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Effect of Methylcyclopentadienyl Manganese Tricarbonyl Injection on the Catalytic Reforming Process
Improvement of the Gasoline Ron in an Oil Refining Installation

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***Abstract*:**

Gasoline is produced by mixing reformat gotten with light essence. The catalytic reforming process that occurs under severe conditions causes damage to the catalysts. To preserve the cycle duration of the catalysts, a Refining Company is planning to reduce the RON (Research Octane Number) of the reformat and to add the MMT (Methylcyclopentadienyl Manganese Tricarbonyl) in abbreviation MMT, to the mix. This additive should improve the gasoline. The present study shows out that for this purpose, the reforming process would operate under less severe condition and would produce a reformat with 92.5 RON instead of 95. The working temperature will be 5°C less and the cycle duration would gain three months with a reduction of the consuming of fuel by the furnace. Under this new working temperature, even so the produced gas phase flow would be less; 1.35 ton per hour instead of the formerly 1.72 ton per hour, it should be richer in hydrogen; 96% instead of 92% obtained formerly. This gas could be directly used in the hydrocracking process.

***Keywords*:** Naphtha; Reformat; MMT; RON; Lead free gasoline; Flow back; Injection.

1. Introduction

Formerly, the Lead Tetra Ethyl (LTE) was added to gasoline after elaboration to ensure a good carburetion to the engine [1, 2]. Since its prohibition for environmental and health problems [3, 4, 5], the refiners produce a fuel named lead free gasoline, characterized by a RON (Research Octane Number).

The N-paraffinic hydrocarbons burn with explosions that cause damage inside the engine. However, iso-paraffinic hydrocarbons burn with harmony and without detonation which ensures proper operation of the engines [6]. The difference between these hydrocarbons is expressed by the RON [7, 8]. This number is determined with a particular engine (CFR) that works at 600 rpm.

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A Refining Company produces lead free gasoline with 91 RON. The process consists in the mixing of reformat with 95 RON to light gasoline with 75 RON. The production of reformat with 95 RON induces operation under very severe conditions; conditions that must bear the catalysts [9, 10]. Therefore, pauses are needed to regenerate the catalysts. These periods of downtime represent losses for the company.

In order to minimise these losses, the company must reduce the number of pauses that are needed by operating under less severe conditions. In such case, the reformat that would be produced would be with less RON. The lead free gasoline so produced would not respect the 91 RON required.

An operation of increasing the RON by use of an additive must so be necessary. It is on this purpose that the use of the MMT molecule as additive is studied. The company is projecting to realize a mix with a reformat with 89 RON and light gasoline. The mix would be boosted by adding MMT to make lead free fuel with 91 RON.

The target of this work is to determine the RON of reformat required and the composition of the mixture to be realized, to elaborate the new operating conditions and establish the technical feasibility of adapting a post for the injection of the additive, on the existing plant.

2. Materials and method

The MMT (Methylcyclopentadienyl Manganese Tricarbonyl) or $C_9H_7MnO_3$ is an organometallic molecule elaborated by AFTON CHEMICAL CORPORATION, a Canadian chemical firm. This product under liquid form presents physical properties such as [9]:

- A very low vapour pressure; 1.8mm Hg at 25°C;
- A stability at high temperature;
- A chemical compatibility with all kind of fuel and components;
- A dew point of freezing at -1° C;
- A flash point at 42 °C;
- Very sensitive to light that makes it to decompose.
- A density of 1.1 at 20°C.

The MMT is used at very feeble concentration, 8 to 36 ppm of manganese and presents the advantage of increasing the RON of fuel. Figure 1 shows the gain in RON compared to lead addition.

To augment the RON of two points, one must add 0.074 g of MMT per liter of gasoline. It ameliorates the quality of gas emitted during refining and is very useful to make the gasoline correspond to the required new speciation.

This molecule is also supposed to protect engine against damages, to improve the efficiency of catalytic converter, to protect valves and to reduce gas emission from engines. The product of the combustion MMT annihilates phosphorus and reduces its deposit on the catalyzers [11].

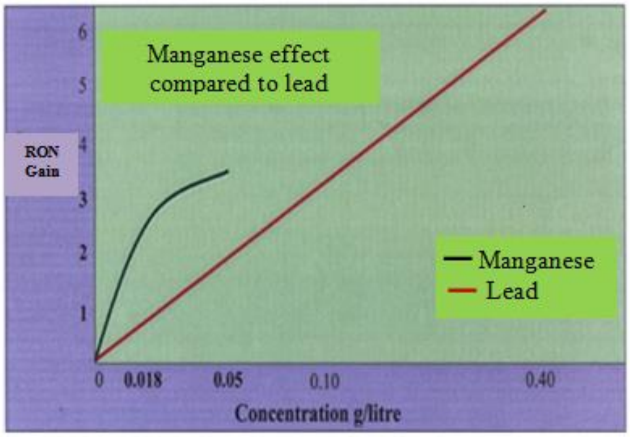

Fig. 1. Effect of MMT on the RON compared to Lead Tetra Ethylated [3].

The MMT is presented under solution state, like a mixture of solvent naphtha light aromatic, 1 2 5-trimethylbenzene, and distillates hydro treated light, N-propyl benzene, Xylen and cumen. The final solution is commercialized under the name of HITEC 3062 Octane Booster and contains 62% MMT and 38% of other components. If the MMT is known for toxicity, its high photosensitivity causes its decomposition into harmless products [12].

This study is focused on the post of unleaded fuel production which process consists on the mixing of light gasoline and catalytic reformat. The determination of the preheating temperature of the naphtha before it enters the reforming reactor to produce a reformat with a given RON was also treated. The chemical engineering software which are PRO II and INSTRUCALC [13, 14] have been used, and data from INFOPLUS [15] that gathers all the parameters of functioning and the speciation of the products elaborated in the firm.

3. Results and discussion

3.1 Effect of the change of the RON on the reforming process

Considering the RON of the reformat and the light gasoline produced, the proportion to be mixed to produce lead free gasoline is given by a mathematic relation. Noting as N_1; N_2 and N_0, the respective RON of reformat, the light gasoline and the lead free gasoline, the proportions are given below (Eq. (1)):

$$N_1 = 95 \qquad \frac{N_1 - N_0}{N_1 - N_2} \times 100 = \%\,LG$$

$$N_0 = 91 \qquad (1)$$

$$N_2 = 75 \qquad \frac{N_0 - N_2}{N_1 - N_2} \times 100 = \%\,(C_5^+)$$

With LG, the light gasoline and C_5^+ indicating the reformat. The calculation gives the respective proportions of 80% C_5^+ for 20% LG. For the same proportion, to attain a RON of 89 the new RON of the reformat can be determined by Eq. (2):

$$\%C_5^+ \times N_1 + \%LG \times N_2 = N_0 \qquad (2)$$

The calculation gives a value of N_1 equal to 92.5. For this value of RON, the new parameters and thermal condition for reformat production are determined and compared to former ones in Table 1.

Table 1
Evolution of the parameters for changing the RON

	95 RON	92.5 RON
Reformat Yield	88.5%	90.50%
Cycle duration	15 months	18 months
Temperature of entry	480°C	475°C

It clearly appears that producing a reformat with 92.5 RON improves the yield and reduces the temperature of entry. The duration of cycle is also improved. According to the feeding flow, the quantity of naphtha treated per year is around 600.000 ton. The yield under the new conditions, the gain in reformat produced is given by:

$$Q_{refor} = \frac{Rdt_{refor} \times Q_{napht}}{100} \quad (3)$$

With Q_{refor} the quantity produced, Q_{napht} the quantity used and *Rdt* the yield under new conditions. The gain per year for the reformat should be of 11.900 ton.

Since the inlet temperature of the furnace decreases of 5°C, this represents a saving in fuel supply. Considering Q_{FG} the flow of the combustible and Q the energy needed to increase the temperature of 5°C, both values are linked by the relation:

$$Q = Q_{FG} \times PCI \quad (4)$$

PCI is the inferior calorific power that is of 11800 kcal/kg. Q is also given by the following relation:

$$Q = M \times C_P \times \Delta T \quad (5)$$

M is the charge of naphtha to be heated and, Cp the specific heat at constant pressure that is 0.724 kcal kg^{-1} K^{-1}. The flow of combustible Q_{FG} thus calculated gives 0.02 ton per hour for unit named U83 which supports a charge of 65 ton per hour, and around 0.003 ton per hour for the other unit named U33 for a charge of 9 ton per hour. For both reforming units, the gain in combustible per year should be of 183 ton. The reformat production induces production of LPG and a hydrogen rich gas phase used for the cracking process. The change in the reformat quality may induce change in these other products.

3.2 Quality of hydrogen phase

The hydrogen produced during the reforming process is of higher purity. Two tests that have concerned the analysis of the gas specimen, elaborated under different RON conditions, 95 and 92.5 are presented in Table 2.

Table 2
Composition of the gas produced under different RON conditions

	95 RON	92.5 RON
CH_4	4.36	1.96
C_2H_4	1.73	1.03
C_3H_5	0.9	0.56
n-C_4H_{10}	0.17	0.11
i-C_4H_{10}	0.21	0.16
n-C_5H_{10}	0.09	0.05
i-C_5H_{10}	0.14	0.10
H_2	92.4	96.03
Molar weight	3.85	3.06

It shows that gas phase produced under condition RON of 92.5, presents a higher purity of hydrogen. The specimen of gas was produced with a flow of naphtha of 50 ton per hour. The flow of gas produced is of 2.35 and 2.2 ton per hour respectively for 95 and 92.5 RON. So, for a charge of 65 ton per hour such as unit U83, the gas flow would be of 3.05 and 2.86 ton per hour respectively for 95 and 92.5 RON. The flow of hydrogen produced is calculated by the following expression:

$$Q_{H2} = \%H_2 \times \frac{M_{H2}}{M_{charge}} \times Q_{charge} \qquad (6)$$

With M_{H2}, the molecular weight of hydrogen, M_{charge} the weight of the charge mass of gas and Q_{charge} the flow of the gas. The calculation of hydrogen flow gives the values of 1.35 and 1.72 ton per hour respectively for 92.5 and 95 RON conditions. So, operation under low RON conditions reduces flow of gas produced but improves the quality of the gas that is richer in hydrogen and can directly be used for the cracking process.

3.3 Effect on the LPG production

The LPG is produced during the reforming process. The lowest the level of cracking is, the less is the LPG production. The change in RON produced, should induce loss of LPG. The exploitation of Table 2 gives the yield of hydro carbides produced for any RON. One finds a yield in hydro carbides C_1, C_2, C_3, and C_4 of 9.3% and 7.7% of the gas produced, respectively for RON 95 and 92.5. The flow of LPG is given by the following relation:

$$Q_{LPG} = \%LPG \times Q_{naphta} \qquad (7)$$

For both reforming units, the loss of LPG production should be around 9500 ton per year. The changing of the RON of the reformat produced would improve the cycle duration by 3 months, reduce the consuming of fuel, ameliorate the yield in reformat and produce a hydrogen richer gas phase, but would cause a lost in LPG production.

3.4 A post adaptation for MMT injection

Since the production of reformat with 92.5RON appears conclusive, the technical approach of realizing the post of MMT injection is undertaken. Figure 2 presents the unit of lead free gasoline production. This station is constituted of pumps and a mixer which is their common point. The bases entering the constitution of the fuel are pumped until mixer, and the solution obtained is stored.

This operation is ensured by the system constituted of centrifuging pumps: P6134 and P6135 for the reformat, P6131 and P6132 for light gasoline. On this installation, the former system for addition of lead still exists.

These operations were located at the aspiration of the pumps P6134 and P6135. The HITEC3062 Octane Booster is available in a kit with a volumetric pump that sucks up the liquid and drives it back to the point of injection. The outlet is endowed of a pipe of 0.75 inch diameter. Therefore, the line would be changed and replaced with a pipe of same diameter. So, the full line should be constituted of two diameters, the first from the volumetric pump to the flow back being with 0.75 inch and the line from the flow back to the mixer with 2 inches diameter.

The technical aspects concern the determination of :

- The injection flow of the volumetric pump;
- The power lost on the line;
- The flow back pressure of the volumetric pump.

In order to gain 2 RON, one has to add 0.074 g/l of MMT of fuel. The mixer is working with a volumetric flow of 600 m^3 per hour, the need for MMT mass flow should be of 44.26 kg per hour. Considering that the HITEC 3062 octane booster contains 62% MMT, the mass flow would be of 71.4 kg per hour. The volumetric flow of HITEC is given by the relation:

$$Q_V = \frac{Q_m}{\rho} \quad (8)$$

With Q_m the mass flow, ρ the HITEC volumetric mass at 25°C. The density of a solution is given by:

$$D = D_T + A(T - 15) \quad (9)$$

With D, the density of the fluid at 15°C, A represents a coefficient that depends on D and D_T the relative density of the fluid at temperature T. When the fluid density at 20°C is known, the density at 15°C is determined equal to 1.1031 then, the density at *25°C* becomes accessible by the Eq. (9). D_{25} so determined is of 1.0969. The ρ value is of 1096.6 kg per m^3. The volumetric flow of HITEC injection calculated with Eq. (8) gives a flow of 0.065 m^3 per hour.

3.5 The pressure loss

The MMT can be injected either at the aspiration of the P6134, or at the aspiration of the P6135. But for more security and to prevent from any malfunctions, both injection posts will be considered. The post on the P6134 will be the principal while the P6135 ones would only be activated anytime that the P6134 should be stopped. To determine the pressure loss on the lines, the calculations have been undertaken using the INSTRUCALC 5.1 software [14]. Therefore, the singularities of the lines from the isometric scheme, the working temperature that's 25°C, the cinematic viscosity of the fluid phase: 1.35 cst, its volumetric flow: 0.065 m^3/h, and the relative density, 1.0969 were needed to inform the software.

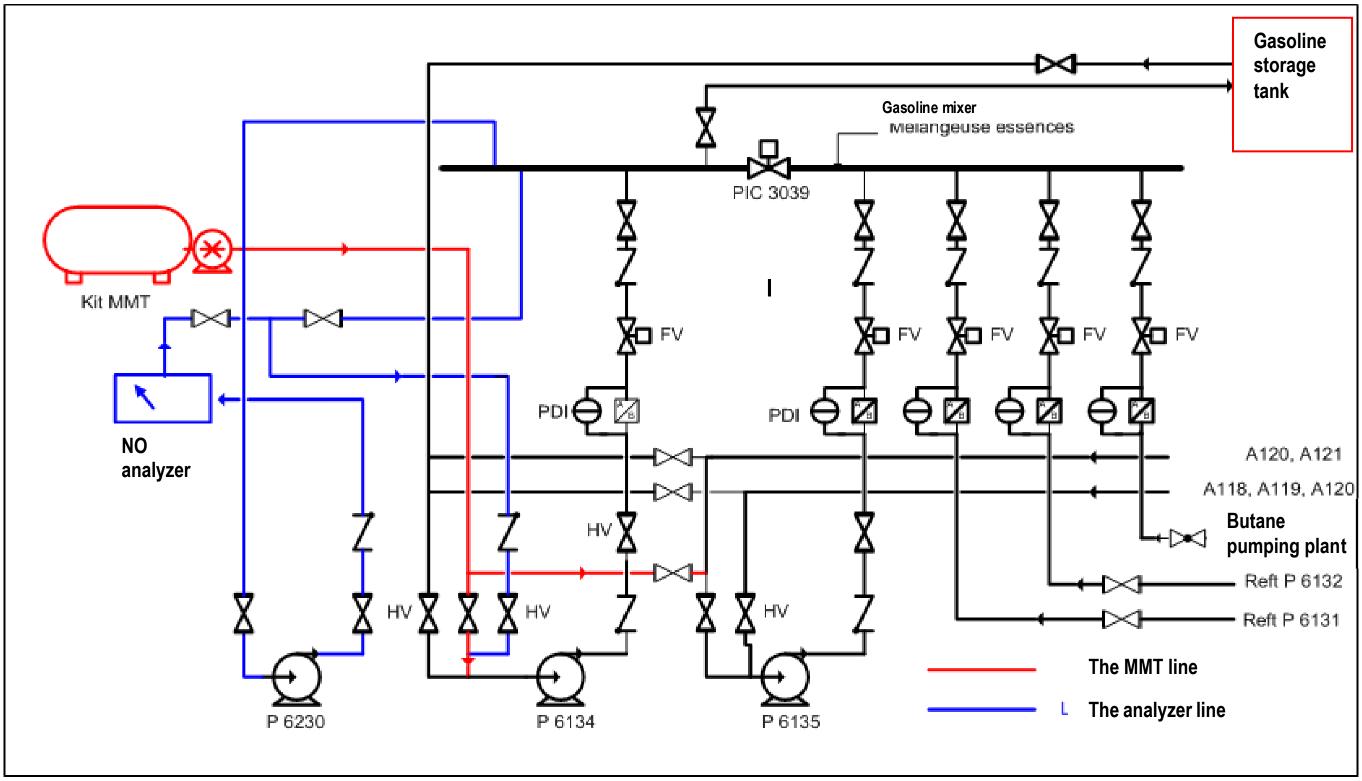

Fig. 2. Gasoline production unity with the projected posts for the MMT injection.

Table 3
Parameters calculated by the INSTRUCALC 5.1 software

	P6134		P6135	
Line diameter in inch	0,75	2	0,75	2
Flow rate in m/s	0,052	0,0083	0,052	0,0083
Reynolds number	819	326,5	819	326,5
Pressure of entry in bar	0	-0,0038	0	-0,035
Outlet pressure in bar	-0,0038	-0,0038	-0,0035	-0,035
ΔP	0.0038	0.00	0.0035	0.00

3.6 Flow back pressure and pressure of injection

The flow back pressure of the pumps P6134 and P6135 is of 1.1 bar eff. So, the volumetric pump pressure of flow should necessary be higher. Figure 3 presents such a system with *Hr* the height of flow back, P_{fb} the pressure of flow back and P_i the pressure of injection. After the isometric considerations for the positioning of the Kit HITEC versus the points of injection, the heights of flow back should be of 1.76 m for the pump P6134 and of 2.025 m for the pump P6135.

The theorem of Bernoulli establishes the relation between the flow back pressure and the injection ones:

$$P_{fb} = P_i + \rho g H_r + 1/2\rho\left(V_i^2 - V_{fb}^2\right) + \Delta P \qquad (10)$$

Considering an injection pressure of 2 bar eff, the pressure of flow back calculated for P6134 and P6135 are respectively 1.81 and 1.78 bar eff. These values stay higher than the pumps pressures of aspiration so that, an injection pressure of 2 bars should be convenient.

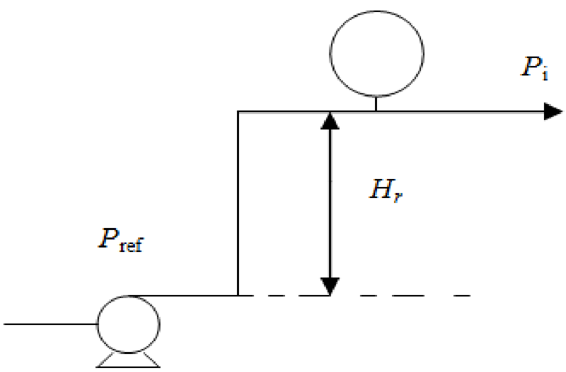

Fig. 3. Scheme of a system with a pressure of flow back and a pressure of injection.

4. Conclusion

This study involved the production of unleaded gasoline with 91 RON. This, from a mixture of reformat and light gasoline of 89 RON. The RON of this mixture would be boosted by the addition of MMT to reach the speciation of unleaded gasoline with 91 RON. This operation will induce less severe conditions of reforming process, thereby would increase the life of the catalysts. Producing reformat with 92.5 RON would result in a decrease of five degrees of the temperature of the oven, which would result in fuel savings.

The gas phase would be produced with a lower flow but will be much richer in hydrogen and could be used directly for the hydro cracking process. However, production of LPG is going to experience a decline of about 1.6% on both units, that's to say a decrease of 9500 T per year.

From technical point of view, it would be easy to adapt the MMT Kit to the old facility formerly used for the addition of lead.

References

[1] J. Hine, S.J. Ehrenson, The effect of structure on the relative stability of dihalomethylenes, J. Am. Chem. Soc. 80(4) (1958) 824-830.

[2] D.F. Caris, E.E. Nelson, A new look at high compression engine, SAE Trans. 67 (1959) 112-124.

[3] R.L. Boeckx, B. Postl, F.J. Coodin, Gasoline sniffing and tetraethyl lead poinsoning in children, Pediatrics 60(2) (1977) 140-145.

[4] I. Romieu, Epidemiological studies of health Effects in: Urban Traffic Pollution; Eds D. Schwela, OZali, E. and Spun. Cambridge (2007).

[5] A. Wagde, Lead in: Air Pollution and Health. Eds S. Ti Holgate, J. M. Samet, H. S. Koren, R. L. Maynard. Academic Press New York (1999).

[6] J.D. Benson, G. Dana, The impact of MMT gasoline additive on exhaust emission and fuel economy of low emission vehicle, SAE Trans. 111(4) (2002) 2023-2062.

[7] N. Petroff, Y. Boscher, J.P. Durand, Determination of composition and octane number of reformat by gas chromatography, Revue Française de Pétrole 43(2) (1988) 259-271.

[8] Improved Octane Measuring Process and Device Publication N°WO/1991/003726 (1991), International Application N° PCT/US 1990/004110.

[9] P. Bourges, F. Garin, G. Maire, G. Szabo, M. Laborde, R. Loutaty, D. Bazin, Etude in situ par analyse EXAFS d'un catalyseur de reformage Pt-Sn/Al_2O_3-Cl, Journal de Physique IV Colloque 6 (C4) (1996) C4-947-C4-956.

[10] P. Bourges, Ageing studies on a reforming bimetallic catalyst., Thesis, University of Strasbourg (France) N° 95STR 13073 (1995).

[11] M. Kitazawa, R. Jarrad, M. Wagner, Oxidative stress and mitochondrial apoptosis in dopamergic cell exposed to methylcyclopentadieneyl manganese tricarbonyl, J. Pharmacol. Exp. Ther. 302 (2002) 26-35.

[12] W. Zheng, H. Kim, Q. Zhad, Comparative toxicokinetic of manganese chloride and methylcyclopentadiene manganese tricarbonyl, Toxicol. Sci. 54 (2) (2000) 295-301.

[13] PROII: Comprehensive process simulation INVENSYS - Operations Management, Copyright Invensys Inc. (2012).

[14] INSTRUCALC: SOFRESID, Rev. 3 (2007). Engineering.com/pdf/logicielpdf-Instrumentation and control.

[15] INFOPLUS, internal data stock, FIRM documents (2015).