

SHORT COMMUNICATION

Capture of hydrogen sulfide from wine fermentation gas for use in the food industry

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Summary

This study dealt with the capture of hydrogen sulfide from wine fermentation gas for use in the food industry. Gas chromatography was used to investigate the H₂S sorption capacity of two commercial sorbents based on the combination of CuO-zeolite and CuO/MnOx, as well as the ability of the examined sorbents to pass aromatic substances. The best results were obtained with the CuO/MnOx-based sorbent, which had the highest overall sorption capacity and was also able to pass positive aromatics, such as higher alcohols and esters. The treated gas, which does not contain unwanted hydrogen sulphide, is suitable for use in the food industry.

Keywords

fermentation gas; hydrogen sulfide; sorbent

CO₂ produced from fermentation processes, including wine fermentation, is a saturated gas, at low to atmospheric pressure [1]. During the fermentation of wine, many volatile aroma-active are formed by yeast metabolism [2–4] and so the fermentation gas is enriched with valuable volatile substances and with off-odours [5–7]. The latter are mainly sulphur compounds including H₂S and dimethyl sulphide (DMS) [8]. Other sensorially undesirable volatiles in wine are 4-vinylphenol and 4-vinylguaiacol, which are formed during fermentation from hydroxycinnamic acids [9]. Off-odours could subsequently worsen the sensorial properties of the product in which the captured CO₂ was used [10, 11].

The biochemical pathway for the formation of hydrogen sulfide is an integral part of the metabolism of wine yeasts [12]. Various methods of H₂S removal were investigated, such as adsorption, scrubbing and biological treatment at low temperatures [13–15]. Among these methods, the dry adsorption process is a readily available, environmentally friendly and economical method [16].

In this study, the hydrogen sulfide sorption capacity of two commercial sorbents was assessed, together with their ability to pass sensorially posi-

tive aromatic substances such as higher alcohols and esters. The results of the study can be used for further research and development of new types of sorbents.

MATERIALS AND METHODS

Chemicals

Captured compressed carbon dioxide, Na₂S·9H₂O (Thermo Fisher Scientific, Waltham, Massachusetts, USA), isoamyl alcohol, isobutyl alcohol, isoamyl acetate, hexyl acetate, ethyl butyrate, ethyl hexanoate and ethyl octanoate (all Sigma Aldrich, St. Louis, Missouri, USA) were used. Commercial sorbents HyProGen GS-6 (CuO/MnOx) and HyProGen GS-23 (CuO-zeolite) from Catalysts and Chemical Specialties (Zorneding, Germany) were used.

Preparation of synthetic fermentation gas with sulfane

Three parts of a cellulose wadding (Batist Medical Productions, Červený Kostelec, Czech Republic) were put into the filter for compressed air model 005A (Parker Domnic Hunter, Gateshead,

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United Kingdom), into which 9 ml of 1 mol·l⁻¹ sodium sulfide solution was soaked. Another piece of cellulose wadding (Batist Medical Productions) was placed on this layer, into which a solution of a mixture of volatile substances in ethanol was soaked (isoamyl alcohol, isobutyl alcohol, isoamyl acetate, hexyl acetate, ethyl butyrate, ethyl hexanoate and ethyl octanoate; 50 µl of each with 1 ml of ethanol). Then, the housing was closed and connected to a pressure cylinder as a source of carbon dioxide and to a keg into which the working gas was collected. The maximum pressure was set to 700 kPa by the reducing valve.

Determination of sulfane

Sulfane concentration was determined using Gastec sorption tubes in conjunction with a GV-110 gas measuring syringe (Gastec, Kanagawa, Japan). Hydrogen sulphide 4HM tubes (Gastec) with a range of 50–800 mg·l⁻¹ were used to determine the sulfane concentration in the working gas. Tubes 4LT (0.1–2 mg·l⁻¹), 4LB (1–6 mg·l⁻¹), 4LK (2–20 mg·l⁻¹) and 4L (10–120 mg·l⁻¹) were used to measure sulfane concentrations in the outlet gas according to increasing concentration.

Determination of volatile organic compounds

The concentration of volatile organic compounds in the inlet and outlet gas was measured by gas chromatography-mass spectrometry (GC-MS) on a Shimadzu GC-17A gas chromatograph (Shimadzu, Kyoto, Japan) coupled to a QP5050A mass detector (Shimadzu) and an Agilent J&W DB-Wax column (25 m × 0.2 mm, 0.2 µm; Agilent, Santa Clara, California, USA). The carrier gas was He with a flow rate of 0.9 ml·s⁻¹ (36 cm·s⁻¹). Gas injection was from a gas-tight syringe of 2.5 ml in splitless mode into the injector at a temperature of 200 °C and an injection time of 0.2 min. The initial separation temperature of 35 °C was maintained for 4 min, followed by a temperature gradient of 15 °C·min⁻¹ up to a value of 200 °C. The total duration of the analysis was 15 min. The detector worked in SIM mode, when fragments 43 (specific for isoamyl alcohol, isobutyl alcohol, isoamyl acetate, hexyl acetate and ethyl butyrate) and 88 (specific for ethyl hexanoate and ethyl octanoate) were monitored.

Design of experiment

The individual sorbents were crushed in a porcelain grinding bowl and sifted through sieves with a mesh size of 0.6 mm and 0.3 mm. An amount of 2 g of the sorbent was weighed into a Pyrex glass column (Corning, New York, New York, USA)

with an inner diameter of 20 mm with a glass frit and a Teflon valve. Working gas was supplied from the storage keg through a control valve with a flow meter. The flow rate of the inlet gas was set to 1 l·min⁻¹ and continuously controlled during the experiment.

RESULTS AND DISCUSSION

Based on a previous study by WEINLAENDER et al. [17], where the sorption capacity of various sorbents was investigated at low temperature, two sorbents based on the combination of CuO-zeolite and CuO/MnO were selected for this experiment. Fig. 1 and Fig. 2 show the sorption capacities of the sorbents.

Fig. 1 shows the total amount of captured hydrogen sulfide. The sorption capacity of the sorbent based on CuO-zeolite was low, only 10 mg

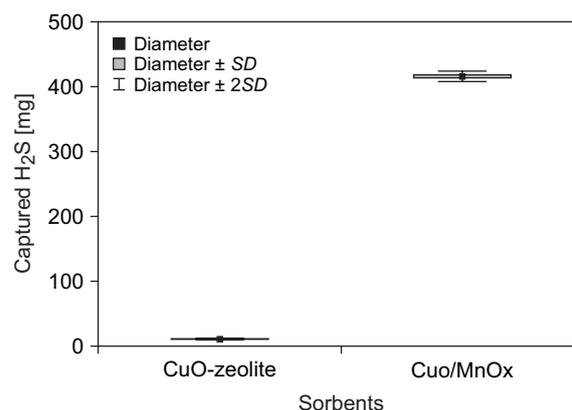


Fig. 1. Amount of captured H₂S by the sorbents.

The results are expressed as milligrams of captured hydrogen sulfide per 2 g of sorbent. SD – standard deviation.

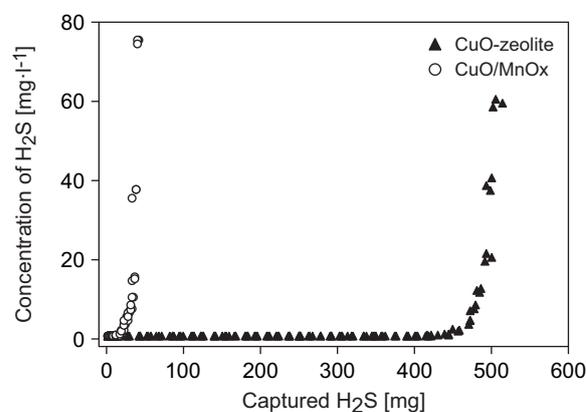


Fig. 2. Concentration of H₂S in outlet gas.

Tab. 1. Concentration of the volatile compounds in the outlet gas.

| Sorbents | Time [min] | Isobutylalcohol [$\mu\text{g}\cdot\text{l}^{-1}$] | Isoamyl acetate [$\mu\text{g}\cdot\text{l}^{-1}$] | Isoamylalcohol [$\mu\text{g}\cdot\text{l}^{-1}$] | Ethyl hexanoate [$\mu\text{g}\cdot\text{l}^{-1}$] | 1- Hexyl acetate [$\mu\text{g}\cdot\text{l}^{-1}$] | Ethyl octanoate [$\mu\text{g}\cdot\text{l}^{-1}$] |
|-------------|------------|---|---|--|---|--|---|
| CuO-zeolite | 0* | 80.51 \pm 0.20 ^f | 87.77 \pm 0.45 ^d | 89.39 \pm 0.07 ^e | 75.17 \pm 0.99 ^f | 76.97 \pm 0.79 ^f | 17.22 \pm 0.12 ^b |
| | 15 | 47.99 \pm 0.08 ^d | 75.16 \pm 1.00 ^c | 26.9 \pm 0.15 ^c | 37.26 \pm 0.14 ^d | 34.17 \pm 0.62 ^d | 4.49 \pm 0.13 ^a |
| | 50 | 3.31 \pm 0.00 ^a | 5.02 \pm 0.08 ^b | 0.96 \pm 0.02 ^a | 4.03 \pm 0.06 ^a | 4.55 \pm 0.10 ^{ac} | 1.06 \pm 0.05 ^a |
| | 80 | 5.63 \pm 0.11 ^a | 3.28 \pm 0.09 ^b | 0.39 \pm 0.02 ^a | 2.25 \pm 0.13 ^a | 2.48 \pm 0.12 ^c | 0.85 \pm 0.09 ^a |
| CuO/MnOx | 0* | 67.22 \pm 4.25 ^e | 79.27 \pm 3.92 ^c | 65.88 \pm 6.56 ^d | 50.33 \pm 5.79 ^e | 51.48 \pm 6.95 ^e | 13.96 \pm 4.55 ^b |
| | 15 | 36.89 \pm 0.62 ^c | 48.92 \pm 1.57 ^a | 21.33 \pm 1.00 ^c | 18.81 \pm 0.42 ^c | 17.41 \pm 0.45 ^b | 2.13 \pm 0.30 ^a |
| | 50 | 30.3 \pm 1.75 ^b | 44.65 \pm 3.78 ^a | 11.41 \pm 0.70 ^b | 12.98 \pm 0.71 ^{bc} | 11.24 \pm 0.45 ^{ab} | 1.22 \pm 0.15 ^a |
| | 80 | 29.89 \pm 2.11 ^b | 45.76 \pm 3.55 ^a | 10 \pm 0.84 ^b | 12.29 \pm 0.87 ^b | 10.45 \pm 0.47 ^{ab} | 1.03 \pm 0.10 ^a |

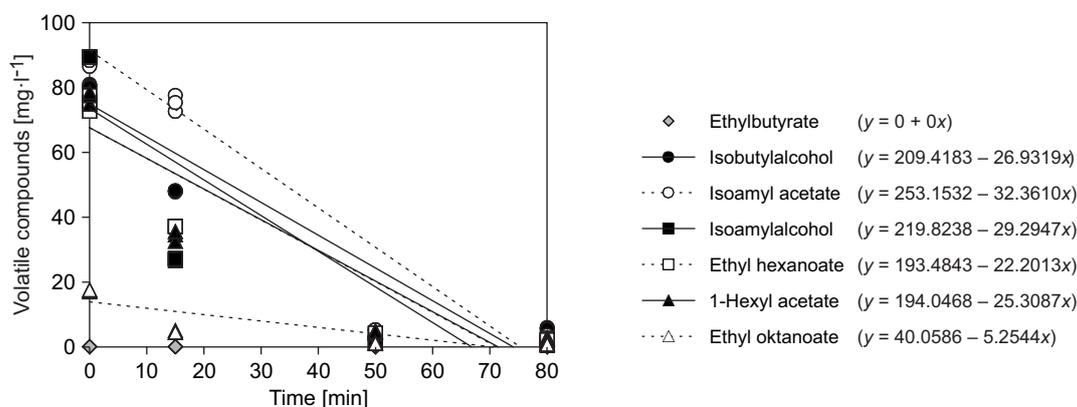
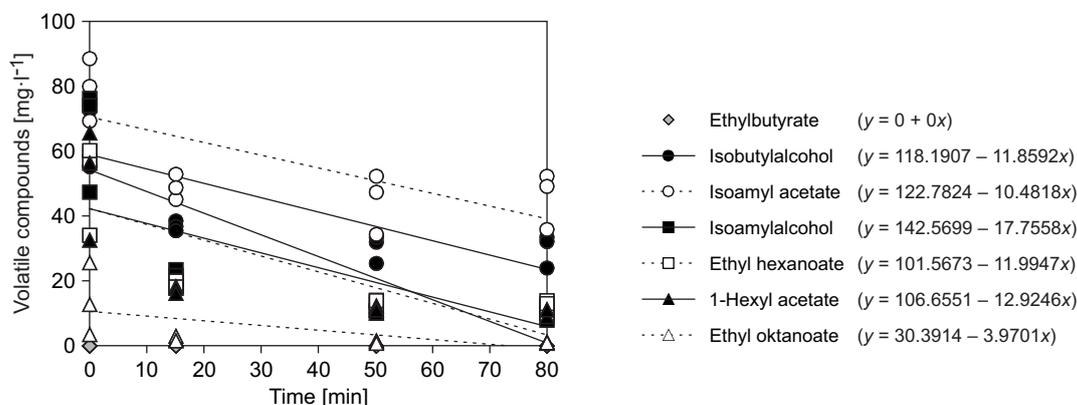
The average values ($n = 3$) were combined by contribution to homogenous groups according to Fisher's test significant difference (LSD) test, where different letters in the same row indicate significant differences ($\alpha = 0.05$).

* – concentration of compounds in inlet gas.

of hydrogen sulfide per 2 g of sorbent, compared to the sorbent based on CuO/MnOx, which captured 420 mg of hydrogen sulfide. Fig. 2 shows the concentration of hydrogen sulfide in the outlet gas as a function of the volume of CO₂ flowed through. While the sorbent based on CuO-zeolite released a significant amount of hydrogen sulfide

already at the beginning, the sorbent based on CuO/MnOx had the ability to adsorb hydrogen sulfide for a longer time and was not saturated too soon.

Concentrations of individual volatile compounds in outlet gas over time are shown in Tab. 1, Fig. 3 and Fig. 4. The concentration of the original

**Fig. 3.** Concentration of individual volatile compounds in outlet gas over time for CuO-zeolite sorbent.**Fig. 4.** Concentration of individual volatile compounds in outlet gas over time for CuO/MnOx sorbent.

gas composition can be seen as the first point of the curve (inlet gas). The concentration of individual aromatic substances gradually decreased over time after passing through the sorbents. Higher concentrations of isoamyl acetate and isobutyl alcohol were determined in the outlet gas when CuO/MnOx-based sorbent was used.

Since 1807, CO₂ is used for production of carbonated beverages, such as carbonated soft drinks, and this application was extended to production of sparkling wines and beer. The CO₂ level in carbonated beverages ranges from 1 % (v/v) in fruit drinks up to 6 % (v/v) in soda drinks [18]. The quality and purity of beverage-grade CO₂ is strictly regulated by The International Society of Beverage Technologists (ISBT) [19]. CO₂ captured from the wine fermentation could be a good source for the production of beverages, but a purification step is essential to remove off-odours, such as H₂S. An additional measure to prevent the formation of volatile sulphur compounds and hydrogen sulphide in wine, it is effective to apply the method of controlled oxidation of must [20].

CONCLUSIONS

The results of this study indicate the possibility to obtain CO₂ from wine fermentation, which would be of good quality for further use in the food industry for the production of carbonated beverages. The sorption capacity of two commercially available sorbents for hydrogen sulfide removal was compared, with better results obtained with the CuO/MnOx-based sorbent. This sorbent had good sorption capacity while passing positive aroma-active volatile compounds, such as higher alcohols and esters. The results of this study are a suitable basis for further research and for preparation of new types of sorbents.

Acknowledgements

This work was supported by project IGA-ZF/2021-ST2005 Capture of fermentation gas during wine fermentation and project CZ.02.1.01/0.0/0.0/16_017/00023 4 Research Infrastructure for Young Scientists.

REFERENCES

1. Gueddari-Aourir, A. – García-Alaminos, A. – García-Yuste, S. – Alonso-Moreno, C. – Canales-Vázquez, J. – Zafrilla, J. E.: The carbon footprint balance of a real-case wine fermentation CO₂ capture and utilization strategy. *Renewable and Sustainable Energy Reviews*, *157*, 2022, article 112058. DOI: 10.1016/j.rser.2021.112058.
2. Ferreira, V. – López, R. – Cacho, J. F.: Quantitative determination of the odorants of young red wines from different grape varieties. *Journal of the Science of Food and Agriculture*, *80*, 2000, pp. 1659–1667. DOI: 10.1002/1097-0010(20000901)80:11<1659::AID-JSFA693>3.0.CO;2-6.
3. Sumby, K. M. – Grbin, P. R. – Jiranek, V.: Microbial modulation of aromatic esters in wine: Current knowledge and future prospects. *Food Chemistry*, *121*, 2010, pp. 1–16. DOI: 10.1016/j.foodchem.2009.12.004.
4. Clarke, R. J. – Bakker, J.: *Wine: flavour chemistry*. Vol. 1. Oxford : Blackwell Publishing, 2004. ISBN: 9781405105309.
5. Colibaba, L.-C. – Cotea, V. V. – Niculuana, M. – Schmarr, H.-G.: Volatile compounds captured in exhaust CO₂ flow during the fermentation of *Busuioacă de Bohotin* wine. *Environmental Engineering and Management Journal*, *11*, 2012, pp. 1895–1900. DOI: 10.30638/eemj.2012.237.
6. Morakul, S. – Mouret, J.-R. – Nicolle, P. – Aguera, E. – Sablayrolles, J.-M. – Athes, V.: A dynamic analysis of higher alcohol and ester release during winemaking fermentations. *Food and Bioprocess Technology*, *6*, 2013, pp. 818–827. DOI: 10.1007/s11947-012-0827-4.
7. Mouret, J. R. – Morakul, S. – Nicolle, P. – Athes, V. – Sablayrolles, J. M.: Gas-liquid transfer of aroma compounds during winemaking fermentations. *LWT – Food Science and Technology*, *49*, 2012, pp. 238–244. DOI: 10.1016/j.lwt.2012.04.031.
8. Casale SA. Method for purification of a CO₂ stream. Inventor: Maffiotti, F. Int. Cl. C01B 32/50. European patent EP3356292B1. 8 August 2018.
9. Ailer, Š. – Serenčák, R. – Kozelová, D. – Poláková, Z. – Jakobová, S.: Possibilities for depleting the content of undesirable volatile phenolic compounds in white wine with the use of low-intervention and economically efficient grape processing technology. *Applied Science*, *11*, 2021, article 6735. DOI: 10.3390/app11156735.
10. MG Gas Products Limited. Recovery of carbon dioxide. Inventor: Cockerill, P. E. Int. Cl. C01B 31/20. European patent EP0720966A1. 10 July 1996.
11. Ailer, Š. – Valšíková, M. – Jedlička, J. – Mankovecký, J. – Baroň, M.: Influence of sugar and ethanol content and color of wines on the sensory evaluation: from wine competition “Nemčičany Wine Days” in Slovak Republic (2013–2016). *Erwerbs – Obstbau*, *62*, 2020, pp. 9–16. DOI: 10.1007/s10341-020-00486-x.
12. Ailer, Š. – Jakobová, S. – Benešová, L. – Ivanova-Petropulos, V.: Wine faults: State of knowledge in reductive aromas, oxidation and atypical aging, prevention, and correction methods. *Molecules*, *27*, 2022, article 3535. DOI: 10.3390/molecules27113535.
13. Gabriel, D. – Deschusses, M. A.: Retrofitting existing chemical scrubbers to biotrickling filters for H₂S emission control. *PNAS*, *100*, 2003, pp. 6308–6312. DOI: 10.1073/pnas.0731894100.
14. Bandosz, T. J.: On the adsorption/oxidation of hydrogen sulfide on activated carbons at ambient tempera-

- tures. *Journal of Colloid and Interface Science*, 246, 2002, pp. 1–20. DOI: 10.1006/jcis.2001.7952.
15. Zhao, Q. – Leonhardt, E. – MacConnell, C. – Frear, C. – Chen, S.: Purification technologies for biogas generated by anaerobic digestion. In: Kruger, C. – Yorgey, G. – Chen, S. – Collins, H. – Feise, C. – Frear, C. – Granatstein, D. – Higgins, S. – Huggins, D. – MacConnell, C. – Painter, K. – Stöckle, C. (Eds.): *Climate friendly farming – Final report. Improving the carbon footprint of agriculture in the Pacific Northwest*. CSANR Research Report 2010-001. Wenatchee : Washington State University, 2010. <<https://csanr.wsu.edu/wp-content/uploads/sites/32/2013/02/CSANR2010-001.Ch09.pdf>>
 16. Bagreev, A. – Rahman, H. – Bandosz, T. J.: Thermal regeneration of a spent activated carbon previously used as hydrogen sulfide adsorbent. *Carbon*, 39, 2001, pp. 1319–1326. DOI: 10.1016/S0008-6223(00)00266-9.
 17. Weinlaender, C. – Neubauer, R. – Hochenauer, C.: Low-temperature H₂S removal for solid oxide fuel cell application with metal oxide adsorbents. *Adsorption Science and Technology*, 35, 2017, pp. 120–136. DOI: 10.1177/0263617416672664.
 18. Mitchell, A. J. (Ed.): *Formulation and production carbonated soft drinks*. New York : Springer, 1991. ISBN: 9780442302870.
 19. Ringo, S. M.: International Society of Beverage Technologists (ISBT) carbon dioxide guidelines. *Master Brewers Association of the Americas – Technical Quarterly*, 39, 2002, pp. 32–35. ISSN: 0743-9407.
 20. Pokrývková, J. – Ailer, Š. – Jedlička, J. – Chlebo, P. – Jurík, E.: The use of a targeted must oxygenation method in the process of developing the archival potential of natural wine. *Applied Sciences*, 10, 2020, article 4810. DOI: 10.3390/app10144810.

Received 16 January 2023; 1st revised 18 July 2023; accepted 18 September 2023; published online 12 November 2023.