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Research Article

Effect of Cetane Number on Specific Fuel Consumption and Particulate Matter and Unburned Hydrocarbon Emissions from Diesel Engines

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This paper discusses the effect of ignition delay time in diesel engines on the formation of particulate matter, using fuel formulations with different sulfur concentrations from various sources. Our findings indicate that the cetane number has a significant influence on particulate matter emissions, especially in engines with mechanical fuel injection. The maximum pressure in the combustion chamber increases as the cetane number increases, favoring the increase in the cracking reactions of high molecular weight fractions remaining in the liquid state and thus increasing the production of particulate matter. In certain conditions, this increase in pressure has a beneficial effect on the thermal efficiency of the cycle. Higher temperatures in the combustion chamber augment the speed of oxidation, reducing unburned hydrocarbon emissions. The ignition delay time of fuel has a strong effect on the formation of particulate matter and on the emission of unburned hydrocarbons.

1. Introduction

Cetane number (CN) is an empirical parameter associated with the ignition delay time of diesel fuels, which is determined by means of standard tests based on the ASTM D613 standard [1]. Ignition delay is the time interval between the start of fuel injection and the beginning of the oxidation reaction. Ignition delay period starts with the injection of fuel and consists of physical and chemical delay periods until the autoignition occurs [2]. Fuels with a high CN have a very short ignition delay time; that is, ignition occurs in a very brief interval of time after injection begins. Conversely, the longer the ignition delay time the lower the CN. The ignition delay time of diesel cycle engines is a fundamental parameter to effectively control the combustion process, allowing for high thermal efficiency through maximum pressures close to 15° after reaching the top dead center (TDC), with which the maximum torque characteristic of Diesel cycle engines is obtained [3]. The ignition delay time is influenced by several physicochemical phenomena associated with the

nature of the fuel, such as molecular structure, volatility, viscosity, surface tension, and mechanical characteristics of the engines, such as compression ratio, pressure of the injection system, and injection angle [4]. Ignition delay time can be expressed in milliseconds or angle of injection after the TDC [5, 6].

Fuels containing high concentrations of *n*-paraffins generally have low ignition delay times since the activation energy to form free radicals and start the oxidation process is low compared to that of isoparaffins and aromatic compounds, which have stable molecular structures and require high temperatures and pressures to begin combustion [7]. The fuel's volatility also has a significant influence on delay time. During injection, fuel in the form of droplets enters into contact with heated air inside the combustion chamber and heat transfer occurs by convection, conduction and radiation. Radiation heat transfer is initially low and the fuel is heated basically by conduction and convection. Upon vaporizing, the fuel removes energy from the droplet itself,

cooling the surroundings and increasing the ignition delay time. Diesel engine fuels with low volatility and high cetane numbers inhibit the formation of a uniform mixture [8], hindering the fuel burning process. High viscosities provide larger droplet diameters and high penetration of the fuel jet. The use of high viscosity fuels hinders vaporization, favoring the formation of large diameter droplets and causing incomplete combustion due to the high penetration of the fuel jet, hindering cold starts and increasing the emission of unburned hydrocarbons (HCs) and particulate matter (PM) [9–11].

Distillation curves provide information that allows fuel quality to be correlated with engine performance. The temperature of 10% of the volatilized gas fractions recovered reflects the ease of vaporization, while the temperature of 90% of these fractions indicates the presence of high molecular weight compounds that will be difficult to vaporize completely, favoring the emission of particulate matter (PM) and unburned hydrocarbon (HCs) [6], and deposits in the engine [12]. Fuels with low CN may also increase PM emissions, since combustion begins in the final stage of the expansion cycle when the temperature inside the chamber diminishes, reducing the speed of oxidation, which in turn increases the concentration of unburned HC's that condense on the surface, causing the mass of particulate matter to increase [9, 13–15].

Sulfur, which is present in the form of mercaptans, is oxidized to form acid sulfate precursor by-products (SO_x) that deposit on the catalyst surface [16–18]. The presence of mercaptans in the concentrations normally found in fuel does not affect the characteristics of self-ignition to any appreciable extent, but the formation of SO_x in the products of combustion favors particle nucleation, contributing to increase PM emissions, while other smaller particles can accumulate and grow due to the hydroscopic effect of fuel sulfur [3, 16, 17, 19, 20].

The CN also affects specific fuel consumption, with a tendency for fuel consumption to decrease as the CN increases due to the higher temperature of the combustion process, improving the thermal performance of the engine [3]. New vehicles equipped with electronically controlled high-pressure fuel injection require fuels with high CN. Smaller engines with high power-to-weight ratios work at high rotations. The new electronically controlled fuel injection systems and postcombustion treatment systems have presented satisfactory results that meet current regulations [21]. However, it should be noted that the great majority of vehicles in circulation in developing countries, including Brazil, are equipped with mechanical fuel injection, whose new diesel oil specifications are not suitable for this type of engines.

This work discusses the effect of the ignition delay time of different formulations of diesel oils sold in Brazil (S50, S500, and S1800) on PM and unburned HC's emissions and on specific fuel consumption, using a single cylinder diesel engine with mechanical fuel injection and pressure sensors located inside the combustion chamber and in the fuel tubing between the injection pump and the injector. The results obtained indicate that the presence of large amounts of sulfur in the fuel slightly increases the emissions of particulate matter, and that ignition delay time has a significant effect on air pollution emissions. As the cetane number increases, the temperature in the combustion chamber increases, favoring the formation of particulate matter due to thermal cracking, which in turn increases the oxidation rates and reduces the emission of unburned HC's and the specific fuel consumption.

2. Experimental

2.1. Fuels. The fuels employed to evaluate the effect of ignition delay time on PM and unburned HC's emissions and on specific fuel consumption in diesel cycle engines are fuels normally commercialized in the Brazilian market by Petrobras. The effect of the cetane number on the formation of PM and unburned HC's and on specific fuel consumption was evaluated based on fuels modified with secondary standards (U17 and T23) supplied by Chevron-Phillips. Table 1 lists the physicochemical properties of the fuels and secondary standards used in this study.

The effect of ignition delay time on specific fuel consumption and atmospheric pollutant (MP and HC's) emissions was evaluated using the fuels that are hereinafter referred to as \$10_50, \$300_45, \$450_44, and \$1400_51, which are classified according to their sulfur content and CN and were modified with the secondary standards (U17 and T23) in order to obtain similar formulations but with altered CN. The sulfur concentration was altered slightly due to the formulation with the secondary standards, whose content differs from that of the base fuels. To this end, the fuels S10_50 and S1400_51, whose CN is close to 50, were modified with the secondary standard U17 to obtain formulations (S10_45 and S1100_45) with a CN of 45. The fuels S300_45 and S450_44 with a CN close to 45 were altered with the secondary standard T23 to obtain formulations (S300_50 and S400_50) with a CN of 50.

2.2. Engine Performance and Sampling Process. The tests to evaluate the ignition delay time, specific fuel consumption, and PM and unburned HC's emissions were performed in a Toyama 7.0 Hp single cylinder engine, 250 cm³, operating at 80% of maximum power, with mechanical fuel injection at 13.5° before TDC, average injection pressure of 150 bar, compression ratio of 21:1, 3600 rpm, and 10% of O2 in the exhaust gases. The ignition delay time was evaluated based on the pressure signals in the fuel line before the injector nozzle and the pressure inside the combustion chamber, using Optrand inductive pressure sensors. The ignition delay time of fuel is the time elapsed between the opening of the injector nozzle and the increase in pressure in the combustion chamber after the TDC resulting from the increase in the number of species due to the oxidation reactions, which corresponds to the inflection point on the pressure curve. A very accurate estimate of the ignition delay time of each analyzed fuel can be obtained by using an oscilloscope to observe the electrical signals of the pressure profiles inside the combustion chamber and injection system captured by the sensors.

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	Specific gravity (kg m ⁻³)	T 10% (°C)	T 50% (°C)	<i>T</i> 90% (°C)	Kinematic viscosity (mm ² s ⁻¹)	Flash point (°C)	Sulfur $(mg L^{-1})$	CN
ASTM	D4052	D86	D86	D86	D445	D93	D7039	D613
S10_50	839,4	209	264	338	2,85	72	10	50
S300_45	850,2	180	268	376	2,89	67,5	327	45
\$450_44	850,2	206	271	357	3,26	68	452	44
S1400_51	825,6	164	259	361	2,41	43	1370	51
U17	783,1	161	177	216	1,10	81	1	18
T23	792,3	218	250	273	2,15	158	127	76

TABLE 1: Physicochemical properties of fuels and secondary standards.

The PM in the exhaust gas flow was measured by direct filtration, using a Macherey-Nagel glass microfiber filter with a diameter of 47 mm and weighing the PM retained in the filter. The gas flow was vacuum-pumped through the filter element, and after it cooled, the flow rate was measured using a Sensirion flow sensor with a nominal capacity of up to $20 \text{ nL} \text{min}^{-1}$. Quantification of the PM in mg m⁻³ was based on the mass of PM retained in the filter divided by the volume of sampled gas, which was obtained by numerical integration of the gas flow. The average temperature of the filter element was 470°C, adjusted with the aid of an oven with electronic temperature control to keep the collected PM dry, while the volatile hydrocarbons condensed after separation from the PM.

The liquid fraction of diesel engine exhaust gases is composed of unburned and partially oxidized hydrocarbons that condense together with the water vapor produced during combustion. Part of the water vapor in the exhaust gases condenses as the gas flow cools after the particulate matter is collected. Total hydrocarbons in the form of methane (CH₄) were quantified using a technique similar to that described in the ASTM D6591 standard [22], by flow oxidation of the sample in an oxygen atmosphere. Carbon dioxide (CO₂) was analyzed in a gas chromatograph equipped with a thermal conductivity detector (Shimadzu GC/TCD-17A).

3. Results and Discussion

Figure 1 presents the pressure profiles in the combustion chamber for the base fuels with the highest CN (S10_50 and S1400_51) and their respective formulations (S10_45 and S1100_45) with lower CN. As can be seen from the pressure profiles in the combustion chamber, as the CN increases the ignition delay time decreases. As the ignition delay time decreases, the maximum pressure during the expansion phase of the combustion process is greater than with fuels with lower CN.

The pressure profile of fuels S300_45 and S450_44, Figure 2, showed a higher ignition delay time than their respective S300_50 and S400_50 formulations. As can be seen, the effect of lowering the CN reduces the maximum pressure after TDC, reducing the torque and the maximum temperature in the chamber, which directly affects the emissions of PM and unburned HC's.



FIGURE 1: Pressure profiles in the combustion chamber for the base fuels with the highest CNs (S10_50 and S1400_51) and their respective formulations (S10_45 and S1100_45) with the lowest CN.



FIGURE 2: Pressure profiles in the combustion chamber for the base fuels with the lowest CN (S300_45 and S450_44) showed a higher ignition delay time than their respective S300_50 and S400_50 formulations.

Figure 3 shows the gas flow through the filter element as a function of sampling time of the fuels S10_50 and S10_45, S450_44 and S400_50. As can be seen, the gas flow through the filter element using an initial differential pressure of 300 mbar set by a needle valve as a function of sampling time indicates that the gas flow remains at a higher level for the fuels with lower CN, resulting in a lower accumulation of PM. A comparison of the fuels with lower CN reveals the opposite effect, reducing the restriction of gas flow through the filter element and indicating that fuels with lower CN reduce PM emissions. Particulate matter in diesel



FIGURE 3: Gas flow through the filter element as a function of time for the fuels S10_45, S10_50, S450_45, and S400_50.



FIGURE 4: Ignition delay time and PM emissions as a function of CN.

cycle engines is formed according to the excess of air used in the combustion process, the composition of the diesel, and the pressure under which the fuel is injected into the combustion chamber. The tests performed in this study used the same excess air with all the fuels (same load and very similar specific fuel consumption).

Figure 4 presents the ignition delay time and PM emissions as a function of CN. As the CN increases, ignition delay time decreases, increasing the emission of PM. The fuels evaluated here possess similar physical and chemical properties, and the parameter that is changed is the CN, which significantly alters the maximum temperature in the combustion chamber, modifying the cracking reactions of the high molecular weight fractions. These high molecular weight compounds are difficult to vaporize, remaining in the liquid state during the combustion process, and are subjected to high temperatures and pressures, contributing to the formation of precursor species for the formation of PM [8, 23]. In general, it was found that an increase of five units in CN leads to an increase of approximately 40% in PM emissions.

In diesel cycle engines with mechanical injection, fuel with a lower CN takes longer to start the combustion



FIGURE 5: Correlation between HC's and CN and a diesel cycle engine with mechanical injection.

process. Thus, the maximum pressure produced by combustion decreases, resulting in lower temperature and thereby diminishing the cracking reactions, reducing the formation of PM. The S300_45 and S450_44 fuels with highest ignition delay time values also present the highest viscosities (2.9 and $3.3 \text{ mm}^2 \text{ s}^{-1}$, resp.), which hinders the process of atomization and formation of a homogeneous mixture, causing the ignition delay time to increase. On the other hand, the molecular structure of the fuel directly affects its ignition quality and hence it's CN. In general, the CN of compounds with a similar number of carbon atoms increases in the following order: n-alkanes> alkenes> cycloalkanes> aromatic alkyls [8]. Moreover, the increase in the size of the molecular chain through the addition of carbon atoms also causes the CN to increase. This can also be observed between the S300_45 and S450_45 fuels and their formulation with the secondary standard T23, whose composition consists of 91% saturated compounds, 2% olefins, and 7% aromatic compounds, while the S10_50 and S1400_51 fuels were modified with the secondary standard U17, which is composed of 78% saturated compounds, 2% olefins, and 20% aromatic compounds.

HC's emissions are mainly the result of flame extinction in the cold regions of the combustion chamber along the walls of the cylinder and are also related with fuel volatility and viscosity. High viscosities lead to larger droplet sizes and reduce the vapor pressure. Figure 5 clearly shows the inverse correlation between HC's and CN and a diesel cycle engine with mechanical injection. In general, it was found that increasing the CN by five numbers leads to a reduction of approximately 20% in HC's emissions.

The maximum pressure in the combustion chamber generates the highest temperatures, while the lowest temperature in the combustion chamber causes increased production of HC's due to the slower speed of oxidation. Fuels with high CN present shorter ignition delay time, providing high temperatures in the combustion chamber, generating larger amounts of PM and increasing the speed of oxidation, with a consequent reduction in HC's emissions.

Figure 6 shows the instantaneous profiles of specific fuel consumption (gkWh⁻¹) as a function of the testing time of the S1400_51 and S1100_45 fuels. In general, there is a slight increase in specific consumption as the CN decreases [10]. Lower specific consumption is achieved with the fuel with high CN. The S1400_51 fuel is formulated basically



FIGURE 6: ESFC (g kWh^-1) of the S1400_51 and S1100_45 fuels as a function of time.

with fractions originating from atmospheric distillation, while the other fuels are formulated using flows originating from fluid catalytic cracking, delayed coking, and highpressure hydrodesulfurization. However, a direct correlation with specific fuel consumption based on the physicochemical properties listed in Table 1 cannot be established. The main indicator is the source of the fuel S1400_51, which, because it is paraffinic, has a higher CN and therefore shows higher emissions of PM and HC's. In general, as the CN increases, the specific consumption shows a clear tendency to decline. In this range of CN (45–50), for each additional number in CN, the specific consumption in g kWh⁻¹ decreases in the same proportion.

4. Conclusions

The CN of diesel fuels has a determining effect on PM and unburned HC's emissions. The increase in ignition delay time observed in fuels with low CN shifts the maximum pressure to angles above 20° after the TDC while simultaneously reducing the maximum temperature in the combustion chamber. This reduction in maximum temperature has a favorable effect because it reduces the cracking reactions of the high molecular weight fractions, thus reducing the emission of PM. On the other hand, with the increase in CN, the maximum pressure after the TDC is observed at angles smaller than 20°, providing a greater torque. This, in turn, translates into lower specific fuel consumption, increasing the thermal cracking reaction which favors the formation of PM and increases the speed of oxidation reactions, reducing the emission of unburned HC's. The presence of sulfur in the fuel slightly increases PM emissions, but the determining effect on PM emissions is tied to the CN, which determines the maximum pressure in the combustion chamber. Overall, it was observed that increasing the CN by one number increases PM emissions by 8% and reduces HC emissions by 4%.

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