear free-energy relationship. *Bulletin Chem. Soc. Japan.*, 56, 1002-1005.
- [2] Alley, E. R. *Water Quality Control Handbook*. 2007. New York, New York: McGraw-Hill.

- [3] Brooke, S., Newcombe, G., Nicholson, B., Klass, G. 2006. Decrease in toxicity of microcystins LA and LR in drinking water by ozonation. *Toxicon*. 48, 1054-1059.
- [4] Burdock, G.A. 1997. *Encyclopedia of Food and Color Additives*. Boca Raton: CRC.
- [5] Cai, L., Rice, S, Koziel, J.A., Jenks, W.S., van Leeuwen, J.(H.). 2015. Further purification of food-grade alcohol to make a congener-free product. *Journal of the Institute of Brewing*, submitted (JIB.20150364).
- [6] Campo, E., Cacho, J, Ferreira, V. 2007. Solid phase extraction, multidimensional gas chromatography mass spectrometry of four novel aroma powerful ethyl esters Assessment of their occurrence and importance in wine and other alcoholic beverages. *J. Chromatogr. A*. 1140, 180-188.
- [7] Garruti, D. S., Franco, M.R.B., da Silva, M. A. A. P, Janzantti, N.S., Alve, G.L. 2006. Assessment of aroma impact compounds in a cashew apple-based alcoholic beverage by GC-MS and GC-olfactometry. *Food Sci. Technol*. 39, 373-378.
- [8] Glab, W. T. 1965. Lignocellulose method and reaction product. U.S. Patent 3,208,864.
- [9] He, S., Xue, G., Wang, B. 2006. Activated sludge ozonation to reduce sludge production in membrane bioreactor (MBR). *J. Hazard. Mater*. 135, 406-411.
- [10] McAloon, A. Taylor, F., Yee, W., Ibsen, K., Wooley, R. 2000. Determining the cost of producing ethanol from corn starch and lignocellulosic feedstocks. National Renewable Energy Laboratory Technical Report NREL/TP-580-28893. (<http://www.nrel.gov/docs/fy01osti/28893.pdf>)
- [11] Lesage, N.; Sperandio, M.; Cabassud, C. 2008. Study of a hybrid process: Adsorption on activated carbon/membrane bioreactor for the treatment of an industrial wastewater. *Chem. Eng. Proces.: Process Intensification*. 47, 303-307.
- [12] Lisitsin, D.; Hasson, D.; Semiat, R. 2008. The potential of CO₂ stripping for pretreating brackish and wastewater desalination feeds. *Desalination*. 222, 50-58.
- [13] Onuki, S., Koziel, J.A., Jenks, W.S., Cai, L., van Leeuwen, J.(H.). 2015. Simultaneous quantification of fermentation volatile byproducts in industrial ethanol with solid-phase microextraction and gas chromatography. *Journal of the Institute of Brewing*, submitted (JIB.20150332).
- [14] Plutowska, B.; Wardencki, W. 2008. Application of gas chromatography-olfatometry (GC-O) in analysis and quality assessment of alcoholic beverages – A review. *Food Chem*. 107, 449-463.
- [15] Rakness, K., Gordon, G., Langlais, B., Masschelein, W., Matsumoto, N., Richard, Y., Robson, C.M., Somiya, I., 1996. Guideline for measurement of ozone concentration in the process gas from an ozone generator. *Ozone Sci. and Eng*. 18, 209-229.
- [16] Renewable Fuels Association. 2014. Annual Industry Outlook, (<http://www.ethanolrfa.org/pages/annual-industry-outlook> (accessed on January 7, 2015))
- [17] Rivas, F. J., Beltrán, F., Gimeno, O., Acedo, B., Carvalho, F. 2003. Stabilized leachates: ozone-activated carbon treatment and kinetics. *Water Res*. 37: 4823-4834.

- [18] Rocha, S. M., Goncalves, V., Evtuguin, D., Delgadillo, I. 2008. Distinction and identification of lignins based on their volatile headspace composition. *Talanta*. 75, 594-597.
- [19] Rohsenow D.J, Howland J. 2010. The role of beverage congeners in hangover and other residual effects of alcohol intoxication: a review. *Curr Drug Abuse Rev.* 3:76-79.
- [20] Sangave, P.C., Gogate, P.R., Pandit, A.B. 2007. Ultrasound and ozone assisted biological degradation of thermally pretreated and anaerobically pretreated distillery wastewater. *Chemosphere*. 68, 42-50.
- [21] Sereďyńska-Sobecka, B., Tomaszewska, M., Morawski, A.W. 2005. Removal of micropollutants from water by ozonation/biofiltration process. *Desalination*. 182, 151-157.
- [22] Shah, M. R., Noble, R.D., Clough, D.E. 2004. Pervaporation–air stripping hybrid process for removal of VOCs from groundwater. *J. Membr. Sci.* 241, 257-263.
- [23] Shibin, X., Shuichun, X, Changqing, Z. 2007. Removal of organic pollutants from 2,2',5,5'-tetrachlorobenzidine (TCB) industrial wastewater by micro-electrochemical oxidation and air-stripping. *J. Hazard. Mater.* 144, 159-163.
- [24] Singh, S., Fan, M., Brown, R.C. 2008. Ozone treatment of process water from a dry-mill ethanol plant. *Bioresource Technol.* 99, 1801-1805.
- [25] Smogrovicova, D., Domeny, Z. 1999. Beer volatile by-products formation at different fermentation temperature using immobilized yeasts, *Process Biochem.* 34, 785-794.
- [26] Sutherland, J., Adams, C., Kekobad, J. 2004. Treatment of MTBE by air stripping, carbon adsorption, and advanced oxidation: technical and economic comparison for five groundwaters. *Water Res.* 38, 193-205.
- [27] Tchobanoglous, G., Burton, F.L., Stensel, H.D. 2003. *Wastewater Engineering*. New York, New York: McGraw-Hill.
- [28] van Leeuwen, J. Pipe-Martin, C. and Lehmann, R. 2003. The South Caboolture Water Reclamation Process. *Ozone Sci & Eng.* 25, 107-120.
- [29] van Leeuwen, J, Sridhar, A., Esplugas, M., Onuki, S., Cai, L., Harrata, A.K. and Koziel, J.A. 2009. Improving biodegradation of organic pollutants with ozonation during biological wastewater treatment. *Ozone Sci. & Eng.* 31, 63-70.
- [30] van Leeuwen, J. 1996. Reclaimed water - an untapped resource. *Desalination*. 106, 233-240.
- [31] van Leeuwen. 2015. Letter to editor: Measuring ozone dosage. *Ozone Sci. and Eng.* 37(2), 191-192.
- [32] Verster J. C. 2006. Congeners and alcohol hangover: differences in severity among Dutch college students after consuming beer, wine or liquor. *Alcoholism: Clinical and Experimental Research* 30 (Suppl. 6): 53A.
- [33] Zhu, W, Koziel, J.A, Cai, L, Brehm-Stecher, B, Özsoy, H. D., van Leeuwen, J. (Hans). 2013. Ozonation-based decolorization of food dyes for recovery of fruit leather wastes, *J. Agric. Food Chem.* 61, 8198-8206.

Figure Captions

Fig. 1. Ozone generation and ethanol treatment setup

Fig. 2. Effects of ozone dose on removal and generation of impurities in industrial EtOH (SPME conditions: 85 μm Carboxen/PDMS fiber; headspace extraction; extraction temperature, 40 $^{\circ}\text{C}$; extraction time, 20 s; agitation time, 10 min; agitation speed, 750 rpm; EtOH dilution ratio, 10%). Part A: low ozone dose. Part B: higher ozone dose.

Fig. 3. Effects of post-ozonation treatment with activated carbon adsorption: treatment time series. SPME conditions: 85 μm Carboxen/PDMS fiber; headspace extraction; extraction temperature, 40 $^{\circ}\text{C}$; extraction time, 20 s, agitation time, 10 min; agitation speed, 750 rpm; EtOH concentration, 10 %. Ozonation condition: 40 mg/L. Activated C adsorption conditions: amount of EtOH, 50 mL; amount of GAC, 1 g; agitation speed, 220 rpm; GAC, F-400. Part A: Effects of adsorption time. Part B: Effects of GAC dose (per 50 mL of EtOH resulting in 2 to 60 g/L dose).

Fig. 4. Effects of post-ozonation air stripping on removal of volatile byproducts in industrial EtOH: stripping ratio vs. % removal. SPME conditions: 85 μm Carboxen/PDMS fiber; headspace extraction; extraction time, 20 s, agitation time, 10 min; agitation speed, 750 rpm; EtOH concentration, 10 %. Stripping condition: 200 mL EtOH sample; flow rate, 500 mL/min.

Fig. 5. Effects of post-ozonation N_2 -based stripping on removal of volatile byproducts in industrial EtOH: stripping ratio vs. % removal. SPME conditions: 85 μm Carboxen/PDMS fiber; headspace extraction; extraction time, 20 s, agitation time, 10 min; agitation speed, 750 rpm; EtOH concentration, 10 %. Stripping condition: 200 mL EtOH sample; flow rate, 500 mL/min.

Fig. 6. Effects of post-ozonation carbon dioxide stripping on removal of volatile byproducts in industrial EtOH: stripping ratio vs. % removal. SPME conditions: 85 μm Carboxen/PDMS fiber; headspace extraction; extraction time, 20 s, agitation time, 10 min; agitation speed, 750 rpm; EtOH concentration, 10 %. Stripping condition: 200 mL EtOH sample; flow rate, 500 mL/min.