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4th Workshop on Diesel Combustion,  
Sponsored by Combustion Research Branch,  
Industrial Environmental Research Laboratory-  
RTP, U. S. Environmental Protection Agency,  
May 14-15, 1980, Cincinnati, Ohio

BNL 27792

MASTER

CONF-800553--2

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SOOT REDUCTION IN DIESEL ENGINES BY CATALYTIC EFFECTS

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#### ABSTRACT

Recent tests at Brookhaven National Laboratory indicate that both small additions of alcohols to the fuel and the presence of platinum surfaces in the combustion chamber can reduce soot emissions in a diesel engine. These tests were conducted over a limited range of operation in a single cylinder CFR engine. Most of the testing was done using pure cetane as a fuel at constant speed and load. Possible major features of the reaction mechanisms for both fuel additives and surface catalyst effectiveness are presented.

#### ACKNOWLEDGEMENT

We are indebted to T. O'Hare, W. Marlow, M. Sansone, J. Barry, J. Hurst, R. Klemm, and C. Waide for their assistance and support. We also wish to thank I. Tang, H. Munkelwitz, F. Salzano, R. Whisker, and A. Berlad for helpful discussions. This research was carried out at Brookhaven National Laboratory under contract with the U. S. Department of Energy.

## INTRODUCTION

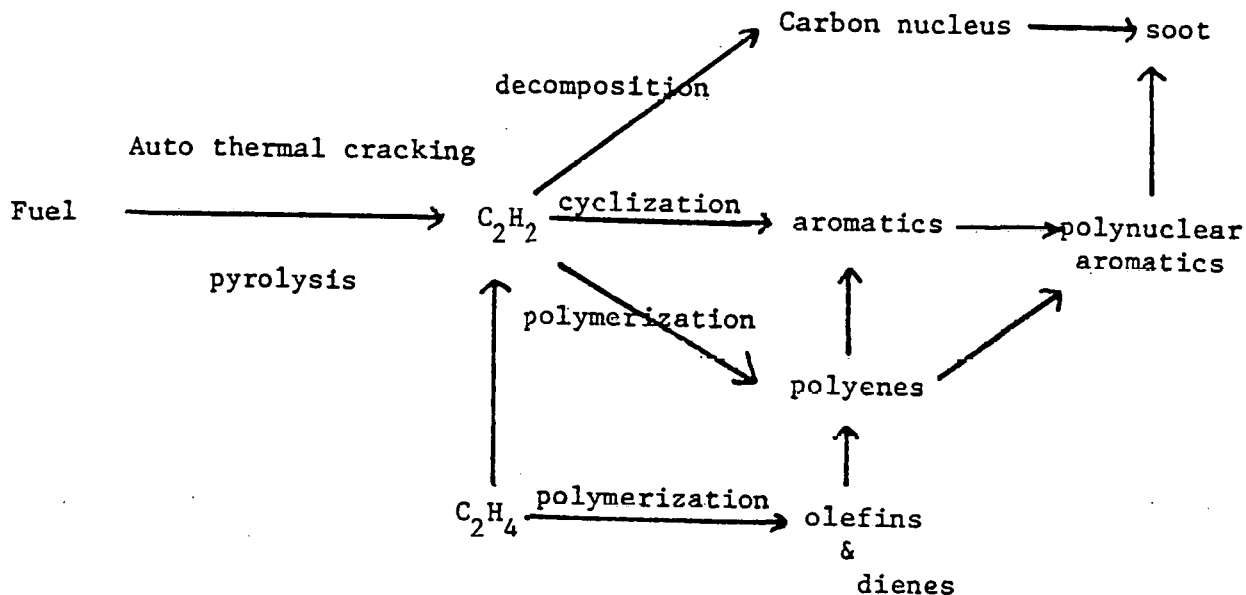
Diesel car sales are climbing in the United States and some manufacturers are predicting that by 1985 25% of the new cars made in the U.S. may be diesel powered (1). The diesel engine's proven fuel economy and lower emissions of unburned hydrocarbons and carbon monoxide makes it a viable alternative to a gasoline automotive plant, but the inherent production of particulate matter (soot) threatens the expanded use of the diesel engine.

Current diesel cars emit about 13 lbs. of particulate matter for every 10,000 miles - 50 times the gasoline auto. High concentrations of these emissions may have a synergistic effect when combined with other carcinogens in the urban environment (2) and this problem may overshadow the diesel's fuel savings.

A variety of methods have been proposed over the years for reducing soot emissions (3). These methods include engine modifications such as fuel injection optimization, combustion chamber shapes and turbocharging; fuel modifications such as the use of water injection, fuel additives, and fuel fumigation; and more recent suggestions which stress exhaust treatments including "trap oxidizers" similar to catalytic converters and various types of replaceable filters. Fuel blending such as methanol-diesel emulsions, as well as separate introduction of methanol, have also been tried.

In the diesel engine the air charge is compressed to a high temperature and pressure, preceding fuel injection and combustion begins spontaneously shortly after. The rate of burning and heat release is controlled by the rate of fuel air mixing. This mixing-limited operation leads to not only many of the diesel's desirable characteristics but also to hot, fuel rich zones despite the air charge being in excess of the stoichiometric requirements. Cracking occurs, leading to soot formation in these fuel rich zones. This can

be perceived as an autothermal cracking process in which heat, from combustion of the fuel, serves to crack the remainder endothermally (similar to the manufacture of ethylene and acetylene via the pyrolysis of hydrocarbons (4)).



All of the soot formed is not emitted as some of it is combusted in later parts of the engine cycle. It has long been recognized that the engine maximum load is limited by excessive smoking at overall air fuel ratios still well above stoichiometric.

Since a precise mechanism of soot formation during combustion in a diesel engine is not completely defined, a tentative approach was formulated relating the partial combustion of liquid hydrocarbons to the initiation of soot formation in the diesel combustion process. There is ample evidence that soot formed in combustion processes consists of a mixture of surface and gas formed carbons (5), therefore, the influence of both homogeneous and wall reactions in the combustion chamber were considered in order to define the fuel and engine properties which contribute to the formation of particulate matter.

#### EXPERIMENTAL

Complete combustion must be attained if soot is to be avoided and the introduction of either oxygen carriers or catalytic surfaces, which would increase the probability of contact between fuel and oxygen could influence the formation of soot in the combustion chamber. The addition of hydroxyl (OH)

carriers to the fuel was felt to be a direct way to verify or illustrate the proposed chemistry. The possible catalytic influence of wall and valve materials to promote the surface ignition of carbon and soot precursor was also investigated.

#### EXPERIMENTAL DETAILS

A standard Waukeska CFR engine coupled to a D.C. dynamometer was used in the tests. Cetane was used instead of diesel oil as fuel for obvious chemical reasons and n-butanol was used as the fuel additive. The engine was operated at the ASTM Cetane number test conditions making a concerted effort to keep the engine operating variables constant. Typical engine operating conditions were: speed, 900 rpm; fuel flow, 13 ml/min., compression ratio, 19:1, (see table for each test).

Sampling of the engine's particulate effluent was done by drawing 15.6 l. p.m. through a 47mm Millipore FA filter directly from the exhaust flow, (see Figure 1). This procedure minimized distortion of the sample and maintained the integrity of the structurally-weak filter with no particulate break-off. The filters were equilibrated at constant humidity and weighed to determine the soot by difference. Duplicate samples were reproducible to better than 10% and at least two samples were taken to each data point.

After the cetane/n-butanol mixtures were studied, the engine was dismantled and platinum was deposited onto the piston crown and valve faces by vacuum sputtering to a thickness of approximately 6,000 Å with an MRC model SEM-8620 RF Bias sputter-etch module. Prior to insertion in the chamber the components were cleaned mechanically in a glassblaster and washed with acetone and alcohol as a final step. Sputter etching was not possible.

#### RESULTS AND DISCUSSION

##### Use of Alchols

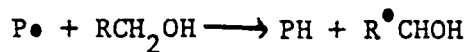
The technology of alcohol fuels utilization in diesel engines is not nearly as advanced as that for spark ignition engines. Since our tentative approach to homogeneous soot formation may be conveniently formulated in terms of the free radical theory of the cracking of hydrocarbons (6), alcohol could suppress the formation of soot by providing species which remove or retard radical fuel pyrolysis intermediates.



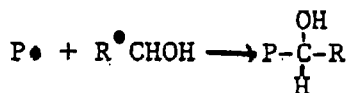
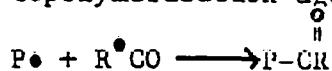
## Alcohols Action

### 1. Radical Retardation

#### a. Transfer agent

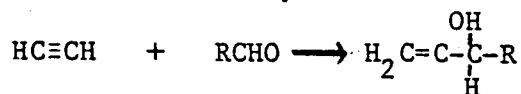


#### b. Copolymerization agent



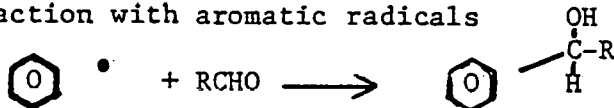
### 2. Precursor Trap

#### a. reaction with acetylene



#### b. inhibits diene cyclization reactions

#### c. reaction with aromatic radicals



The observed data as presented in Figure 2, reveal a rapid and then gradual decrease in soot with n-butanol addition with an optimum 30-40% reduction at ~ 7% n-butanol addition. Similar results were observed when using conventional diesel fuel and ethanol mixtures (Figure 3).

Although recent tests using methanol and ethanol/diesel emulsions have shown particule reduction (7,8), to our knowledge this represents the first systematic investigation of specific alcohol addition versus reduction of soot particulates in a diesel engine. These results seem to support our concept of controlling the gas-phase mechanism of soot formation utilizing the radical retarding effect of alcohols.

## Use of Metals

Catalytic combustion can promote the oxidation of long chain hydrocarbons and soot precursors minimizing polymerization reactions which result in soot formation.

The mechanism by which metal containing fuel additives reduce smoke is obscure (9), but British Petroleum tests suggest that successful soot suppressants lower the soot ignition temperature while other ineffective additives yield little change in this temperature (10).

Alkaline-earth metal fuel additives such as barium salts affect homogeneous soot formation in a manner similar to that proposed for alcohols. These metals which reduce soot in all oxygen-fuel ratios, act by the gas-phase catalysis of the decomposition of hydrogen or water vapor to yield hydroxyl radicals (11).

Other effective metal fuel additives such as molybdenum, tungsten and chromium perform only at high oxygen-fuel ratios, ( $>.9$ ) suggesting a different mechanism for their action (11). It is our contention that these metals act as surface catalysts in the combustion process.

Early exploratory work on surface combustion has shown that hot surfaces have the capability of accelerating combustion at the boundary region between gaseous and solid phases (12). Considering that the nature of the reactor wall has a significant effect on the rate of carbon formation and, the composition of the exit gas in a cracking reactor (13), the oxidation properties of the combustion chamber surface could determine the quantity and quality of the particulate emissions in a diesel engine.

Since an oxidation catalyst serves as the source of oxygen transferred to the reactant molecule, the most important property generally ascribed to a combustion catalyst is its ability to dissociate oxygen molecules into adsorbed oxygen atoms. If the formed oxide can be reduced by the hydrocarbon to a lower oxide or the metallic state, the metal will function as an active catalyst.

We wish to propose a novel yet simple mechanism which would provide a unified picture capable of explaining or predicting catalyst behavior. The basis for this hypothesis was generated from various studies in slow combustion,

which neglected wall effects in elucidating the mechanism and understanding the chemistry of combustion (14).

This proposal starts with the assumption that oxygen must become activated upon a surface, M (step A). This may be the metal in catalyzed combustion or even the walls of the reaction vessel. It has been found that reaction initiation in the absence of walls may be severe (15) and most radical mechanisms use the walls to convert intermediates to products (6).

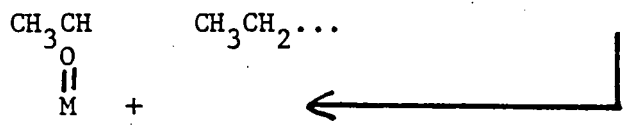
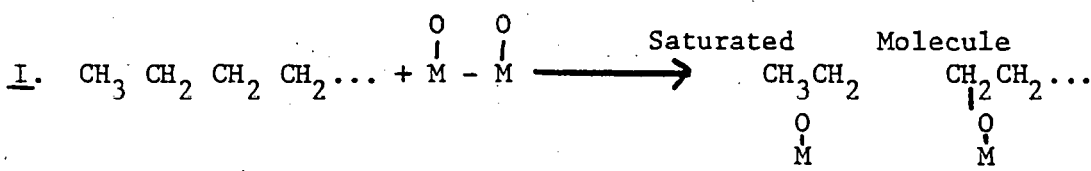
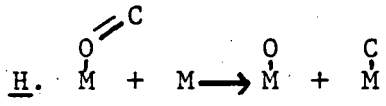
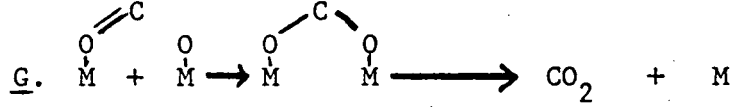
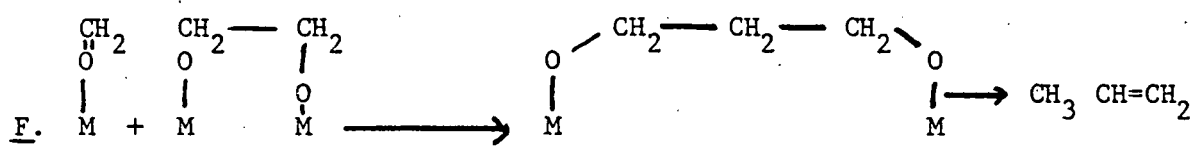
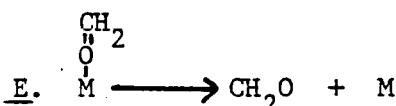
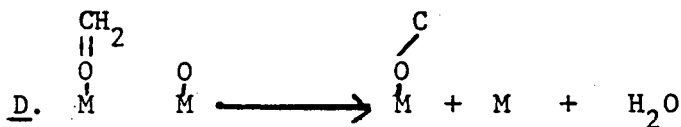
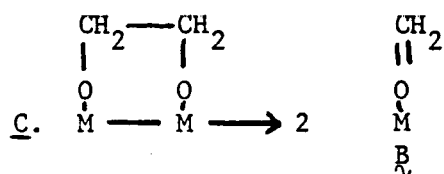
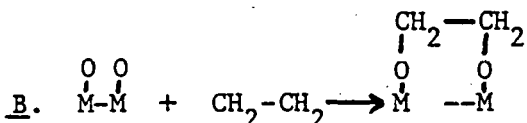
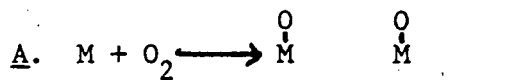
The carbonaceous material (e.g., ethylene in diagram) reacts with the surface oxygen forming a saturated intermediate (B) which undergoes carbon-carbon bond cleavage to give the oxymethylene species, (C). This would be associated with the induction period of combustion, and would be an exothermic reaction. This species would explain why formaldehyde, which would chemisorb on a surface in this manner, is responsible for branching (F) in the combustion of many simple fuels (16). Similarly, saturated hydrocarbons could form acetaldehyde as an intermediate (I). The addition of formaldehyde or acetaldehyde to a hydrocarbon combustion reaction should eliminate the induction period and indeed this is the case in the oxidation of ethane (17). The possible reaction paths of the oxymethylene intermediate result in the various products observed in the slow combustion of ethylene (16).

Carbon dioxide arises from the reaction of the oxygen coordinated carbon monoxide with surface oxide (G). This step is consistent with the mechanism of carbon monoxide oxidation (18). Carbide or soot formation occurs (H) when the adjacent surface oxide is not present (e.g., thru reduction). If the oxide site were available soot formation would be reduced.

An interesting feature of this scheme is that it is closely related to the recently proposed oxide Fischer-Tropsch (F-T) mechanism (19). Since both proposals assume similar reaction intermediates correlations of metal catalysts should be noted. Indeed, metals that form strong oxides are not good F-T catalysts and will inhibit the oxidation of carbon. This relationship is particularly attractive in the examination of controlled combustion for chemical conversion.

In view of the well known combustion catalytic effects of platinum (20) the coating of the combustion chamber surfaces with platinum was tried.

The platinum coated combustion surface produced ~ 40% reduction in soot with no alcohol addition. Addition of alcohol to the platinized reactor was found to further reduce soot with reduction up to ~ 80% being measured (see Figure 4).



The cyclic oxygen transfer mechanism appears to offer reasonable explanations of these results since the free energy decrease on reduction of iron oxides with carbon (or hydrocarbons) is less than that for the reduction of platinum oxide. Because platinum will markedly lower the ignition temperature of carbon (21) and promote ultralean combustion of hydrocarbons, (20) soot and unburned fuel reaching the platinized combustion chamber surface could be partially or completely oxidized leading to reduced particulate emissions. Heterogeneous reactions of this sort will be limited by the amount of carbon reaching the surface by molecular and turbulent transport but may produce products which also affect the homogeneous chemistry. That is, reaction intermediates initially formed at the surface, breakoff to take part in homogeneous reactions. This chemistry would be similar to the action of alcohol described earlier.

After eight hours of continuous operation the platinum coated surface was lost, and the observed soot emission found to be identical with the original iron surfaced piston and valves. Although the precise mechanism by which the platinum was removed is unknown, we believe that surface impurities such as, iron carbon and oxide may have caused problems in the platinum adhesion since no stringent cleaning of the piston crown was performed prior to coating. Thermal expansion differences or excessive vibration would also have deleterious effects (22).

The short service life may also be ascribed to penetration by poisons or oxygen through the catalytic lining with resulting pitting or corroding of the iron alloy composing the piston. To overcome this a hard, smooth, non-catalytic and non-absorbative cap of low corroding properties (e.g., chrome-iron) should be interposed between the catalyst and the coated body (23).

#### CONCLUSION

This work towards reducing soot emission from diesel engines suggests that both homogeneous and heterogeneous approaches are feasible. The homogeneous approach consisted in mixing small quantities of alcohol with the fuel and the heterogeneous approach consisted of coating parts of the combustion chamber (bounding) surface with an oxidation catalyst like platinum. Both approaches produced significant reductions in soot emissions. These tests were conducted

over a small range of operation in a single cylinder engine (a CFR type), with most of the testing done using pure cetane as fuel at constant speed, and load. Although the engine and test conditions are not representative of an automotive diesel engine, the results may be useful to assess the feasibility of soot reduction in automotive and truck diesel engines, using these methods.

The major features of the reaction mechanisms proposed for both fuel additive and surface catalyst effectiveness could be applied to various combustion problems.

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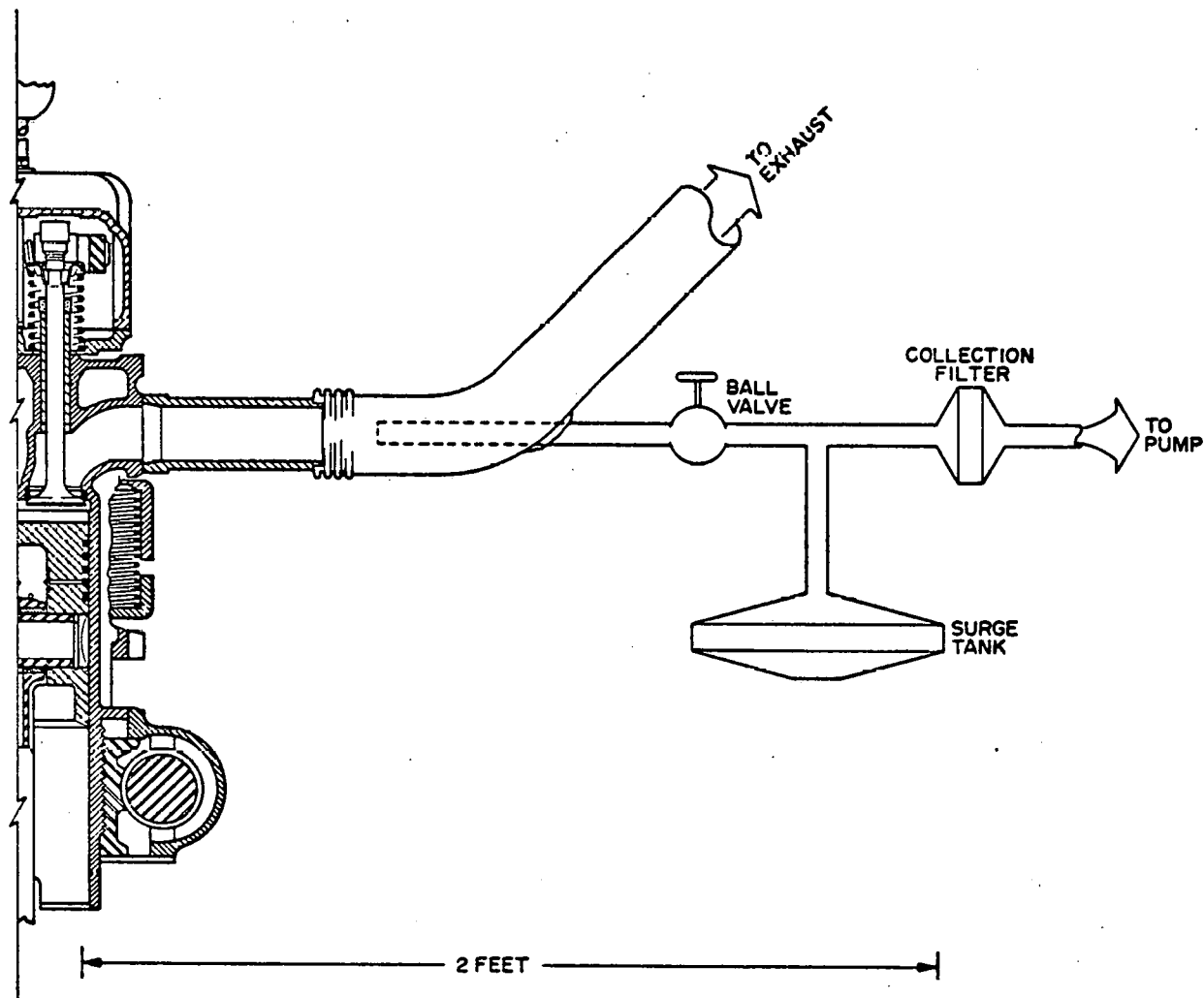


FIGURE 1, SAMPLING SYSTEM

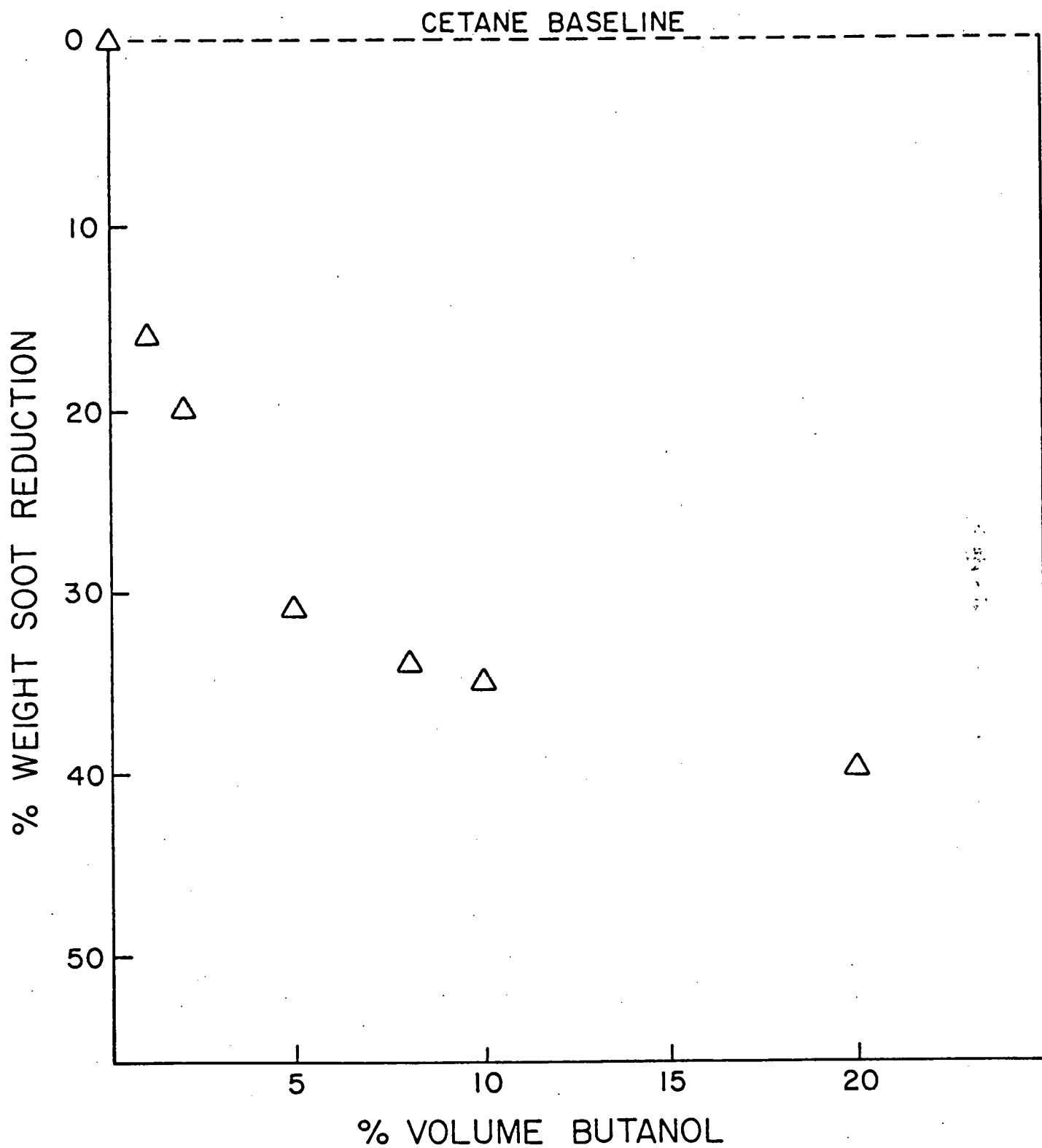


FIGURE 2. BUTANOL ADDITION TO CETANE

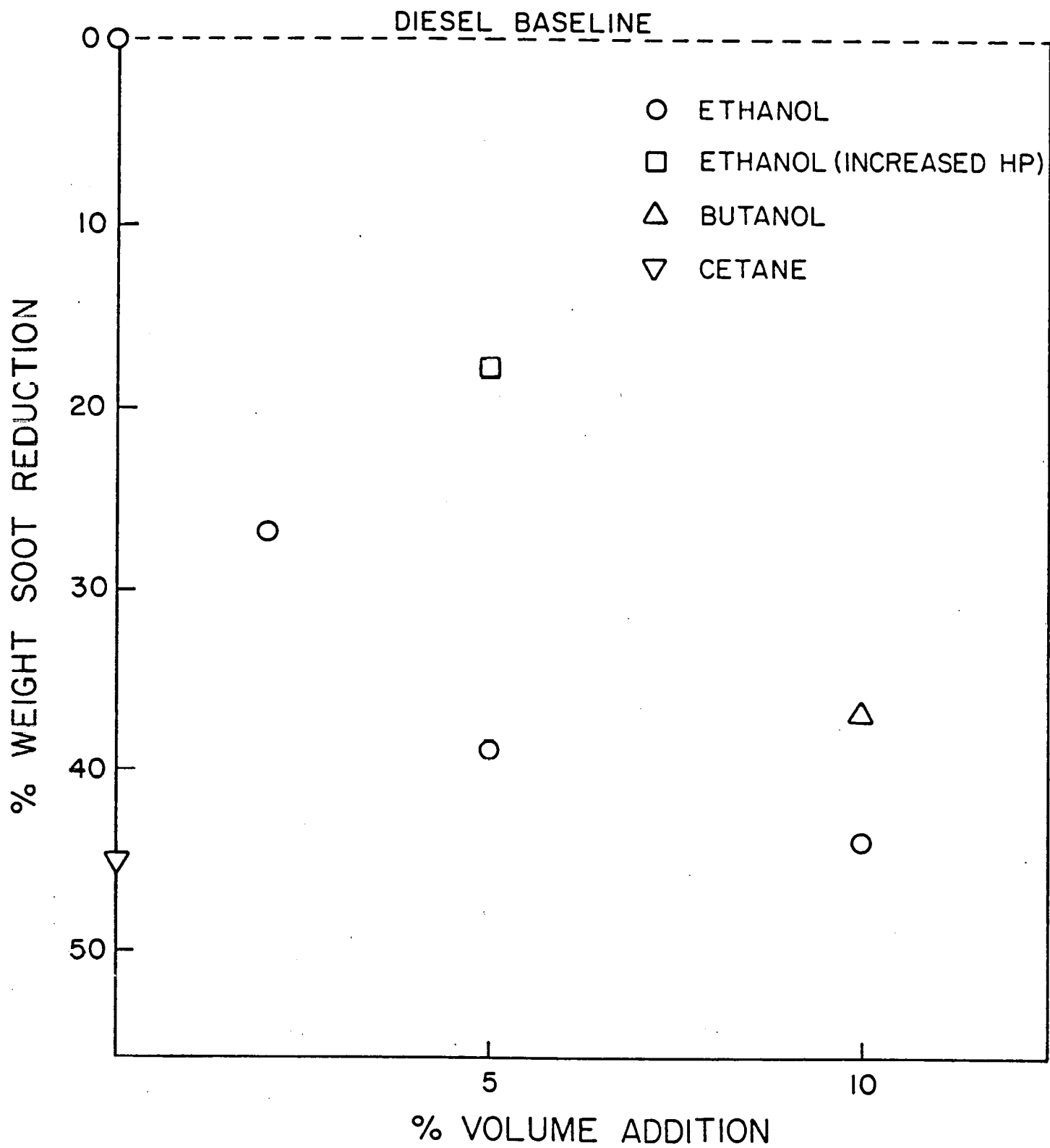


FIGURE 3. DIESEL FUEL DATA

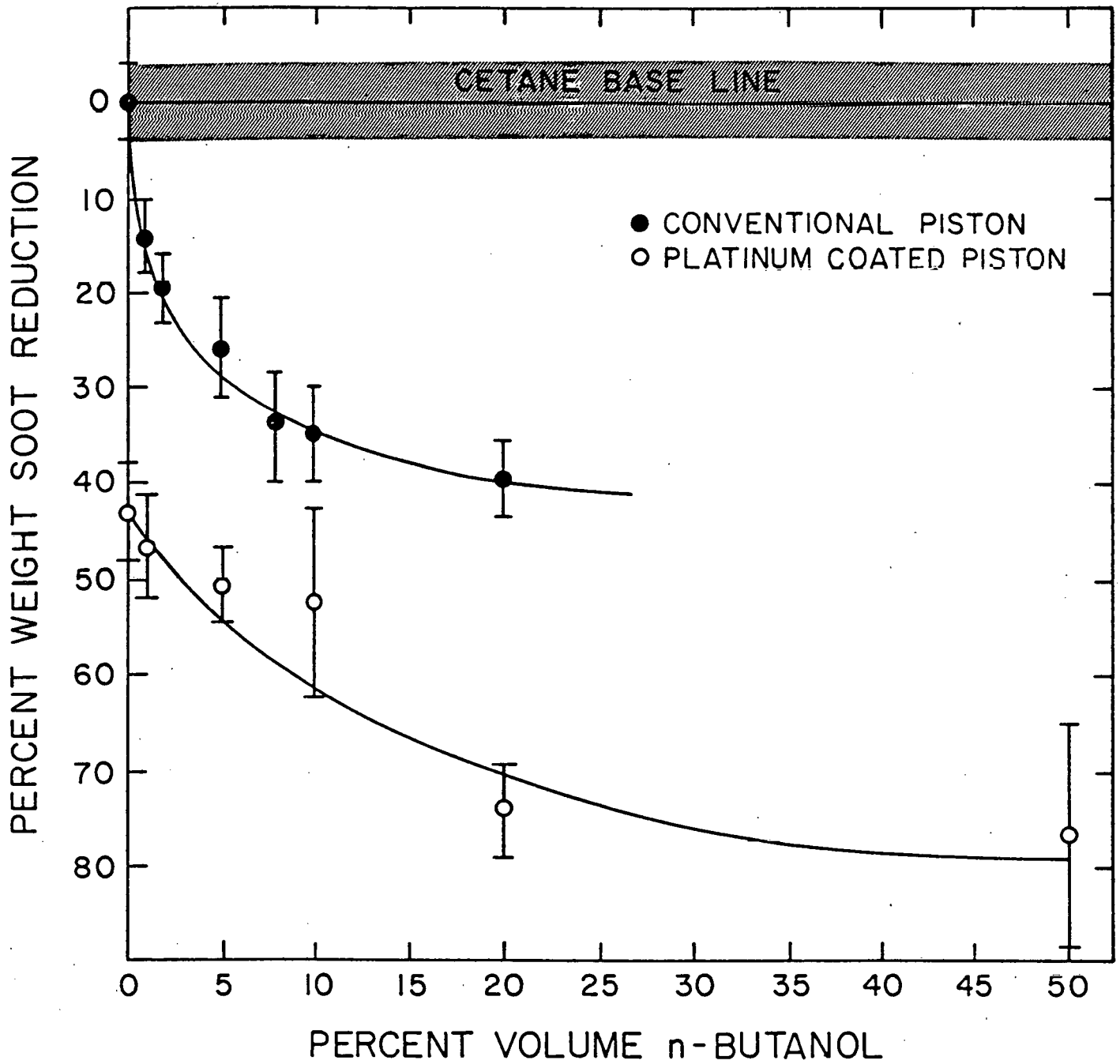


FIGURE 4. EFFECT OF CATALYST (PLATINUM)

TABLE I  
 SOOT EMISSION MEASUREMENTS AS A FUNCTION OF  
 ADDITION OF N-BUTANOL TO A CONVENTIONAL (IRON) CFR ENGINE

PERCENT ALCOHOL ADDITION	SOOT (mg) <sup>a</sup>	ENGINE OPERATING CONDITIONS			
		HP	RPM	INJECTION <sup>b</sup> ADVANCE	IGNITION <sup>b</sup> DELAY
0	1.15	2.8	890	8.4	5.2
1	1.00	3.0	895	8.7	4.7
2	.94	2.9	925	8.8	4.7
5	.86	2.9	880	7.8	4.6
8	.77	2.7	880	7.5	4.7
10	.76	2.6	890	8.2	4.7
20	.70	2.4	900	7.4	5.3

<sup>a</sup>Soot samples taken for 30 seconds (see experimental section for details).

<sup>b</sup>In degrees.

TABLE II  
 SOOT EMISSION MEASUREMENTS AS A FUNCTION OF ADDITION OF N-BUTANOL TO CFR  
 ENGINE WITH PLATINUM COATED PISTON CROWN AND VALVE FACES

PERCENT ALCOHOL ADDITION	SOOT (mg) <sup>a</sup>	ENGINE OPERATING CONDITIONS			
		HP	RPM	INJECTION <sup>b</sup> ADVANCE	IGNITION <sup>b</sup> DELAY
0	.66	2.8	930	9.2	4.7
1	.62	2.7	890	8.3	4.7
5	.57	2.6	890	8.2	4.9
10	.55	2.5	920	8.3	5.2
20	.31	2.1	885	7.4	5.2
50	.28	1.9	930	7.2	5.7
0 <sup>c</sup>	1.13	2.5	915	8.2	4.5
2 <sup>c</sup>	.96	2.6	910	7.9	5.0
15 <sup>c</sup>	.76	2.3	885	7.5	5.2

<sup>a</sup>Soot samples taken for 30 seconds (see experimental section for details).

<sup>b</sup>In degrees.

<sup>c</sup>Platinum coating lost from surfaces.