"COMMERCIAL-SCALE DEMONSTRATION OF THE LIQUID PHASE METHANOL (LPMEOH™) PROCESS"

TOPICAL REPORT
"Peroxide Formation of Dimethyl Ether in Methanol Mixtures"

November 1997

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for
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Prepared for the United States Department of Energy
Pittsburgh Energy Technology Center
Under Cooperative Agreement No. DE-FC22-92PC90543

Patents cleared by Chicago on 18 April 1996.

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Abbreviations/Acronyms/Definitions

AFDU - Alternative Fuels Development Unit
cc - cubic centimeters
DME - dimethyl ether
DOE - U.S. Department of Energy
eqn - equation
H₂O₂ - hydrogen peroxide
lb - pounds
LP - limited partnership
LPMEOH™ - Liquid Phase Methanol™ process
ml - milliliter
mol% - mole percent
MTBE - methyl tertiary butyl ether
nm - nanometers
Partnership - Air Products Liquid Phase Conversion Company, L.P.
ppm - parts per million
psi(g) - pounds per square inch (gauge)
raw methanol - methanol made from syngas by the LPMEOH™ process without distillation
Executive Summary

As part of the DOE-sponsored cooperative agreement "Commercial-Scale Demonstration of the Liquid Phase Methanol (LPMEOH™) Process" (DE-FC22-92PC90543), a research study on peroxide formation from dimethyl ether in methanol, was carried out. Organic peroxides could form when dimethyl ether in methanol is stored for three to six months at a time.

The objective of this work was to determine the level of peroxide formation from dimethyl ether in reagent grade methanol and raw methanol at room temperature under 3 atmospheres (45 psig) of air. Raw methanol is methanol made from syngas by the LPMEOH™ process without distillation. Aliphatic ethers tend to react slowly with oxygen from the air to form unstable peroxides. However, there are no reports on peroxide formation from dimethyl ether.

After 172 days of testing, dimethyl ether in either reagent methanol or raw methanol (a sample from the DOE'S Alternative Fuels Development Unit (AFDU) located in LaPorte, TX) at room temperature and under 60 - 70 psig pressure of air does not form detectable peroxides. Lack of detectable peroxides suggests that dimethyl ether or dimethyl ether and methanol may be stored at ambient conditions.

Since the compositions of ~1.3 mol% or ~4.5 mol% dimethyl ether in methanol do not form peroxides, these compositions can be considered for diesel fuel or an atmospheric turbine fuel, respectively.
INTRODUCTION

Air Products Liquid Phase Conversion Company, L.P. (the Partnership) has begun a commercial-scale demonstration of the Liquid Phase Methanol (LPMEOH™) Process at Kingsport, Tennessee. In addition, the production of dimethyl ether (DME) as a mixed coproduct with methanol in the same equipment is being planned at the end of the LPMEOH™ demonstration. This report describes work done to determine the level of peroxide formation from dimethyl ether in methanol. Certain ethers are known to react slowly with oxygen from the air to form unstable peroxides. However, there are no reports on peroxide formation from dimethyl ether.

BACKGROUND

Aliphatic ethers tend to react slowly with oxygen from the air to form unstable peroxides. These α-hydroperoxy ethers (eqn 1) are obtained readily from the autoxidation of most ethers containing α-hydrogens. These peroxides may detonate when concentrated by evaporation or distillation or when disturbed by heat, shock, or friction.

\[
\text{ROCH}_2\text{R'} + \text{O}_2 \rightarrow \text{ROCHR'} - \text{O}_2
\]

Commonly used ethers such as ethyl ether, isopropyl ether, tetrahydrofuran, and p-dioxane are prone to form explosive peroxides on prolonged storage and exposure to air and a radical initiator. An exception to the above peroxide-forming tendency of ethers is methyl tertiary-alkyl ethers such as methyl tertiary-butyl ether (MTBE).

One of the simplest of the ethers is dimethyl ether, a flammable, colorless gas at room temperature and atmospheric pressure. Its stability and non-oxidative behavior make it ideal for use as a propellant gas for various applications such as perfumes and air refreshers in spray cans of carbon or stainless steel. It is shipped as a liquefied gas under its own vapor pressure of 77 psig at 20°C. However, no data could be found on the peroxide-forming nature of dimethyl ether or dimethyl ether in methanol.

The storage test described below was conducted in stainless steel cylinders. Stainless steel has three major metal components: iron, chromium and nickel. The chromium forms an oxide layer to cover the surface against formation of iron oxides. Commercial storage vessels would be constructed of carbon steel in which chromium and nickel are absent. Therefore, the metal oxide layer on carbon steel is oxides of...
iron. An extensive literature search did not reveal any references citing the formation of peroxides from ethers and oxygen catalyzed by iron oxides. Therefore, stainless steel cylinders were used in the 172-day test for peroxide formation from dimethyl ether.

**TEST PROCEDURE**

Five compositions were prepared according to the amounts summarized in Table 1. Methanol was either reagent-grade or raw methanol as produced at the Alternative Fuels Development Unit (AFDU) located in LaPorte, TX. Raw methanol is methanol made from syngas by the LPMEOH™ process without distillation. Each sample described in Table 1 was added to a 500-cc stainless steel Whitey cylinder, and then each cylinder was pressurized to approximately 60 psig with air. This amount of air contains sufficient oxygen to react with 58% of the dimethyl ether in samples A and B and 16% of the dimethyl ether in samples C and D. The added components had an approximate volume of 80 ml. Each cylinder was monitored weekly for any pressure drop.

The concentration of dimethyl ether in samples A and B is 1.3 mol%. Samples C and D have 4.8 mol% dimethyl ether. These concentrations are being considered for diesel fuel and an atmosphere turbine fuel, respectively.

<table>
<thead>
<tr>
<th>Table 1. Dimethyl Ether and Methanol Compositions</th>
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</thead>
<tbody>
<tr>
<td>Composition</td>
</tr>
<tr>
<td>Dimethyl ether</td>
</tr>
<tr>
<td>Methanol (reagent)</td>
</tr>
<tr>
<td>Methanol (raw - from LaPorte AFDU)</td>
</tr>
<tr>
<td>Initial Pressure (psig) (26 July 1995)</td>
</tr>
</tbody>
</table>
PEROXIDE ASSAY

The assay for hydrogen peroxide (H₂O₂) gave a reproducible calibration curve of absorbance vs H₂O₂ concentration. This curve in Appendix I shows a linear dependence for the KI absorbance measured at 358 nanometers (nm) and the H₂O₂ concentration expressed in parts per million (ppm). Parts per million of H₂O₂ is based on weight. The procedure is as follows:

Reagents:
10% acetic acid in isopropanol
2.78% potassium iodide in de-ionized water, sparged with nitrogen
Hydrogen peroxide (20 ppm H₂O₂) stock solution

To a series of digestion tubes were added 10 ml of acetic acid solution and 1 ml of standard or sample. The digestion tubes were placed in a hot water bath (>90°C). When samples came to temperature, 10 ml of potassium iodide solution was added to each tube. The tubes were covered with parafilm and allowed to heat for 30 minutes. The digestion tubes were removed from the water bath and made up to a total volume of 25 ml with isopropanol and mixed with a Vortex mixer. The digestion tubes were then placed in a cold-water bath. After 50 minutes the samples were analyzed by UV/VIS spectrophotometer using isopropanol as the blank and reading absorbancy at 358 nm.

DATA AT 172 DAYS

The data in Table 2 show zero peroxides within the error bar established for the assay (see footnotes at bottom of Table 2).

Table 2. Peroxide Determination After 172 Days

<table>
<thead>
<tr>
<th>Samples</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Final Pressure (psig)*</td>
<td>60</td>
<td>59</td>
<td>64</td>
<td>66</td>
<td>59</td>
</tr>
<tr>
<td>(15 January 1996)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ppm as H₂O₂**</td>
<td>-0.67</td>
<td>-0.16</td>
<td>-0.47</td>
<td>-0.02</td>
<td>-0.07</td>
</tr>
<tr>
<td>ppm as H₂O₂***</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Dependent on laboratory temperature.
** Average of two values; all values were slightly negative.
*** The error bar is +0.33 to -0.58 ppm. Therefore, in all samples there is 0 ppm H₂O₂ within experimental error.
CONCLUSION

The reagents used in the assay hydrolyze any α-hydroperoxy ether formed from the reaction of dimethyl ether and oxygen to H₂O₂. The H₂O₂ is then detected by a reaction between H₂O₂ and potassium iodide to form potassium tri-iodide, which has a characteristic absorption at 358 nm in the ultraviolet part of the light spectrum. Within experimental error of the assay, dimethyl ether does not form peroxides in methanol when the concentration of dimethyl ether is 1.3 and 4.8 mol%. Therefore, it would be expected that at atmospheric pressure there would be even less of a chance for peroxide formation because the concentration of oxygen is less.

DME is a volatile component (vapor pressure of 77 psig at 20°C), which either needs to be kept under pressurized storage or refrigerated conditions. Both under pressurized storage and under refrigerated conditions, the stored DME is very unlikely to pick up any oxygen from the environment. Under pressurized storage, oxygen cannot migrate into the system. Under refrigerated conditions, the solubility of oxygen in DME will limit the process of peroxide formation.

Lack of detectable peroxides suggests that dimethyl ether or dimethyl ether and methanol may be stored at ambient conditions. Storage of dimethyl ether at ~1.3 mol% and ~4.5 mol% in methanol would be adequate for consideration of these compositions for diesel fuel and an atmospheric turbine fuel, respectively.
Appendix I
Report Number (14): DOE/PC/90543--T11

Publ. Date (11): 199711

Sponsor Code (18): DOE/FE, XF

JC Category (19): UC-101, DOE/ER