Interest of combining an additive with diesel–ethanol blends for use in diesel engines

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Abstract

Two organic additives were selected for their different physico-chemical parameters to study the behaviour of a diesel–ethanol mixture. These compounds had a glycerol skeleton bearing heteroatoms and amino-ether, hydroxyl, nitrate and nitramine functional groups. Properties directly related to engine parameters (viscosity, cetane number, heat content, volatility) and those characterising fuel quality (homogeneity, cold properties, anticorrosiveness and volatility) were investigated. Fuel formulations were prepared with 2% additive and ethanol contents between 10 and 20% in volume in relation to the diesel fuel. Blends, with or without additive, are compared in two diesel engines with direct and indirect injection. Engine behaviour seemed to be improved in the presence of additives with a reduction of pollutant emissions in exhaust gas, cyclic irregularities and ignition delay. No trouble shooting, knocking or vapor-lock phenomenon were encountered during this study. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Diesel-fuelled engines have the disadvantage of producing soot, particles and nitrogen oxides and are now subjected to increasingly severe legislation following revision of the standards by Auto oil [1]. The required levels are difficult to achieve through engine design alone. Even with high-grade fuels, catalytic systems are being extensively investigated to remove particulates. But, there are still problems in the operation of these. The introduction of oxygenated compounds such as alcohols into diesel fuel is still today the best way to have results in matter of pollution.

The use of ethanol in diesel engines is, to begin with, unusual in that the ignition capacity of the diesel fuel is hindered by ethanol.

The initial investigations into the use of ethanol in diesel engines were carried out in South Africa in the 1970s [2] and continued in Germany and the United States during the 1980s [3,4]. Most of these works relate a reduction in the smoke and particle levels emitted in the exhaust [5]. This point, of increasing importance today, alone justifies the incorporation of ethanol into fuels.

This approach does however merit a careful investigation as, in the future, it may enable the constraints regarding pollution to be respected.

The presence of ethanol generates different physico-chemical modifications on fossil fuel, notably reductions of cetane number, of viscosity as well as of gross heat. Several possibilities can be considered to make compatible the technology of a diesel engine with the properties of the ethanol-based fuels.

The experiments describing the addition of ethanol into diesel engines occurred under the following conditions:

- When the ethanol content of the prepared mixture was 20–40%, high concentrations of additives needed to be used to stabilise the mixture or attain the required cetane number [6]. Choosing a suitable organic additive meets with several difficulties. Certain compounds (alkyl peroxides) show reduced efficacy in the presence of ethanol [7] or are not even miscible in fuel–alcohol blends.
(polyethylene glycol dinitrates). Procetane molecules may often be difficult to handle (alkyl nitrates) or involve complicated methods of synthesis (tetrahydrofurfuryl nitrate) [8]. In fact, additives doted of a specific action and which need to be present in high amounts, are only of limited interest.

- A higher percentage ethanol content necessitated the instigation of double-injection device or so-called ‘dual fuel’ or ‘fumigation’ systems [9]. Gaseous pollutants and combustion noise levels are significantly reduced, but the complexity to control these devices is restricting.

- Using 100% ethanol required both considerable technical modifications and recourse to a powerful procetane and lubricant additive [10]. Experiments of this type gave good results with up to 80% fewer particles and easy vehicle maintenance. However the costs of implementation were, in practice, often an obstacle.

Therefore, in 1995 [11], another approach was studied. Mixtures with reduced ethanol content (10–20%) were prepared. The properties were adjusted by adding a small amount of organic polyfunctional additives. The major interests for this option is the absence of technical modifications, a limited loss of heat content and the ease of implementation.

This same approach was also recently chosen by Archer Daniel Midland (ADM), number 1 producer of ethanol in the United States. Tests are carried out on a bus fleet in Chicago involving an 80% diesel, 15% ethanol and 5% additive mixture supplied by Pure Energy.

The key factor then resides in using additives that present a perfect compatibility with ethanol blends and that are effective at a low content.

In view of the modifications conferred on diesel fuel by the presence of ethanol, the selected additive will intervene at several levels. It will be required to:

- make up the cetane number, reduced by the addition of ethanol, to ensure that the ignition properties are satisfactory;
- intensify the viscosity to ensure adequate lubrication of the injection pumps;
- stabilise the mixture in the presence of a high water content, to ensure fuel homogeneity under all conditions.

Therefore, the organic molecules which have been selected are likely to confer plurifunctional properties because of their polyfunctional chemical nature. Two molecules are identified for performance and ease of production. These are 1-octylamino-3-octyloxy-2-propanol (A1) and the dinitrated derivative N-(2-nitrate-3-octyloxy propyl), N-octyl nitramine (A2) [11]. As these compounds showed complementary physico-chemical characteristics and performance, they were then combined, each at a level of 1%, within the same formulation [12,13].

The properties of the resulting fuel mixture were determined for ethanol contents of 10–20% by volume with the additive content fixed at 2%.

Before using this four-component mixture in an engine, the required properties of a diesel fuel needed to be verified.

2. Fuel properties

2.1. Experimentation

2.1.1. Raw materials

The mixtures consisted of commercial diesel fuel and ethanol of agricultural origin supplied by the ‘Dock’ (France) alcohol company, to which compounds A1 and A2 were added. These organic glyceryl additives were produced in a laboratory pilot plant as described in the protocol [11].

2.1.2. Tests

The chemical properties were assessed by VERNOLAB (Verneuil-sur Avre, France). The analyses were performed in accordance with current standards.

Cetane numbers were determined through NF M07-035 (engine CFR). Kinematic viscosities were conducted using the procedure given in ASTM D445 standard. Dynamic viscosities were measured with a Carri-Med CSL 100 (Rheo) controlled stress Rheometer. NF 07-042 and NF M07-015 standards were used for Cloud Filter Plugging Point and corrosiveness measures, respectively. Heat contents were determined with NF M07-030 and distillation curves performed according to ASTM D86.

Surface tensions were investigated with a Tensimat n3 Prolabo automatic stabiliser tensiometer as well as with an experimental method.


A number of properties of diesel fuel must be maintained within certain limits to ensure its successful burning. These properties include viscosity, cloud point, cetane number, heat content, and boiling point. Compatibility, corrosiveness and freezing point are additional properties introduced by blending ethanol and diesel fuel.

3.1. Interfacial properties of the additives

The critical micellar concentrations (CMC) for the selected additives were: CMC(A1) = 1.5 × 10−3 mol l−1 and CMC(A2) = 9.5 × 10−3 mol l−1 in EtOH/H2O (1:1) at 25°C.

It can be deduced from this that such molecules have a high tensioactive capacity, the CMC values being within the 10−3–10−4 mol l−1 range of known surfactants such as SDS (sodium dodecyl sulphate) or C10E5 with the formula CH3(CH2)9O[CH2(CH2)5OH]12. A1 exhibits greater tensioactive properties than A2. However the latter
possesses nitrate and nitramine groups which have a beneficial effect on the cetane number. As a result, A1 and A2 exert a synergistic effect, firstly, by ensuring compatibility of the diesel–ethanol components [14] and secondly as proctane agents of the diesel–ethanol mixture, due to their oxygenating and nitrating capacities.

3.2. Study of diesel ethanol compatibility in the presence of additive

Absolute ethanol is highly soluble in diesel fuel at contents of approximately 0–30% and 70–100%. Within these zones of miscibility we observed cloudiness in the mixture followed by separation, when the water content of the ethanol exceeded 1%. The occurrence of this phenomenon has therefore to be prevented by using additives.

Table 1 shows that the stability of a diesel–ethanol mixture left in air is increased in the presence of A1 and A2.

This test also confirms the greater surfactant potential of A1 in relation to A2.

These results require comment. The surfactant properties of the glyceric compounds A1 and A2 defer the maximum permissible water content by developing a microemulsion between the water and organic phase. To do this, the amphiphilic structures become aligned at the diesel/ethanol–water interface, thereby reinforcing the structural affinities between the various components of the mixture. The hydrocarbon moieties of these molecules constitute the hydrophobic portion of the structure due to their strong affinity with diesel fuel. The glyceryl skeleton bearing the ether, hydroxyl and amine groups represents the hydrophilic head which becomes oriented towards the ethanol–water phase. These surfactants are therefore non-ionic and lead to the formation of stable, homogeneous emulsions (Fig. 1).

In fact, introducing additives with emulsion-forming properties increases the flexibility of use of ethanol in diesel fuel.

3.3. Heat content

The reduction in heat content of the mixture, compared to that of diesel fuel, is only a few percents (Table 2), which may at the most have an effect on volume consumption.

3.4. Viscosity

With ethanol contents of 10–20%, this viscosity does not exceed the required minimum for diesel fuel (2 cSt at 40°C). The use of an additive is nevertheless recommended to improve lubrication.

At ambient temperature one third of the viscosity lost by adding ethanol can be recovered by using an additive (Table 3).

It can be seen that above 40°C, the increase in viscosity acquired by using additives is further enhanced (curve c in Fig. 2).

This phenomenon can be attributed to the occurrence of polycondensation reactions between molecules under the effect of temperature. This hypothesis is corroborated by the profile of the differential scanning calorimetry curves in thermal analyses [11].

It would seem, in fact, that on contact with a metallic surface heated to more than 40°C, (temperature frequently

<table>
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<tr>
<th>Mixture without additive</th>
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<tr>
<td>Mixture + 2% A1</td>
<td>7</td>
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<tr>
<td>Mixture + 1% A1 + 1% A2</td>
<td>6</td>
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Table 2

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<th>Gross heat content (MJ/kg)</th>
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<tr>
<td>Diesel</td>
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<tr>
<td>Diesel + 10% ethanol + 1% A1 + 1% A2</td>
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<tr>
<td>Diesel + 15% ethanol + 1% A1 + 1% A2</td>
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<tr>
<td>Diesel + 20% ethanol + 1% A1 + 1% A2</td>
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<th>Dynamic viscosity at 40°C (mPa s)</th>
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<tr>
<td>Diesel</td>
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<td>Diesel + 15% ethanol</td>
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<td>Diesel + 15% ethanol + 1% A1 + 1% A2</td>
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<td>Gain in viscosity at 20°C</td>
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<td>Gain in viscosity at 40°C</td>
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<td>Gain in viscosity at 50°C</td>
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reached inside an engine), the presence of additives results in the formation of a lubricant film with beneficial anti-wear properties. One can imagine that this behaviour in contact with the measuring plate of the rheometer (hot surface) will also occur during engine running (friction of parts within the engine shafts). Finally, additives act favorably on the blend viscosity as well as on its lubricant properties.

3.5. Cetane number

The linear changes in cetane number that occur in relation to ethanol content are shown in Fig. 3. It should be remembered that a high cetane number ensures good cold starting, reduced noise and an increase in engine life.

Table 4 gives the cetane numbers for mixtures containing 10, 15 or 20% ethanol, measured on the CFR engine.

The additives keep the cetane number above 45, which ensures suitable ignition.

3.6. Antifreeze properties

Table 5 shows that the cold properties of mixtures containing additives are somewhat better than those of commercial diesel fuel.

The ethanol confers good fuel fluidity at low temperature.

The interest of the additive is to prevent any risk of mixture separation when the temperature drops.

3.7. Anticorrosive properties

The tests showed that steel and copper cylinders immersed in the ternary mixture were not corroded (score 1A), even in the presence of hydrated ethanol.

Blends have been performed with hexadecane as hydrocarbon base in order to preclude the need for anticorrosion additives in commercial diesel fuel.

Although there is no real risk of corrosion from the ethanol, the metallic structures always need to be protected from any traces of water present in the fuel. The test mixture was therefore compatible with these requirements.

3.8. Volatility

It can be seen from Fig. 4 that the addition of ethanol modifies the shape of the distillation curve at temperatures below 200°C. The diesel–ethanol-additive blends tested

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<th>CFPP (°C)</th>
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<td>−14</td>
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<td>−19</td>
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<td>−18</td>
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nevertheless satisfy the specifications as regards the distilled volumic fractions.

The increased volatility of the mixture is also apparent as a lower flash point at ambient temperature. Although this does not have a direct effect on engine performance, such mixtures would be subjected to the legislation concerning fuel handling.

In conclusion, this study demonstrates the positive role of the A1 and A2 additives in a diesel–ethanol mixture. The compatibility-enhancing, rheologic, procetane, antifreeze and corrosion-inhibiting properties ensure normal running of the diesel engine under all conditions. As the resulting formulations were compatible with the requirements of a standard diesel engine, they could then be subjected to engine tests.

4. Engine tests

It is generally acknowledged that ethanol reduces the smoke and particle contents of the exhaust. But how would additives, with their nitrated and oxygenated glyceric structures, affect this when present at a level of 2%?

Previous work already carried out on diesel/ethanol blends accords with the following observations:

- Under operation DI engines are more sensitive than IDI engines to the fuel’s cetane number [15].
- Diesel/ethanol blends with low ethanol content (less than 15%) have little effect on the content of pollutant gases from IDI engines whereas a reduction is observed with DI injection engines [16].
- Adding ethanol leads to a reduction in the smoke and particles levels emitted in the exhaust [5].

Two types of tests were chosen according to the literature data. The performance of a mixture containing 10% absolute ethanol, which had little effect on cetane number, was examined using the DI engine. In this case, the ‘cetan effect’ does not mask the impact of the additive.

A mixture containing 20% absolute ethanol, was used in an IDI injection engine to demonstrate the role of the additive in maintaining combustion quality. IDI engines are little affected by the variations in the cetan number. Moreover, a low ethanol rate would not enable to observe significant reductions of exhaust fumes.

Within the framework of this study, the two standard fuels are the diesel fuel and the diesel fuel–ethanol blends. The investigated criteria are the maximum power, the ignition delay, the cyclic dispersion, the composition of exhaust fumes as well as the Bosch smoke number.

4.1. Equipment

The testing equipment was an electric brake Schenck W150 associated with a Horiba-Mexa 9000 DEGR gas analysis bay.

The data system was operated by an RTI 860 Analog Device which enabled 1000 points to be recorded per engine cycle (that is a resolution of 0.72 C.A). The acquisition of 1000 points in 50 successive cycles was initiated with a crank angle detector (Leine and Linde). Both the instant pressure in the combustion chamber and the needle deflection signal were recorded during data acquisition. The pressure was measured with a Kistler piezo-electric pressure sensor type 6123 (0–250 bars) coupled to a Kistler 5007 amplifier. The needle deflection signal was recorded with a Somitronic Surfasan-type sensor linked to a Sigma Diesel Ala 100-type amplifier. This produced an analog signal proportional to needle deflection.

These data were then processed using the Cycledel software developed by ESEM (Orléans, France). This programme calculated the mean and standard deviation for each of the 1000 points in the 50 cycles for each variable, chamber pressure and needle deflection, and provided the corresponding curves in relation to crankshaft angle (CA).

There are two types of diesel engine, namely direct injection (DI) and indirect injection (IDI) engines depending on whether the fuel is directly injected or not injected into the principal combustion chamber.

- Direct injection (DI) engine. The test engine was an
air-cooled single cylinder HATZ (667 cm$^3$). The 1D80 model presents $100 \times 85$ mm$^2$ as bore × stroke with a compression of 18:1. The engine rated at 10 kW power at a speed of 3000 rpm. The Bosch 4-hole nozzles type 150S1146 was set at 265 bar.

- **Indirect-injection (IDI) engine.** The test engine was a 4-cylinder (1870 cm$^3$) RENAULT water-cooled of F8Q 706 model. The values for bore × stroke was $80 \times 93$ mm$^2$ with a compression ratio of 21.5:1. The engine rated at 50 kW at 4500 rpm. The engine used a injection pump CAV roto diesel. Bosch pintle nozzle type DNOSD189 set at 135 bar.

4.2. Procedure

With the DI engine, data have been collected from six measuring points. The cycle was: 1700 and 3000 rpm at full load followed by 3000 rpm no load, 9000 rpm at idle speed and 1700 rpm no load. Then, the first point 1700 rpm at full load was repeated. At each point, the engine was stabilised for 5 min and the parameters then recorded at the sixth minute. Table 6 shows the series of tests and the fuels’ characteristics.

The procedure cycle was different with the IDI engine. Between two measures at 4000 rpm full load, 8 points were recorded every 500 rpm from 4500 to 1000 rpm. This sequence of 10 points was used for 75, 50, 25 and 0% load of the engine.

4.3. Results and discussion

Although the engines were different, an air-cooled single cylinder and a water-cooled multi-cylinder, running in both were not affected by the presence of ethanol in blends. No problem of vaport-lock in injection pumps and lines, no knocking or trouble shooting appeared.

The influence of specifically developed additives was studied on the two types of diesel engines currently on the market.

4.3.1. Tests on hatz DI engine

Fig. 5 confirms that the presence of 10% ethanol led to a little reduction in maximum power (full load) of approximately 5% due to the loss of heat content. Thus, at the same rated power output, the overconsumption of ethanol blends in relation with diesel fuel alone is only 3%.

Despite the difference in measured cetane number, ignition delay was little affected by the presence of ethanol, with or without the additive (Fig. 6). The blend diesel fuel–ethanol-additive thus presents a suitable ignition delay. No
significant differences between the fuels were apparent for the levels of NO\textsubscript{x} recorded.

Examination of the CO levels did not reveal any notable differences between diesel fuel and diesel containing 10% ethanol. But, thanks to additive, the CO level is reduced particularly at no load, which is interesting for urban vehicles.

Moreover, the A\textsubscript{1} and A\textsubscript{2} additives play a role in reducing HC contents but do not bring them to the level of diesel fuel (Fig. 7).

Finally, the introduction of 10% absolute ethanol into this direct injection engine led to a slight drop in maximum power, but had no effect on the gases emitted, excepted an HC increase.

Introducing an additive makes up the cetane number, reduces the increase in HC and leads to a decrease of CO up to 20% in relation to diesel fuel alone.

4.3.2. Tests on the RENAULT IDI engine

With the same mechanical adjustments and fixed air and fuel parameters, the cyclic dispersion reveals the unevenness of the operations due mainly to the fuel in a given engine and the point of operation in question. This irregularity may not be apparent between the overall comparative performances of the two fuels but does affect the emission of pollutants.

The data logging system records 1000 points per cycle and 50 consecutive cycles. The dispersion of the recorded
parameters at any one moment in the cycle can be determined by comparing the 50 values.

Fig. 8 shows a greater dispersion observed with diesel +20% ethanol mixtures than with diesel alone, particularly at idle speed without load.

The addition of A1 and A2 significantly improved cyclic regularity with full load. The additives also reduced irregularity at idle speed without totally achieving the performance observed with diesel alone (Fig. 9). Combining the two additives then improves cyclic uniformity.

Fig. 10 confirms that the presence of 20% by volume of absolute ethanol reduced the maximum power by approximately 11% due to the loss of heat content. At the same rated power output, the over-consumption with the blends was around 7%.

Fig. 9. Cyclic dispersion, idle speed, no load (DI engine).

Fig. 10. Power measured on IDI Renault engine.
The ignition delays are increased by adding ethanol. The additives tend to shorten these delays by improving the cetane number. Moreover, a shorter starting-up time was systematically observed showing that the cold starting is improved with additives.

The CO and HC contents are increased by the addition of 20% ethanol but the additives correct this tendency particularly the HC content. In the presence of ethanol the NO\textsubscript{x} contents are always lower than in diesel fuel alone (Fig. 11).

Finally it can be said that using a diesel mixture containing 20% by volume of absolute ethanol (99\%), in this IDI engine leads to an 11% due to the loss of maximum power. The ignition delays are longer, the cyclic irregularity is increased, and the CO and HC contents are augmented. Only the NO\textsubscript{x} and smoke contents are reduced.

Introducing a specific additive improves ignition delay, reduces cyclic irregularity, brings back the CO and HC contents and at the same time conserves the decrease in NO\textsubscript{x} and smoke contents.

In fact, additives annul the disruption resulting from ethanol addition and strengthen the observed beneficial effects. Ethanol and additives have a synergic effect regarding some properties and a complementary effect for other properties.

5. Conclusions

The Bosch smoke number was measured for all three fuels with the engine at full load. With the diesel + ethanol mixture, an average reduction of 45% in this number was apparent for the entire range of engine operations. The introduction of 20% ethanol then generates a lower soot emission. This can be explained by the oxygenated fraction contributed by the ethanol, which means that the excess air is then 16% higher than that of diesel. The additives bring the smoke number up again although it still remains 35% lower than that of diesel alone (Fig. 12).

The first phase of this work led to the targeting of two multifunctional organic additives which have favourable effects on the physico-chemical properties associated with injection, ignition and combustion of fuel mixtures containing 10–20% ethanol. The disadvantages associated with the diesel–ethanol blend are overcome, thanks to the complementarity of the two molecules. These non-ionic surfactants act simultaneously by reducing the interfacial tension in liquid medium (homogeneity of the diesel/ethanol mixture) as well as the fluid/metal interfacial tension (lubrication).

The engine tests in the second phase show that the presence of such additives is justified whatever the engine
type (DI or IDI) and whatever the level of added ethanol between 10 and 20%. This type of blend, by only producing a very low reduction in maximal power, in fact results in overall gains with regard to polluting gases at the same time as engine performance [17,18].

Moreover, the efficacy of the additives would in fact authorise a low mass level of 2% in the diesel–ethanol blend. In these conditions, the selected additives confer an advantage which helps to make diesel–ethanol mixtures attractive.

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References