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Petrol in Nigeria: a fuel or a killer?“ Is shift to hydroisomerisation not overdue?”

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ABSTRACT

The paper reports key issues associated with the used of leaded gasoline (petrol) in Nigeria. While many global countries have indicated strong commitment for a shift to most suitable and environmentally sustainable gasoline upgrading option (i.e hydroisomerisation), addition of 0.6-0.74 g/L of tetraethyl lead remain the only upgrading option given priority in Nigeria, due to government negligence. Millions of people have suffered from various associated illness with numerous number of deaths, especially in young children below the age of seven. The soils, foods and waters are severely polluted in the major trafficking communities. The availability of favorable factors such as adequate infrastructure and capital for hydroisomerisation in the country indicated the process to be a long overdue process that was neglected due to poor government concern and serious corruption problem in the energy industry. It is therefore recommended here that the public should put the issue in the fore front of the current protest for lucrative workers’ salary.

Introduction

Since the discovery of the high efficiency properties of automobile engines fed with “anti-knocks” by the automotive industry in the early 90s, the search for the most appropriate of these additives has been intensified. This focused primarily on striking a balance between enhancing the octane properties of the fuel, economic viability and environmental sustainability. Tetraethyl lead (TEL) was the first key gasoline anti-knock that received rapid global acceptance since the discovery of its application by Thomas Midgely in 1921 (Nadim et al., 2001), especially due to relatively cheap cost of production. However, although TEL is still in used in many developing countries, either due to government negligence or capital and infrastructural challenges, health and environmental threats necessitate its phase-out towards the end of 20th century by developed nations. Subsequently other measures were developed as replacement. These include the addition of methylcyclopentadienyl manganese tricarbonyl (MMT), oxygenates such as methyl tertiary butyl ether (MTBE) and ethanol and aromatic compounds. MMT combustion involved the emission of manganese dioxide (MnO_2), a serious pollutant that causes severe respiratory problems and hypertension. Oxygenates and aromatics produce carcinogens. The aromatics have also recorded destruction to catalytic converters in the automobile engines (Mokaya et al., 1997; Lincoln, 2000; Moushey and Smirniotis, 2009).

The only alternative option that remains most acceptable and is increasingly gaining global attention is the “isomerisation” of the linear alkanes in the gasoline feed to their corresponding isomers by a process called hydroisomerisation. While numerous studies have been carried out in many parts of the world on the process and its economic feasibility to petroleum refineries, little is available in Nigerian records despite the global ranking of the country in terms of oil production, consumption and environmental and health challenges. The paper therefore tailors key issues of why a shift to the hydroisomerisation process is necessary and how it can promote sustainable human development in Nigeria.

Leaded Gasoline in Nigeria

While several other octane enhancers are used in different parts of the world, Nigeria is one of the global countries that recorded the used of highest TEL concentration as the only gasoline octane promoter (Table 1). However, subsequent to the “Clean Air Act” of 1996 and beyond that saw complete phase-out of TEL in UK, USA, New Zealand and Canada, the Nigerian government promulgated an initiative titled “Phasing-out leaded gasoline in Nigeria, 2002” as a response to the World Bank Clean Air Initiative in sub-Saharan African cities in 2001.

Leaded gasoline in Nigeria contain lead in the concentration range of 0.65 to 0.74 g/L, the initiative proposed to reduce the concentration to 0.15 g/L and finally to zero level. However, numerous studies revealed that, the initiative is just on paper (Orisakwe, 2009) due to government negligence. The consequences have been severe environmental problems.

Lead pollution from automobile emissions in Nigeria had been extensively studied and documented in various Nigerian and international publications. Nriagu et al. (1997) investigated blood lead levels in 87 children aged 1-6 years from Kaduna state. An average of 10.6 µg/dl was found, with some children having up to 30 µg/dl. The values exceed the maximum allowed limit of 10 µg/dl recommended by Centre for Disease Control (CDC) and correlated linearly with the distance of house from highly trafficking roads, as well as, whether a family owns a car or not. At the beginning of 21st century Federal Environmental Protection Agency (FEPA) of Nigeria examined the lead concentrations in soils from roads, markets and motor parks of Lagos, Aba, Abuja, Ibadan, Kaduna and Port Harcourt.

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The results revealed elevated and health threatening concentrations (Table 2). It could be seen that the highly trafficking cities of Lagos, Ibadan and Kaduna recorded the highest lead levels.

Recently, Ogunstein and Smith (2007) found in Otukpo that 35% of 306 children (1-6 years) examined had blood lead level exceeding the CDC limit, with some having up to 31.8 µg/dl. Although there was good correlation with other industrial sources, the highest exposures were attributed to gasoline sources. Orisakwe (2009) have argued that all categories of people in the country are seriously affected. He reported one of the worst studies, with all the respondents having lead levels exceeding the CDC guidelines (Table 3).

Shridhar et al. (2011) reported high degree of contamination in different samples from Ibadan and Lagos. Drinking waters exhibited up to 2.16 mg/L, foods contained 18.5 mg/Kg and soil samples from residential and mechanic areas showed 81.91-4060.7 and 140.0-5454.6 mg/Kg respectively. The highest concentrations in all cases correlated linearly with level of traffic and gasoline usage.

Consequences of Lead Exposure

Exposure to lead has been identified to have severe health consequences. Adults have shown sleeplessness, muscular weakness, fatigue, headache, body rashes and subsequent death (Galadima and Garba, 2011). Children are particularly the most vulnerable to brain damage and sudden death. Millions of these cases have been reported to date, the most recent is the "tragic Zamfara lead poisoning, 2010" that claimed the lives of over 500 children and leaves many with severe mental deformations in just seven months. The affected children showed unusual and frightening symptoms (Galadima et al., 2011a).

"Gastro-intestinal upset, skin rashes, changes of mood; some were lethargic, some partially paralyzed and some had became blind and deaf. The worst affected were coming to small Ministry of Health Clinics with seizure that could last for hours and would some times lead to coma and then often to death" (Figures 1a-c).

Figures 1a, b & c: Children from Zamfara state, Nigeria suffering from lead poisoning, being treated at the Ministry of Health Clinics by experts from Blacksmith Institute and Médecins Sans Frontières.

Ignorance is a serious factor that is increasingly contributing to the problem. For example, a study by Adebamowo et al. (2006) showed that majority of the 600 people interviewed in Ibadan, a key city with many schools and high level of education, did not have a satisfactory knowledge about lead exposure in residential areas, how to prevent it and the role of nutrition in diminishing the impact of exposure. People consider emissions from automobile exhausts as normal as breathing air. Children are allowed to play in polluted soils and waters and in most cases absorb lead through their regular hand to mouth activities.

Analysis and treatment cost for the exposed individuals is also a factor that should be considered. The affected people are mostly poor, living below a US Dollar daily and therefore cannot afford the internationally recommended chelation therapy for treating lead poisoning. Serious corruption on the other hand, hinders the government ability to fully finance hospitals, dispensaries and post-secondary health institutions, limiting the availability of trained health personals. Total reliance on foreign aids (see for example figure 1a-c) cannot solve the problem, and consequently the people area alarmingly dyeing of the poisoning.

The various reported literature indicated the used of leaded gasoline to be the major source of lead poisoning in Nigeria, the key question that remain unanswered is "should we allow this to continue or protest for a shift to a sustainable option?".

Gasoline Upgrading by Hydroisomerisation

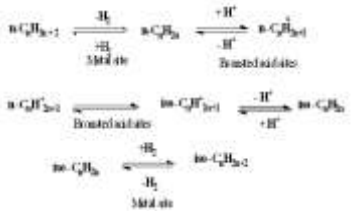
While lead poisoning remains a silent killer in Nigeria, a shift to hydroisomerisation in countries like USA and UK indicates an alarming decreased in exposure for both adults and children. For example, a comprehensive study titled National Health and Nutritional Examination survey conducted by US Centers for Disease Control and Prevention confirms that the mean blood lead level in the US decreased from 16 µg/dl to 3 µg/dl (i.e from severely toxic to non-toxic level) following the leaded gasoline phase-out (Nadim et al., 2001). The hydroisomerisation process which does not require the addition of any life threatening chemical, involved the conversion of the linear alkanes in the gasoline feed to their corresponding isomers because the latter have higher octane numbers (Table 4). It occurs over a bifunctional heterogeneous catalyst (scheme 1) at high hydrogen pressure ($\geq$ 20 bars), although recent studies indicated that the reaction can be achieved at atmospheric pressure (Kinger et al., 2002; Woltz et al., 2006; Moushey and Smirniotis, 2009; Komatsu, 2010) . The mechanism of the process involved three elementary steps.

I. The alkane is dehydrogenated,

II. Then the alkene formed is adsorbeds on a Bronsted acid site, forming an alkoxy group (a carbenium ion in the transition state), which isomerises and eventually desorbs.

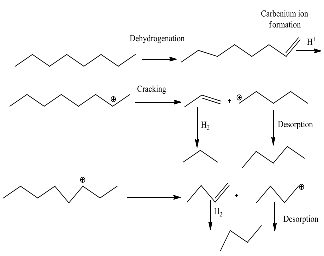
III. Finally, the iso-olefin is hydrogenated to the iso-alkane.

Therefore, the catalysts are bifunctional, with a metal (e.g. Pt, Pd, Ni) catalyzing the hydrogenation/dehydrogenation step and an acidic function for the formation and isomerisation of the alkoxy group/carbenium ion. The metal component also helps reduce catalyst deactivation by hydrogenating coke precursors. The isomer yield is limited by the thermodynamic equilibrium between the iso and n-isomers. As the former are thermodynamically the more favoured at lower reaction temperatures, the reaction temperature should be as low as possible.



Scheme 1: Bifunctional route to hydroisomerisation process.

Since the initial commercialization of the hydroisomerisation process at the begining of 20th century, the refineries and associated research organizations have intensified the search for the most appropriate catalysts. Chlorinated alumina and Freidel Craftcatalysts such as $AlCl_3$ were the first materials employed (Galadima et al., 2009). They are active at low temperatures but were abandoned due to serious corrosion and disposal problems. Heteropoly acids, their salts and metal-modified derivatives have been tested given good isomerisation selectivity (Ono, 2003). However, thermal stability, acid sites titration and poor resistance to poisons even in trace quantities limited their continuous exploitation. Oxides of molybdenum and tungsten are only partly studied, but the available literature indicated the materials to exhibit long induction period (could be up to 24 hours in some cases). Pt and Pd loaded zeolites, especially the mordenites, are the most accepted hydroisomerisation catalysts in used today. However, although modification is possible, hydrocracking and hydrogenolysis on the active sites remain a serious problem with these materials (see scheme 2 for example). The refineries also proposed a shift to cheaper materials of better or comparable activity. These, will require the refineries to focus on the evaluation of molybdenum carbide catalyst systems. The carbide materials are generally cheaper than zeolites, and if appropriately designed can yield better activities. They have been previously tested in refining processes such as aromatization, hydrodesulfurisation (HDS) and hydrodenitrogenation (HDN), yielding good activity. They are thermally stable and with good structural properties suitable for hydroisomerisation (Gomes et al., 2005; Galadima et al. 2011b).



Scheme 2: Examplified mechanistic cracking/hydrogenolysis of n-octane over metal-zeolite catalysts.

Prospects of Nigerian Refineries for Hydroisomerisation

Modern refineries are currently designed with in-built units for the hydroisomerisation process. In Nigeria, Warri and old Port Harcourt refineries were built without these units, however, the new Port Harcourt and Kaduna refineries possess these compartments but yet the hydroisomerisation process is not given any emphasis. As modification to the former is also possible, the process should have been in proper used in the country for over a decade. The refineries if appropriately utilized can supply unleaded gasoline to not only Nigeria but also some sub-Saharan African countries due to adequate refining capacities (Table 5). Less than 50% of the total production would be required for the country daily, indicating that over 250,000 bpd are available for export. Shifting to the process is also economically cheaper. Lofgren and Hammar (2000) showed that for the European Union countries the price of gasoline fell significantly with the phasing-out of TEL. They attributed the failure of global countries that still used TEL to ignorance of its economic feasibility.

The huge cost of obtaining TEL would be eliminated and on the other hand, the catalysts required for the hydroisomerisation process are already in used in the refineries for related purposes, they can be recycled and reused. This in totality can have significant positive effect for the common man, by decreasing the net costs of purchasing the fuel and goods and services.

Conclusions and Recommendations

Lead poisoning associated with combustion of leaded gasoline is a silent killer in Nigerian communities that seems to be given inappropriate consideration due to peoples' ignorance, unconceivable government negligence and the worst corruption problem in the petroleum sectors. It is particularly disappointing to see that *"despite the government claim of phasing out leaded gasoline in the last ten years, this product is still in 100% circulation, crippling human development and rendering the product a KILLER rather than a fuel"*. The most acceptable hydroisomerisation option used in other countries is a long overdue process that was neglected in Nigeria despite the existence of several factors favoring its implementation. There are adequate infrastructures, capital and conducive atmosphere for the process. Despite the relevance of the process in mitigating lead poisoning, it is economically cheaper and can promote access to refining jobs by many jobless science and engineering graduates through establishment of more refineries and research organizations. The latter can work unanimously with the refineries in evaluating the most appropriate catalyst materials and reaction conditions. Conclusively, the Nigerian public should include this issue in the current protest for new minimum wage and the re-inclusion of fuel subsidy.

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Table 1: Amount of TEL in gasoline by country.
***Source:* Thomas and Kwong (2001)**

Country	TEL Concentration, g/L
Nigeria	0.65-0.74
Algeria	0.60
South Africa	0.33
Libya	0.60
Morocco	0.30
Tunisia	0.50
Sudan	0.40
United Kingdom (UK)	0.00
United States of (USA)	0.00
Highest in the World	1.0

Table 2: Lead levels in soils from some Nigerian cities. *Source*: Enemari (2001).

City	Lead Concentration (mg/Kg)
Lagos	24.9-121.61
Ibadan	22.41-121.61
Kaduna	14.40-126.81
Abuja	5.24-89.92
Port	28.38-67.78
Harcourt	2.34-55.01
Aba	

Table 3: Blood lead levels in Nigerian people by category. *Source:* Orisakwe (2009).

Category of Respondents	Blood lead level (μg/dl)
Factory workers	17.0±4.0
Secondary school	35.0±7.9
students	18.1±6.4
Traffic warders	11.4 to 25.0
Others	

Table 4: Octane numbers of some alkanes and their isomers.

Compound	Octane Number
n-Hexane	26.00
2-Methylpentane	73.50
3-Methylpentane	74.30
2,2-dimethylbutane	93.40
2,3-dimethylbutane	94.30
n-Heptane	0.00
2-Methylhexane	45.00
3-Methylhexane	55.80
3-Ethylpentane	69.30
2,3-dimethylpentane	89.00
n-Octane	-15.00
2-methylheptane	23.80
3-methylheptane	45.00
2,2,4-Trimethylpentane	100.00

Table 5: Nigerian refineries and their capacities

Refinery	Capacity (bpd)
Kaduna Refining and Petrochemical Companies	110,000
Old Port Harcourt Refining Company Limited	60,000
New Port Harcourt Refining Company Limited	150,000
Warri Petrochemical and Refining Company Limited	125,000
Total	445,000