Selective sulfides removal in new make spirit using silver-exchanged zeolite Y

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Abstract: Even infinitesimal amounts of sulfide compounds such as dimethyl sulfide (DMS), dimethyl disulfide (DMDS) and dimethyl trisulfide (DMTS) are critical as unwanted smell components in new make sprit of malt whisky. It takes ages for these sulfides to vanish during the maturation in oak casks. New technology using silver-exchanged zeolite Y (Ag-Y) to remove these sulfides selectively without any reduction of aroma components has been developed. As a small amount of silver ions dissociated from Ag-Y must be trapped, the sodium zeolite Y (Na-Y) bed has been installed downstream of the Ag-Y bed in new process.
Keywords: Silver exchanged zeolite, Adsorptive sulfur removal, New make spirit.

1. Introduction

Adsorption technology to remove sulfur compounds completely has been studied and utilized in various industrial areas. For hydrogen production from liquefied petroleum gas (LPG) for fuel cell, sulfur compounds must be removed to the ppb level, as sulfur poisoning on catalysts used in the system is crucial. It was reported that silver-exchanged zeolite β is effective adsorbent for DMS, DMDS and t-butyl mercaptane (TBM) at room temperature[1].

Target sulfur compounds are sulfide with unpleasant smell in new make sprit of malt whisky. These sulfides are produced mostly during distillation. During the maturation in oak casks, it takes about 1 year for DMS to disappear, but for DMDS 6 to 10 years, and DMTS 10 or more years[2]. As the concentration of DMDS is much higher than DMTS, our main target is DMDS to be removed. In order to achieve high adsorbed amount of sulfur, more silver ions with highly dispersed state would be required. Zeolite Y normally with more ion-exchange sites than zeolite β was investigated with changing metal loadings.

2. Experimental

Ag-Y was prepared by ion exchange method using silver nitrate aqueous solution. Amount of silver loaded on zeolite was measured by quantitative analysis of X-ray fluorescence method. For single column test, Ag-Y was filled in a column and new make spirit was processed into the fixed bed at 10 h^{-1} of the liquid hourly space velocity (LHSV).

Sulfide compounds, esters and fusels in feedstocks and products were then quantitatively determined using a head space gas chromatography mass spectrometer.

A test with two columns in series was carried out to evaluate long term duration. First column was filled with Ag-Y and second column was filled with Na-Y. Besides sulfides, esters and fusels in products, the concentration of silver was also measured by quantitative analysis of inductively coupled plasma method.

3. Results and discussion

Single column test of Ag-Y with 13.8 wt% silver loading was conducted with charging new make sprit containing 2.01 ppm of DMS, 0.36 ppm of DMDS and 0.004 ppm. All sulfide compounds were removed completely as shown in Figure 1 (a). On the other hand, aroma components such as esters and fusels did not change at all (Figure 1 (b), (c)). Therefore Ag-Y is a suitable adsorbent to remove sulfides selectively. Figure 2 shows the effect of silver loadings to zeolite Y on sulfides adsorption. DMS is removed in an early stage at increasing silver loading, but DMDS and DMTS are adsorbed in a later stage. And the adverse effect of temperature was observed for DMS adsorption and the positive for DMDS. So the adsorption behaviors of DMS and DMDS are different, and the former is more like physical adsorption, the latter seems to be chemical adsorption.

A test with tandem columns of Ag-Y and Na-Y was carried out to evaluate their durations at LHSV 5 h^{-1}. Main target to be reduced is DMDS and the removal ratio was maintained more than 90 % over 700 hours as shown in Figure 3. Moreover, non-detectable leakage of silver (less than 10 ppb) at the outlet of Na-Y column was also confirmed during the test. At the last period of the test, the sampling between Ag-Y and Na-Y was measured and the contribution of second column for DMDS removal was observed. It is noted that Na-Y from the top of second column was transforming into Ag-Y which can adsorb DMDS.

A pilot scale test consisting of two columns each packed with 0.02 m^3 of Ag-Y and two columns with the same volume of Na-Y was conducted to obtain enough volume of product for the maturation in casks. During maturation for 14 months, the concentration of DMS was decreasing rapidly but not of DMDS at all without processing in the pilot system as expected. The maturation test will be continued to confirm the quality of product using this technology for commercial application.

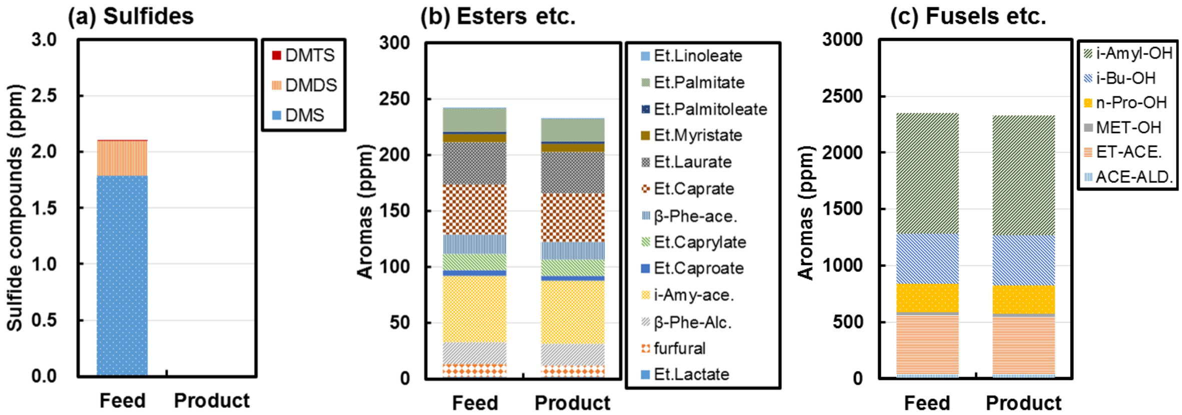

Figure 1. Feed and product components of single column test using Ag-Y

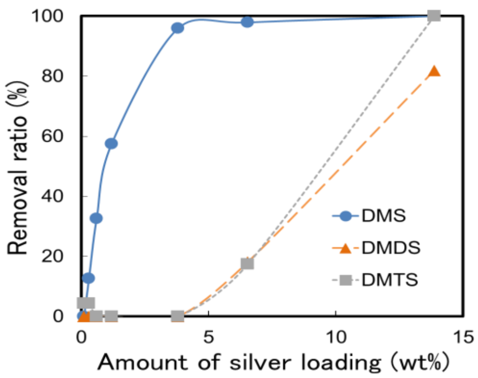

Figure 2. Effect of silver loadings on sulfides removal

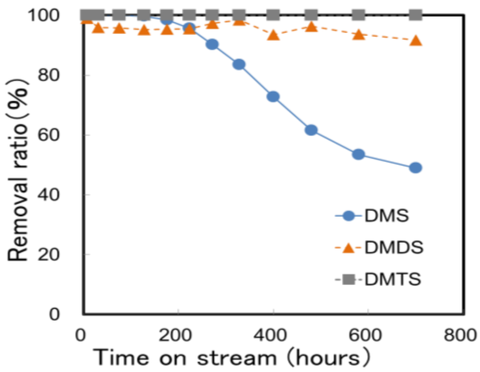

Figure 3. Duration test with tandem columns of Ag-Y and Na-Y

4. Conclusions

It takes ages that sulfide compounds in new make sprit vanish during the maturation in oak casks. New technology to remove sulfide compounds before the maturation has been developed. Ag-Y is a suitable adsorbent to remove sulfide compounds selectively without any reduction of aroma components. A small amount of silver ions dissociated from Ag-Y is captured completely in the consecutive bed of Na-Y. A pilot scale test has been carried out successfully and the maturation test will be continued to confirm the improvement of product quality within an appropriate period using this technology.

References

1. K. Takatsu, G. Takegoshi, H. Kastuno, Y. Kawashima, H. Matsumoto, J. Jpn, Petrol, Inst. 50(4) (2007) 200.
2. M. Masuda, K. Nishimura , Journal of Food Science 47 (1981) 101.