



## Upgrading of LCO by partial hydrogenation of aromatics and ring opening of naphthenes over bi-functional catalysts

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### ABSTRACT

Available options to upgrade LCO to diesel fuel are: i) aromatic saturation (ASAT) ii) mild hydrocracking and iii) aromatic saturation followed by selective ring opening (SRO) of naphthenic structures. Although the above mentioned routes lead to significant product quality enhancement, they suffer from several disadvantages. Hydrocracking leads to significant yields in gasoline-range products, ASAT is characterized by a relatively high consumption of hydrogen with only limited improvement of product quality in terms of density and cetane properties, ASAT + SRO route leads to higher improvements of product quality but it requires a very high hydrogen consumption which strongly affects the economics of the process.

An alternative upgrading route consists in partial polyaromatic compound saturation and selective opening of both naphthenic and benzo-naphthenic structures to produce less condensed naphthenic structures and alkyl-benzenes respectively. In this case the hydrogen needed to improve product quality at the same level, of cetane properties and density, is lower in comparison with ASAT.

This paper reports the results obtained during a research program aimed at upgrading LCO via selective ring opening. The hydroconversion of a low sulfur hydrotreated LCO has been studied over iridium and platinum loaded on different supports. The results of this study indicate that the properties of products heavily depend on the characteristics of the support and the metal used. The data obtained with the Ir/amorphous silica-alumina (MSA) show the possibility to get a clear increase of CN and decrease of density in comparison with the mere aromatic saturation. The practical consequence of this result is the possibility of producing products with CN and density similar to products obtained by complete dearomatization but still containing a significant percentage of aromatic structures so allowing a consistent saving of hydrogen.

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### 1. Introduction

Environmental awareness is causing a worldwide significant enhancement of fuel quality in order to meet new tighter automotive emission standards. The reduction of polycyclic and total aromatic hydrocarbon content and the increase of cetane number (CN) of diesel fuel are measures that most likely will be taken in the near future to further diminish diesel engine exhaust gas emissions. Current EU legislation on fuel quality [1] establishes maximum Polycyclic Aromatic Hydrocarbons (PAH) content of 11 wt.% and minimum CN of 51 for diesel fuel; however, a proposal to set the maximum PAH limit at 8 wt.% or lower is under evaluation. As a consequence of likely stricter future regulations, severe limitations to the use in diesel fuel blending of high aromatic streams, such as those from cokers and catalytic cracking units or coming from bitumen derived synthetic crude oils, could be necessary if new upgrading processes are not introduced in refining cycle. Commercially proven refining technol-

ogies addressing highly aromatic middle distillates upgrading are Aromatics SATuration (ASAT) and hydrocracking. By using commercial noble metal based hydrodearomatization catalysts, aromatic compounds are saturated to produce naphthenic compounds [2]. In this way the product quality can be properly enhanced only when most of the aromatic carbons are saturated; in any case CN increase and density reduction are limited. Moreover, the maximum achievable improvement is strictly a function of feed composition and it is not always possible to obtain products that are suitable to be conveniently blended in diesel pool. On the other end, not selective hydrocracking improves the quality of middle distillates by saturating aromatic rings and cracking naphthenic structures but is characterized by extensive production of hydrocarbons not boiling in the diesel range [3–5]. A recently proposed alternative route [6] that is able to overcome part of the problems related with the above mentioned upgrading process, is saturation of aromatic structures followed by selective ring opening (SRO) of naphthenic structures to produce alkanes having the same carbon number. In this case the improvement in terms of density and CN is the highest achievable but hydrogen consumption associated with this process is very high. A variation of the latter approach is represented by only partial

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hydrogenation of aromatic structures coupled with selective opening of naphthenic rings in benzo-naphthenic structures. This process can limit the high hydrogen consumption associated with complete saturation of aromatic rings while allowing a significant improvement of product quality [7].

While theoretically SRO is a promising route to upgrade low value feed to high quality products its practical realization represents a challenge because SRO is characterized by a complex chemistry where besides the structure of the feed, the selectivity, distribution and composition of the final products heavily depend on operating conditions and characteristics of the catalytic system [8,9]. In the case of metal-catalyzed system, activity and selectivity for ring opening reaction strongly depend on the type of metal [6,10]. Several studies carried out with model compounds show that ring opening activity and selectivity of alkyl-cyclopentanes and alkyl-cyclohexanes follow the order iridium>platinum>nickel>>ruthenium. Moreover ring opening of six-membered rings occurs at lower rate and less selectively than of five-membered rings [11,12]. Metal-catalyzed ring opening can occur via two main mechanisms: multiplet and dicarbene mechanism [13]. On well dispersed platinum ring opening occurs through multiplet mechanism where all the endocyclic C–C bonds, regardless the substitution, have the same probability to be broken. Differently, with iridium loaded catalysts the dominant mechanism is dicarbene where the secondary endocyclic C–C bonds are preferably broken in comparison with the secondary–tertiary and tertiary–tertiary endocyclic C–C bonds. As a consequence of the different operating mechanism, ring opening products from Pt based catalysts are less isomerized than products from Ir based catalysts. This fact has consequences on the cetane properties and density that are affected by the branching degree of the molecules. Although on Ir catalyst the dicarbene mechanism dominates during methyl-cyclohexane conversion, large deviations from this mechanism have been observed for different supports and degree of substitution of naphthenes [6,14]. Particle size and crystal morphology as well are known to show a remarkable effect. It has been reported that Pt displays a different behavior according to the dispersion and the level of metal loading [13] whereas Ir and Rh seem to be less sensitive to the particle size. Besides the above mentioned factors also support exerts a strong influence: the interaction with metal particles can change their electronic properties and the presence of acid sites can heavily change the chemistry of the process [15]. On bi-functional catalysts (i.e. catalytic system characterized by the presence of acid sites and hydrodehydrogenating function) the reacting system is characterized by the presence of reactions occurring via carbenium intermediate (i.e. isomerization,  $\beta$ -scission). Santana et al. [16] pointed out that a wide range of ring opening products can be formed by ring opening of naphthenic structures and improvement of cetane number is not a straightforward task but requires the development of extremely selective catalyst for the scission of substituted C–C bonds in naphthenic structures in order to minimize branching degree of ring opening products. As highlighted by McVicker et al. [6], a critical step in determining the selectivity and distribution of ring opening products is the ring contraction reaction of six-membered rings to alkyl-substituted cyclopentanes. The main reason for this is the higher ring opening selectivity to molecules with the same carbon atoms and higher ring opening rate of five-membered structures in comparison with six-membered rings. Following this line of reasoning it was suggested that for SRO reaction a bi-functional catalyst with a suitable acid function for the ring contraction step and a metal function for the ring opening of the so formed cyclopentanes is necessary. An example in this direction is given by the results obtained by McVicker [6] with alkyl-substituted cyclopentanes and alkyl-substituted cyclohexanes.

Oil derived middle distillates are complex mixtures of thousands of different compounds. The aromatic, naphthenic and benzo-naphthenic fractions are made up of five- and six-membered rings bearing different length alkyl groups and with condensation degree ranging

between 1 and 3–4 fused rings depending on the final boiling point and on the characteristics of the oil. Owing to the complexity of the feedstock and of the chemistry the results of hydroconversion over a bi-functional catalyst aimed at enhancing the contribution of the selective ring opening on the overall chemical transformations are hardly predictable.

While extensive works have been carried out on model compounds [10], few data are available in literature for real feedstock conversion. The present paper is focused on comparing the hydrocarbons distribution and the chemical–physical properties of products obtained in hydroconversion of a hydrodesulfurized commercial Light Cycle Oil (LCO) over noble metal bi-functional catalysts.

## 2. Experimental

### 2.1. Catalyst preparation

Three different supports with varying acidity density have been prepared: a ZSM-12 zeolite, an amorphous mesoporous silica alumina (MSA) and an aluminum borate ( $\text{Al}_2\text{O}_3\text{-B}$ ). A highly dealuminated ultra stable Y zeolite ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$  mol/mol) HSZ-390HUA, supplied from Tosoh Corporation, has been evaluated too. Catalyst preparation procedures have been reported hereafter.

#### 2.1.1. ZSM-12 (MTW)

Zeolite ZSM-12 was synthesized according to recipes described in Ref. [17] using the following procedure: 127 g of tetra-ethylammonium hydroxide at 40% by weight, in aqueous solution, is added to 24 g of demineralized water. 4 g of sodium aluminate at 56% by weight of  $\text{Al}_2\text{O}_3$  is then added. The limpid solution thus obtained is poured, under stirring, into 350 g of Ludox HS 40 colloidal silica. After brief stirring, a limpid homogeneous gel is obtained which is poured into a 1 l autoclave made of AISI 316, equipped with an anchor stirrer. The gel is left to crystallize under hydrothermal conditions at 160 °C for 60 h. At the end of this phase, the autoclave is cooled to room temperature. The slurry obtained is homogeneous, with a milky appearance. The slurry is centrifuged. The discharged solid is washed by redispersion in water, centrifuged again, dried at 120 °C and calcined at 550 °C for 5 h. Upon X-ray diffraction analysis, the solid obtained proves to consist of pure ZSM-12. The solid obtained is subsequently exchanged into ammonia form by treatment with a solution of ammonium acetate 3 M. Upon subsequent calcination at 550 °C, for 5 h, the zeolite in acid form is obtained. The final Si/Al ratio, determined by chemical analysis, was 50.

#### 2.1.2. Mesoporous silica alumina

The MSA was prepared as described in Ref. [18]. 23.5 l of demineralized water, 19.6 kg of aqueous solution at 14.4% by weight of TPA-OH and 1200 g of aluminum tri-isopropoxide are introduced into a 100 l reactor. The mixture is heated to 60 °C and maintained under stirring at this temperature for 1 h, in order to obtain a limpid solution. The temperature of the solution is then brought to 90 °C and 31.1 kg of tetraethyl silicate is rapidly added. The reactor is closed and the stirring rate is regulated at about 1.2 m/s, the mixture being maintained under stirring for 3 h at a temperature ranging from 80 to 90 °C, with thermostatic control to remove the heat produced by the hydrolysis reaction. The pressure in the reactor rises to about 0.2 MPa. At the end, the reaction mixture is discharged and cooled to room temperature, obtaining a homogeneous and relatively fluid gel having the following composition molar ratios:  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50.5$  TPA-OH/ $\text{SiO}_2 = 0.093$   $\text{H}_2\text{O}/\text{SiO}_2 = 15$ .

The product is left to rest for about 6–8 h and is then dried by maintaining it in a stream of air at 100 °C until the weight becomes constant. It is finally calcined in a muffle at 550 °C for 8 h in air. In this way, a porous solid is obtained, with acidic characteristics, essentially consisting of silica alumina with a molar ratio  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 50.2$ , a BET

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