

An Evaluation of the Speciated Exhaust Emissions Associated with South African Gasolines in an EU4 Vehicle

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ABSTRACT

An EU4 compliant vehicle was tested according to the ECE R83.05 procedure, with dilute and speciated modal analysis, on a European EN228:2004 gasoline and 3 South African gasolines, one of which is a synthetic gasoline made from coal using the Fischer-Tropsch process.

The synthetic fuel had broadly similar regulated emissions to the EN228 fuel while the two South African crude derived fuels had significantly higher HC and NO_x emissions. The synthetic fuel's exhaust olefins were similar to the EN228 fuel and aromatics were significantly lower than all the other fuels. The photochemical reactivity of the synthetic fuel was seen to be similar to the EN228 while the South African crude derived fuels were significantly higher.

INTRODUCTION

South Africa is in a unique situation in terms of vehicle technologies and transportation fuels. The national vehicle parc contains a broad cross section of technologies including older, pre emissions legislation technologies and the latest technologies conforming to the latest emissions legislations. The fuel landscape is even more unique in that there is a mix of fuels made in conventional refineries, made from crude oil, as well as significant quantities of synthetic fuel made from coal and natural gas. The mix of fuels is further complicated by the fact that the majority of fuel sold in the country is done so at altitudes of over 1200 meters above sea level. Thus these fuels have octane grades and volatility specifications suitable for these altitudes. The overall fuel specifications in South Africa still lag those in the highly regulated markets in some areas such as sulphur content.

The synthetic derived fuels are significantly different in their makeup to those derived from crude oil. While it has extremely favourable properties such as zero sulphur and lower comparative aromatics, the historically produced Sasol synthetic gasoline had higher levels of olefins. Although olefins should not be a challenge in

any future Sasol plants they are known to be highly reactive photochemical precursors [1]. Previous work on the emissions from synthetic fuels which was performed specifically to determine the impact of fuel octane on regulated emissions, had considered older technology vehicles and had not included exhaust speciation [2]. An investigation was thus conceived to evaluate the relative emissions performance, including relative photochemical reactivity of typical South African market fuels in a relatively advanced emissions controlled vehicle.

BACKGROUND

PHOTOCHEMICAL SMOG AND GROUND LEVEL OZONE – Polluted urban airsheds have long been associated with visible smog and high levels of ozone [3]. The visible smog has been identified as being due to a series of reactions with the precursors being various hydrocarbon species and oxides of nitrogen, in the presence of ultraviolet light, and is thus referred to as photochemical smog. The reaction chain is complex but products of the reaction include ozone (O₃) and NO₂; ozone is an irritant and NO₂ is a visible yellow/brown substance which leads to the visible smog [3]. As vehicles are known emitters of both of the chemical precursors, they have been targeted as the main contributors and this is one of the main factors in the institution of stringent vehicle emissions legislation.

EMISSIONS LEGISLATION – Strict vehicle emissions legislation has been implemented in developed markets such as Europe, the United States, some parts of Asia and Australasia. The legislation directly limits the total emissions of certain pollutants from the vehicle when driven over a predefined driving cycle. Vehicle emissions legislation has been accompanied by evolving fuel specifications which ensure that the market fuels are appropriate for the vehicles and specifically the various forms of exhaust after treatment: these are the so called enabling specifications. However, many countries around the world have not implemented emissions legislation or are lagging behind the most developed regions of the world in this regard. South Africa is

currently implementing a phased approach to catch up and is following the European specifications, although significantly lagging behind. Since January 2008, legislation requires all newly sold vehicles to be at the Euro 2 level or better, and the intention is to increase the level of emissions legislation until it is on par with Europe. Even though the legislation is relatively new, and only at the Euro 2 level, a significant number of vehicles sold currently and in the past number of years have been at much higher levels of emissions conformance, including at the highest level. This is because significant numbers of the vehicle sold are fully imported from developed markets.

The international emissions legislation limits the total permissible emission of a small number of pollutants, namely carbon monoxide, hydrocarbons and oxides of nitrogen and for diesel vehicles, particulate matter. It has long been understood that in terms of photochemical smog, the relative reactivity of the mix of hydrocarbons taking part in the chemical reactions can be more important than the amount of the hydrocarbons [3]. For this reason there is an increased awareness of the reactivity and there is some indication that legislators will attempt to control the reactivity as well as the total emissions in future legislation [1, 4].

PHOTOCHEMICAL REACTIVITY – As indicated above, it is not only the amount of hydrocarbons present in an airshed which is important in terms of the photochemical reactions, but their relative reactivities [1]. This has been well understood for some time and much research has been undertaken to identify the worst offending species and to assign appropriate reactivity factors to the most important hydrocarbons. Carter has been researching this aspect for many years and has developed a thorough understanding of the chemistry associated with photochemical smog [1]. The issue is complicated due to the fact that the reactivity of a given hydrocarbon is a function of the various concentrations of the other species in the airshed into which it is emitted. Thus there is no single reactivity which can be easily assigned to a given hydrocarbon. Carter has devised a reactivity scale which is widely used in studies of this nature. The scale is the Maximum Incremental Reactivity or MIR, and this essentially rates each hydrocarbon based on its highest reactivity given all possible variations of airshed.

OVERVIEW: SYNTHETIC GASOLINE

Sasol is the only commercial scale producer of finished transportation fuels made from coal with the so called Coal to Liquids or CTL process. Sasol's Secunda plant in the north-eastern part of South Africa produces gasoline, diesel and chemicals using Sasol's proprietary High Temperature Fischer-Tropsch (HTFT) process. A brief summary of the important property differences is presented here for completeness.

The HTFT process produces a synthetic crude which is a mix of aliphatic hydrocarbons and downstream refinery

processing is used to manufacture the finished transport fuels as well as other high value chemical products. The finished unleaded gasoline has nominal octane specifications of 93 RON and 83 MON. The fuels made in this process are very low in sulphur as the HTFT process itself is sulphur intolerant and thus effective sulphur removal from the gasified coal is utilised. Typical sulphur levels in the finished gasoline are less than 0.0010 % m/m or 10 ppm. Prior to the latest process upgrades at these facilities, the product was characteristically high in olefin content and contained up to 30 % m/m olefins while octane specifications are met with the addition of oxygenates in the form of TAME (tertiary amyl methyl ether) and reforming which raises the aromatic content. Typical values for these components would be oxygen content of 0.14 % m/m and aromatics at 29 % m/m. The relatively low aromatic fuel is also relatively low in density with typical values being in the region of 0.72 kg/l.

It is relevant to note that the significant altitude difference exceeding 1200 m between coastal regions and the highly populated inland regions of South Africa have resulted in a two level octane structure for the country. Coastal octane grades are 95 RON while the main grades retailing inland are 93 RON. The Sasol synthetic fuel products are marketed almost exclusively inland at the 93 RON specification, while crude derived fuels are manufactured at both octane levels.

TEST METHODOLOGY

FUELS - The test fuels matrix was made up of three market representative fuels from South Africa and one European market fuel conforming to EN228:2004. Two of the South African fuels came from crude based refineries of coastal origin, and the synthetic fuel from Sasol's synthetic fuels refinery in Secunda, which is at altitude and inland from the coast.

The fuels were analysed and speciated using Gas Chromatography – Mass Spectrometer and Gas Chromatography – Flame Ionisation Detection. The synthetic fuel contains oxygenates in the form of TAME (tertiary amyl methyl ether) at a nominal 13.5 % m/m, while the European fuel was found to have 2.8 % m/m of MTBE (methyl tertiary butyl ether) and 2.7 % m/m of ETBE (ethyl tertiary butyl ether). Neither of the South African crude derived test fuels was found to contain any significant quantities of oxygenates. The results of the analyses are presented below in Table 1.

The fuel olefin, aromatic and paraffin contents of all the fuels are indicated in the table. In terms of ozone forming potential, the short chain olefins are known to be especially reactive and thus significant [1]. The breakdown of the olefin content of the fuels is thus presented by carbon number.

At the time of execution of this project in 2005, heavy metal based additives were permitted in South African unleaded gasoline, and two of the fuels contained

manganese at levels of 18 and 14 mg/l in the form of methylcyclopentadienyl manganese tricarbonyl or MMT. The Sasol HTFT process manufactures gasolines with very low total sulphur. The synthetic fuel thus has the lowest total sulphur content of all the fuels evaluated, including the European fuel conforming to the EN228:2004 specification. The two South African crude derived test fuels have relatively high sulphur levels at 0.0323 and 0.1114 % m/m, this second fuel was marginally above the South Africa limit, which at the time that these tests were undertaken in 2005 was 0.10 % m/m. This limit has since been reduced to 0.050 % m/m for unleaded gasoline (January 2006).

The South African fuels were sampled in winter, and they reflect this with the elevated vapour pressures. Similarly, the European fuel was also sampled in winter and is shown to conform to the EN228 class C specification.

Table 1 Test Fuel Analysis

Property	Units	Results			
		Crude 1 Coastal	Crude 2 Coastal	Synthetic 1 Inland	EN228 European
Density @ 20° C	kg/l	0.7551	0.7568	0.7224	0.7326
Distillation corr to 101.325 kPa					
IBP	° C	35	35	39	30
10% evap	° C	52	57	58	42
50% evap	° C	115	112	93	88
90% evap	° C	164	168	140	152
FBP	° C	201	203	181	194
Residue	vol %	1.0	1.0	1.0	1.0
Reid vapour pres (RVP)	kPa	72	71	61	
Vapour Pressure DVPE	kPa				86.1
Octane rating					
Research Octane	RON	95.6	97.2	93.7	95
Motor Octane	MON	86.1	86.6	84.4	84.8
Flexible volatility index (RVP + 0.7E70)		90	84	77	
Total Sulphur	% m/m	0.0323	0.1114	0.0002	0.0008
Manganese content	mg/l	-	18	14	-
Olefin content	% m/m	7.6%	11.0%	19.2%	3.9%
Aromatic content	% m/m	34.6%	38.7%	25.3%	29.8%
Paraffinic content	% m/m	57.8%	50.3%	55.5%	66.3%
Olefinic breakdown					
C ₄	% m/m	1.6%	2.1%	0.8%	
C ₅	% m/m	2.3%	3.9%	4.3%	
C ₆	% m/m	1.7%	2.9%	6.9%	
C ₇	% m/m	0.8%	1.0%	3.8%	
C ₈₊	% m/m	1.1%	1.1%	3.3%	
Oxygenates					
TAME	% m/m			13.6%	
MTBE	% m/m				2.8%
ETBE	% m/m				2.7%

VEHICLE - An EU 4 compliant test vehicle was chosen for the investigation specifically to evaluate the performance of relatively advanced vehicle technologies from an emissions control perspective. While vehicles of this technology level are not necessarily prevalent in the existing vehicle parc in South Africa, they are being sold in increasingly significant numbers. Furthermore this technology is more representative in terms of international relevance.

The vehicle used was a 2004 MY, Toyota Corolla with 5 speed manual transmission and a 1.4 litre displacement engine. The vehicle indicated approximately 4300 km on the odometer at the onset of the project.

Several tests were performed initially to ensure that the vehicle was repeatably compliant with the EU 4 emissions limits.

TEST METHOD - The vehicle emissions testing was performed according to the ECE R83.05 directive (EU 4) procedure. Conventional CVS (constant volume sampling) bag sampling was performed as per the legislated test procedure. Simultaneously, raw and dilute modal analyses were performed. The dilute modal analysis uses the conventional gas analysers to continuously sample and measure the gas concentrations in the dilution tunnel of the CVS system. This provided a second-by-second record of the regulated pollutants emitted.

The raw modal analysis was performed by a SESAM FT-IR system (System for Emissions Sampling and Measurement Fourier Transform – Infra Red spectroscopy). This is a multi-component gas analyser which measures a sample of the raw exhaust gas using the FT-IR principle of operation. In this application the sample was a post-catalyst sample and thus can be considered as a tailpipe sample. These results thus provide a speciation of the tailpipe emissions. The unit was calibrated to provide the following 21 species:

CH₄, H₂O, NMHC, MECHO, SO₂, COS, HCHO, NO, NO₂, N₂O, NH₃, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₄H₆, NC₅, IC₅, C₆H₆, C₇H₈ and C₃H₈

The stipulated driving cycle used for the testing was the NEDC2000 (New European Driving Cycle) which was made up of two distinct phases. Phase 1 comprises a cold start of the vehicle from a pre-conditioned 22° C, followed by the driving of 4 consecutive, identical driving sequences. This phase, known as the ECE or urban driving cycle, is characterised by relatively low average speeds, engine loads and exhaust temperatures and a number of stop and pull away events. This is intended to simulate typical city or urban driving conditions from a cold start, and thus captures tailpipe emissions produced prior to the catalyst attaining the necessary minimum operating temperature to be effective in emissions reduction. Phase 2, known as the Extra Urban Driving Cycle (EUDC), is characterised by higher maximum and average speeds and is intended to simulate highway driving conditions. The general characteristics of the driving cycle are presented below in Table 2. Both portions of the driving cycle produce a result in g/km for each of the emissions measured. A combined result is then generated from a distance weighted sum of these two intermediate results. It is this

single combined result which is used for the vehicle regulatory process.

It is important to note that the legislated driving cycle is primarily intended to evaluate the relative emissions performance of vehicles for the application of vehicle emissions regulation. While the driving cycle is historically based on typical vehicle usage patterns, it does not necessarily simulate the typical in use emissions of vehicles: essentially the relative weighting of the two portions of the driving cycle is relatively arbitrary. This does not detract from the primary purpose of the testing process, but caution should be applied when using these results to directly infer real in-use differences in emissions performance of vehicles and especially fuels. For this reason, where practical, the results of both the ECE and EUDC portions of the driving cycle are presented separately here and not only the combined result.

Table 2 Characteristics of the NEDC2000 driving cycle.

ECE - urban driving cycle (all 4 repeats)		
Duration	(s)	780
Number stop / pull away events	(-)	12
Maximum speed	(km/hr)	50
Average speed	(km/hr)	18.7
Distance	(km)	4.052
EUDC - extra-urban driving cycle		
Duration	(s)	400
Number pull away events	(-)	1
Maximum speed	(km/hr)	120
Average speed	(km/hr)	62.6
Distance	(km)	6.955

TEST PROTOCOL - As the vehicle history was unknown at the time of testing, three repeat tests were performed using the European EN228 fuel. This was done to ensure that the vehicle emissions were stable, conformed to the EU 4 emissions levels and to indicate test repeatability. The test fuels were then tested once each in the following order: synthetic, South African crude 2 (SA crude 2), South African crude 1 (SA Crude 1). Two consecutive bracket tests on the European EN228 fuel were conducted at the end of the test series.

The testing protocol followed was as specified by the ECE R83.05 procedure, including the vehicle preconditioning run and controlled temperature soak period. A thorough flushing procedure was used to minimise any fuel carryover effects between the fuels.

It was appropriate to consider the test process in light of the fact that the test was being used to compare fuels, whereas the legislated test is inherently intended to be a vehicle test using a defined reference fuel: it is used to indicate whether vehicles meet the legislated emissions levels. Amongst other factors, the pre-conditioning run, which comprises driving the vehicle through the prescribed NEDC2000 driving cycle prior to the

temperature controlled soak, is intended to achieve the following:

- allows the vehicle control system to adapt to the fuel used for the test
- ensures that the evaporative control canister is purged, according to the engine control strategy, prior to the temperature soak.

The first of these aspects is important as the vehicle will run in an open-loop fuel control mode until the engine is warm enough to provide acceptable driveability without the requirement for rich air-fuel ratios, which can take of the order of 30 to 100 seconds. Modern vehicles overall emissions can be dominated by the tailpipe emissions during this period. Thus if a fuel with different C:H:O ratio is run without the engine control having undergone the necessary adaptations, the emissions can be significantly different during this phase. It is very likely that the engine control unit will make the necessary adaptations to the test fuel during the preconditioning run and this is assumed to be the case. Thus when the test procedure is used to evaluate fuels, it is ensured that the engine will operate consistently and as intended in terms of stoichiometry.

The second of these aspects should similarly not influence the test procedure in terms of the ability to differentiate the performance of different fuels.

DISCUSSION AND INTERPRETATION OF MEASUREMENTS

REGULATED EMISSIONS – The regulated emissions for gasoline vehicles are hydrocarbons (HC) oxides of nitrogen (NO_x) and carbon monoxide (CO). The results of the eight tests are presented below in Table 3 and Figure 1. The results are presented separately for the entire test (combined) and for the two distinct phases of the test, the lower speed initial ECE portion (Phase 1) and the higher speed EUDC portion (Phase 2). Considering Figure 1, it is apparent that for all three of the regulated emissions there are significant differences between the fuels.

Considering the reproducibility and sensitivity of the test, it is seen from the first three results, all for EN228, that there is good test repeatability. Considering the combined results of the three regulated emissions, differences of greater than 0.02 for HC, 0.08 for CO and 0.001 for NO_x can be considered significant.

It is apparent from Figure 1 that the two South African crude derived fuels have significantly higher HC and NO_x emissions than both the synthetic fuel and the EN228 fuel and that this trend is seen in both phases of the test. For the HC emissions a consistent trend is noted with Phase 1 dominating the combined result for all of the tests. This is not noted for NO_x whereby the first phase dominates for the EN228 and synthetic fuels but the second phase dominates for both of the South African crude derived fuels. Carbon monoxide emissions indicate a slightly different trend whereby the synthetic

Table 3 Emissions results for the regulated emissions and carbon dioxide.

Results: Combined (g/km)								
Fuel	European EN228	European EN228	European EN228	Inland 1 Synthetic	S.A. Crude 2	S.A. Crude 1	European EN228	European EN228
Test Order	1	2	3	4	5	6	7	8
HC	0.040	0.042	0.042	0.044	0.079	0.070	0.047	0.048
CO	0.833	0.817	0.898	1.080	0.826	0.827	0.985	1.033
NO _x	0.006	0.007	0.006	0.007	0.071	0.044	0.018	0.018
CO ₂	169.1	163.6	163.9	160.6	167.3	169.2	162.6	164.6

Results: Phase 1 (ECE) (g/km)								
Fuel	European EN228	European EN228	European EN228	Inland 1 Synthetic	S.A. Crude 2	S.A. Crude 1	European EN228	European EN228
Test Order	1	2	3	4	5	6	7	8
HC	0.101	0.106	0.106	0.113	0.148	0.135	0.100	0.103
CO	1.449	1.387	1.486	1.427	0.509	0.576	1.239	1.406
NO _x	0.012	0.015	0.014	0.015	0.034	0.027	0.021	0.017
CO ₂	208.6	197.9	198.9	194.4	204.7	206.2	197.7	201.0

Results: Phase 2 (EUDC) (g/km)								
Fuel	European EN228	European EN228	European EN228	Inland 1 Synthetic	S.A. Crude 2	S.A. Crude 1	European EN228	European EN228
Test Order	1	2	3	4	5	6	7	8
HC	0.004	0.004	0.004	0.004	0.039	0.032	0.017	0.015
CO	0.467	0.479	0.547	0.876	1.012	0.974	0.837	0.815
NO _x	0.003	0.003	0.002	0.002	0.093	0.055	0.016	0.018
CO ₂	145.6	143.3	143.1	140.7	145.4	147.5	142.1	143.2

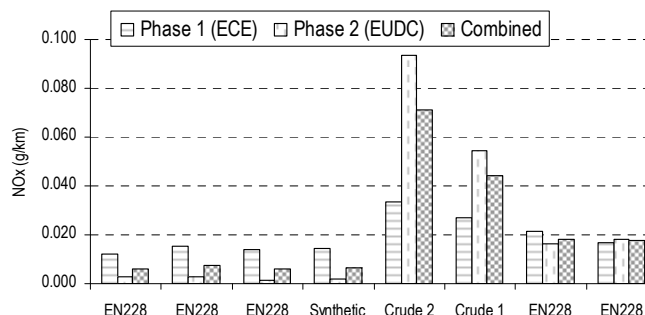
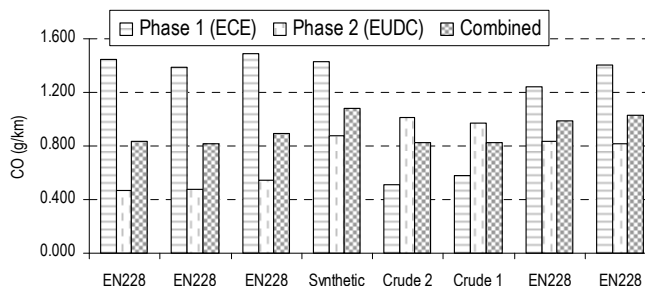
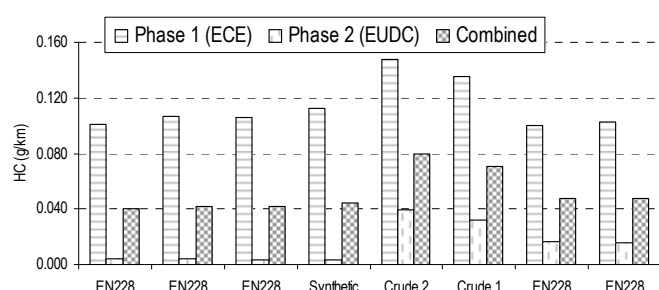


Figure 1 Regulated emissions results.

fuel is the highest emitter, and the South African crude derived test fuels are similar to the EN228 in terms of the combined result. However, the phase specific emissions are again different for the two South African crude derived fuels whereby these fuels have higher CO emissions during the second phase than the first and the synthetic fuel and the EN228 have higher emissions during the first phase than the second.

Subsequent analysis revealed that the order of the fuel testing influenced the results and for this reason the order shown in diagrams reflects the chronological order in which the tests were conducted. The order of the testing was reference EN228 (three tests), SA synthetic, SA crude 2, SA crude 1, bracket EN228 (two tests).

An interesting trend is immediately apparent when considering Figure 1. As stated above, the expected reproducibility and sensitivity of the test is of a high standard as indicated by the three consecutive EN228 tests performed at the outset of the trial. Comparing

these results with the two bracket tests with EN228 at the end shows a shift in emissions greater than the indicated repeatability of the test procedure. The overall effect seems to be dominated by an increased emission during the second phase of the test. The second phase is characterised by a fully warmed catalytic converter and thus shifts in emissions during this phase are usually related to shifts in catalyst efficiency.

As previously noted, two of the fuels had relatively high sulphur levels (0.0323 and 0.1114 % m/m). The effect of sulphur on catalyst efficiency is well known [4]. Sulphur is known to act as a catalyst inhibitor[†] and as a poison[†]. The effects are seen in terms of increased catalyst light-off temperature and in reduced conversion efficiencies. Catalyst formulation and application differences can influence the specific response to fuel

[†] Catalyst inhibitor – the effect is reversible by removal of the offending species from the feed-gas

[†] Catalyst poison – the effect is not reversible