

THE PERFORMANCE OF DI-TERTIARY-BUTYL PEROXIDE AS CETANE IMPROVER IN DIESEL FUELS

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Abstract

Increasing the cetane number of diesel fuel, either by lowering aromatic content of the fuel through hydrotreating and/or by addition of chemical cetane improvers, is a cost-effective option to reduce diesel engine emissions. It is generally recognized that chemical cetane improvement additives represent a low cost alternative to aromatic reduction. Although both methods significantly reduce engine emissions, deep hydrotreating tends to adversely affect some fuel properties. We are evaluating the performance of a peroxide based cetane improver for diesel fuel. A comparison is made between the performance of di-t-butyl peroxide and the conventional cetane improver, 2-ethylhexyl nitrate. Correlation between the cetane response of the peroxide with the different fuel properties is discussed. Both the additives significantly reduce all regulated and unregulated emissions including NOx emissions. The NOx emissions from the peroxide treated fuels are consistently lower than those for the nitrate treated fuels at similar cetane level. The chemistry for the synthesis of di-t-butyl peroxide is discussed.

Introduction

The implementation of stringent diesel engine emissions regulations is growing worldwide. In the United States, the 1990 Clean Air Act mandates lowering oxides of nitrogen (NOx) emissions to 4.0 grams per horsepower-hour (g/hp-hr) in 1998. Future proposals by EPA call for a further reduction of a combined NOx and HC to 2.5 g/hp-hr for the year 2004 for heavy-duty trucks and buses. Such emission reduction will require a combination of new engine technology and economically viable low emission diesel fuels.

It is widely accepted that increasing the cetane number represents one option for production of cleaner burning diesel fuels. Numerous studies, including the Coordinating Research Council VE-1 and VE-10 programs, have demonstrated that increasing the cetane number of the fuel significantly reduces all the regulated emissions.¹ Increasing the cetane number of diesel fuel can be achieved by lowering aromatic content of the fuel through hydrotreating and/or by addition of chemical cetane improvers. It is generally recognized that chemical cetane improvement additives represent a low cost alternative to obtaining higher cetane number achieved through aromatic reduction. Moreover, deep hydrotreating to reduce aromatics tend to adversely affect some fuel properties, e.g., waxing and cold flow.²

Chemical cetane improvers are those compounds that readily decompose to form free-radicals, which in-turn promote the rate of initiation. This increased rate of chain initiation leads to improved ignition characteristics of diesel fuel. Chemicals selected from alkyl nitrates, certain peroxides, tetraazoles, and thioaldehydes can serve as cetane improvers. Due to their low costs, alkyl nitrates have played the most significant role in commercial use. 2-Ethylhexyl nitrate (EHN) has been used as a commercial cetane improver for a number of years and today is the predominant cetane improving additive in the marketplace. Di-tertiary-butyl peroxide (DTBP) was first recognized as an effective cetane improver in the 1940's.³ Due to its higher cost, DTBP has not achieved the same wide spread usage as EHN. New technology has been developed by ARCO Chemical Company that will substantially reduce the cost of DTBP to a level comparable to that of EHN. Moreover, DTBP has a potential advantage over alkyl nitrates in reducing NOx emissions since it does not contain nitrogen.⁴ DTBP is currently used in limited amounts in an after market fuel treatment package.⁵ This fuel additive package containing DTBP, has been evaluated, certified and approved for use by the Department of the Navy.⁶

Synthesis

Dialkyl peroxides can be synthesized by the reaction of an alcohol and/or an olefin with an organic hydroperoxide, using an acidic catalyst. In the process developed at ARCO Chemical Company, t-butyl alcohol and/or isobutylene is reacted with t-butyl hydroperoxide in the presence of an acidic resin catalyst.⁷

Cetane Response

Cetane response, which may be defined as the relationship between the change in cetane number of the fuel and the concentration of the cetane improver, is a key factor for commercial acceptance of a cetane improver. We have studied, in details, the cetane response of DTBP in a variety of commercial diesel as well as in various diesel fuel blend stocks, worldwide.⁸ The relative effectiveness of DTBP versus the commercial cetane enhancer, EHN, was determined in numerous base fuels with varying fuel properties as well as different blend stocks.

On an average, DTBP is between 85% to 90% as effective as EHN in increasing cetane number of diesel fuels.

It is also very important to understand the relation between the diesel fuel composition or properties and its cetane response for DTBP. We have developed a predictive cetane response equation for DTBP based on various fuel properties, viz., aromatics, mid-range distillation point (T_{50}), flash point, and pour point. The regression equation describing the change in cetane number due to the addition of DTBP is:

$$\Delta C = (39.8727 + 0.02335 \cdot Z_2 - 0.0823 \cdot Z_3 + 0.1405 \cdot Z_4 - 0.0777 \cdot Z_5) \\ + (-0.1176 \cdot Z_3 + 0.0430 \cdot Z_5) \cdot X + (-0.1190 \cdot Z_4 - 0.0113 \cdot Z_5) \cdot X^2$$

with $R^2 = 0.889$ and $RMSE = 1.6846$

where ΔC = expected change in cetane number,
 X = concentration of additive (wt%)
 Z_2 = flash point ($^{\circ}F$)
 Z_3 = aromatics (wt%)
 Z_4 = pour point ($^{\circ}F$)
 Z_5 = mid-range distillation point, T_{50} ($^{\circ}F$)

Thus, given the values for appropriate fuel properties, the above equation can be used to predict, within their limits of uncertainty, the expected change in cetane number due to the addition of a specific amount of DTBP. However, it is recommended that this equation be used within the valid range of the experimental data used to generate it and the results not be extrapolated beyond an additive concentration of 0.75 wt%. Since this equation reduces to a simple quadratic form on substitution of the fuel properties, it can also readily be solved to determine the amount of additive required to increase the cetane number of the fuel by a desired amount.

Although the cetane response equation was generated based on several fuel properties, statistically, the two most influential fuel parameters were the aromatic content and the mid-range distillation temperature (T_{50}).

The cetane response of DTBP was inversely related to the aromatic content of the fuel. Thus, low aromatic fuels will respond well to the additive. On the contrary, fuels with high aromatic content or highly aromatic blend stocks like light cycle oil (LCO) or light cycle gas oil (LCGO) will respond very poorly to cetane improvers. Indeed, a highly aromatic (87%) LCGO blend stock did not respond at all to either of the cetane improvers, DTBP or EHN. Assuming the cetane improvers react through formation of free radicals to accelerate combustion, this low response for the aromatics may be attributed to the higher activation energy required for the nitrate or peroxide free radicals to react with an aromatic fragment compared to an aliphatic hydrocarbon fragment of the fuel. This, in fact, follows a similar trend for natural cetane for different fuel fragments, where aromatics have poor natural cetane numbers while straight chain aliphatic hydrocarbons have the highest natural cetane numbers.

The relationship between the cetane response of the two additives for the different fuels and the mid-range distillation temperature of the fuel is less clearly understood. In general, it was observed that the lighter fuels respond better to cetane improvers compared to the heavier fuels, especially at low additive levels. More work is needed to understand this effect.

It must be emphasized that although the cetane response equation, described here, use the base diesel fuels' properties to compute the expected change in its cetane number, the relationship between these changes and the fuel properties are by no means causal. Rather, the fuel properties are merely manifestations of some other more fundamental attributes of the fuel.

Engine Emissions

Numerous studies by the Coordinating Research Council and others have shown that increasing the cetane number through the use of additives reduces all regulated emissions.¹ The Coordinating Research Council's VE-10 program addressed the effect of cetane additives on diesel emissions.⁹ The first part of this study, using two different 1994 heavy-duty engine technologies, demonstrated that the use of cetane improvement additives produces significant reduction in carbon monoxide and oxides of nitrogen emissions, with hydrocarbon and particulate matter being either unaffected or slightly reduced. Cetane additives including DTBP and EHN at levels up to 1.25 wt% were included in the continuation of this study using 1998 engine technology. Even using 1998 engine technology, having lower emissions than any diesel engine on the road today, increasing the cetane number with either EHN or DTBP reduced all engine emissions.

ARCO Chemical Company has conducted extensive testing on the effects of cetane additives on emissions from heavy-duty diesel engines.¹⁰ This testing was conducted on a 1991 Detroit Diesel Series 60 heavy-duty diesel engine, typical of an engine currently in service, using the 1992 Federal Test Procedures for transient testing of heavy-duty engines. A total of four

fuels, representative of those currently commercially available, were used. The properties of the four test fuels are described in Table 1. One of these fuels, designated C, is a standard 2-D fuel, which meets the requirements for a diesel engine certification fuel as defined in CFR 86.1313-94(b)(2). The effects of both the cetane improvers, including a mixture of the two additives in fuel C, on engine emissions are summarized in Table 2.

Table 1: Test Fuels Properties

Property	Fuels			
	A	B	C	D
Cetane Number (D613)	46	41	43	38
Aromatics, vol% (D1319)	20	25	32	35
Sulfur, wt%	0.01	0.01	0.03	0.01
API Gravity, (D287)	37.9	35.4	35.7	33.4
Distillation Range (D86)				
IBP, °C	200	168	178	181
50% Point (T50), °C	243	247	259	248
EP, °C	328	333	334	344

Table 2: Effect of Cetane Improver on Regulated Emissions

Base Fuel	Additive	Additive Level (wt%)	Increase in Cetane Number	Hydrocarbon	Carbon Monoxide	NOx	Particulate Matter
A	EHN	0.40	10	- 41%	- 27%	- 1.9%	11%
	DTBP	0.50	11	- 43%	- 29%	- 2.2%	12%
B	EHN	0.70	15	- 59%	- 40%	- 2.8%	0.7%
	DTBP	0.80	16	- 58%	- 40%	- 3.9%	2.5%
C	EHN	0.60	9	- 60%	- 37%	- 1.9%	2%
	DTBP	0.65	10	- 59%	- 36%	- 5%	- 4%
	EHN/DTBP	0.31	10	- 59%	- 37%	- 2.6%	- 6.6%
D	EHN	0.65	10	- 75%	- 47%	- 2.8%	- 40%
	DTBP	0.75	10	- 77%	- 49%	- 3.3%	- 40%

As evident from the results increase in cetane number can significantly reduce hydrocarbon and carbon monoxide emissions in all the fuels. The NOx emission from the cetane improved fuels showed a small reduction compared to the base fuels, with the limited number of tests used for these study. The NOx emissions from the peroxide treated fuels, although not statistically significant, were lower than that from the nitrate treated fuels, in each of the base fuels. The peroxide produced about 0.5% to 3% lower NOx when compared to the nitrate at the same cetane level. These results indicate that when blended to comparable cetane numbers, DTBP produces lower NOx emissions than EHN. This trend is not only observed in this work but also in other works with different fuels, different engines, and using different international test protocols.

Gaseous Toxics Emissions

The use of a cetane enhancer substantially reduces the four gaseous toxic emissions of 1,3-butadiene, benzene, formaldehyde, and acetaldehyde.¹⁰ Typical reductions in these four gaseous toxic emissions achievable by increasing the cetane number of a fuel by ten numbers, which on average required 0.65% cetane improver, vary from 30% to 70%.

Ozone Forming Potential

Complete speciation of the volatile hydrocarbons, aldehydes and ketones into C₁-C₁₂ fractions was included as part the test program conducted by ARCO Chemical Company. Using standard Minimum Incremental Reactivity (MIR) values, the ozone forming potential was calculated.¹⁰ Typical reductions in the ground level ozone forming potential achieved by a ten number increase in cetane using additives is between 50% to 75%. With ground level ozone, a major cause of smog, becoming an increasing problem in metropolitan areas, significant reductions

in ground level ozone attributed to diesel engine emissions can be obtained through the use of cetane improvers.

Soluble Organic Fraction of Particulate Matter

The use of DTBP produces substantial reductions in the soluble organic fraction of the particulate matter.¹⁰ These reductions in the soluble organic fraction of the particulate matter are expected in-turn to reduce the emissions of both polyaromatic hydrocarbons and nitrated polyaromatic hydrocarbons.

Thermal and Oxidative Stability

A cetane improvement additive that is thermally or oxidatively unstable under actual conditions impacts on the fuel quality and could lead to poor engine performance resulting from the decrease in cetane number or fuel degradation. Thus, for commercial acceptance the peroxide based cetane improvement additives must be stable, thermally and oxidatively, at actual use temperatures.

The thermal stability of DTBP was demonstrated by determining the effects of heating on the treated fuels and also by measurement of the decomposition rates in a low sulfur diesel fuel.⁸ A fuel treated with DTBP showed no statistically significant loss in cetane number after heating for 100 hours at 92°C. The half-life for DTBP at 70°C in diesel fuel is in excess of 10,000 hours, with greater than 97% of the additive remaining after nearly 700 hours. Even at 100°C, the half-life of DTBP in diesel fuel is over 300 hours. Even though the rate of thermal decomposition of the peroxide is five to ten times faster than the nitrate, the peroxide additive is very stable under typical fuel system temperatures.

Additives can cause diesel fuel degradation if they are not oxidatively stable. The oxidative stability of DTBP was demonstrated by the standard ASTM methods. Both the accelerated oxidative stability test (D274)¹² and the long term storage stability test (D4625)¹³ did not show any gum formation in most of the diesel fuels tested. In some inherently unstable fuels degradation was observed. But they can be controlled easily by addition of very small amount of antioxidants.

Conclusion

Increasing the cetane number by addition of chemical cetane improvement additive is a cost effective way to produce cleaner burning diesel fuels. A peroxide based cetane improvement additive, di-*t*-butyl peroxide, can be very effective as a cetane improver. DTBP can be synthesized cheaply by the reacting isobutylene with *t*-butyl hydro peroxide. It is comparable in performance to 2-ethylhexyl nitrate, the cetane improver currently used commercially. DTBP has the potential of reducing NO_x emissions more than the nitrate at comparable cetane level. The additive is thermally and oxidatively stable in diesel fuels at typical fuel systems temperatures.

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