International Journal of Engineering and Applied Sciences

www. eaas-journal.org

PRODUCTION OF ULTRA-LOW SULPHUR GASOLINE AND ASSESSMENT OF THE EFFICIENCY OF FERROCENE ANTIKNOCK ADDITIVE

Fahed Salem Khamis[1], Todor Vasilev Palichev[2]

Department of Technology of Oil and Gas, "Aden University" Ataq-Yemen[1]

Department of Industrial Technologies and Management, "Prof. Dr. A. Zlatarov University" Bourgas, Bulgaria[2]

abumario@gmail.com[1]; tovpal@abv.bg[2]

ABSTRACT

The present research was focused on the production of stock gasoline with ultra-low sulphur content up to 10 ppm (Euro-5 Standard) by blending of different gasoline streams produced in the Lukoil Nentochim Bourgas (LNHB) refinery units as well as on the study on the efficiency of ferrocene antiknock additives.

Some recipes for the production of stock gasoline A92, A95 and A98 commercial grade on the basis of component streams produced in LNHB refinery units and satisfying all specifications of the European regulation were elaborated. Thus, the gasoline blending provides a great potential benefit to the refinery in view of minimizing operating costs and product quality improvement.

It has been proved that the efficiency of the additive is a function of the total content of alkanes and particularly of that of paraffin in the blended gasoline. The higher is its content the higher the additive efficiency is.

It was found that the maximum increase in RON by using ferrocene antiknock additive can be up to five points and the maximum increase in MON – up to 2.9 points.

KEYWORDS: Euro-5, ferrocene antiknock additives, gasoline, ultra-low sulphur.

INTRODUCTION

Current and future legislation worldwide is forcing refiners to lower the sulphur in gasoline to ever lower levels (Brown and Evans, 2007). The European Union will cut the sulphur content of all gasoline and diesel to meet the 10 ppm limit from the start of 2009 according to Directive EC (2003).

Other countries around the world generally aim to harmonize their fuel and emissions regulations with Europe. With few exceptions, the trend around the world appears to be towards the eventual requirement for the production of a sulphur-free gasoline (defined as less than 10 ppm) (Brown and Evans, 2007).

The non-hydrogen consuming desulphurization processes can be grouped into three categories; biodesulfurization, separation, and oxidative desulphurization (Liotta and Han, 2003; Blumberg *et al*., 2003).

The production of ultra-low sulphur fuels, less than 10 ppm, by hydrodesulphurization, both conventional and the newer selective processes, requires high temperature, high pressure equipment, modelling and optimization of refinery gasoline blending, representing a significantly higher capital expenditure than that required to produce low sulphur, 500 ppm, fuel (Barsamian, 2008; Ivanov and Argirov, 2005; Ivanov *et al*., 2010; Musaev and Nikitin, 2006; Fatoni, 2006).

 ISSN 2305-8269

International Journal of Engineering and Applied Sciences

www. eaas-journal.org

In order to increase the quality of the current gasoline fuels and to comply with the ecological norms, another option, in addition to the optimization of production technologies, is the use of additives.

The purposes of the present paper are two: the first one aims to study the possibilities for the production of ultra-low sulphur stock gasoline up to 10 ppm sulphur according to Euro-5 Standard (2008) by optimum using of various gasoline fractions from the LNHB refinery units and the second one – to evaluate the efficiency of ferrocene antiknock additive.

MATERIALS AND METHODS

The first aim of our research, i.e. production of ultra-low sulphur stock gasoline was accomplished by using the following component streams produced in the LNHB refinery units:
1- Product of fluid catalytic cracking (FCC);
2- Product of catalytic reforming (CR);
3- Product of alkylation installation (AI);
4- Products of methyl *tert*-butyl ether production (MTBE).
5- Straight-run gasoline (low-octane gasoline (LOG), obtained by the primary petroleum distillation.

By blending of the above-pointed products in a system for mixing of the semi-finished products denoted as MIK 4000 C gasoline blends were obtained, which were further tested according to the methods described in Euro-5 standard.

For the purpose of the second aim – to study the efficiency of ferrocene antiknock additive two types of base gasoline were used:
1-Stock regular gasoline A92
2-Light low-octane gasoline from straight distillation (fraction with initial boiling point - 100^{o}C).
3-Ferrocene antiknock additive, kindly provided by LNHB.

The mixing of 30% of the straight-run light low-octane gasoline with 70% regular gasoline A92 gave a gasoline blend denoted by us as mixture A. To gasoline A92 and mixture A was added industrial ferrocene antiknock additive and the obtained fuels were tested following the methods for evaluation of the motor octane number (MON) and research octane number (RON), as required by Euro-5 standard.

RESULTS AND DISCUSSION

1. First aim:

The current motor gasoline is produced by blending of the products from isomerization of light straight-run gasoline, FCC, CR, AI and products from the production of MTBE.

The application of the proposed recipes could increase the potential benefit of LNHB since it is very important for each refinery to utilize all products thus avoiding the accumulation of some and shortage of others.

The proposed by us base recipes for the production of stock gasoline A92H; A95H and A98H in LNHB are shown in Table 1.

The physicochemical indices of the obtained fuels, according to the recipes given in Table 1, are presented in Table 2.

Gasoline A92H is in compliance with Euro-4 Standard (2005), i. e. it has a content of sulphur to 50 ppм and can be used for export in countries in which Euro-5 Standard is still not implemented. Gasoline fuels A95H and A98H meet the norm of sulphur content of to 10 ppm as Euro-5 standard states. For the production of gasoline A98H we have not added low-octane components since they cannot ensure the obtaining of the required values for the RON and MON.

The results in Table 2 reveal that using the proposed recipes for the production of motor gasoline A92, A95 and A98 from components produced in LNHB refinery units can be obtained gasoline blends meeting all requirements of the European norm.

2. Second aim:

In order to successfully accomplish the second aim, i. e. to increase the economic profit, which means the production of high-octane gasoline by using of lower amounts of high-octane components (alkylate and MTBE) produced in lowest amounts

 ISSN 2305-8269

International Journal of Engineering and Applied Sciences

www. eaas-journal.org

and are limited for the production of motor gasoline A95H, A98H grade, the use of additives improving the antiknock properties of the fuels is required.

Due to the proved hazardous effect of lead-containing octane improvers on the human health they were not utilized in the composition of the modern motor gasoline (Walsh, 2007). They were replaced by octane-improving additives on the basis of manganese and Iron. The studies have shown that the exposure of humans to the effect of manganese can lead to adverse impacts on the nervous system (Walsh, 2007). It has not been established that iron-containing additives have such a hazardous effects on the human health and the environment as lead-and manganese-containing additives. In view of this, our second aim was to study the efficiency of the provided by LNHB ferrocene antiknock additive.

The data for the hydrocarbon composition and octane number for the utilized by us base gasolines are presented in Table 3.

The data of Table 3 show that the addition of the fraction initial boiling point-100^{o}C to A92-gasoline (RON 92.5) affects strongly the octane number of the obtained mixture. The calculated mixed octane numbers of mixture A, assuming that the octane number is a linear combination of the relative volume part and the octane numbers of the individual components, amounts to 83.7 according to the research method and 75.9 – by the motor method. We have obtained experimentally octane number of 79.8 by the research method and 74.2 - by the motor method. This confirms the established earlier regularities at gasolines blending, i. e. that the calculated octane number of a given mixture from several components can be used only as an approximate estimation. The real octane number is a function not only of the individual hydrocarbon composition, but also of their quantitative ratio and mutual effect.

Industrial ferrocene antiknock additive was added to A92 gasoline and mixture A in a concentration up to 3000 ppm. Higher concentrations of the additive were avoided due to the information provided by the company producer of the additive that over this dosage there is a possibility of arising of problems in the exploitation of the modern gasoline engines.

The change in the octane number of the doped with additive gasoline is demonstrated in Figs 1 and 2.

The data of Figs 1 and 2 indicate that the additive efficiency is higher with respect to RON. The slope of the RON change depending on the additive concentration for the two gasoline blends varies between 0.0014 and 0.0016, whereas the slope of the change in MON ranges within 0.0006 – 0.0009. Thus the additive leads to preferential increase in RON than in MON of the gasoline blends. These data show also that the slope of the change in the octane number is different for the different gasoline blends.

In our attempt to find some correlation between any of the gasoline parameters and the efficiency of the ferrocene antiknock additive, we have established that the additive action is a function of the total content of saturated hydrocarbons, particularly of paraffins in the gasoline blend. The higher the content is in the blended gasoline, the higher the efficiency of ferrocene antiknock additive is.

It has been also found that the addition of ferrocene antiknock additive to the studied gasoline blends results in increasing of the octane number. At 1000 ppm additive concentration in sample A, the increase of RON is 2.8 and of MON - 1.0 points, whereas for A92 gasoline the increase of RON is 2.0 and that of MON is only 0.7 points.

The research demonstrates that the maximum increase of RON using the ferrocene antiknock additive for sample A is 5.0 points, and for A92 gasoline - 4.2. The maximum increase in MON is lower and it amounts to 2.9 for sample A and 1.6 – for gasoline A92.

CONCLUSIONS

1. Some production recipes of stock motor gasoline of A92, A95 and A98 commercial grade using the component streams manufactured in Lukoil-Neftochim Bourgas refinery units and meeting all requirements of the EN have been proposed. These preparations allow the maximum realization of the refinery quantitative and qualitative potential.

International Journal of Engineering and Applied Sciences

www. eaas-journal.org

2. It has been proved that the efficiency of the ferrocene antiknock additive depends on the total content of saturated hydrocarbons, particularly of paraffins in the doped gasoline. The higher is the content of the additive in the gasoline blend the higher is the efficiency of the ferrocene antiknock additive.

3. It has been established that the maximum increase of RON in the presence of ferrocene antiknock additive can reach up to 5.0 points and the maximum increase in MON – 2.9 points.

REFERENCES

1. Barsamian, A. J. 2008. Optimize fuels blending with advanced online analyzers. Hydrocarbon Processing. 87. (9): 121-122.
2. Blumberg, K. O., Walsh, M. P. and Pera, C. 2003. Low-Sulfur Gasoline & Diesel: the Key to Lower Vehicle Emissions. www.walshcarlines.com/conventfuels.html.
3. Brown, M. and Evans, M. 2007. FCC Gasoline Sulphur Reduction Using Catalyst Additives Mechanisms and Commercial Experiences. The 17th Annual Saudi Arabia - Japan Symposium "Catalysis in Petroleum Refining & Petrochemicals", Nov. 11-12, Dhahran, Saudi Arabia.
4. Fatoni, R 2006. Modelling and optimisation of refinery gasoline blending. Jurnal Teknik Gelagar. 17, (2): 125-133.
5. Ivanov A. I. and Argirov G. S. 2005. Refining technology achievements to produce environmentally friendly gasoline. Oxidation Communication. 28. (2): 253-272.
6. Ivanov, S. V., Manchuk, N. M. and Ahremova, D. A. 2010. Catalytic alkylation of branched alkanes by alkenes for the obtaining of high-octane gasoline components. Neft i Gaz. (2): 48-60 (in Russian).
7. Liotta, F. J. and Han, Y. Z. 2003. Production of Ultra-Low Sulfur Fuels by Selective Hydroperoxide Oxidation. Annual Meeting. March: 23-25.
8. Musaev, A. A. and Nikitin, V. A. 2007. Optimal process control of commercial grade fuel mixture in flow. Instrumentation and systems. 4: 5-11.
9. Walsh, M. P. 2007. The Global Experience With Lead in Gasoline and the Lessons We Should Apply to the Use of MMT. American Journal of Industrial Medicine. 50: (11), 853–860.

November 2012. Vol. 1, No.1 ISSN 2305-8269

International Journal of Engineering and Applied Sciences

www. eaas-journal.org

Table 1: Base recipes for the production of motor gasoline

No of mixture	*Component concentration, %m/m*				
	FCC	*CR*	*AI*	*MTBE*	*LOG*
Mixture No 1 (A92H)	*60*	*30*	*0*	*0*	*10*
Mixture No 2 (A95H)	*50*	*25*	*15*	*5*	*5*
Mixture No 3 (A98H)	*40*	*25*	*25*	*10*	*0*

Table 2: Physicochemical indices of the obtained stock gasoline and the corresponding requirements

Parameters	*Requirements for:*			*Base fuels*		
	A92	*A95*	*A98*	*Mixture 1*	*Mixture 2*	*Mixture 3*
1. Density at 15 ^{o}C, kg/m3	*720.0 to 775.0*	*720.0 to 775.0*	*720.0 to 775.0*	*750.3*	*748.7*	*746.2*
2. RON	*min. 92*	*min. 95*	*min. 98*	*92.8*	*95.8*	*98.3*
3. MON	*min. 82*	*min. 85*	*min. 87*	*82.3*	*85.2*	*87.5*
4. Sulphur, mg/kg	*max.50*	*max.10*	*max.10*	*12.7*	*7.3*	*6.8*
5. Benzene, % v/v	*max.1*	*max.1*	*max.1*	*0.91*	*0.83*	*0.76*
6. Oxygen content, % m/m	*max. 2.7*	*max. 2.7*	*max. 2.7*	*0.6*	*0.8*	*1.3*
7. Content of:						
arenes, %v/v	*max. 35*	*max. 35*	*max. 35*	*33.8*	*31.0*	*28.1*
olefins, %v/v	*max.21*	*max. 18*	*max. 18*	*20.1*	*15.9*	*13.5*
8. Distillation characteristics, Up to 70^{o}C dist. %v/v						
summer	*20.0-48.0*	*20.0-48,0*	*20.0-48,0*	*24.2*	*25.7*	*26.3*
winter	*22.0-50.0*	*22.0-50.0*	*22.0-50.0*	*24.8*	*25.1*	*26.1*
to 100 ^{o}C dist., %v/v	*46.0-71.0*	*46.0-71.0*	*46.0-71.0*	*48.9*	*48.1*	*50.1*
to 150 ^{o}C dist., %v/v	*min. 75.0*	*min. 75.0*	*min. 75.0*	*81.3*	*80.3*	*78.4*
end of boiling, ^{o}C	*max. 210*	*max. 210*	*max. 210*	*197.5*	*196.2*	*195.7*
residue, % v/v	*max. 2*	*max. 2*	*max. 2*	*1.4*	*1.2*	*0.9*
9. Vapor pressure,						
summer, kPa	*45.0-60.0*	*45.0-60.0*	*45.0-60.0*	*51.9*	*55.3*	*58.4*
winter, kPa	*50.0-80.0*	*50.0-80.0*	*50.0-80.0*	*63.6*	*65.8*	*67.2*

Table 3: Hydrocarbon composition and octane number values of the studied gasoline

Hydrocarbon composition and octane number	*Gasoline A92*	*Fraction (initial boiling point-100^{o}C)*	*Mixture A*
PONA analysis, %m/m			
Paraffins	*37.6*	*73.3*	*49.7*
Olefins	*21.1*	*0.4*	*13.2*
Naphthenes	*6.9*	*26.1*	*9.8*
Arenes	*35.3*	*1.9*	*25.9*
Group hydrocarbon composition (ASTM D-1319 – FIA method), %v/v			
Saturated	*41.7*		*58.7*
Olefins	*21.1*		*14.6*
Arenes	*35.3*		*28.8*
Octane number			
Research method (RON)	*92.5*	*63.2*	*79.8*
Motor method (MON)	*82.4*	*60.6*	*74.2*

International Journal of Engineering and Applied Sciences

www. eaas-journal.org

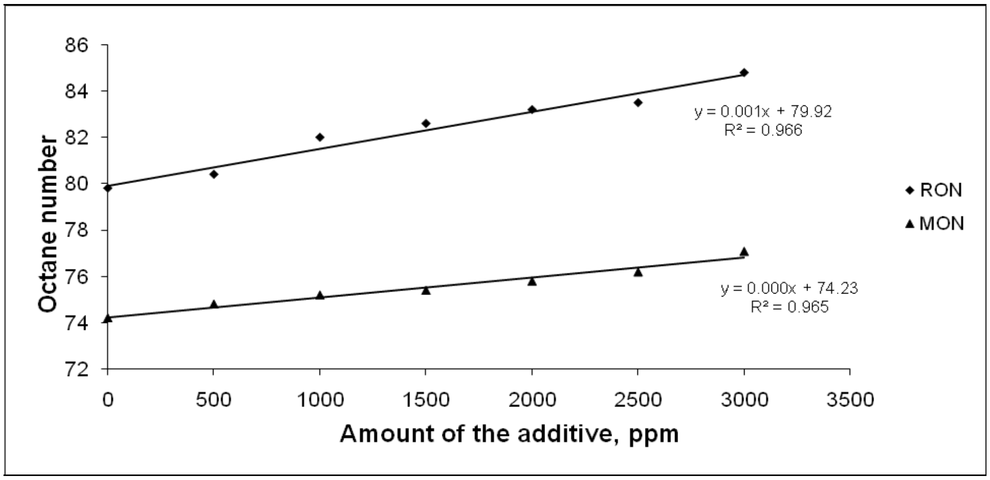

Fig. 1: Dependence of RON, MON of mixture A on the concentration of the ferrocene antiknock additive

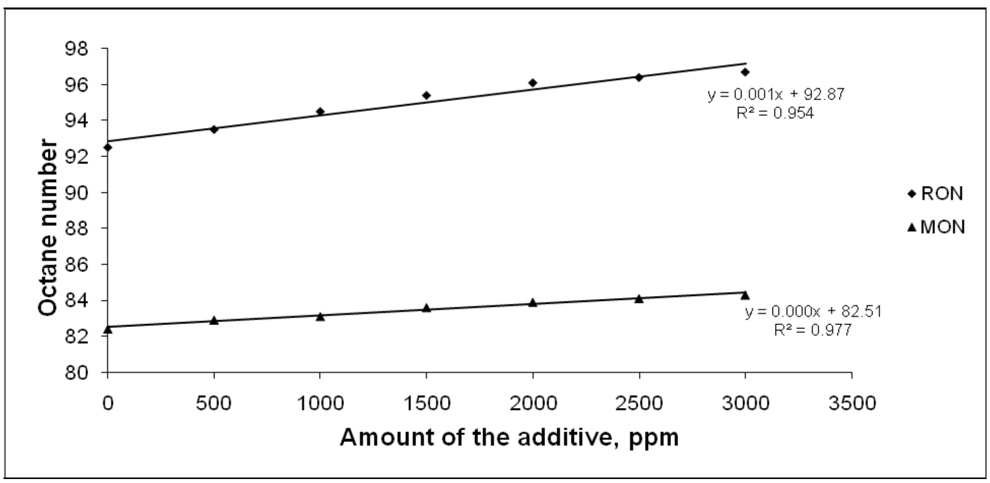

Fig. 2: Dependence of RON and MON of A92 gasoline (RON 92.5) on the concentration of ferrocene antiknock additive