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

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14 **KEYWORDS:** Gasoline, Autoxidation, Stability, Deposits, GDI, PFI, PetroOxy, RSSOT,
15 Autoclave, Manganese, Sulfur, DMDS, MMT, VWEA111, M102E, injectors, valves
16

17 **ABSTRACT**

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

22 the oxidation stability of a non-additised standard European gasoline SP95 Euro 6 containing
23 10%v/v Ethanol (SP95E6E10) complying with the EN228 standard and the impact of additives
24 such as methylcyclopentadienyl manganese tricarbonyl (MMT) and dimethyl disulfide (DMDS)
25 on deposits formation to mimic other world market fuels such as Africa or China. The stability of
26 these fuels was compared to a commercial Nigerian gasoline which has higher sulfur content (800
27 mg/kg) to evaluate the sulfur effect on deposits formation. The fuel degradation tendencies
28 (Induction Period, IP) obtained from PetroOxy apparatus and Autoclave reactor were compared to
29 the real engines tendencies to form deposits. The deposits targeted are those created on the injector
30 nozzle of a VW EA111 engine (direct injection), and on the valve using a M102E engine (indirect
31 injection). PetroOxy results show the negative impact of DMDS and MMT on the IP of the
32 gasoline, SP95 E10 ULG Euro 6: IP decrease of up to 30%. Comparison of the IP results in
33 PetroOxy and Autoclave with the results of the direct injection (VW EA111) and indirect injection
34 (M102E) engine tests suggests that the PetroOxy results follow the trend of the mass of deposits
35 formed on the valves of the indirect injection, M102E, engine tests, with the IP decreasing as the
36 valve deposits mass increases. On the contrary, the Autoclave results seem to follow the trend of
37 the results of the direct injection, VW EA111 engine tests: IP decreases when the injection time
38 increases. These features could allow us to identify fuel tendencies to form deposits on specific
39 spare parts based only on laboratory scale methods, helping to optimize and to target the
40 maintenance operation and preventing failures or damages on real engine systems.

41

42 **INTRODUCTION**

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

45 or pyrolysis [2]; hydrolysis [3]; and microbiological contamination [4]. More specifically,
46 autoxidation stability of fuels refers to the tendency of a fuel to degrade from the oxidation of its
47 compounds. Fuel degradation by autoxidation can lead to the formation of insoluble products and
48 deposits of various origins and compositions in the tank, combustion systems and injection systems
49 [1]. Deposits formed as a result of the autoxidation process are generally obtained at $T < 300^{\circ}\text{C}$.
50 Therefore, deposits related to autoxidation process indicates the degradation of organic compounds
51 at low temperatures in the presence of oxygen. Several authors have studied the physical and
52 chemical characteristics of gasoline with and without additives and its impact on several
53 combustion process such as auto-ignition [5,6], heat release [7], soot precursors and soot formation
54 [8], among others. All these features can lead to deposits formation at different parts of gasoline
55 engine such as injector nozzle [9–11], spark plug [12,13], intake valves [11,14,15], and combustion
56 chamber walls [11]. Ganeau et al. [16] have studied the formation of deposits in pistons using
57 standard gasoline in an optical engine. They studied the mechanisms leading to gasoline deposits
58 formation on pistons and identified mainly two pathways: liquid-film path or the soot path [17].
59 For the liquid-film path, the work showed that the formation of the deposit by the liquid film was
60 conditioned by the evaporation rate of the liquid film, the surface roughness and material does not
61 have an impact on the formation of the deposit via the liquid-film path. For the soot path,
62 thermophoresis and inertial deposition seems to be the main mechanisms involved in deposition
63 process. The results showed that an increase in the surface temperature reduced the deposition of
64 soot [17]. However, Ganeau's work did not establish the chemical process involved during liquid-
65 film deposits formation and the analytical methods used, Infrared absorption spectroscopy (FTIR-
66 ATR) and Raman Spectroscopy, were not able to identify the chemical trends. Kinoshita et al [18]
67 studied the process of deposit build-up on injector nozzles and also showed that surface

68 temperature plays an important role in the nature of the deposit formed. Indeed, they propose that
69 the residual fuel film on the nose surface after injection and after combustion can form more or
70 less adherent deposits depending on the temperature, i.e. for a $T_{\text{surface}} > T_{90}$ of the
71 fuels, thicker and more adherent deposits are formed, whereas $T_{\text{surface}} < T_{90}$ the deposits are
72 "washed off" during the next injection and do not adhere to the surface. However, this hypothesis
73 has not been confirmed by other studies and the mechanism of deposit formation remains a subject
74 of study. Nevertheless, the residual fuel remaining in contact with the hot metal surface of the
75 injector nozzle and valves certainly leads to the degradation of its compounds by the autoxidation
76 process, especially during the engine shutdown (soaking) phases [19]. This feature has been
77 observed during studies on the injection bench, and so without the influence of combustion
78 products on deposits, for diesel and biodiesel fuels [19,20] as well as kerosene [21]. Nevertheless,
79 there is a lack in the literature about gasoline autoxidation in liquid phase at low temperature and
80 the link of this fuel degradation mechanism to the deposits that can be observed in different parts
81 of the real engines. Also, there is a need to identify analytical methods that would be able to predict
82 the gasoline deposits formation tendencies by using lab scale tests instead of using engine tests
83 that are expensive and time consuming.

84 Gasoline is mainly composed of paraffins, olefins, naphtenes, aromatics and oxygenated
85 compounds. In other fuels autoxidation studies, it has been shown that the presence of
86 unsaturations in the alkyl chain (e.g. olefins) as well as the presence of heteroatoms, such as S, N
87 or O, are parameters favoring the free radical mechanism in the propagation phase [1,22,23]. N-
88 alkanes, iso-alkanes, cycloalkanes, and aromatics are also sensitive to oxidation depending on the
89 temperature and pressure conditions [24–26]. In addition to fuel base compounds, impurities such
90 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

112 Ethanol (SP95E6E10) and the impact of additives such as methylcyclopentadienyl manganese
113 tricarbonyl (MMT) and dimethyl disulfide (DMDS) on gasoline oxidation stability. The stability
114 of these fuels was compared to a commercial Nigerian gasoline which has higher sulfur content
115 (800mg/kg) to evaluate its impact on stability. The fuel degradation tendencies (Induction Period,
116 IP) obtained from PetroOxy apparatus and Autoclave reactor were compared to the real engines
117 tendencies to form deposits. The deposits targeted are those created on two different injection
118 system technologies: the injector nozzle of a VW EA111 engine (direct injection), and on the valve
119 of a M102E engine (indirect injection).

120

121 **EXPERIMENTAL METHODS**

122 *Fuel Matrix*

123 The fuel matrix is composed of two commercial gasolines: one from European market and one
124 from Nigerian market (*See supplementary material for more details*). The European gasoline
125 chosen was the SP95 ULG E10 Euro 6 (hereafter named as SP95E10) used as reference. This fuel
126 presents a low quantity of sulfur (<10ppm) and 10%v/v of ethanol (EtOH). Two blends were
127 performed using the additives methylcyclopentadienyl manganese tricarbonyl (MMT) and the
128 dimethyl disulfide (DMDS) to obtain the fuels SP95+Mn (20 mg/kg of Manganese) et SP95+S
129 (500 mg/kg of Sulfur). These blends were used to mimic world market fuels other than Europe
130 such as Africa or China. By adding MMT and DMDS to the neat SP95 gasoline, the impact of
131 manganese and sulfur compounds can be more specifically appreciated respectively. It is true that
132 DMDS sulfur compound is different from those naturally present in a fuel from refining operations,
133 but it allows to appreciate the direct impact of added sulfur compared to neat SP95E10. The

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

140

141 **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

142

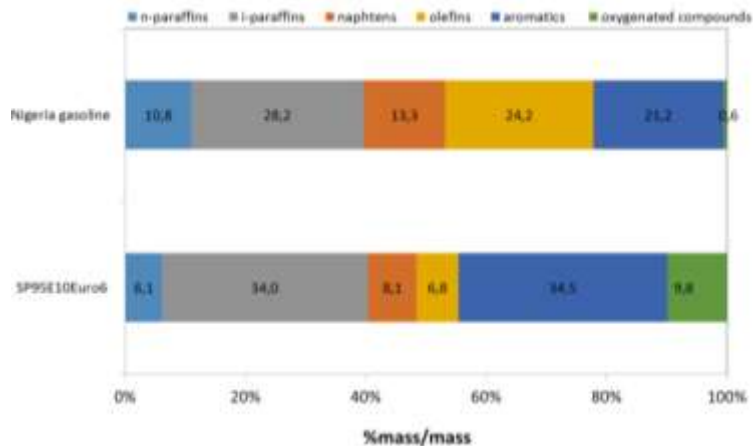


Figure 1. Chemical composition of Nigerian and SP95 gasolines

143
144
145

146 *Oxidation Stability Tests*

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

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

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

$$164 \quad \frac{-d[O_2]}{dt} = -\frac{d[RH]}{dt} = A \cdot e^{\frac{-E_a}{RT}} \cdot [RH] \quad \text{Equation 1}$$

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

$$168 \quad \frac{[\Delta O_2]_{IP}}{IP} = A \cdot e^{\frac{-E_a}{RT}} \cdot ([RH]_{t_0} - [RH]_{IP}) \quad \text{Equation 2}$$

169 where $[RH]_{t_0} = \frac{\rho}{M}$, with ρ is the fuel's density and M the molar mass. Considering that the oxygen
 170 is the main component in the gas phase, it is possible to calculate the oxygen consumption by
 171 volume of fuel at IP by:

$$172 \quad \frac{[\Delta O_2]_{IP}}{IP} = \frac{P_{max} - P_{IP}}{RT} \cdot \frac{V_{TOT} - V_{liq}}{V_{liq}} \quad \text{Equation 3}$$

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

$$176 \quad \ln \left[\frac{[\Delta O_2]_{IP}}{t \cdot [RH]_{t_0, IP}} \right] = -\frac{E_a}{RT} + \ln A \quad \text{Equation 4}$$

177

178 *Autoclave reactor*

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

187 The autoclave is an inert reactor designed to carry out chemical reactions at temperature and
188 pressure with operating limits close to 300 °C and 500 bar. In this study, a volume of 50 mL of
189 sample is placed in a cell with a total volume of 250 mL. The idea is to be in the same conditions
190 in terms of O₂/fuel ratio as the PetroOxy test. The fuel is first stirred with a rotation system
191 followed by pressurization using an inert gas, Argon. Then the temperature is raised to the desired
192 temperature. Once the test temperature has been reached, the inert gas is flushed by introducing
193 oxygen into the cell. The replacement of the gas is very fast and does not disturb the course of the
194 test. As soon as the system is stable, a few seconds after purging the inert gas with O₂, the oxidation
195 kinetics are very similar to those obtained with PetroOxy. Oxygen is therefore consumed over time
196 by the oxidation of the fuel and the time to reach a 10% drop from P_{max} and recorded as IP. The
197 main difference in comparison with PetroOxy is the possibility to take gas and liquid samples
198 during the test and, in this way, monitor the progress of fuel degradation. Here, only liquid
199 samplings are analyzed using Fourier-Transform Infrared Spectroscopy (FTIR) to achieve the
200 chemical composition variation during oxidation. More information about Autoclave procedure
201 can be found elsewhere.[3–5]

202

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

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

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

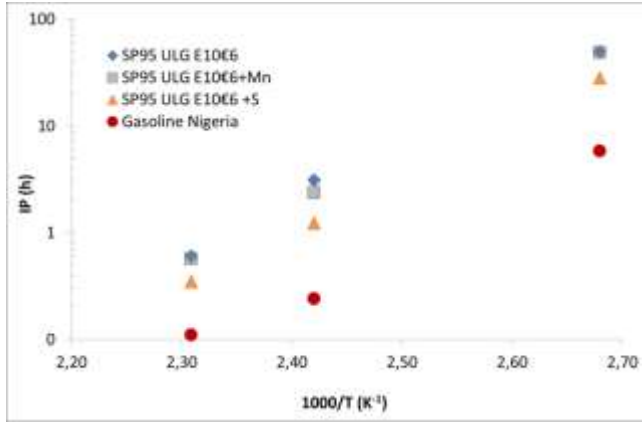
224 standardized test method, referred as CEC F-05-93, allows the assessment of the deposits
225 formation tendency of the intake system of the indirect injection engine, in particular the intake
226 valves and the combustion chamber. The test engine is a Mercedes Benz M102E in-line, 4-
227 cylinder, 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 $\log(\text{IP})$ 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 E_a values of our samples are within
243 the E_a range of pure compounds such as isoalkanes that have E_a comprised in a range from 15-
244 45kcal/mol depending on the level of hydrocarbon branching[5]. It is also similar to the E_a

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



247
248 **Figure 2.** Induction Period variation as a function of 1000/T

249
250 It is noteworthy that fuels containing higher sulfur amount present lower stability. Indeed, at 160°C
251 the SP95+S has lower IP than SP95 and SP95+Mn but the variation is within the standard deviation
252 of the analysis. However, at 140°C the IP decrease is evident being ~60% lower than the fuel
253 without S, and at 100°C the IP of the S-additivated fuel is ~42% lower than the IP of the fuel
254 without S. The results of the Nigeria petrol stability are even lower: -83% at 160°C, -93% at 140°C
255 and -88% at 100°C. These results could be due to the higher amount of sulfur but also the higher
256 amount of olefins and naphthenes of the Nigerian gasoline in comparison to the standard SP95 fuel
257 and, on the other hand the SP95 has higher aromatics content. Based on the literature, the di-
258 aromatics and mono-aromatics present much higher stability than naphthenes [21] which is in line
259 with our observations.

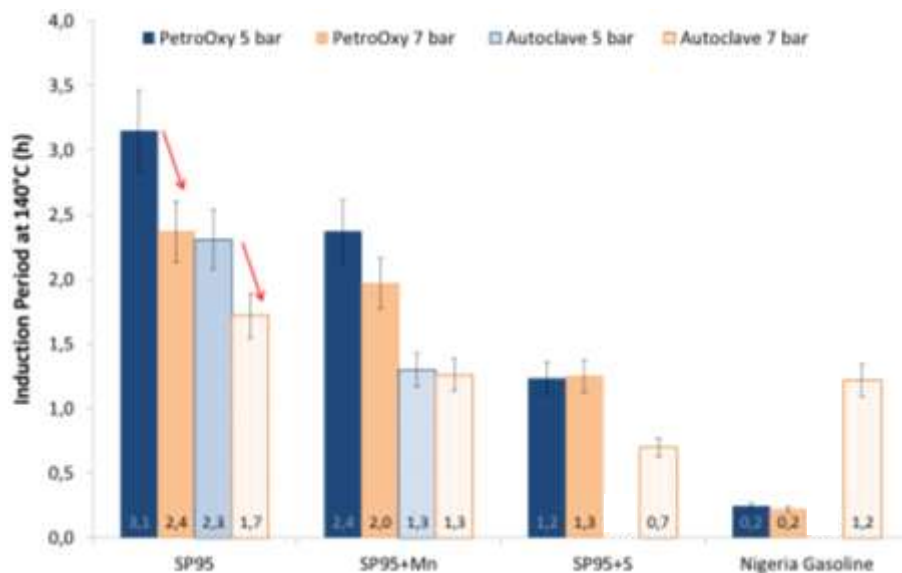
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261

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

Fuel	T (°C)	IP (h)	Ea (kcal/mol)	A (cm³/(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		

263

264 By analyzing the PetroOxy and Autoclave results at 5 and 7 bar (Figure 3) the first trend that can
 265 be distinguished is the impact of the pressure variation for fuel SP95, using both methods, the fuel
 266 stability decrease with a higher pressure. Nevertheless, the effect seems to be mitigated in the
 267 presence of additives. The mechanisms involved in this process is out of the focus of the present
 268 study and need further investigation. The other feature that can be observed is the difference
 269 between PetroOxy and Autoclave results. Even with the same O₂/fuel ratio into the reactors,
 270 Autoclave results are more severe than PetroOxy, the stability is around 50% lower when tested
 271 within an autoclave. This indicates that the fuel stirring has an important impact on the results,
 272 indeed the fuel oxidized into a PetroOxy cell is static whereas the fuel into the autoclave reactor is
 273 in a turbulent flow. This is an important feature to help to identify the best method to represent the
 274 deposits formation at different spare parts of the engine, i.e. the PetroOxy could better represent
 275 the oxidation that is observed in an environment where the fuel is stored (e.g. tank) or remains
 276 static in contact with a hot surface (e.g. injectors during soaking); and, on the other hand, the fuel
 277 oxidized into an autoclave reactor could represent better the phenomena leading to deposits on
 278 engine parts where there is fuel flowing.



279
 280 **Figure 3.** Comparison of IPs from PetroOxy (filled columns) and Autoclave (groove columns) at
 281 5 bar (blue) and 7 bar (orange)
 282

283 It is important to highlight that the fuels containing large amount of sulfur compounds (SP95+S
 284 and Nigerian gasoline) presented an unusual behavior in Autoclave reactor during oxidation at
 285 140°C and 5 bar: the IP is not achieved even after more than 60h aging, i.e. there is no consumption
 286 observed of the gas phase. In this case, two hypotheses can be made: (1) the fuels are not oxidized
 287 or (2) the oxidation produces some highly volatile products, going to the gas phase and so biasing
 288 the measurement. Since the fuels obtained after the test have all presented color changes indicating
 289 that they suffered chemical changes, it is possible to conclude that the second hypothesis is
 290 preferred, i.e. for fuels SP95+S and Nigeria oxidation products in the gas phase balance the oxygen
 291 consumption into the liquid.

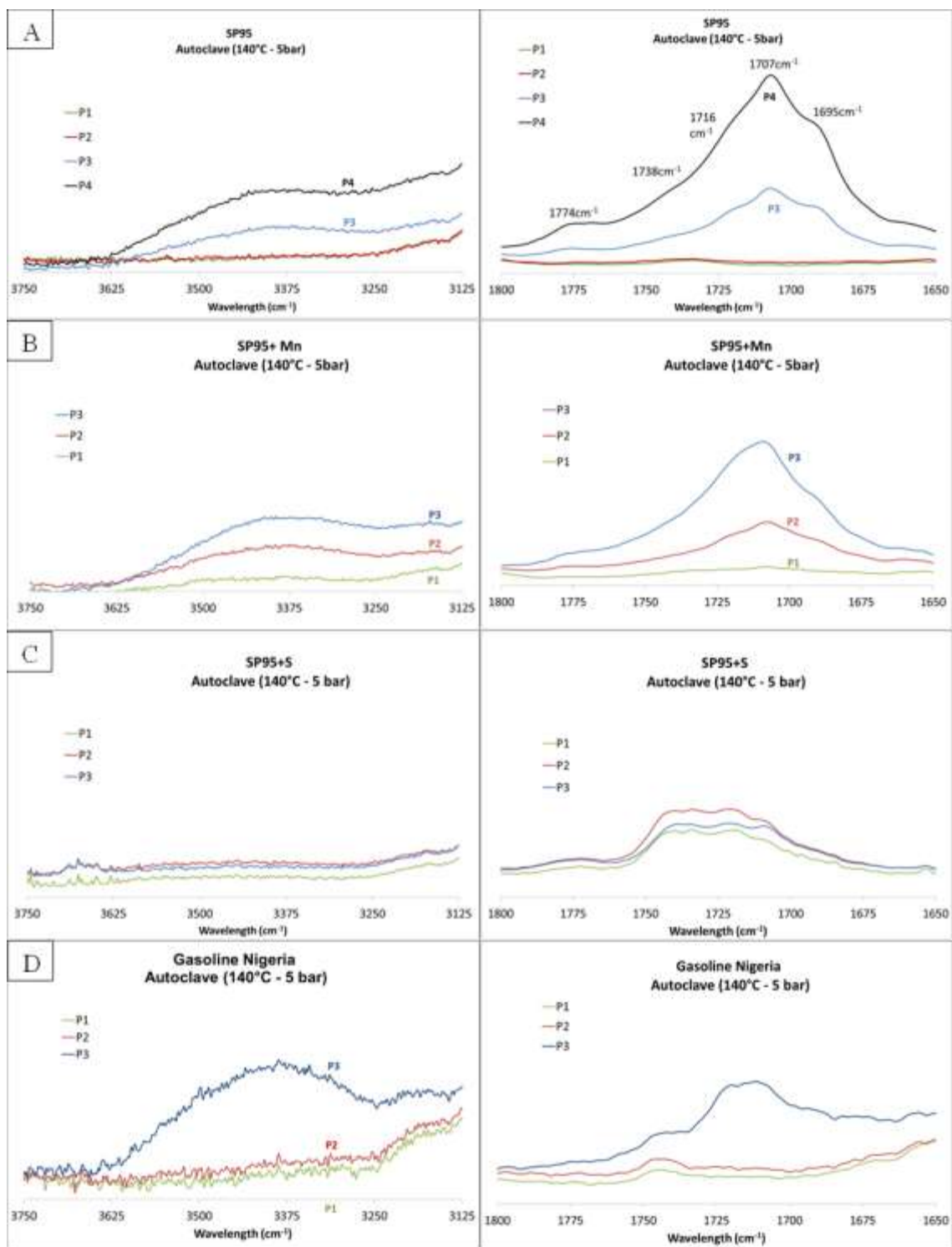
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293 *Chemical Analysis of the Liquid Phase*

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

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

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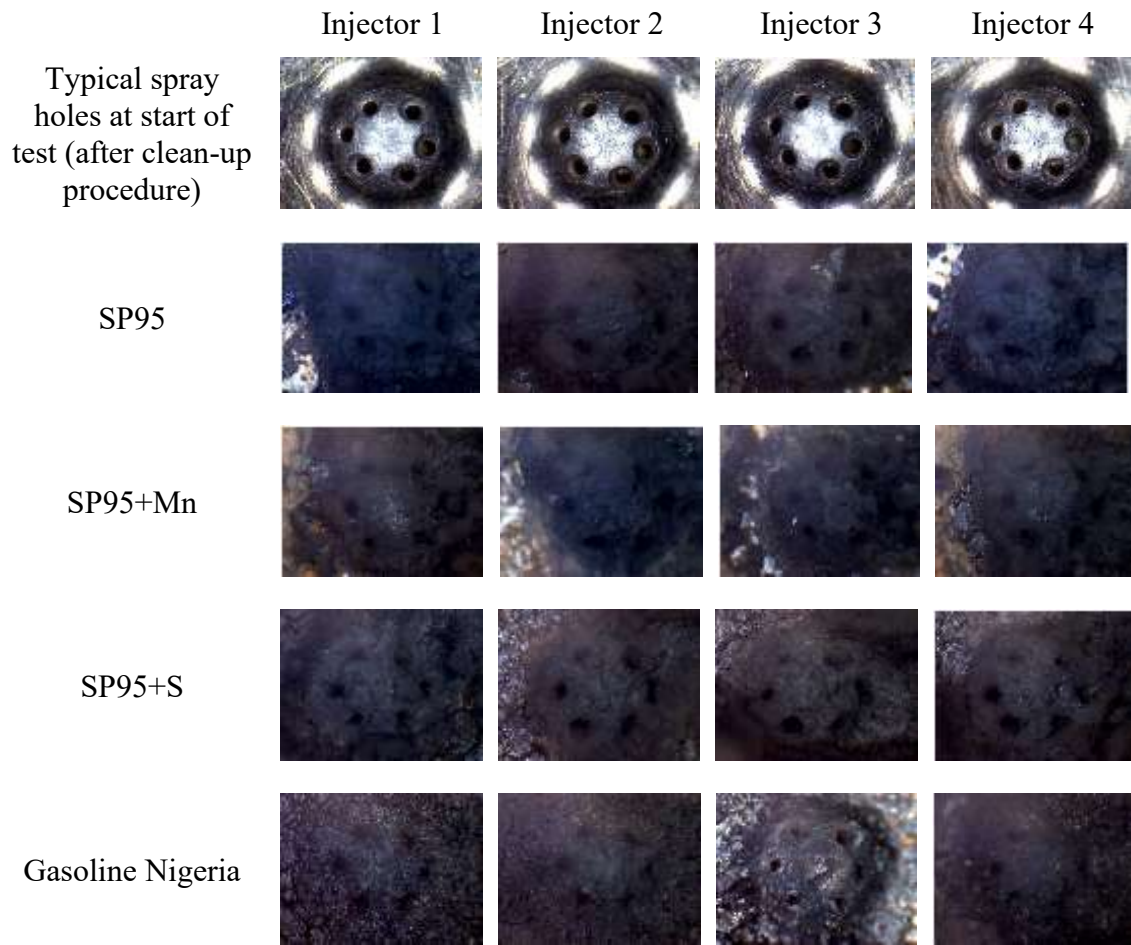


315
 316 **Figure 4.** FTIR spectra of oxidized fuels at Autoclave reactor, 140°C and 5 bar: (A) SP95, (B)
 317 SP95+Mn, (C) SP95+S and (D) Nigeria. (left) zoom at region 3600-3120cm⁻¹ and (right) zoom at
 318 region 1800-1650cm⁻¹
 319

320 *Engine tests*

321 *Direct Injection, VWEA111*

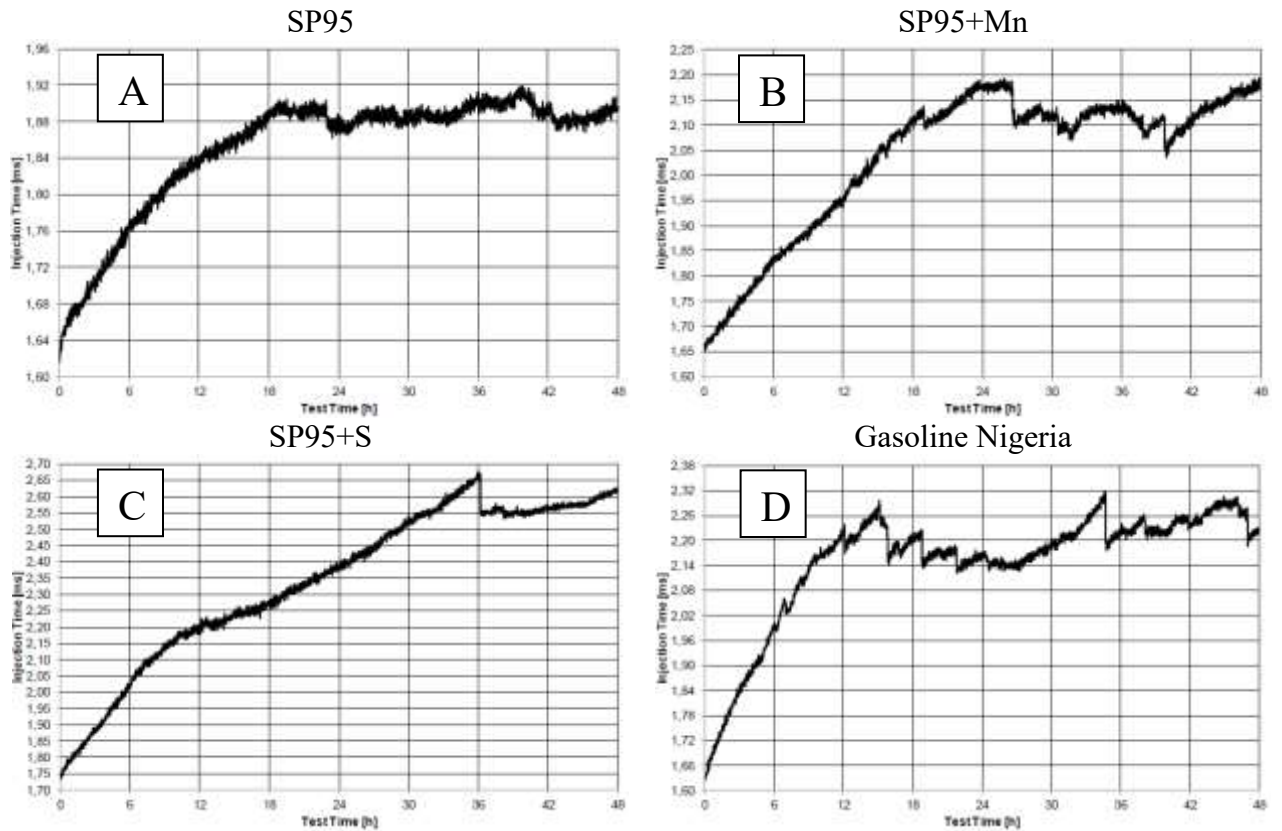
322 The direct injection VWEA111 engine tests were performed with the 4 different gasolines. Figure
323 5 shows the spray holes at the end of the 48-hours test.



324 **Figure 5.** Spray holes at end of test (48 hours)
325

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

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



330 **Figure 6.** Injection time in milliseconds during Keep Clean test: (A) SP95, (B) SP95+Mn, (C)
331 SP95+S and (D) Nigeria
332

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

336

337 **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%

338

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

346

347 *Indirect Injection, M102E*

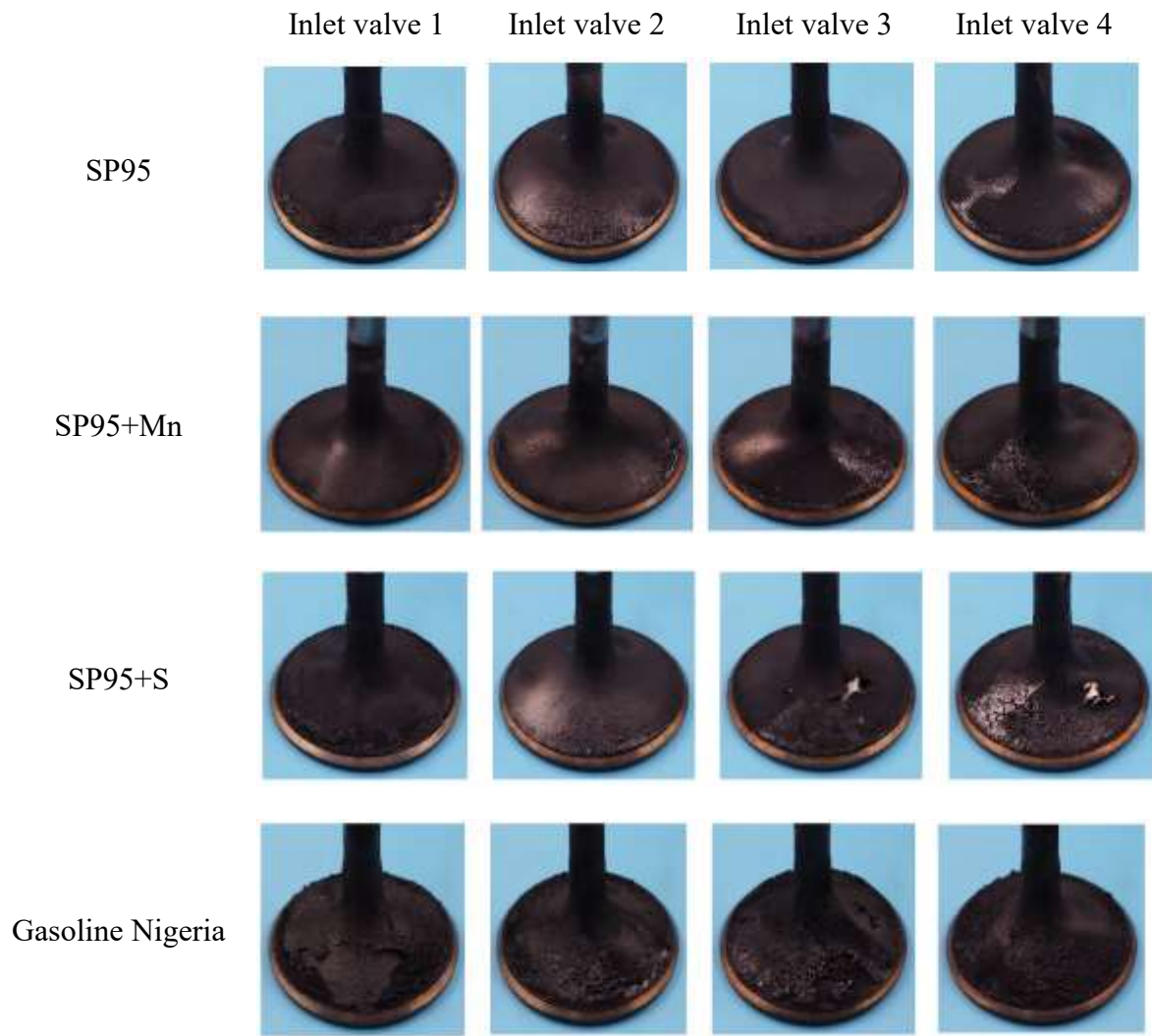
348 The pictures of the inlet valves and the cylinder heads after running the M102E engine tests are
349 presented in Figure 7 and Figure 8.

350

351

352

353



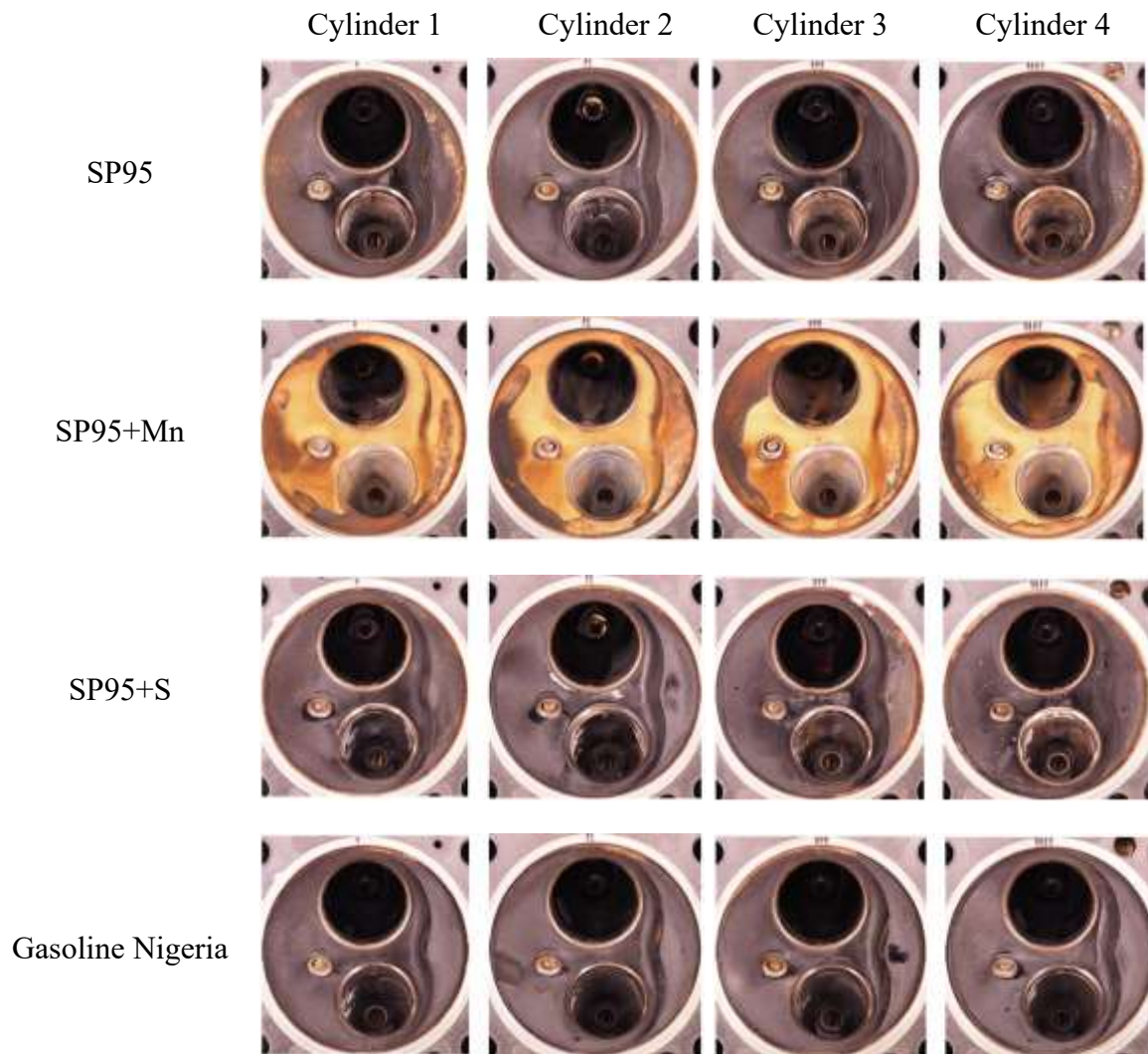
355 **Figure 7.** M102E inlet valves at end of test
356

357

358

359

360

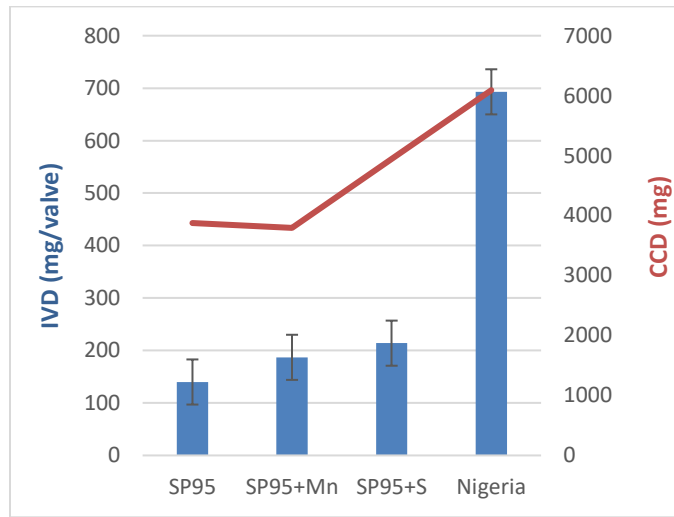


362 **Figure 8.** M102E cylinder heads at end of test
 363

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

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

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



373 **Figure 9.** M102E intake valve deposits (IVD) and total combustion deposits (TCD) at end of test
374
375

376 The test precision is defined in the precision statement of the test method F-05-93 in Section 11:
377 Precision for F-05-93 is ± 43 mg per valve for deposit of fuels without additives and 12 mg/valve
378 for deposit of fuels with additives. The precision is evaluated during the latest round robin. In our
379 case, the methylcyclopentadienyl manganese tricarbonyl (MMT) and the dimethyl disulfide
380 (DMDS) were not considered as additives but rather as contaminants of the original SP95 fuel,
381 hence the ± 43 mg precision retained. The total combustion deposits consisting of the sum of piston
382 top deposits and cylinder head combustion deposits (CCD) are also given for information purposes
383 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*

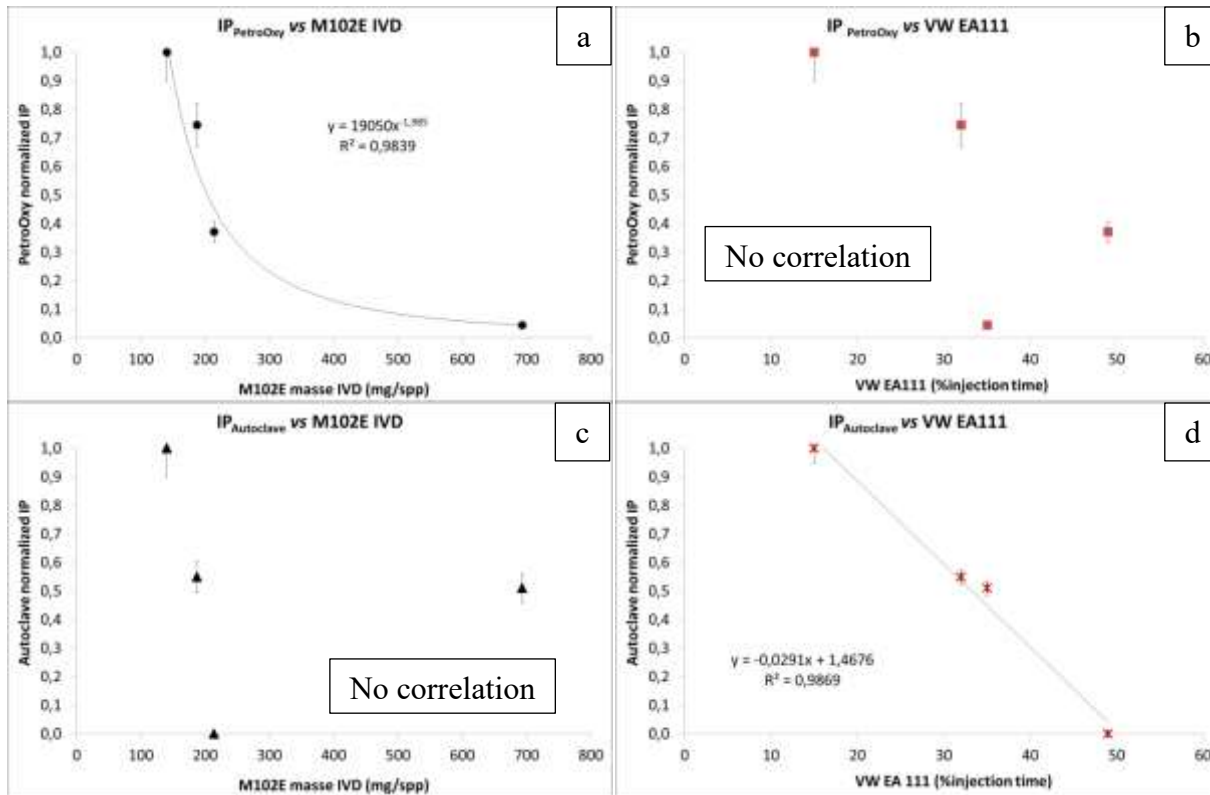
403 As discussed previously, by comparing the PetroOxy and Autoclave results it is clear that they do
404 not follow the same oxidation process, in most cases, the stability is around 50% lower using
405 Autoclave reactor than using a PetroOxy reactor.

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

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

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

424



425

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

428

429 CONCLUSION

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

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

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

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

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

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

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

473

474 **ABBREVIATIONS**

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

478

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484

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