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Gasoline Oxidation Stability: deposits formation tendencies evaluated by PetroOxy and Autoclave methods and GDI / PFI engine tests

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KEYWORDS: Gasoline, Autoxidation, Stability, Deposits, GDI, PFI, PetroOxy, RSSOT, Autoclave, Manganese, Sulfur, DMDS, MMT, VWEA111, M102E, injectors, valves

ABSTRACT

Deposits formation from the gasoline autoxidation process has attracted more and more attention since the emergency of new systems operating at higher pressure range and higher temperatures imposing new fuel constraints, and so favoring the appearance of deposits on different engine parts in contact with the fuel (e.g. injection systems, valves, pumps, piston). This study aims to evaluate

the oxidation stability of a non-additised standard European gasoline SP95 Euro 6 containing 10%v/v Ethanol (SP95E6E10) complying with the EN228 standard and the impact of additives such as methylcyclopentadienyl manganese tricarbonyle (MMT) and dimethyl disulfide (DMDS) on deposits formation to mimic other world market fuels such as Africa or China. The stability of these fuels was compared to a commercial Nigerian gasoline which has higher sulfur content (800 mg/kg) to evaluate the sulfur effect on deposits formation. The fuel degradation tendencies (Induction Period, IP) obtained from PetroOxy apparatus and Autoclave reactor were compared to the real engines tendencies to form deposits. The deposits targeted are those created on the injector nozzle of a VW EA111 engine (direct injection), and on the valve using a M102E engine (indirect injection). PetroOxy results show the negative impact of DMDS and MMT on the IP of the gasoline, SP95 E10 ULG Euro 6: IP decrease of up to 30%. Comparison of the IP results in PetroOxy and Autoclave with the results of the direct injection (VW EA111) and indirect injection (M102E) engine tests suggests that the PetroOxy results follow the trend of the mass of deposits formed on the valves of the indirect injection, M102E, engine tests, with the IP decreasing as the valve deposits mass increases. On the contrary, the Autoclave results seem to follow the trend of the results of the direct injection, VW EA111 engine tests: IP decreases when the injection time increases. These features could allow us to identify fuel tendencies to form deposits on specific spare parts based only on laboratory scale methods, helping to optimize and to target the maintenance operation and preventing failures or damages on real engine systems.

INTRODUCTION

Fuel stability refers to the ability of a hydrocarbon to preserve its physical and chemical properties over time. Different fuel degradation mechanisms can be distinguished: autoxidation [1]; cracking

or pyrolysis [2]; hydrolysis [3]; and microbiological contamination [4]. More specifically, autoxidation stability of fuels refers to the tendency of a fuel to degrade from the oxidation of its compounds. Fuel degradation by autoxidation can lead to the formation of insoluble products and deposits of various origins and compositions in the tank, combustion systems and injection systems [1]. Deposits formed as a result of the autoxidation process are generally obtained at T < 300°C. Therefore, deposits related to autoxidation process indicates the degradation of organic compounds at low temperatures in the presence of oxygen. Several authors have studied the physical and chemical characteristics of gasoline with and without additives and its impact on several combustion process such as auto-ignition [5,6], heat release [7], soot precursors and soot formation [8], among others. All these features can lead to deposits formation at different parts of gasoline engine such as injector nozzle [9–11], spark plug [12,13], intake valves [11,14,15], and combustion chamber walls [11]. Ganeau et al. [16] have studied the formation of deposits in pistons using standard gasoline in an optical engine. They studied the mechanisms leading to gasoline deposits formation on pistons and identified mainly two pathways: liquid-film path or the soot path [17]. For the liquid-film path, the work showed that the formation of the deposit by the liquid film was conditioned by the evaporation rate of the liquid film, the surface roughness and material does not have an impact on the formation of the deposit via the liquid-film path. For the soot path, thermophoresis and inertial deposition seems to be the main mechanisms involved in deposition process. The results showed that an increase in the surface temperature reduced the deposition of soot [17]. However, Ganeau's work did not establish the chemical process involved during liquid-film deposits formation and the analytical methods used, Infrared absorption spectroscopy (FTIR-ATR) and Raman Spectroscopy, were not able to identify the chemical trends. Kinoshita et al [18] studied the process of deposit build-up on injector nozzles and also showed that surface

temperature plays an important role in the nature of the deposit formed. Indeed, they propose that the residual fuel film on the nose surface after injection and after combustion can form more or less adherent deposits depending on the temperature, i.e. for a $T_{surface}$ greater than T90 of the fuels, thicker and more adherent deposits are formed, whereas $T_{surface}<T90$ the deposits are "washed off" during the next injection and do not adhere to the surface. However, this hypothesis has not been confirmed by other studies and the mechanism of deposit formation remains a subject of study. Nevertheless, the residual fuel remaining in contact with the hot metal surface of the injector nozzle and valves certainly leads to the degradation of its compounds by the autoxidation process, especially during the engine shutdown (soaking) phases [19]. This feature has been observed during studies on the injection bench, and so without the influence of combustion products on deposits, for diesel and biodiesel fuels [19,20] as well as kerosene [21]. Nevertheless, there is a lack in the literature about gasoline autoxidation in liquid phase at low temperature and the link of this fuel degradation mechanism to the deposits that can be observed in different parts of the real engines. Also, there is a need to identify analytical methods that would be able to predict the gasoline deposits formation tendencies by using lab scale tests instead of using engine tests that are expensive and time consuming.

Gasoline is mainly composed of paraffins, olefins, naphtenes, aromatics and oxygenated compounds. In other fuels autoxidation studies, it has been shown that the presence of unsaturations in the alkyl chain (e.g. olefins) as well as the presence of heteroatoms, such as S, N or O, are parameters favoring the free radical mechanism in the propagation phase [1,22,23]. N-alkanes, iso-alkanes, cycloalkanes, and aromatics are also sensitive to oxidation depending on the temperature and pressure conditions [24–26]. In addition to fuel base compounds, impurities such as the presence of metals, even in very small quantities, can also have an impact. In this context,

91 the experimental methods employed to evaluate diesel, biodiesel and kerosene can be adapted and
92 used to study gasoline autoxidation process.

93 Several methods have been identified in the literature for the study of gasoline stability [27–31].
94 In this study, two liquid-phase oxidation methods were selected: a standard method, ASTM
95 D7525, which describes the Rapid Small Scale Oxidation Test (RSSOT) known as the PetroOxy
96 test, and the "Autoclave" method developed at IFPEN. The induction period (IP) of the fuels
97 obtained from both methods can be compared to the tendencies observed to deposits formation in
98 real engines to correlate the autoxidation process and deposits formation.

99 Two standardized gasoline engine bench tests have been used for the study of the deposits
100 formation tendency:

101 - For indirect injection spark ignition engines, the Mercedes Benz M102E method
102 (standardized test method CEC F-05-93) gives access to the measurement of the intake
103 valve deposits (IVD)

104 - For direct injection spark ignition (DISI) engines, the new injector fouling test in the
105 process of being proposed to CEC (standardized test method TDG-F-113), by using a
106 widespread used version of the EA111 engine developed by Volkswagen AG, gives
107 information on a measured variable called the injection time (duration) linked to the
108 injectors fouling.

109 The first part of this study was dedicated to the kinetic study of gasoline autoxidation to obtain
110 kinetic parameters that will be later used on modeling gasoline degradation. The second part was
111 to evaluate the oxidation stability of a standard European gasoline SP95 Euro 6 containing 10%v/v

Ethanol (SP95E6E10) and the impact of additives such as methylcyclopentadienyl manganese tricarbonyl (MMT) and dimethyl disulfide (DMDS) on gasoline oxidation stability. The stability of these fuels was compared to a commercial Nigerian gasoline which has higher sulfur content (800mg/kg) to evaluate its impact on stability. The fuel degradation tendencies (Induction Period, IP) obtained from PetroOxy apparatus and Autoclave reactor were compared to the real engines tendencies to form deposits. The deposits targeted are those created on two different injection system technologies: the injector nozzle of a VW EA111 engine (direct injection), and on the valve of a M102E engine (indirect injection).

EXPERIMENTAL METHODS

Fuel Matrix

The fuel matrix is composed of two commercial gasolines: one from European market and one from Nigerian market *(See supplementary material for more details)*. The European gasoline chosen was the SP95 ULG E10 Euro 6 (hereafter named as SP95E10) used as reference. This fuel presents a low quantity of sulfur (<10ppm) and 10%v/v of ethanol (EtOH). Two blends were performed using the additives methylcyclopentadienyl manganese tricarbonyl (MMT) and the dimethyl disulfide (DMDS) to obtain the fuels SP95+Mn (20 mg/kg of Manganese) et SP95+S (500 mg/kg of Sulfur). These blends were used to mimic world market fuels other than Europe such as Africa or China. By adding MMT and DMDS to the neat SP95 gasoline, the impact of manganese and sulfur compounds can be more specifically appreciated respectively. It is true that DMDS sulfur compound is different from those naturally present in a fuel from refining operations, but it allows to appreciate the direct impact of added sulfur compared to neat SP95E10. The

Nigerian petrol contains 820mg/kg of sulfur and is representative of exiting fuels on the African market *(See supplementary material for details about sulfur speciation)*. The chemical composition of all fuels are listed in Table 1 below. Complementary chemical analysis of the fuels in presented on Figure 1. To note that Nigerian petrol has higher amount of naphthenes (cycloalkanes) and olefins whereas the SP95 presents notably higher content of aromatics and oxygenated compounds.

Table 1. Fuel Matrix: physical and chemical analysis of base fuels

Test Name	Method	Analyte	Unit	SP95E10Euro6 (reference fuel)	Nigerian gasoline
Density at 15°C	NF EN ISO 12185	Density at 15°C	kg/m^3	747.9	734.3
Reid Vapor Pressure at 37.8°C	NF EN 13016-1	ASVP at 37.8°C	kPa	57.8	53.9
Distillated percentage at 70°C		% distillated at 70°C	% v/v	42	21.7
Distillated percentage at 100°C		% distillated at 100°C	% v/v	59	58.6
Distillated percentage at 150°C		% distillated at 150°C	% v/v	92	95
Sulfur content	NF EN ISO 20846	S content	mg/kg	<10	820
Gum content of light and middle distillates fuels	NF EN ISO 6246	Before washing	mg/100mL	5	1
		After washing	mg/100mL	<1	<1
Oxidation induction period of gasolines	NF EN ISO 7536	Oxidation induction Period	min	>360	341

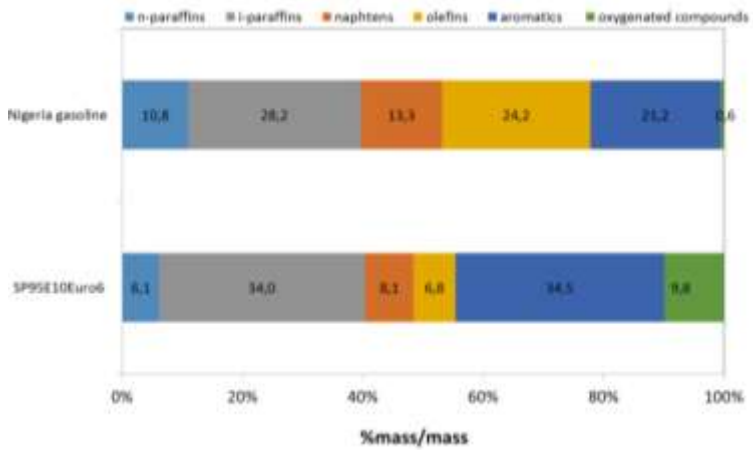

Figure 1. Chemical composition of Nigerian and SP95 gasolines

Oxidation Stability Tests

Rapid Small-Scale Oxidation Test (RSSOT), also known as PetroOxy test

For gasolines, the standard PetroOxy method (ASTM D7525) consists in placing 5mL of a sample in a cell with a total volume of 25mL. Once the lid is closed, the sample is subjected to an initial oxygen pressure of 500kPa and heated to 140°C. As the temperature rises, the pressure in the cell increases until a maximum pressure (Pmax) is reached which varies with the fuel. Then, the cell pressure decreases with the consumption of oxygen by the sample caused by the fuel oxidation process. As soon as the pressure reaches a value of -10% in relation to Pmax, the test shall stop. The time required to reach this pressure drop is noted as the Induction Period (IP) of the fuel. According to this method, the IP therefore gives information on the fuel's resistance to oxidation, i.e. the longer the IP, the more stable is the fuel. To carry out the kinetic study the tests were done at three temperatures:100°C, 140°C and 160°C at 5 bar as well as 140°C at 7 bar. The stability of the fuels was also evaluated under two atmospheres: Oxygen and Argon. Each fuel was tested three times at the different conditions to obtain the standard deviation. To calculate the

Activation Energy (Ea) and the kinetic constants the method proposed by Bacha et al [2] was used. It uses the simplified global kinetic mechanism of fuel oxidation to calculate the global kinetic rate constant from the different oxidation steps. The rate of oxygen consumption in the PetroOxy gas phase is used to calculate the Ea following the Arrhenius equation:

$$\frac{-d[O_2]}{dt} = -\frac{d[RH]}{dt} = A.e^{\frac{-Ea}{RT}}.[RH] \qquad \textbf{Equation 1}$$

where RH represents the fuel, A corresponds to the pre-exponential factor, Ea is the activation energy, R is the gas constant and T is the temperature. The variation of oxygen pressure into PetroOxy cell reactor can be obtained from the Pmax until IP according to Equation 2:

$$\frac{[\Delta O_2]_{IP}}{IP} = A.e^{\frac{-Ea}{RT}}.([RH]_{t0} - [RH]_{IP}) \qquad \textbf{Equation 2}$$

where $[RH]_{t0} = \frac{\rho}{M}$, with ρ is the fuel's density and M the molar mass. Considering that the oxygen is the main component in the gas phase, it is possible to calculate the oxygen consumption by volume of fuel at IP by:

$$\frac{[\Delta O_2]_{IP}}{IP} = \frac{Pmax - P_{IP}}{RT}.\frac{V_{TOT} - V_{liq}}{V_{liq}} \qquad \textbf{Equation 3}$$

Where V_{tot} is the total PetroOxy cell volume, V_{liq} is the sample volume, P_{IP} is the pressure in kPa measured at IP. Therefore, we may calculate the following relationship (Equation 4) to obtain the Ea and A:

$$\ln\left[\frac{[\Delta O_2]_{IP}}{\tau.[RH]_{t0}.IP}\right] = -\frac{Ea}{RT} + \ln A \qquad \textbf{Equation 4}$$

Autoclave reactor

The IFPEN autoclave is a reactor in which a fuel oxidation method has been developed to meet the need for the analysis of compounds produced during the oxidation of fuels under test, which is very difficult and time consuming to achieve with standardized tests such as PetroOxy. The IFPEN autoclave allows to carry out gas and liquid phase sampling during the test. Therefore, it is possible to follow chemical kinetics of the reaction in both phases. To minimize equilibrium changes due to the sampling, oxygen is added to compensate for the pressure loss which is typically close to 1 bar. Preliminary tests have demonstrated a negligible impact of this oxygen addition on the overall kinetics considering the measurement uncertainties.[25,26,32]

The autoclave is an inert reactor designed to carry out chemical reactions at temperature and pressure with operating limits close to 300 °C and 500 bar. In this study, a volume of 50 mL of sample is placed in a cell with a total volume of 250 mL. The idea is to be in the same conditions in terms of O_2/fuel ratio as the PetroOxy test. The fuel is first stirred with a rotation system followed by pressurization using an inert gas, Argon. Then the temperature is raised to the desired temperature. Once the test temperature has been reached, the inert gas is flushed by introducing oxygen into the cell. The replacement of the gas is very fast and does not disturb the course of the test. As soon as the system is stable, a few seconds after purging the inert gas with O_2, the oxidation kinetics are very similar to those obtained with PetroOxy. Oxygen is therefore consumed over time by the oxidation of the fuel and the time to reach a 10% drop from Pmax and recorded as IP. The main difference in comparison with PetroOxy is the possibility to take gas and liquid samples during the test and, in this way, monitor the progress of fuel degradation. Here, only liquid samplings are analyzed using Fourier-Transform Infrared Spectroscopy (FTIR) to achieve the chemical composition variation during oxidation. More information about Autoclave procedure can be found elsewhere.[3–5]

Endurances Tests: Direct Injection (VW EA111) and Indirect Injection (M102E) engine tests

VW EA111 test: This CEC test is being developed by Volkswagen. The proposed test addresses injector deposits in direct injection spark ignited engines (DISI) and the deposit control ability of gasoline, so that it can be used to evaluate the performance of neat or additivated gasolines. The test engine is the VW EA111 1.4L TSI (CAVE) engine with 132kW, representing the Skoda version of the EA111 engine family, developed by Volkswagen AG. The twin charged engine is equipped with a supercharger and a turbo charger, including charge air cooler. The test procedure is performed with new 6-hole injectors, type 03C906036E/F from Bosch or Magneti Marelli. The injector run-in procedure is performed at high load for 4 hours. The test procedure is a steady state test at an engine speed of 2000 rpm and a constant torque of 56 Nm (=5 bar mean effective pressure). The thermostat is in serial condition. Nozzle coking is measured as change of injection timing. Due to nozzle coking, the hole diameter of the injector holes is reduced, and the injection time adjusted by the Engine Control Unit (ECU) accordingly. The injection time in milliseconds is a direct readout from the ECU via ECU control software. The keep-clean procedure employed lies on a phase of 48 hours deposit formation with the fuel to be tested, with a continuous measurement of the increase of injection time. A linear trend calculation at start of test and end of test defines the nozzle coking during 48 hours of keep clean test. The result is expressed as a percent of increased injection time. The longer the injection time, the dirtier the injectors are.

M102E test: All engines progressively accumulate engine deposits as a result of the normal gasoline combustion process. Combustion chamber deposits (CCD) and intake valves deposits (IVD) are originated primarily from fuel and to some extent from the engine lubricating oil. The

224 standardized test method, referred as CEC F-05-93, allows the assessment of the deposits
225 formation tendency of the intake system of the indirect injection engine, in particular the intake
226 valves and the combustion chamber. The test engine is a Mercedes Benz M102E in-line, 4-
227 cylinder, 4-stroke, 2.3L gasoline engine mounted on a computer controlled test-bed having 1 Hz
228 data logging capability and usual services such as exhaust extraction, fuel flow measurement,
229 temperature and pressure measurements, etc. The engine is operated for a period of 60 hours under
230 cyclic conditions, simulating stop and go operation, with the inlet valve pegged to prevent rotation.
231 The ability of a gasoline or a gasoline formulation to influence deposit formation on the inlet valves
232 is determined. The results are expressed by the weight of the deposits accumulated during the test
233 on the intake valves and in terms of merit rating. The lower the amount of deposits on the valve
234 (measured in mg/valve) at the end of the test, the better the gasoline fuel.

235

236 **RESULTS AND DISCUSSION**

237 PetroOxy at 100°C, 140°C and 160°C as a function of the temperature is presented in Figure 2 and
238 the associated kinetic data is shown on Table 2. The IP behavior follows the Arrhenius law with a
239 linear relationship of log(IP) vs 1/T which is valid for all fuels. The IP decreases with the
240 temperature increase. The activation energies are quite similar from 21-25 kcal/mol but the pre-
241 exponential factor obtained for the Nigerian fuel is two orders of magnitude higher than the
242 standard SP95 and the S- and Mn-additivated samples. The Ea values of our samples are within
243 the Ea range of pure compounds such as isoalkanes that have Ea comprised in a range from 15-
244 45kcal/mol depending on the level of hydrocarbon branching[5]. It is also similar to the Ea

calculated for diesel and biodiesel samples (from 18-25 kcal/mol)[2] depending on the fuel feedstock.

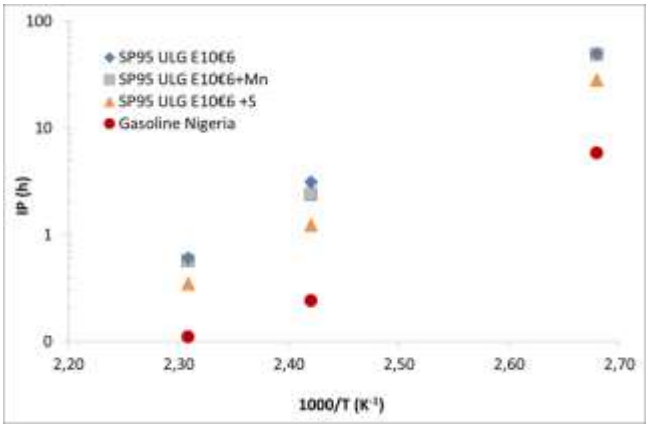

Figure 2. Induction Period variation as a function of 1000/T

It is noteworthy that fuels containing higher sulfur amount present lower stability. Indeed, at 160°C the SP95+S has lower IP than SP95 and SP95+Mn but the variation is within the standard deviation of the analysis. However, at 140°C the IP decrease is evident being ~60% lower than the fuel without S, and at 100°C the IP of the S-additivated fuel is ~42% lower than the IP of the fuel without S. The results of the Nigeria petrol stability are even lower: -83% at 160°C, -93% at 140°C and -88% at 100°C. These results could be due to the higher amount of sulfur but also the higher amount of olefins and naphtenes of the Nigerian gasoline in comparison to the standard SP95 fuel and, on the other hand the SP95 has higher aromatics content. Based on the literature, the di-aromatics and mono-aromatics present much higher stability than naphtenes [21] which is in line with our observations.

Table 2. Activation Energy in kcal/mol and pre-exponential factors of the different gasolines

Fuel	T (°C)	IP (h)	Ea (kcal/mol)	A (cm^3/(mol.s))
SP95	160	0.6 ± 0.02	21.7	1.8E+06
	140	3.1 ± 0.11		
	100	49.4 ± 2.2		
SP95+Mn	160	0.6 ± 0.01	22.2	3.7E+06
	140	2.4 ± 0.19		
	100	48.7 ± 5.7		
SP95+S	160	0.4 ± 0.02	22.1	5.6E+06
	140	1.2 ± 0.13		
	100	28.2 ± 1.1		
Nigeria	160	0.1 ± 0.0	25.0	5.9E+08
	140	0.2 ± 0.0		
	100	5.8 ± 0.1		

By analyzing the PetroOxy and Autoclave results at 5 and 7 bar (Figure 3) the first trend that can be distinguished is the impact of the pressure variation for fuel SP95, using both methods, the fuel stability decrease with a higher pressure. Nevertheless, the effect seems to be mitigated in the presence of additives. The mechanisms involved in this process is out of the focus of the present study and need further investigation. The other feature that can be observed is the difference between PetroOxy and Autoclave results. Even with the same O_2/fuel ratio into the reactors, Autoclave results are more severe than PetroOxy, the stability is around 50% lower when tested within an autoclave. This indicates that the fuel stirring has an important impact on the results, indeed the fuel oxidized into a PetroOxy cell is static whereas the fuel into the autoclave reactor is in a turbulent flow. This is an important feature to help to identify the best method to represent the deposits formation at different spare parts of the engine, i.e. the PetroOxy could better represent the oxidation that is observed in an environment where the fuel is stored (e.g. tank) or remains static in contact with a hot surface (e.g. injectors during soaking); and, on the other hand, the fuel oxidized into an autoclave reactor could represent better the phenomena leading to deposits on engine parts where there is fuel flowing.

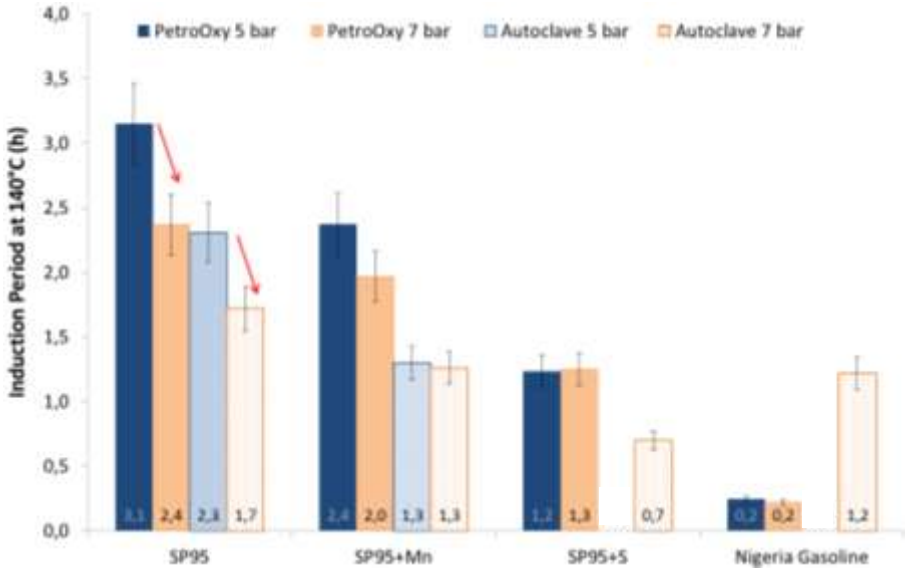

Figure 3. Comparison of IPs from PetroOxy (filled columns) and Autoclave (groove columns) at 5 bar (blue) and 7 bar (orange)

It is important to highlight that the fuels containing large amount of sulfur compounds (SP95+S and Nigerian gasoline) presented an unusual behavior in Autoclave reactor during oxidation at 140°C and 5 bar: the IP is not achieved even after more than 60h aging, i.e. there is no consumption observed of the gas phase. In this case, two hypotheses can be made: (1) the fuels are not oxidized or (2) the oxidation produces some highly volatile products, going to the gas phase and so biasing the measurement. Since the fuels obtained after the test have all presented color changes indicating that they suffered chemical changes, it is possible to conclude that the second hypothesis is preferred, i.e. for fuels SP95+S and Nigeria oxidation products in the gas phase balance the oxygen consumption into the liquid.

Chemical Analysis of the Liquid Phase

The infrared spectrum was recorded for the liquid samples taken during the Autoclave tests (Figure 4). Qualitatively, two zones of interest can be observed between the initial sample (P1) and the sample obtained at IP (P3 or P4) for the four fuels: the region between 1780 and 1710 cm^{-1} and the region between 3650-3120 cm^{-1} corresponding, respectively, to functional groups containing carbonyls (e.g. carboxylic acid, aldehydes, ketones, esters) and to hydroxyl group (-OH) of alcohols and carboxylic acids functional groups.

It is noteworthy that fuel SP95+S presents a different profile in comparison to both SP95 and SP95+Mn. There is no evident variation in the region from 3600-3120 cm^{-1} indicating the absence of alcohols or carboxylic acids whose vibrations were clearly observed for the SP95 and SP95+Mn samplings. In addition, the region from 1800-1650 cm^{-1} for this fuel also present a different spectra profile: for fuels SP95 and SP95+Mn there is an important vibrational band centered at 1707 cm^{-1} with at least four shoulder peaks at 1774 cm^{-1}, 1738 cm^{-1}, 1716 cm^{-1} and 1695 cm^{-1}, also the intensity of these bands increases clearly from the beginning of the oxidation (P1) until the end; in the case of sulfur additivated fuel, there is a large vibrational range from 1750-1675 cm^{-1} but it is very similar for all samplings, and so, does not seem to correspond to an important increase of oxidation products, which is in agreement with the observation of 3600-3120 cm^{-1} region that does not present any variation during samplings. This observation is in line with the one presented previously for the IP results (Figure 3), if the oxidation products were mainly in the gas phase, the liquid samplings would not present a significant spectra variation, it is exactly what is observed at FTIR analysis of the liquid phase.

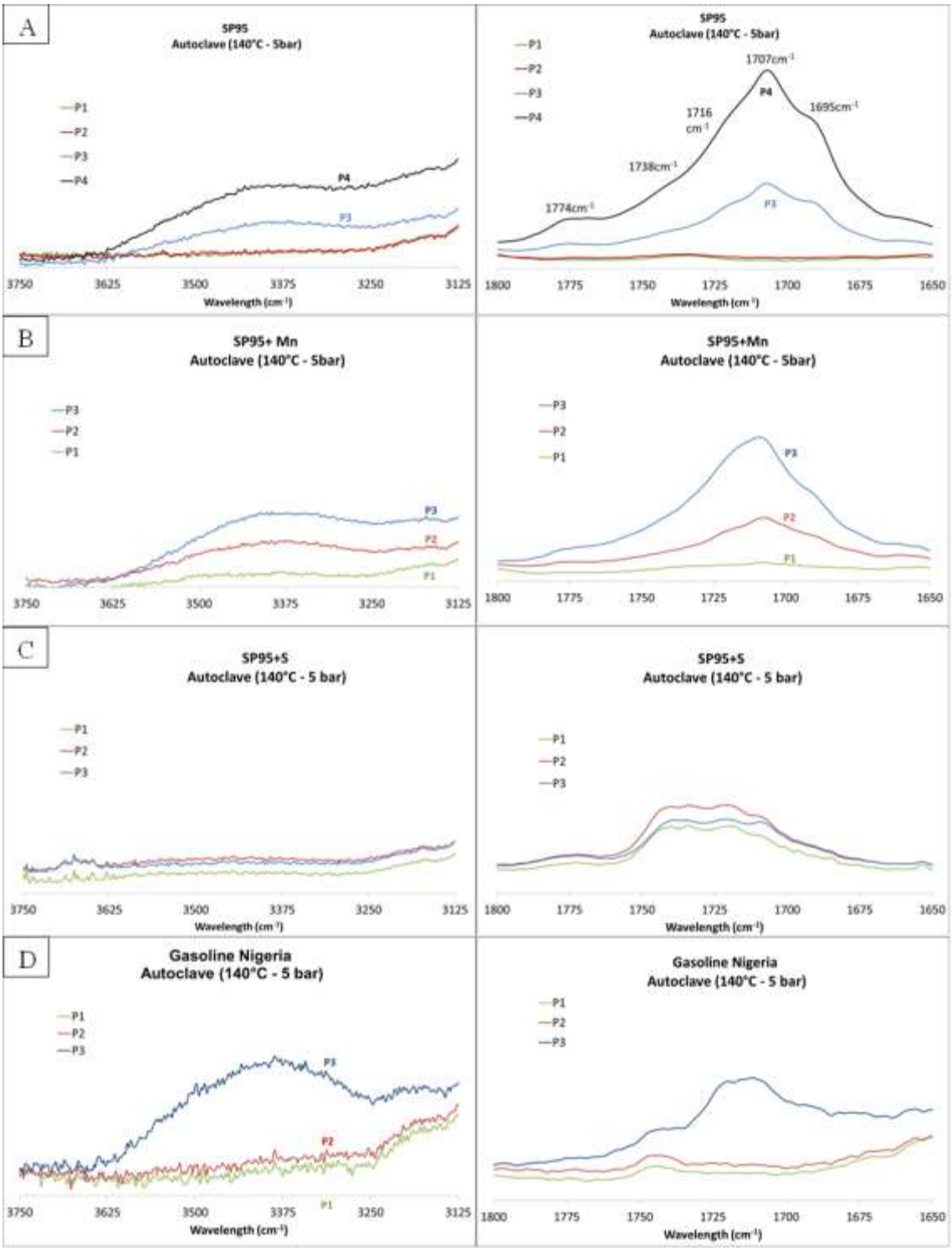

Figure 4. FTIR spectra of oxidized fuels at Autoclave reactor, 140°C and 5 bar: (A) SP95, (B) SP95+Mn, (C) SP95+S and (D) Nigeria. (left) zoom at region 3600-3120cm^{-1} and (right) zoom at region 1800-1650cm^{-1}

Engine tests

Direct Injection, VWEA111

The direct injection VWEA111 engine tests were performed with the 4 different gasolines. Figure 5 shows the spray holes at the end of the 48-hours test.

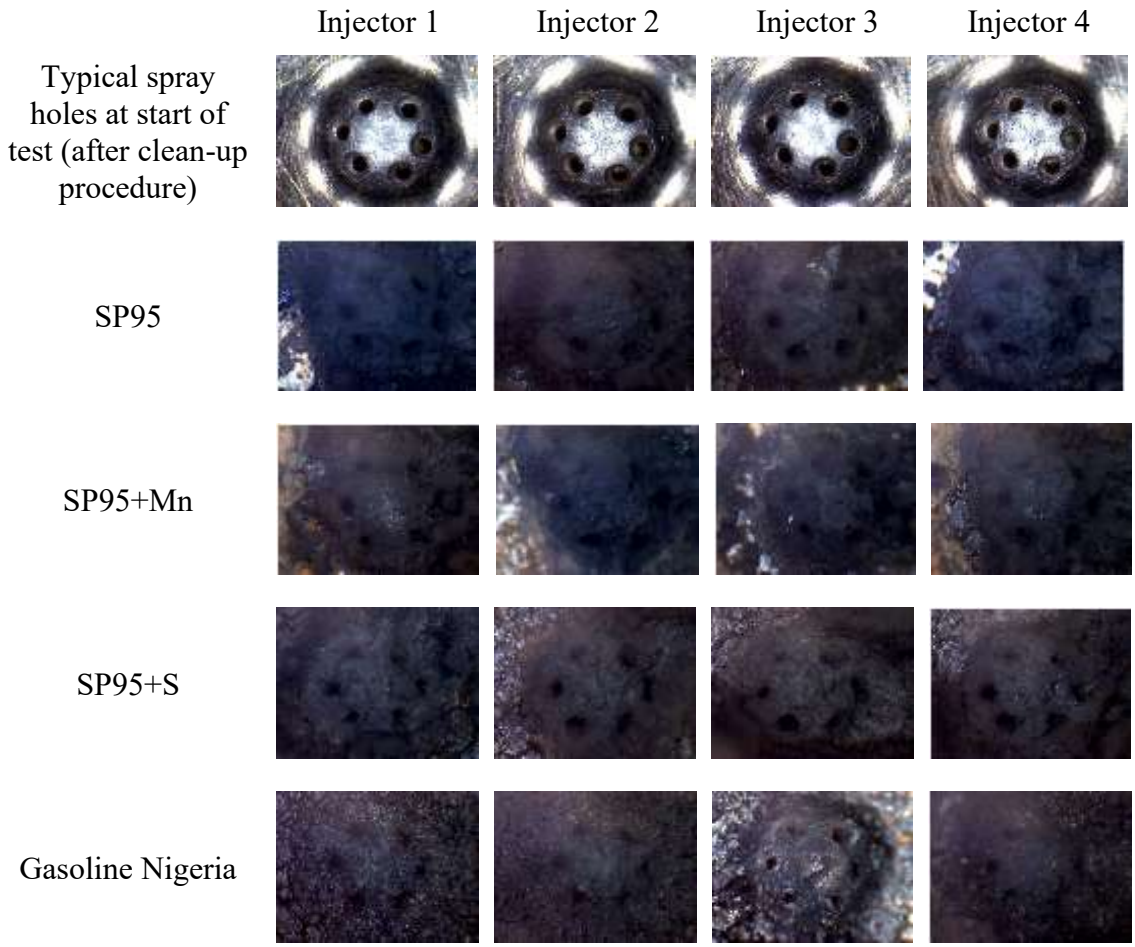

Figure 5. Spray holes at end of test (48 hours)

The pictures clearly indicate a real coking of the injectors spray holes at the end of the 48 hours of keep clean test whatever the gasoline employed. There is no evident difference between the fuels, based only on the quantity or morphology of the deposits.

The graphs showing the injection time during the keep clean test are presented in Figure 6.

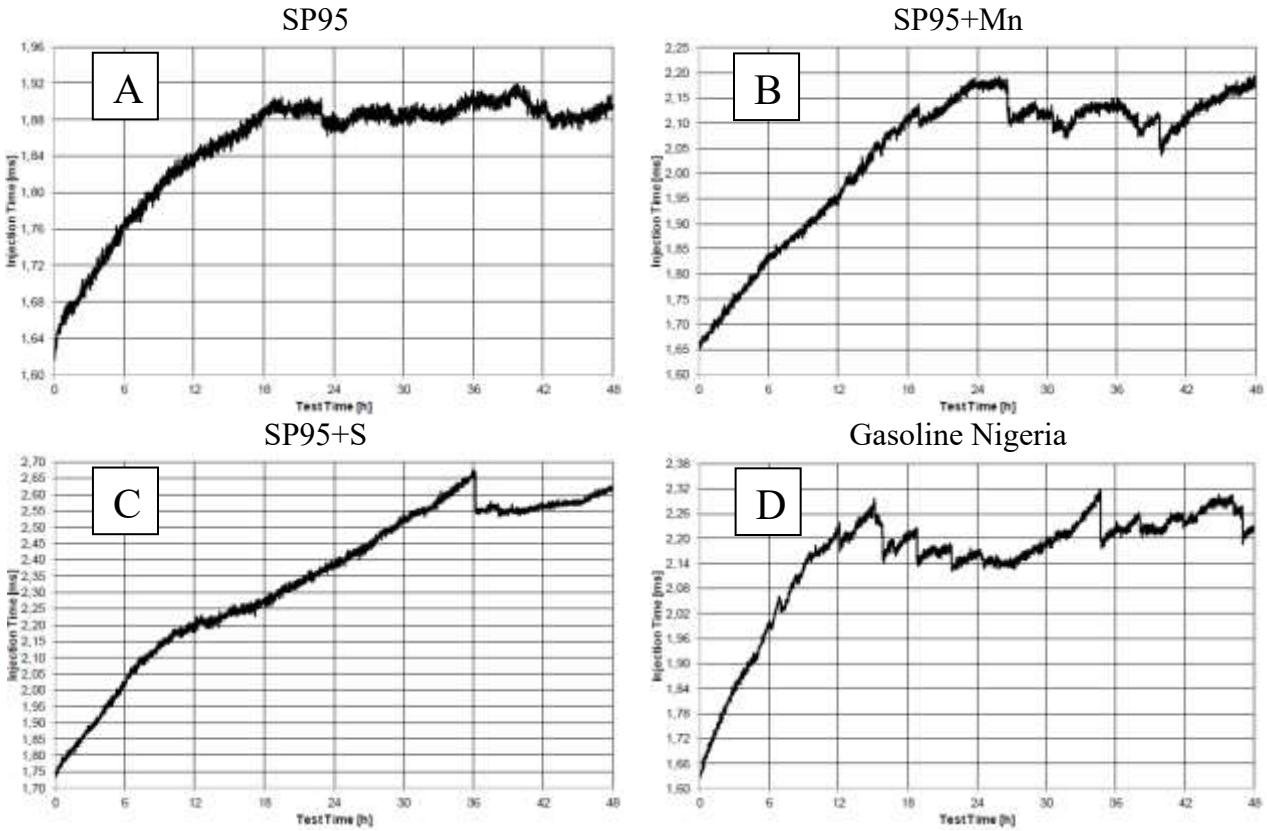

Figure 6. Injection time in milliseconds during Keep Clean test: (A) SP95, (B) SP95+Mn, (C) SP95+S and (D) Nigeria

The SP95+Mn and SP95+S profiles show a more progressive fouling of the injector holes with a less steep slope in the injection time evolution. As explained previously, an increase of the injection time was calculated from these curves for each test. The values are reported in Table 3.

Table 3. Calculated increase of injection time in percent

Fuel	Calculated increase of injection time
SP95	15%
SP95+Mn	32%
SP95+S	49%
Nigeria	35%

The greatest calculated increases of injection time at the end of test were observed for the SP95+S and Nigerian fuels. In the same trend as the data obtained in terms of stability on the PetroOxy tests, These results could be due to the higher amount of sulfur but also the higher amount of olefins and naphtenes of the Nigerian gasoline in comparison to the standard SP95 fuel. In this VWEA111 engine test, the SP95+S fuel appears to be a fuel strongly favoring the nozzle coking of the injectors. To a lesser extent, the SP95+Mn and Nigerian fuels generate a moderate nozzle coking with a 32% and 35% calculated increase of injection time respectively.

Indirect Injection, M102E

The pictures of the inlet valves and the cylinder heads after running the M102E engine tests are presented in Figure 7 and Figure 8.

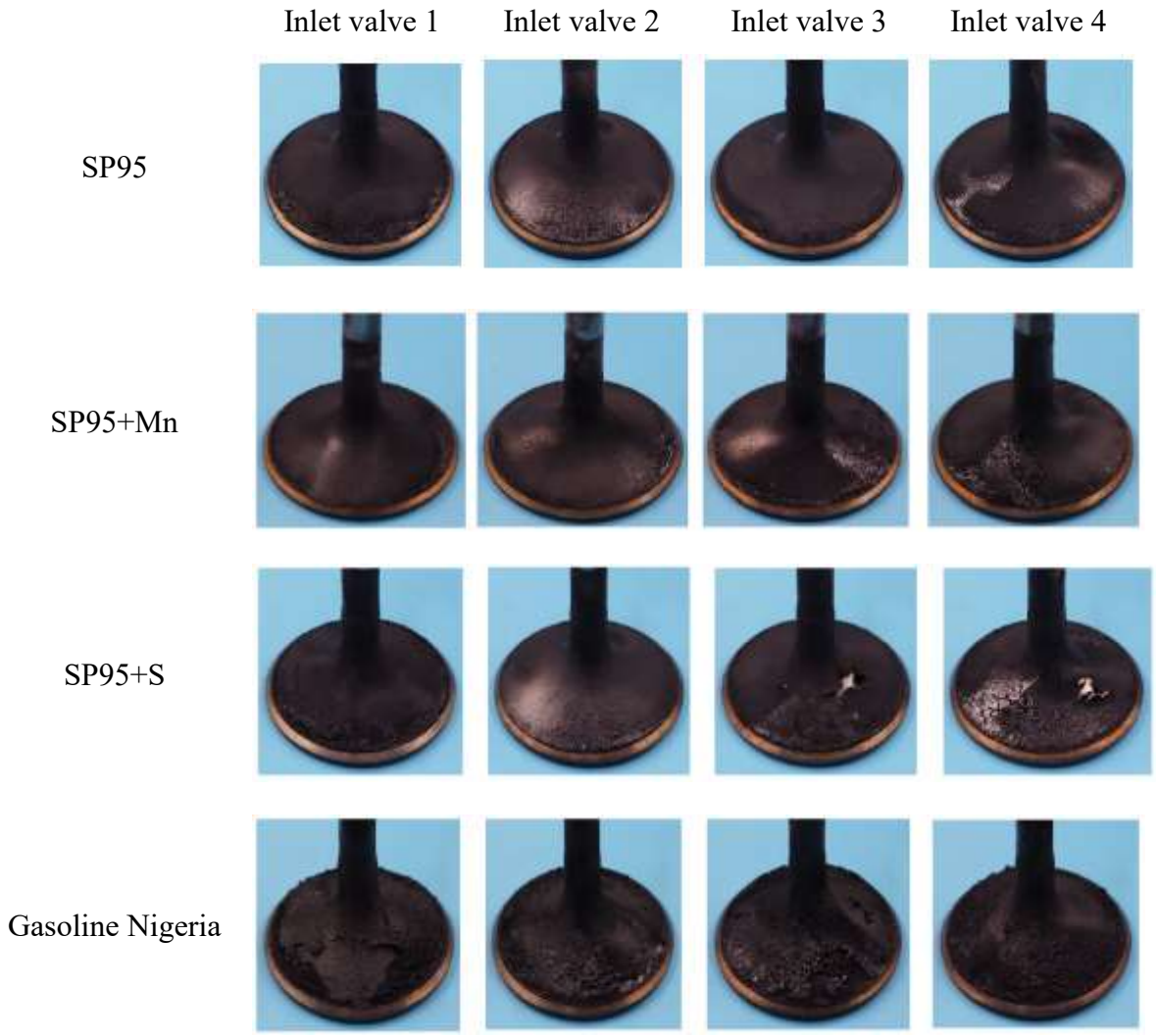

Figure 7. M102E inlet valves at end of test

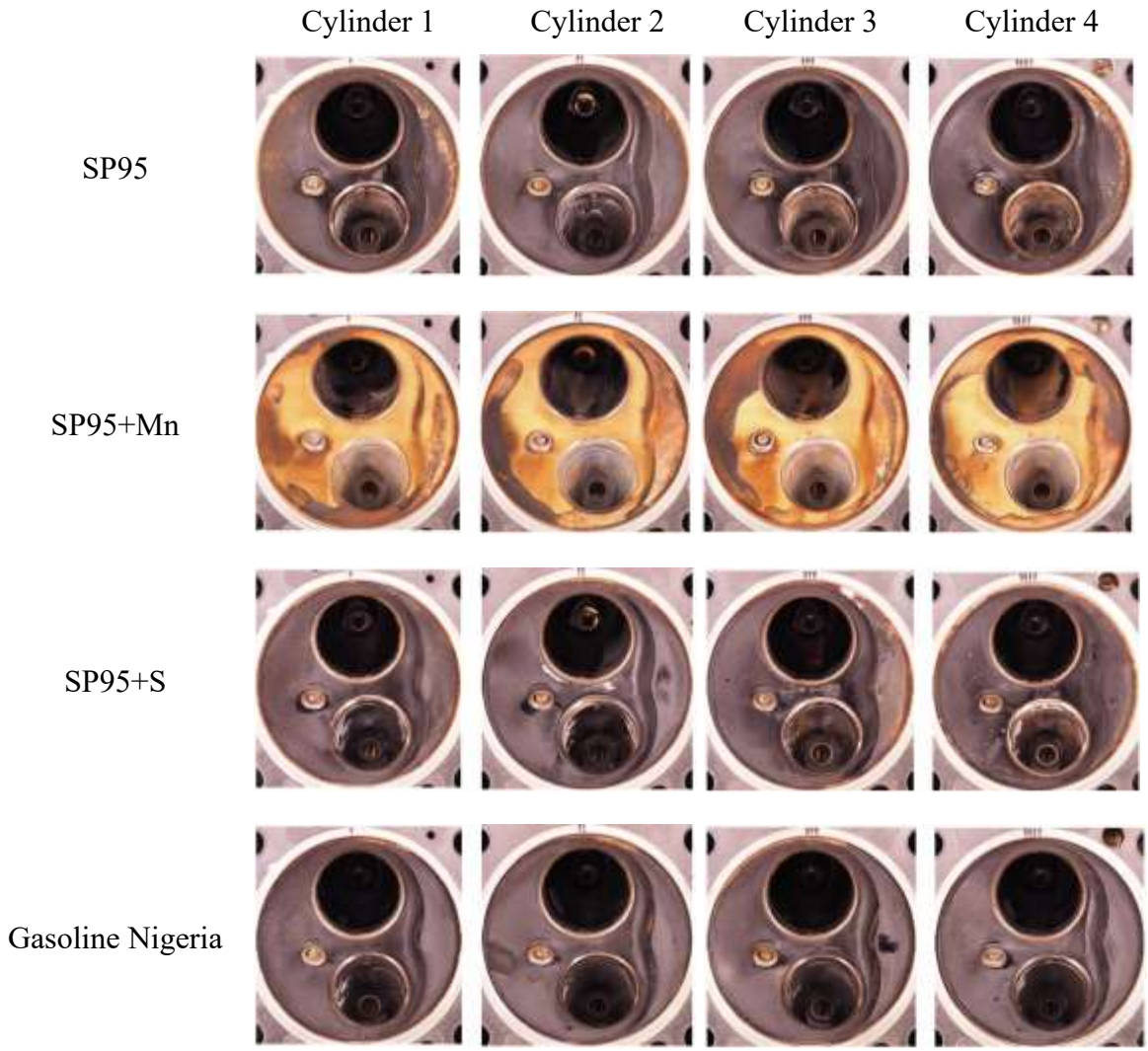

Figure 8. M102E cylinder heads at end of test

The Nigerian gasoline appears to be the fuel that generates more deposits. Clearly, the presence of a significant proportion of sulfur compounds, olefins and naphthenes generates more deposits as in the case of direct injection engine tests. It can be noted that the use of SP95+Mn induced a strength reddish-brown coloration of the combustion chamber as well as the exhaust valves (not shown here). This is a well-known phenomenon as the manganese oxides from combustion of

MMT-containing fuels contribute to reddish-brown deposits that form on engine and exhaust components, including catalysts.[6]

For a better comparison, the M102E results expressed as an amount of deposits per inlet valve are presented in the Figure 9.

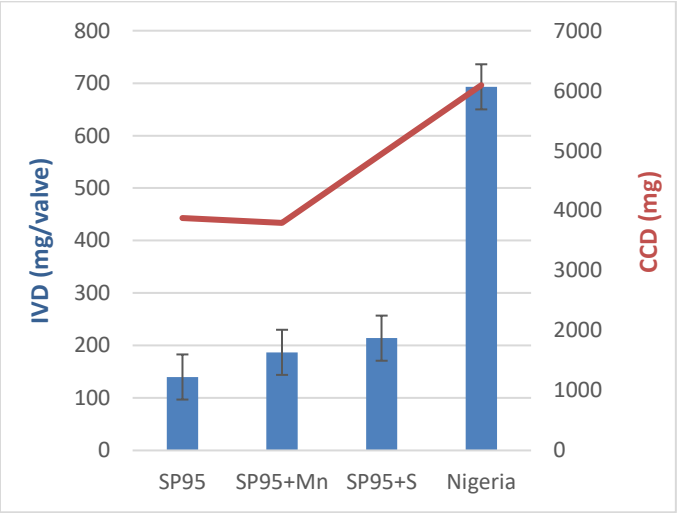

Figure 9. M102E intake valve deposits (IVD) and total combustion deposits (TCD) at end of test

The test precision is defined in the precision statement of the test method F-05-93 in Section 11: Precision for F-05-93 is ± 43 mg per valve for deposit of fuels without additives and 12 mg/valve for deposit of fuels with additives. The precision is evaluated during the latest round robin. In our case, the methylcyclopentadienyl manganese tricarbonyl (MMT) and the dimethyl disulfide (DMDS) were not considered as additives but rather as contaminants of the original SP95 fuel, hence the ± 43 mg precision retained. The total combustion deposits consisting of the sum of piston top deposits and cylinder head combustion deposits (CCD) are also given for information purposes with the same trend as IVD.

384 These results confirm that the presence of sulfur compounds promotes the IVD and TCD
385 formation and suggests the nature of the S-derived compounds impacts quantitatively this
386 phenomenon. A compositional analysis by Gas Chromatography coupled with Sulfur
387 Chemiluminescent Detection was thus performed to identify the S species in the Nigerian fuel.
388 The analysis revealed the significant presence of C0-, C1-, C2-, C3- thiophenes,
389 tetrahydrothiophenes, C0-, C1-, C2- benzothiophenes, mercaptans, sulfides, disulfides but the
390 absence of DMDS. Consequently, the DMDS added as a contaminant in the SP95 fuel plays a
391 minor role in the IVD/TCD formation. It is noteworthy that some authors [33,34] have identified
392 thiophene type compounds in gasoline deposits. Nevertheless, they considered that these
393 compounds are known not to affect deposit formation of fuels. More recent work [35,36] on jet
394 fuels autoxidation process have investigated the sulphur effect on deposits formation and
395 evidenced the impact of sulphur: the induction period, measured by PetroOxy, increase by
396 increasing mercaptan and di-tert-butyl-disulphite content. It seems that sulphur is acting slowing
397 down the time necessary to start the deposits formation. The authors have also shown that sulphur
398 impact overwhelms the aromatic impact.[36] These results indicate that the structure of the sulphur
399 molecule under study has a great impact by promoting or avoiding deposits formation. The role of
400 thiophenes as contaminants in gasoline fuels should be considered for further investigation.

401

402 *Gasoline Oxidation Stability and Engine Deposits: A Comparison*

403 As discussed previously, by comparing the PetroOxy and Autoclave results it is clear that they do
404 not follow the same oxidation process, in most cases, the stability is around 50% lower using
405 Autoclave reactor than using a PetroOxy reactor.

By normalizing the IP results and comparing to the engine tests (Figure 10) it is possible to obtain a 1st order correlation (R^2=0.9839) between the PetroOxy test and the deposits mass formed using the indirect injection M102E engine (Figure 10a), whereas no correlation can be found with the VWEA111 engine test (Figure 10b). On the other hand, for the IP from Autoclave reactor there is a linear correlation (R^2=0.9869) between the IP and the VWEA111 engine test (increase of the injection time in percentage) (Figure 10d) and no correlation with the M102E test (Figure 10c).

These results could indicate that deposits formed at the back face of the inlet valve using the engine M102E could be related to the fuel oxidation probably due to fuel stagnation, and consequently, fuel soaking in contact with a hot metallic surface favoring the deposits growth. Indeed, in Port Fuel Injection engine as M102E, fuel injection takes place over the back face of the inlet valve, when it is in a closed state during the exhaust stroke. Thus, a simple PetroOxy test could help to predict the tendency of the fuel to form this type of deposit. By contrast it means also that PetroOxy results is not adequate to identify the fuel tendency to form deposits at the nozzle injector in a direct injection engine.

On the contrary, these results could indicated that the deposits obtained in the VWEA111 are somehow related to the fuel flow and the fuel tendency to form deposits could be better predicted by using a simple apparatus like Autoclave stirring reactor which is much easier and cheaper to operate than an injection bench for example.

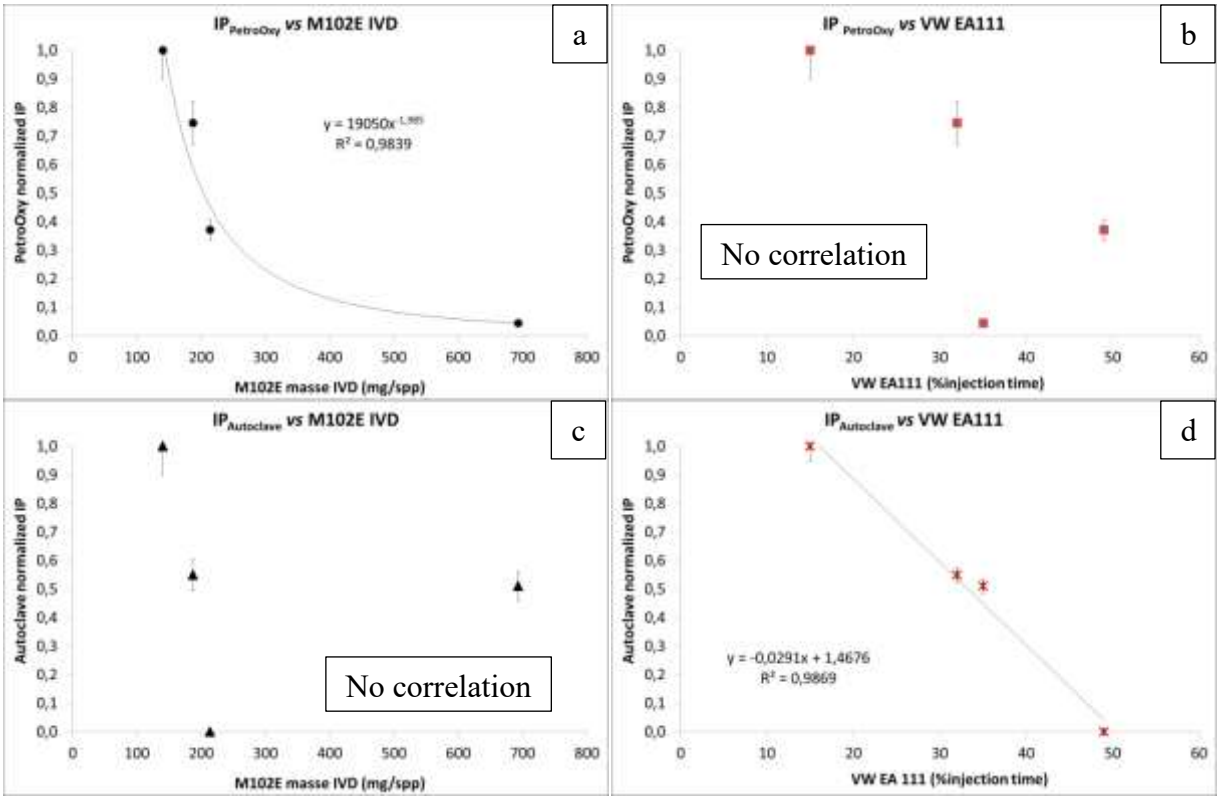

Figure 10. Comparison of IP and deposits: (a) $IP_{PetroOxy}$ *vs* M102E mass IVD, (b) $IP_{PetroOxy}$ *vs* VWEA111, (c) $IP_{Autoclave}$ *vs* M102E mass IVD, (d) $IP_{Autoclave}$ *vs* VWEA111

CONCLUSION

The aim of this study was to evaluate the oxidation stability of a standard European gasoline SP95 Euro 6 E10 and the impact of additives such as methylcyclopentadienyl manganese tricarbonyl (MMT) and dimethyl disulfide (DMDS) on deposits formation. The stability of these fuels were compared to a commercial Nigerian gasoline which has higher sulfur content (800mg/kg) to evaluate the sulfur effect on deposits formation. The oxidation stability obtained from PetroOxy and Autoclave Stirring Reactor were compared to the real engines tendencies to form deposits. The deposits targeted are those created on the injector nozzle of a VW EA111 engine (direct injection), and on the intake valve using a M102E engine (indirect injection).

The oxygen consumption at 100°C, 140°C and 160°C was monitored in the PetroOxy cell. This information was used to determine global rate constants of oxidation, using a simple global kinetic model. The Activation Energy for gasoline oxidation in the liquid phase was about 21-25 kcal/mol.

The induction period from PetroOxy test shows the negative impact of DMDS and MMT on the IP of the standard gasoline SP95 E10 ULG Euro 6: IP drops ~20% with MMT and ~30% with the DMDS.

PetroOxy and Autoclave results do not show the same trend with the fuels IP being around 50% lower when tested within the autoclave. This indicates that the oxidation mechanisms involved are not the same and the fuel stirring has an important impact on the results. This feature is in line with the comparison of the IP results in PetroOxy and Autoclave with the results of the direct injection (VW EA111) and indirect injection (M102E) engine tests. The results suggest that the PetroOxy IP follow the trend of the mass of deposits formed on the valves of the indirect injection, M102E, engine tests, with the IP decreasing as the valve deposits mass increases which is well correlated to a 1st order equation. On the contrary, the Autoclave results seem to follow the trend of the results of the direct injection, VW EA111 engine tests: IP decreases linearly when the injection time increases.

Indeed, the fuel oxidized into a PetroOxy cell is static whereas the fuel into the autoclave reactor is in a turbulent flow. This is an important feature to help to identify the best method to represent the deposits formation at different spare parts of the engine, i.e. the PetroOxy could better represent the oxidation that is observed in an environment where the fuel is stored (e.g. tank) or remains static in contact with a hot surface (e.g. inlet valves for PFI engines or injectors during soaking); and, on the other hand, the fuel oxidized into an autoclave reactor could represent better the

phenomena leading to deposits on engine parts where there is fuel flowing. Therefore, the results could indicate that deposits formed at the indirect injector of engine M102E could be related to the fuel oxidation probably due to fuel stagnation, and consequently, fuel soaking in contact with a hot metallic surface favoring the deposits growth. Thus, a simple PetroOxy test could help to predict the tendency of the fuel to form this type of deposit.

In addition, the results also indicate that the deposits obtained in the direct injection VWEA111 are somehow related to the fuel flow and the fuel tendency to form deposits could be better predicted by using a simple apparatus like Autoclave stirring reactor which is much easier and cheaper to operate than an injection bench. All the detailed chemical mechanisms involved in these processes are not on the scopus of the present study and will be further investigated in the future. A better comprehension of these processes could allow us to identify fuel tendencies to form deposits on specific spare parts based only on lab scale methods, helping to optimize and to target the maintenance operation and preventing failures or damages on real engine systems.

ABBREVIATIONS

IP, Induction Period; SP95, Standard European gasoline SP95 Euro 6 containing 10%v/v Ethanol; MMT, methylcyclopentadienyl manganese tricarbonyl; DMDS, dimethyl disulfide; SP95+Mn, SP95+20mg/kg of MMT; SP95+S, SP95+500mg/kg of DMDS.

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