Using Biodiesel Fuels to Reduce DPM Concentrations; DPM Results Using Various Blends of Biodiesel Fuel Mixtures in a Stone Mine

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ABSTRACT: This paper discusses a collaborative effort among Mine Safety and Health Administration (MSHA), Industry, and the Kentucky Department of Energy to test diesel particulate matter (DPM) emissions and exposures when using various blends of biodiesel fuels in two underground stone mines. The study was initiated by the industry partner, with MSHA and National Institute for Occupational Safety and Health (NIOSH) providing support for study design, data collection, and sample and data analysis. Project funding was provided by Carmeuse North America, Inc., and the Kentucky Department of Energy through the Kentucky Clean Fuels Coalition.

The study evaluated mine DPM emissions when using various biodiesel to diesel fuel mixtures. Two types of biodiesel were evaluated, a recycled vegetable base biodiesel fuel mixture and a soy based biodiesel fuel mixture. Baseline conditions were established using 100% low sulfur No. 2 diesel.

1 INTRODUCTION

Diesel particulate surveys were conducted at the underground Maysville Limestone Mine, Maysville, Kentucky and Black River Limestone Mine, Butler, Kentucky. The purpose of the study was to evaluate the effect of utilizing biodiesel fuel mixtures on diesel particulate emissions and personal exposures in underground nonmetal mines. Management of Carmeuse North America, Inc., had obtained outside funding to evaluate the effectiveness of biodiesel fuels. The Kentucky Clean Fuels Coalition coordinated the funding, to conduct the surveys, which was provided from two outside sources. This funding was provided by The Kentucky Division of Energy and by Griffin Industries, Inc.

Two types of biodiesel fuels were studied. They were a recycled vegetable oil (RVO) and a virgin soy oil (VSO). Various concentrations of each fuel were tested. The biodiesel fuel mixtures and baseline study were tested during normal underground mining operations. The studies were jointly conducted by MSHA personnel and Carmeuse North America, Inc., personnel. MSHA personnel involved in these studies were from the Pittsburgh Safety and Health Technology Center, Dust Division and Metal and Nonmetal Mine Safety and Health, Southeastern District.

Table 1 shows the dates and the biodiesel fuel mixtures studied at the Maysville Limestone Mine.

Table 1. Maysville Mine Biodiesel Fuel Mixtures

Date	Biodiesel Fuel
DEC 10-12, 2002	20-80% biodiesel mixture (RVO)
JAN 7-9, 2003	50-50% biodiesel mixture (RVO)
FEB 4-6, 2003	No. 2 low sulfur diesel fuel (baseline)
APR 1-3, 2003	50-50% biodiesel mixture (VSO)

Table 2 shows the dates and the biodiesel fuel mixtures studied at the Black River Limestone Mine.

Table 2. Black River Mine Biodiesel Fuel Mixtures

Date	Biodiesel Fuel
MAR 18-19, 2003	No. 2 low sulfur diesel fuel (baseline)
APR 8-9, 2003	35-65% biodiesel mixture (RVO)
APR 29-30, 2003	35-65% biodiesel mixture (VSO)

Each study period lasted for two weeks. During the study period, all the underground diesel equipment was fueled using the appropriate blend of biodiesel fuel. The first week of each study was used to purge the equipment and fuel distribution system from the previous fuels used. Sampling was conducted during the second week of the survey.

2 BACKGROUND

2.1 *Maysville Limestone Mine*

The Maysville Mine, located in Mason County, Kentucky, is an underground limestone mine owned and operated by Carmeuse North America, Inc. The Camp Nelson Limestone formation is mined. The mine operates two 10-hour production shifts per day to produce approximately 3.5 million tons of limestone annually. The active mining area is approximately 1,000 feet deep. Mined entries are approximately 45 to 50 feet wide with the final mining height ranging from 50 to 60 feet. The limestone deposit is mined using a regular room-and-pillar, heading-and-bench mining method. The headings are approximately 20 to 24 feet high and the bench ranges in height from 30 to 40 feet. This process results in a mine layout consisting of an upper level, which eventually was shot down to the lower level creating room heights over 60 feet.

A conventional mining system, where the limestone is drilled and blasted, was used to advance heading or mine the benches. This process consisted of drilling the face or the floor and then loading the drilled holes with ammonium nitrate and fuel oil (ANFO). The blasting sequence was initiated at the end of each shift. A two-hour idle period followed blasting to allow for the gasses and other contaminants to be removed by the ventilation system. The broken stone was then loaded at the faces by front-end-loaders into 40-ton haulage trucks. The trucks transported the material to a crusher and a belt feeder. The conveyor system carried the stone from the crusher area and out of the mine via an 18° slope. On the surface, the stone was further crushed and screened. The diesel equipment used to mine limestone included: front-end-loaders, haul trucks, scalers, roof bolters, face drills, a grader, a dozer, a water truck, a service truck, an explosives truck, fork lifts, and tractors.

Primary airflow was induced into the mine using ventilation fans located underground at the base of two vertical shafts. The intakes were the elevator shaft and the 1 West shaft, located off of the M-roadway in 1 West drift between panel 4 North and 4 South. Each fan installation consisted of a set of fans that worked in parallel with each other, installed side-by-side.

The ventilation system induced an average mine airflow of approximately 878,000 cubic feet per minute (cfm) for the months of December, January, and February. An average mine airflow of approximately 892,000 cfm was calculated during the baseline survey and 748,000 cfm for the tests conducted during the month of April. The change in airflow was the result of a change in natural ventilating pressures (NVP) occurring between the baseline survey and the VSO 50-50% survey. Surface air temperature changed from 40° Fahrenheit during the baseline survey to 85° Fahrenheit during the VSO 50-50% survey. During the baseline survey, NVP assisted with the mine mechanical ventilation, but during the VSO 50-50%, NVP worked against the mine mechanical ventilation.

Air entered the mine at the elevator shaft and the 1 West intake shaft. Air was then coursed to the working areas by air walls. Air walls were constructed of conveyor belting material approximately 10-feet long and anchored to the mine roof. Recycled fines, or waste rock, that had been brought back into the mine were then placed under the belting to complete the air wall. Freestanding auxiliary fans, which had no ductwork or tubing assisted ventilating the working panels. Intake air was coursed throughout the mine to two exhaust areas: an exhaust shaft and the belt slope. An average airflow of 629,000 cfm was measured exhausting out of the main exhaust shaft and an average of 249,000 cfm was measured exhausting out the slope for the months of December, January, and February. During the baseline survey, an average airflow of 640,000 cfm was measured exhausting out of the main exhaust shaft and an average of 250,000 cfm was measured out of the slope. During the VSO 50-50% survey, an average airflow of 530,000 cfm was measured exhausting out of the main exhaust shaft and an average of 220,000 cfm was measured exhausting out of the slope. The exhaust shaft was located between 1 North and 2 North panels and the slope was located near the elevator shaft.

2.2 *Black River Limestone Mine*

The Black River Mine, located in Pendleton County, Kentucky, is an underground limestone mine, also owned and operated by Carmeuse North America, Inc. The Camp Nelson Limestone formation is mined. The mine operates two 10-hour production shifts, 4 days per week to produce approximately 2.5 million tons of limestone annually. The limestone deposit is mined using a regular room-and-pillar, heading-and-bench mining method. The headings are approximately 24 feet high and the bench ranges from 30 to 40 feet in height. Mined entries are 30 to 40 feet wide. This process results in a mine layout consisting of an upper level which eventually is shot down to a lower level.

A conventional mining system where the limestone is drilled and blasted was used to mine the limestone deposit. This process consisted of drilling the face or the floor and then loading the drilled holes with ANFO. The blasting sequence was initiated at the end of each shift. A two-hour and fifteen-minute idle period followed blasting to allow for the gasses and other contaminants to be removed by the ventilation system. The broken stone was then loaded at the faces by front-end-loaders into haulage trucks. The trucks transported the material to a jaw crusher which fed onto the mine belt. The belt conveyor system carried the stone from the crusher area out of the mine via the exhaust air slope. On the surface, the stone was further crushed and screened. The diesel equipment used to mine limestone included: front-end-loaders, haul trucks, scalers, face drills, a roof bolter, a grader, a grease rig, a water truck, a service truck, an explosives truck, and tractors.

Primary airflow was induced into the mine at two intake locations. Air was then coursed to the working areas by air walls and auxiliary fans. The free-standing auxiliary fans, which had no ductwork or tubing assisted ventilating the working panels. Intake air was coursed throughout the mine to two exhaust areas: an exhaust shaft and the belt slope. Airflow varied from 147,000 cfm to 179,000 cfm exhausting out of the main exhaust shaft during the study and varied from 67,000 cfm to 109,000 cfm exhausting out of the slope.

2.3 *Biodiesel*

Biodiesel is a methyl ester product produced by combining methanol oil or feedstock, then adding a catalyst. Glycerin is spun off during the refining process with the remaining product being termed a mono-alkyl ester known as biodiesel. Biodiesel can be made from a variety of feedstocks including soybeans, rapeseed, canola, and palm oil as well as from recycled vegetable oils. The RVO, more commonly referred to as "yellow grease", was supplied by Griffin Industries, Inc. The VSO was supplied by Peter Cremer North America.

3 SAMPLING LOCATIONS

3.1 *Maysville Limestone Mine*

Six area and five personal samples were collected during each day of the study. Area samples were collected at two main intake locations: one at the bottom of the elevator shaft and one at the outlet end of the dual intake fans located at the 1 West shaft. Return samples were also taken: two side-by-side samples at the bottom of the return shaft and another two side-by-side samples approximately 400 feet up the slope entry.

Five personal samples were collected on each shift and included drillers, roof bolters, scalers, loaders, truck drivers, and a powderman. Smoking was permitted underground in the mine. There were not enough nonsmokers working production, therefore smokers and nonsmokers were selected for sampling.

3.2 *Black River Limestone Mine*

Seven area samples and five personal samples were collected during each day of the study. Area samples were collected at the two main intake locations: near the North intake airshaft and the South intake airshaft. Return side-by-side area samples were also taken at the bottom of the return airshaft and the exhaust slope. The North jaw crusher dump point was also sampled. Five personal samples were collected on each shift. Although individual workers were selected based on availability, the same occupations were sampled for each phase of the study. Occupations sampled were a loader operator, two truck drivers, a scaler, and a roof bolter. Smoking was permitted underground in the mine. Since individual workers varied at the occupations during different phases of the test, their smoking and nonsmoking designations changed.

4 ANALYTICAL

4.1 *Sampling Confidence Range*

The study sampling was designed to determine whether concentration reductions were significant at the 95% confidence level. Prior to the test, it was assumed that the baseline exhaust concentration would be approximately 400 µg/m^3 with a standard deviation of 20% and the reduction from biodiesel fuel would be approximately 20%. A "t-test" was used to determine whether reductions were significant. The critical "t" values for a 95% confidence limit range from 2 to 3. Using the following "t-test" equation:

$$t = \frac{x_i - x_o}{s \big/ (n)^{\frac{1}{2}}}$$

where:

x_i = initial concentration
x_o = final concentration
s = standard deviation
n = sample size

Solving for the sample size "n" gives:

$$n = \frac{t^2 \times s^2}{(x_i - x_o)^2} = \frac{2.5^2 \times (80)^2}{(400-320)^2} \approx 6\ samples$$

To allow for variability and mine operational delays, a sample size of 6 was selected. This resulted in the collection of 2 samples per day for 3 days at each of the mine exhaust air locations (shafts and slope). The critical "t" value at 95% for a two-sided test with 5 degrees of freedom (6 - 1 samples) is 2.571. This value was used in the analysis of the data to confirm significance.

4.2 *Sampling Procedure*

Individual area and personal samples were collected with SKC, Inc., diesel particulate sampling cassettes. This cassette includes a submicron impactor and a quartz fiber filter. All sampling units used 10-millimeter nylon preseparator cyclones. Samples were collected using SKC pumps and MSA Elf's calibrated and operated at 1.7 liters per minute (Lpm) of airflow.

The airborne carbon samples were analyzed by MSHA, Pittsburgh Laboratory and NIOSH, Pittsburgh Research Laboratory according to NIOSH Method 5040. Elemental carbon (EC), organic carbon (OC), and total carbon (TC) values were determined from the samples collected. This method uses a thermal/optical carbon analyzer to determine the OC and EC matter per square centimeter of filter surface. Separation of different types of OC is accomplished through temperature ramping over time and controlled atmospheric conditions. Carbonaceous minerals are separated at a temperature of 750°C (fourth OC peak). The carbonaceous mineral content, evolved at the 750°C peak, was subtracted from the OC portion of the analysis using the software capability of the analytical program. OC and EC were added together to obtain the TC. A field blank correction was also applied to the carbon measurements. If the field blank correction resulted in a negative carbon measurement, the carbon measurement was defaulted to zero. Concentrations of carbon were calculated from the following formulas:

$$carbon\ conc.\,(\mu g/m^3) = \frac{C(\mu g/m^3)\times A(cm^2)\times 1{,}000\left(\frac{L}{m^3}\right)}{1.7\,Lpm \times Time\,(min.)}$$

and

$$TC = EC + OC\ or\ \ TC = EC \times 1.3$$

where:

C = The corrected OC or EC, concentration measured in the thermal/optical carbon analyzer.

A = The surface area of the filter media used. The surface area of the filters is 8.04 cm^2.

All area sample concentrations were based on actual sampling time resulting in time weighted averages (TWA's). For MSHA enforcement activities, normal MSHA Metal and Nonmetal protocol is to base all personal samples as shift weighted averages (SWA's). SWA calculations use 480 minutes as the sampled time regardless of the time sampled. The personal samples are reported as SWA's.

5 RESULTS AND DISCUSSION

Table 3 contains the TWA summary of the average area DPM sampling for the Maysville Mine survey.

Table 3. Maysville Mine Average Area Samples

	Baseline		RVO 20-80%		RVO 50-50%		VSO* 50-50%	
	TC= ECx1.3 ($\mu g/m^3$)	TC= EC+OC ($\mu g/m^3$)	TC= ECx1.3 ($\mu g/m^3$)	TC= EC+OC ($\mu g/m^3$)	TC= ECx1.3 ($\mu g/m^3$)	TC= EC+OC ($\mu g/m^3$)	TC= ECx1.3 ($\mu g/m^3$)	TC= EC+OC ($\mu g/m^3$)
Weighted Return	352	321	235	225	109	121	178	175
Percent Reduction	---	---	33%	30%	69%	62%	49%	45%
*results adjusted for changes in airflow and intake concentrations								

The weighted average DPM concentrations were obtained by multiplying each location's air quantity by its respective DPM concentrations, and then dividing the sum of these products by the combined total air quantity. Concentrations and percent reductions based on TC = EC + OC or TC = EC x 1.3 were similar.

The total exhaust airflows were similar for the baseline, RVO 20-80%, and RVO 50-50% surveys; therefore, a comparison of concentrations can be used to assess the impact of these blends of biodiesel fuels. The VSO 50-50% survey was conducted under different weather conditions with warm spring weather outside. The baseline survey was conducted during the mid-winter weather conditions. The weather conditions significantly affected the amount of air ventilating the mine. Total return air quantities measured during the baseline survey averaged 892,000 cfm. This average air quantity was reduced to 748,000 cfm during the VSO 50-50% survey. The air quantity ventilating the mine has a direct affect on the DPM concentrations in the mine. Because the airflows are different in these two surveys, the comparison of effectiveness must be made using the total mass of particulate emitted. This value is obtained by multiplying the concentration by the airflow.

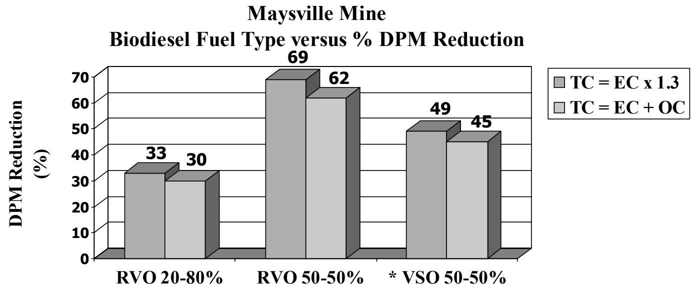
Table 4 contains the TWA summary of the average area DPM sampling for the Black River Mine survey.

Table 4. Black River Mine Average Area Samples

	Baseline		RVO 35-65%		VSO* 35-65%	
	TC= ECx1.3 ($\mu g/m^3$)	TC= EC+OC ($\mu g/m^3$)	TC= ECx1.3 ($\mu g/m^3$)	TC= EC+OC ($\mu g/m^3$)	TC= ECx1.3 ($\mu g/m^3$)	TC= EC+OC ($\mu g/m^3$)
Weighted Return	693	626	480	439	582	526
Percent Reduction	---	---	31%	30%	16%	16%
*concentrations adjusted due to decrease in airflow						

The airflows during the baseline and RVO 35-65% surveys were similar; therefore, a direct evaluation of DPM concentrations can be made. A direct comparison of DPM concentrations could not be used to assess the VSO 35-65% survey, because during this survey there was a decrease in airflow due to the changes in the natural ventilation of the mine. For this comparison the mass of diesel particulate (airflow times concentration) from the baseline was compared to the mass diesel particulate from the VSO 35-65% test.

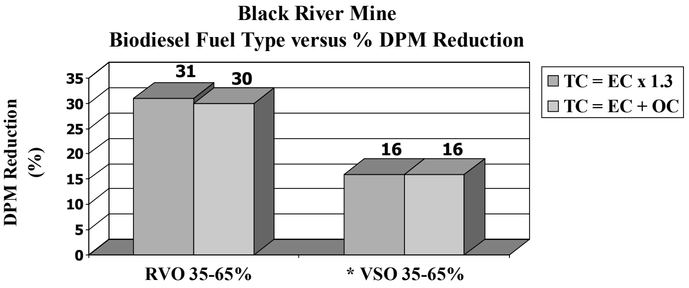
Figure 1 shows a graph of the biodiesel fuel type versus percent DPM reduction for the Maysville Mine. The percent DPM reductions are shown for the RVO 20-80%, RVO 50-50%, and VSO 50-50% surveys for TC = EC x 1.3 and TC = EC + OC. The biodiesel fuels were shown to be effective in the decrease of DPM exposures with the greatest DPM decrease utilizing RVO 50-50%.



* adjusted for changes in airflow and intake concentrations

Figure 1. Graph of Biodiesel Fuel Type Versus Percent DPM Reduction

Figure 2 shows a graph of the biodiesel fuel type versus percent DPM reduction for the Black River Mine. The percent DPM reductions are shown for the RVO 35-65% and VSO 35-65% surveys for TC = EC x 1.3 and TC = EC + OC. The biodiesel fuels were shown to be effective in the decrease of DPM exposures with the greatest DPM decrease utilizing RVO 35-65%.



*concentrations adjusted due to decrease in airflow

Figure 2. Graph of Biodiesel Fuel Type Versus Percent DPM Reduction

Table 5 shows the SWA summary of the average personal DPM concentrations inside and outside of the cabs for the Maysville Mine using TC = EC x 1.3. This TC formula was used for all personal sample calculations because it removes all carbonaceous interferences.

Table 5. Maysville Mine Average Personal DPM Concentrations Inside and Outside of Cab; TC = EC x 1.3 ($\mu g/m^3$)

	Baseline	RVO 20-80%	RVO 50-50%	VSO 50-50%
Average Workers Inside of Cab	220	219	89	212
Percent Reduction	---	0%	60%	4%
Average Workers Outside of Cab	300	208	216	313
Percent Reduction	---	31%	28%	(4%)

Table 6 shows the SWA summary of the average personal DPM concentrations inside and outside of the cab for the Black River Mine using TC = EC x 1.3. This TC formula was used for all personal sample calculations because it removes all carbonaceous interferences.

Table 6. Black River Mine Average Personal DPM Concentrations Inside and Outside of Cab; TC = EC x 1.3 ($\mu g/m^3$)

	Baseline	RVO 35-65%	VSO 35-65%
Average Workers Inside of Cab	1,611	731	967
Percent Reduction	---	55%	40%
Average Workers Outside of Cab	1,369	771	1,013
Percent Reduction	---	44%	26%

Personal samples had many variables affecting their exposure to DPM concentrations; therefore, they are not as useful in determining the effectiveness of the biodiesel fuels as are the area samples.

Nitrogen dioxide (NO_2) diffusion tubes were also collected with all of the samples taken. The highest concentrations of NO_2 recorded were 1.5 parts per million (ppm) on the high scaler and the loader operator. The roof bolter, the downhole driller, and the loader operator had concentrations of 1.0 ppm. These numbers did not significantly change from survey to survey. There was no indication that NO_2 concentrations increased during the RVO 20-80%, RVO 50-50%, and VSO 50-50% surveys from the baseline survey.

6 FINDINGS

6.1 *Maysville Limestone Mine*

The Maysville Mine reductions in the weighted exhaust TWA DPM biodiesel concentrations from the baseline survey using TC = EC x 1.3 were as follows:

- RVO 20-80% indicated a 33% reduction
- RVO 50-50% indicated a 69% reduction
- VSO 50-50% indicated a 49% reduction

The average personal SWA DPM biodiesel concentrations showed a reduction from the baseline survey, except for the VSO 50-50% survey when outside of the cab. The findings of the biodiesel fuel percent reduction from the baseline survey for inside and outside of the cab using TC = EC x 1.3 were as follows:

- RVO 20-80% indicated a 0% inside cab
- RVO 20-80% indicated a 31% outside cab
- RVO 50-50% indicated a 60% inside cab
- RVO 50-50% indicated a 28% outside cab
- VSO 50-50% indicated a 4% inside cab
- VSO 50-50% indicated a (4%) outside cab

6.2 *Black River Limestone Mine*

The Black River Mine reductions in the weighted exhaust TWA DPM biodiesel concentrations from the baseline survey using TC = EC x 1.3 were as follows:

- RVO 35-65% indicated a 31% reduction
- VSO 35-65% indicated a 16% reduction

A direct comparison of DPM concentrations could not be used to assess the VSO 35-65% survey, because there was a decrease in airflow due to the changes in the natural ventilation of the mine; therefore, the mass of the diesel particulate from the baseline survey was compared to the mass of the diesel particulate from the VSO 35-65% survey.

The average personal SWA DPM biodiesel concentrations showed a reduction from the baseline survey. The findings of the biodiesel fuel percent reduction from the baseline survey for inside and outside of the cab using TC = EC x 1.3 were as follows:

- RVO 35-65% indicated a 55% inside cab
- RVO 35-65% indicated a 44% outside cab
- VSO 35-65% indicated a 40% inside cab
- VSO 35-65% indicated a 26% outside cab

7 CONCLUSIONS

The use of biodiesel fuel mixtures reduces DPM concentrations in underground nonmetal mines:

- Two entire underground limestone mines had been switched over to various blends of biodiesel fuel mixtures. Subsequent DPM sampling has shown reductions in the weighted exhaust DPM concentrations at both mines from all biodiesel mixtures tested.
- The RVO 50-50% had the greatest reduction in DPM concentration. This mixture had a 69% reduction in TC.
- The VSO mixtures also showed reductions, but it was not as effective as the RVO at similar blends.

The use of biodiesel fuels did not have any significant effect on NO_2 concentrations.