

Oxidation Process Enhances Oil Recycling From Cuttings Waste

Rahul Dixit, M-I SWACO; Karen McCosh, M-I SWACO; G.A. Addicks, M-I SWACO; Ivan Batinic, M-I SWACO

Copyright 2008, AADE

This paper was prepared for presentation at the 2008 AADE Fluids Conference and Exhibition held at the Wyndam Greenspoint Hotel, Houston, Texas, April 8-9, 2008. This conference was sponsored by the Houston Chapter of the American Association of Drilling Engineers. The information presented in this paper does not reflect any position, claim or endorsement made or implied by the American Association of Drilling Engineers, their officers or members. Questions concerning the content of this paper should be directed to the individuals listed as authors of this work.

Abstract

Cuttings produced while drilling with invert-emulsion drilling fluids can be treated in several ways to reduce the hydrocarbon content prior to disposal. One such treatment involves the use of thermal or kinetic energy to vaporize the hydrocarbon component. The oil content of the treated cuttings is reduced and the material classified as non-hazardous for re-use or disposal. The vaporized hydrocarbon fraction is condensed, separated and collected for re-use as a base for new drilling fluids.

The recovered oil from such processes is often dark with a strong odor due to degradation of components in the drilling fluid. Oxidation processes however can reduce the color intensity and remove offensive odors to produce oil with improved properties for re-use. For example, ozone is a powerful oxidizing agent used in thousands of municipal plants, commercial and industrial installations as an oxidant. Injection of an ozone stream into the oil promotes reaction via direct and indirect oxidation mechanisms to remove the malodorous compounds.

Laboratory-scale testing identified controlling parameters for ozone treatment of oil and allowed development of a larger treatment system. A corona discharge is used to apply energy to oxygen-bearing gas to produce ozone at the desired concentration. The ozone is injected into a continuous flow of oil passing through a vessel where the oxidation reactions occur. This paper presents data from lab and field studies showing the effectiveness of the treatment system, the improvement of color and odor of treated oil and the enhancement to cuttings treatment technology.

Introduction

Thermal-desorption technology for the treatment of oil contaminated drill cuttings has proven to be a time-honored process successfully employed in various parts of the world.¹⁻³ The process involves indirect heating of the cuttings in an inert atmosphere to the boiling temperature of the hydrocarbon components, where desorption of both hydrocarbon and water from the solid materials occur. The vapor phase is subsequently cooled and condensed, with the hydrocarbon and water fractions separated.

The hydrocarbon fraction recovered from this process can be reused or recycled, often as the base for new invert-emulsion drilling fluids. The recovered oil is typically dark in color. A pungent, sulfur-like or burnt odor is also often associated with the thermally recovered fluids. Jones, Sanders and Chambers⁴ reported the presence of volatile components in the thermally recovered fluids using head-space gas chromatography-mass

spectrometry (GC-MS) technique. Possible sources of the volatiles are from the partial oxidation of hydrocarbon fraction, thermal breakdown of drilling fluid additives, and contamination of the drilled cuttings with crude from the reservoir. Reducing the odor of the recovered oil will increase the acceptance of this fluid for use in drilling fluid systems and this was the main driver to explore possible treatment solutions.

Creating a quantifiable method for the measurement of both the initial and neutralized odor is challenging and highly subjective. The level at which such odors become tolerable or offensive differs for each individual. No analytical method is currently available but measurement of Volatile Organic Compounds (VOC) measurement can be used to provide a less-subjective method to monitoring volatile materials which may contribute to the odor of the material.

One method used to treat the thermally recovered oil is clay filtration, where the clay acts to absorb organic materials which may be malodorous. Studies on the long-term effectiveness of such treatment to this particular hydrocarbon stream are not widely available. The large quantity of waste generated is considered unattractive along with the logistical challenges associated with filling and emptying filter pods. Therefore an alternative method for odor removal was investigated, using the powerful oxidant ozone to improve the odor and aesthetic qualities of the thermally recovered oil without negatively impacting the hydrocarbon distribution and properties of the recovered oil. Initial laboratory studies investigated the suitability of this process and successful trials led to the development of a full-scale process using the oxidation potential of ozone to treat thermally recovered oil.

Theory

Ozone is a powerful oxidant used in wastewater treatment systems to oxidize and remove contaminants. If a similar technique were applied to the treatment of non-aqueous liquids without significantly affecting their physical properties, ozone could remove molecules that significantly contribute to the dark color and odor of thermally recovered oil. Ozone (O₃) is a naturally occurring allotrope of oxygen (Fig. 1) which is chemically unstable. It readily decomposes to molecular oxygen (O₂) plus an oxygen atom with an oxidation state of ⁻², rendering it highly capable of drawing electrons or oxidizing other species.

The oxidation reaction can occur through a two-step process called ozonolysis (Fig. 2). In the first step ozone reacts with unsaturated molecules such as alkenes, unsaturated esters and

unsaturated fatty acids through cycloaddition reactions, generating ozonide (or molozonide) which is extremely unstable. In the second step, the ozonide decomposes to carbonyl products such as aldehydes, ketones, and carboxylic acids by either reductive or oxidative reactions.⁵ Many of the resulting carbonyl compounds have an acidic odor which are often pleasant and markedly different from the burnt odor of a thermal process.

Ozone will not react with the aliphatic hydrocarbons predominant in recovered oil and therefore the physical properties such as viscosity and API gravity should not be affected. Thus, the ozonolysis reaction can be used to react the unsaturated molecules thereby decreasing odor and color.

Laboratory-Scale Studies

Laboratory-scale test equipment (Fig. 3) was developed to investigate the effect of ozonolysis on thermally treated oil. Ozone is generated as a direct result of electrical discharge from a corona discharge element. This corona-discharge causes the oxygen molecule to split and form two oxygen radicals. These radicals can combine with oxygen molecules to form ozone. The generator was capable of producing an ozone concentration of 0 to 100%, depending upon the voltage applied to the corona tube. Compressed oxygen having a dew point of -60°F (-51°C) was used as the feed gas to prevent simultaneous formation of nitrogen oxide compounds from water vapor. The ozone generated was sparged into the test liquid contained in a 1-litre Pyrex reaction kettle, through a 2-micron cylindrical metal frit. Ozone monitors measured the inlet and outlet concentrations of ozone from which ozone consumption could be determined. Residual ozone exiting the reaction vessel was passed through a column packed with magnesium oxide, causing decomposition to oxygen and release to the atmosphere.

Oil recovered from cuttings treated by a commercially operating high-temperature thermal process was treated using the laboratory-scale equipment. The untreated sample was almost black and opaque with a pungent sulfur like charred odor. The sample was treated with ozone and the color and odor monitored qualitatively. To determine the optimal reaction time and ozone concentration required to reduce odors from the sample without over treatment, the sample volume, gas flow rate, inlet pressure, and ozone concentration was controlled and the reaction run for 30, 60 or 90 mins. The operating conditions were: sample volume 500 mL; gas feed rate 1.625 L/min; inlet pressure 1.3 psig; ozone concentration 100% at ambient temperature. After each 30-min time period, the reaction was halted and a sample removed for analysis. The specific gravity of the oil was determined using a standard American Petroleum Institute (API) method.⁶ The Paraffin, Isoparaffin, Olefin, Napthenic and Aromatic (PIONA) content of the samples was determined by GC-MS.⁷ The Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) content were also determined using standard analytical techniques.⁸ The presence of residual and non-residual odors were qualified using an American Society for Testing and Materials (ASTM) method.⁹ The color of each sample was also determined using ASTM method.¹⁰ Flash point measurement was made using the Pensky-Martens closed cup method.¹¹

Data and Results

Initial treatment of recovered oil showed that after 45 min of ozone treatment at 100% ozone concentration, the oil became noticeably lighter and the odor was greatly reduced. After 4 hr of treatment, the oil was transparent with a faint yellow color and was devoid of sulfur odors. However, the reduced odor had been replaced with a rancid, acidic, and somewhat fruity odor suggesting that over-treatment had occurred. Therefore, optimization of ozone concentration and reaction time was critical for the success of the ozonolysis process in this application.

Addition of 2.71 g of ozone to 500 mL of sample reduced the odor, although it was still distinctly charred (Table 1) and the color had lightened. Increasing the ozone dose to 5.82 g further improved the properties. The sample was over-treated when 9.12 g of ozone was used, determined by the presence of a sharp pungent and acidic odor. Quantitative color measurement confirmed the reduction in color intensity (Table 2). Compositional analysis (Table 2) shows that ozone treatment had little deleterious effect upon the overall hydrocarbon distribution of the oil. The most significant change in fluid composition is the depletion of olefins and the accumulation of species which include acids, aldehydes, ketones, and alcohols. This is consistent with the expected reaction of ozone at the carbon-carbon double bond on olefin molecules and with the increase in acidic odors detected. The addition of ozone to the oil sample did not significantly affect the flashpoint as compared to the untreated sample.

The studies showed that ozone treatment to reduce color and odor was effective and determined that a stream of ozone at 100% concentration could reduce odors to non-offensive levels within 1 hr on 500 mL of oil. This translates to 5.82-g/hr ozone or 13,866-ppm/hr ozone. This result allowed development of a continuous process on a larger scale for commercial operations.

Field-Scale Studies

The field tests were a great success and have shown the potential of the ozone treatment technology in treating thermally recovered oil with the oxidation of organic compounds to enhance final product quality. These tests also have confirmed that the ozone treatment technology can be run as a continuous process with excellent consistency and system stability.

The data recorded and experience gained during the testing phase met or exceeded all initial pre-test expectations. The lack of analytical methods to quantify odor meant that the reduction in odor was determined qualitatively using the nose. The test populations were selected from a variety of backgrounds and with direct involvement or experience handling of hydrocarbon fluids. Of the three discrete locations that participated in this evaluation trial, 95%, 85% and 84% of the participants ranked the ozone-treated thermally recovered oil as less offensive than untreated oil (Fig. 4). It is further noted that 70%, 35% and 33% considered the ozone-treated thermally recovered oil to be less offensive in odor than virgin diesel oil (Fig. 5).

The samples were analyzed for VOC content which was recorded as a function of the concentration of ozone used to treat that sample (Fig. 6). The results show that the lowest levels of VOC content were achieved at 45-g/hr ozone. The methodology

may provide a possible non-subjective way to measure odor removal.

Conclusions

Initial laboratory studies and field tests were used to prove that ozone treatment was a viable process to remove odor and color associated with thermally recovered oils. The studies showed that ozone concentration must be closely controlled to successfully reduce the color and odor of the oil. Over-treatment must be prevented to avoid buildup of compounds which give the oil an acidic odor. These findings determined operational parameters and allowed the development of a larger treatment process which could operate in a continuous manner.

It is recommended that a more detailed study be carried out to provide a non-subjective method to monitor and possibly quantify odor levels.

Acknowledgments

The authors would like to thank the management of M-I SWACO for their permission to publish this paper. A special thanks to Mukesh Kapila and Richard Bingham for encouragement and guidance in this work.

Nomenclature

API = American Petroleum Institute
 ASTM = American Society for Testing and Materials
 GC-MS = Gas Chromatography-Mass Spectrometry
 PIONA = Paraffin, Isoparaffin, Olefin, Napthenic and Aromatics
 BTEX = Benzene, Toluene, Ethyl Benzene, and Xylene
 VOC = Volatile Organic Compounds

References

- Zupan, T. and Kapila, M. "Thermal Desorption of Drill Muds and Cuttings in Ecuador: The Environmental and Financially Sound Solution." SPE 61041, SPE International Conference on Health, Safety, and the Environment in Oil and Gas Exploration and Production, Stavanger, 26-28 June 2000.
- Antle, G., Gover, P. and Pruett, J.O. "Integrated Waste Management: Successful Implementations of Thermal Phase Separation Technology for Oil- and Synthetic-Based Cuttings and Drilling Fluid Waste." SPE 80595, SPE/EPA/DOE Exploration and Production Environmental Conference, San Antonio, Texas, 10-12 March 2003.
- Pierce, D., Gaddis, C. and Wood, B. "Lessons Learned From Treating 500,000 Tons of Oil-Based Drill Cuttings on Five Continents." IADC/SPE 99027, IADC/SPE Drilling Conference, Miami, Florida, 21-23 February 2006.
- Jones, T.G.J., Sanders M.W. and Chambers, B.D. "Improvements in the Analysis of Thermally Recovered Drilling Fluid Base Oils from Drilled Cuttings." SPE 74166, International Conference on Health, Safety, and Environment in Oil and Gas Exploration and Production, Kuala Lumpur, Malaysia, 20 -22 March 2002.
- Reusch, W. *Virtual Textbook of Organic Chemistry*. (2007). Available at: www.cem.msu.edu/%7Ereusch/VirtualText/addene2.htm (Last accessed February 14, 2008).
- API RP 131: *Recommended Practices, Standard Procedures for Laboratory Testing of Drilling Fluids*, 7th ed. American Petroleum Institute (February 2004).
- ASTM D6730-01(2006)e1: *Standard Test Method for Determination of Individual Components in Spark Ignition by 100-Metre Capillary (with Precolumn) High-Resolution Gas Chromatography*. ASTM (2006).
- EPA8260B, Volatile Organic Compounds by Gas Chromatography Mass Spectroscopy (Dec. 1996, Rev. 2).
- ASTM D1296-01(2007): *Standard Test Method for Odor of Volatile Solvents and Diluents*. ASTM (2007).
- ASTM D1500-04: *Standard Test Method for ASTM Color of Petroleum Products (ASTM Color Scale)*. ASTM (2004).
- ASTM D93-07: *Standard Test Methods for Flash-Point by Pensky-Martens Closed Cup Tester*. ASTM (2007).

Table 1 – Effect of Ozone Concentration of Recovered Oil Properties

Reaction Time (min)	Total Ozone Addition (g)	Ozone Flow Rate (ppm/hr)	Properties After Treatment		
			Color	Odor	Density (g/cm ³)
0	0	0	Dark brown	Charred	0.8400
30	2.71	6,460	Brown	Low charred odor	0.8095
60	5.82	13,866	Orange-brown	Paraffinic	0.8315
90	9.12	21,716	Orange-yellow	Acidic, pungent	0.8355

Table 2 – Chemical Analysis of Untreated and Treated Oil				
Property	Reaction Period (min)			
	0	30	60	90
PIONA tests				
Total paraffins (wt%)	23.93	23.22	26.05	23.38
Total isoparaffins (wt%)	36.24	36.53	37.45	34.55
Total aromatics (wt%)	11.24	11.21	11.24	8.69
Total naphthenics (wt%)	18.43	19.08	17.19	18.33
Total olefins (wt%)	6.25	5.52	3.66	5.88
Other* (wt%)	3.91	4.44	4.41	9.17
BTEX tests				
Benzene (ppm)	0.001	0.001	0.001	<0.001
Toluene (ppm)	0.006	0.005	0.006	0.005
Ethylbenzene (ppm)	0.005	0.005	0.005	0.005
Xylene (ppm)	0.018	0.034	0.041	0.037
Total BTEX	0.030	0.045	0.053	0.047
Color	7.5	4.5	3.5	2.0
Hydrocarbons				
C4 to C8 (% conc.)	0.17	0.14	0.23	0.28
C9 to C13 (% conc.)	21.91	24.08	23.35	23.16
C14 to C18 (% conc.)	47.65	46.94	46.48	46.18
C19 to C23 (% conc.)	23.98	22.84	23.47	23.57
C24 to C28 (% conc.)	5.17	4.97	5.30	5.46
C29 to C33 (% conc.)	0.85	0.79	0.90	1.01
C34 to C44 (% conc.)	0.28	0.23	0.27	0.33
C45 to C49 (% conc.)	not detected	not detected	not detected	not detected
Flashpoint (°F)	190	190	193	192

* Other compounds detected as acids, aldehydes, ketones and alcohols

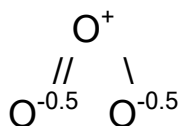


Figure 1 - Ozone Structure.

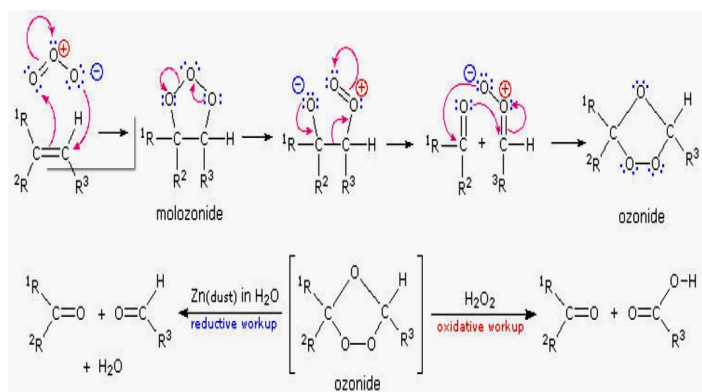


Figure 2 – Ozonolysis Reaction Mechanism.

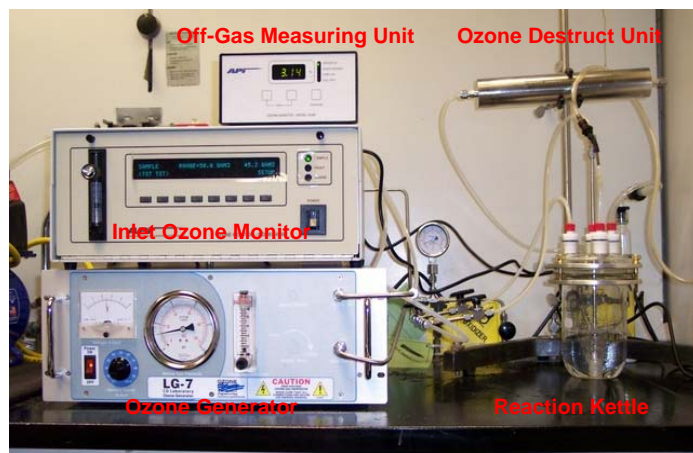


Figure 3 – Ozonolysis Lab-Scale Equipment.

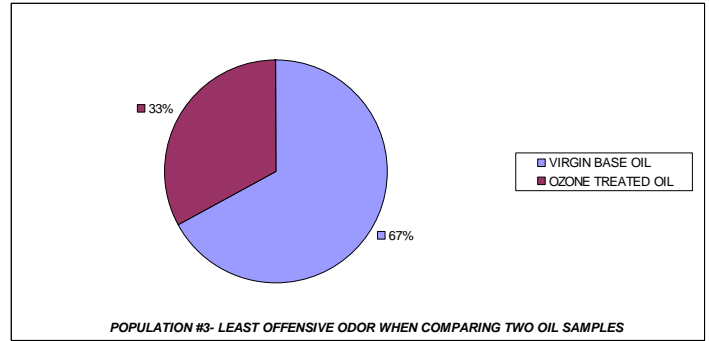
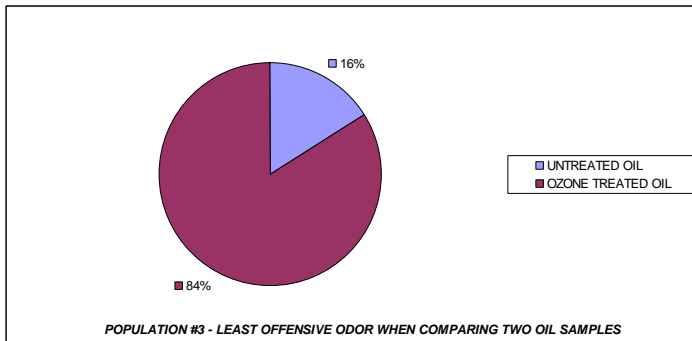
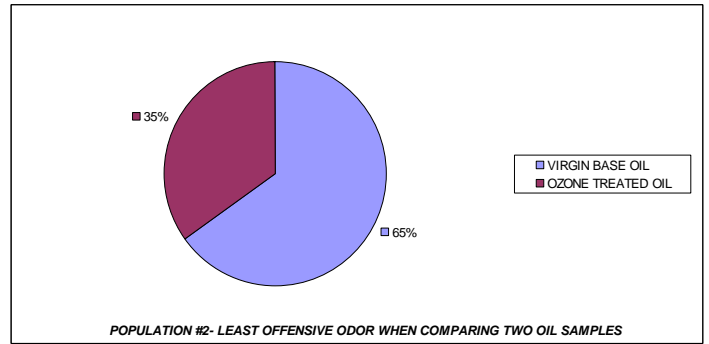
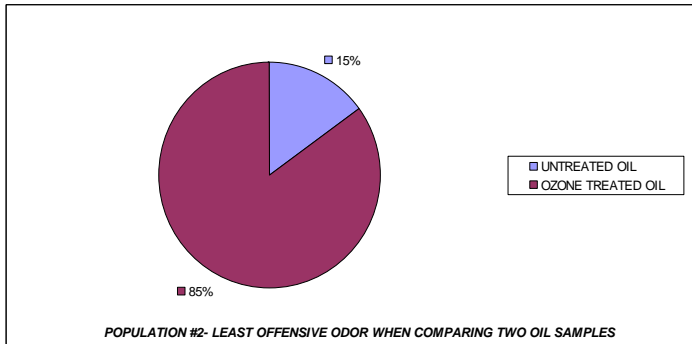
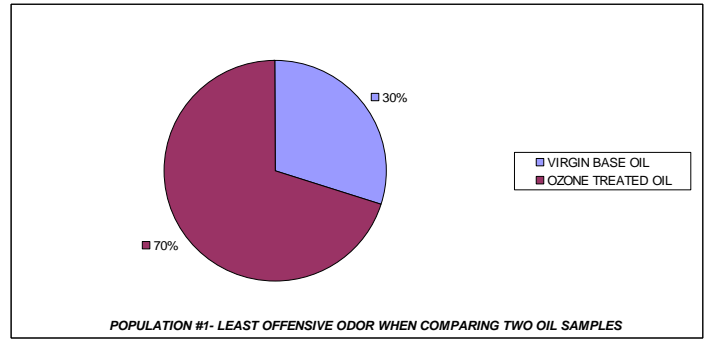
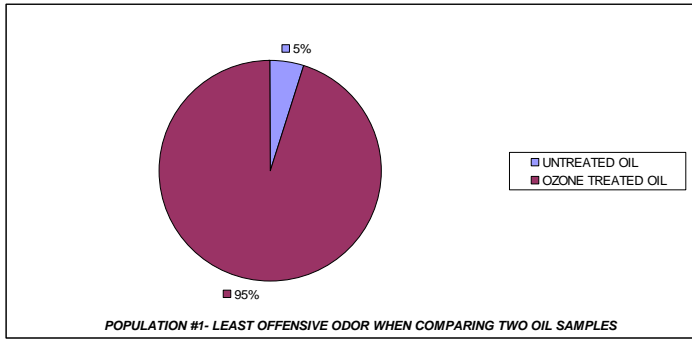


Figure 4 – “Smell test” results (untreated oil versus ozone-treated oil).

Figure 5 – “Smell test” results (virgin oil versus ozone-treated oil).

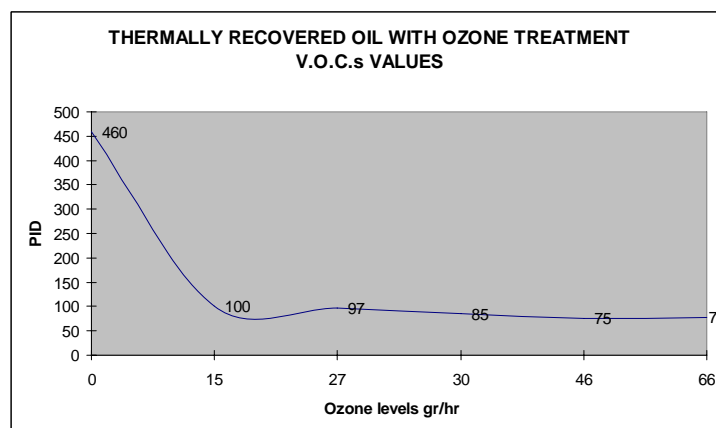


Figure 6 - V.O.C. Test Results.