462c Energy Efficient Vapor Phase Oxidation of Methanol Using Ozone and Catalytic Reactor

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The pulp and paper industry releases more than 144 million tons of Volatile Organic Compounds (VOCs) per year. A big portion of this effluent, 66+ % is released to air making it the fourth highest contributor of VOC emissions to the atmosphere by industry sector [1]. The current practices by the pulp and paper industry generally involve collecting and burning the non-condensable waste gas streams, which contain methanol and other VOCs, in a thermal oxidizer. This practice adds loading to the on-site boiler and energy consumption due to extensive ductwork between the emission source and boiler in integrated Kraft mills. This project investigates ozone-enhanced catalytic oxidation as a low temperature, low energy method that could be applied to treat non-condensable waste gas streams at their source. We specifically investigated the effectiveness of vanadia/titania (V2O5/TiO2) catalysts for the oxidation of methanol. V2O5/TiO2 catalysts are effective in selective catalytic reduction (SCR) reactions in the destruction of VOCs [2,3,4], extending to the oxidation of methanol. Effects of major process parameters including residence time, ozone / methanol ratio, and reaction temperature were investigated. Qualitative and quantitative analyses of methanol and reaction products showed the effluent stream is predominantly methyl formate and carbon dioxide. Our experimental results show that ozone-enhanced catalytic oxidation is a feasible method to treat VOC emissions at temperatures less than 200 C. Greater than 98 percent of the initial methanol concentration (approximately 1.5 mol% in air) was degraded at 150oC using ozone and V2O5/TiO2 catalyst. The activation energy of methanol using the V2O5/TiO2 catalyst was 6.6 kJ/mol. At 150oC, catalysts with a V/Ti ratio = 0.05 is most active without ozone, but V/Ti = 0.01- 0.05 act approximately the same with ozone. The study emphasizes that reaction conditions have a significant impact on the selectivity to methyl formate, indicating process optimization is critical. Generally, the addition of ozone to this reaction decreases the selectivity toward methyl formate and increases the selectivity toward carbon dioxide. The selectivity towards methyl formate (MF), the most predominantly formed byproduct identified in this study, was increased at lower temperatures (100 C) and higher residence times (0.1 seconds), and in the presence of the V2O5/TiO2 catalyst.

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