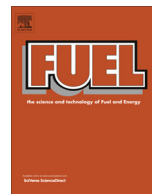


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Selective ring opening of naphthenes: From mechanistic studies with a model feed to the upgrading of a hydrotreated light cycle oil

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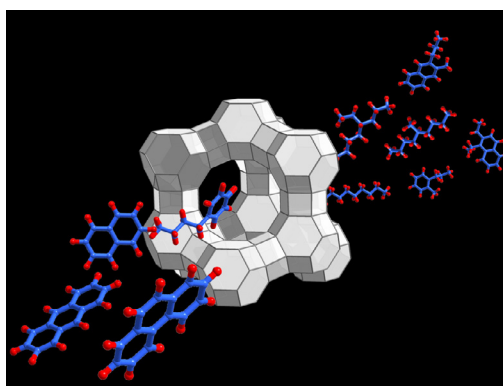
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HIGHLIGHTS

- Iridium and platinum based catalysts, with high selective ring opening selectivity were used to upgrade a hydrotreated LCO.
- Hydroconversion of hydrotreated LCO resulted in a strong decrease of condensed naphthenic structures.
- Changes in chemical structure led to a remarkable increase of Cetane Index with relatively low cracking yields.
- It is shown the possibility to upgrade aromatic rich streams to products meeting the Cetane Number specification of gasoil.
- Testing ring-opening catalysts with decalin enables to investigate the main factors affecting the ring-opening reaction.

GRAPHICAL ABSTRACT



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ABSTRACT

The catalytic hydroconversion of desulfurized and dearomatized light cycle oil (DeAr-LCO) with a Cetane Index (CI) of 41.7 was investigated at 7.0 MPa and in the temperature range from 290 to 350 °C in a down-flow fixed bed reactor. Two catalysts made up, respectively, of 3 wt% iridium and 4 wt% platinum loaded on Y zeolite exchanged with Na were used. The hydroconversion of DeAr-LCO over the above-mentioned catalysts resulted in a remarkable change of chemical structure of the feed with a strong decrease of condensed naphthenic structures and a concomitant increase of alkyl substituted cyclohexanes and open-chain alkanes. In the case of tests carried out with the platinum-based catalyst the alkanes concentration passed from 21% in the feed to 44% in the product obtained at the highest conversion levels. GCxGC-MS analyses showed that the hydrocracking associated with the hydroconversion process was relatively modest and that the observed changes in chemical composition were mainly the consequence of the selective ring opening pathway of naphthenic structures. The results clearly show that along with the changes in chemical structure during hydroconversion the products are characterized by a higher CI. For the platinum- and iridium-based catalysts an increase of CI of 11 and 7 units, respectively, was observed at a gasoil yield of 80 wt%. The positive results indicate that the use of a metal function with a high hydrogenolytic activity and selectivity coupled with a properly tuned concentration and strength of the Brønsted acidic sites can lead to remarkable improvements in the cetane properties of gasoil cuts. The practical consequence of this result is the possibility of upgrading aromatic-rich streams to products meeting the current Cetane Number specification of gasoil.

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1. Introduction

Environment-related issues are nowadays for sure a powerful driving force for the improvement of current refinery processes or the development of new routes for upgrading refinery cuts. The ongoing need to lower tail pipe emissions, call for the use of cleaner fuels characterized by a cleaner combustion allowing a more efficient post-treatment of the exhaust gas. As for the gasoil, the reduction of the sulfur content from 500 to 10 ppm we have witnessed in the last two decades, has been accompanied by a progressive tightening of automotive emission standards concerning other pollutants. Particularly, the introduction of Euro 5 standards in 2009 [1] reduced the emission of particulate matter of diesel vehicles from 25 to 5 mg km⁻¹, and subsequently EU specifications for polyaromatics in diesel fuel passed from 11% to 8% while a lower limit of 2% is presently a matter of debate [2]. As a consequence of 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 the refining cycle. Nowadays, the low Cetane Number (CN) and the high density often hinder the use of all Light Cycle Oil (LCO) produced in Fluid Catalytic Cracking (FCC) units as blending component in the gasoil pool, and consequently a part of it is valorised as a component to lower the viscosity of fuel oil. Besides this critical factor, European refineries are in need to shift in the near future the product slates to meet the higher diesel demand caused by the continuous increase of diesel-powered passenger vehicles market share observed in the last years [3]. The gasoil/gasoline ratio sales have shown a steady increase in the recent past, and it is most likely that this trend will continue in the near future. Thus European refineries are facing the twofold problem of increasing the production of diesel and improve its quality. In these circumstances, a possible option to increase middle distillate production is an increase in the LCO yields of FCC units together with its upgrading to products suitable for the diesel pool [4]. The options presently available addressing highly aromatic middle distillates upgrading are aromatics saturation (ASAT) [5,6] and hydrocracking [7–9]. However, even in the case of complete saturation of the aromatic structures, the increase of the Cetane Index (CI) is insufficient to meet the specification required for diesel fuel [5,10,11]. On the other hand, hydrocracking produces middle distillate with improved quality but fatally leads to an undesired production of lighter distillates. A more recent approach which potentially can lead to the highest achievable improvement in terms of yields, combustion characteristics of the products and environmental impact, is saturation of the aromatic structures followed by the selective breaking of endocyclic C–C bonds of naphthenic structures so formed to produce alkanes with the same number of carbon atoms as the starting molecule. Although accompanied by a high hydrogen consumption, as depicted in Fig. 1, the complete ring opening of naphthenic structures would lead to significant improvements in the Cetane Number and a remarkable decrease of the soot formation tendency [13,14].

Furthermore, the decrease of boiling point amounting to 40–50 °C would allow to increase the production of gasoil by upgrading the lighter fraction of Heavy Cycle Oil (HCO). Upgrading of refinery cuts via Selective Ring Opening (SRO) has been actively investigated in the past by ExxonMobil [15–17] and, more recently, by UOP [18,19]. However, none of the patents examined presents data concerning the improvement of cetane properties of distillate cuts following the hydroconversion via SRO.

While theoretically SRO is a promising route to upgrade low-value feeds to high-quality products its practical realization represents a challenge because SRO is characterized by a complex

chemistry, and not all effects of the different factors affecting the selectivity, the distribution and the composition of the products have been fully elucidated yet. The difficulties of improving the Cetane Number of diesel fuels by SRO have been examined by Santana et al. [20]. In this paper, the authors considered the cetane properties of products formed by the possible reaction pathways of decalin during hydroconversion on both acid and bifunctional catalysts, the latter with a metal function presenting a high hydrogenolysis activity. The main conclusion of their analysis was that with catalysts working according to the known reaction pathways, the isomerization degree of isodecanes formed is such that it is not possible to obtain a substantial increase of the Cetane Number compared to that of decalin. Significant improvements of cetane properties could be obtained only with a catalyst showing a high selectivity in breaking substituted C–C bonds. Although the conclusions in the case of decalin conversion are correct from a theoretical point of view we notice that the situation with refinery cuts is much more complex and in view of the higher molecular weight of the latter, the negative effect of isomerization could be less pronounced than in the case of decalin. Furthermore, it should be mentioned that the results of a recent paper [21] suggest that it is possible by increasing the “selective ring opening” pathway of tetralin-like structures to alkylbenzene structures to obtain products with the same Cetane Number of a completely dearomatized LCO still containing 20 vol% of aromatic structures.

With few exceptions [22–24] literature available on selective ring opening concerns model compounds with single C₅ or C₆ ring or two condensed rings. Besides the classical review by Gault [25] reporting the state of the art till the early ‘80s, three excellent reviews have been recently published on this subject by Weitkamp [12], Du et al. [26] and Do et al. [27].

Compositional characteristics of LCO [5,9] indicate that the most abundant structures consist of aromatics with two fused aromatic rings, consequently model compounds consisting of two aromatic fused rings or structures derived from partial or total hydrogenation are more suitable than 1ring compounds to investigate LCO upgrading via SRO. A large number of publications dealing with the selective ring opening (SRO) of multi-ring structures, such as decalin, tetralin, perhydroindan, or naphthalene, has appeared in the last 15 years. The catalysts employed in these studies can be classified into three categories:

- (i) Monofunctional acidic catalysts [28–30].
- (ii) Bifunctional catalysts made up of a metal function on an acidic support [29,31–44].
- (iii) Monofunctional metal catalysts made up of a noble metal on a non-acidic support [30,45,46]. Monofunctional acidic catalysts are the least appropriate for ring opening of decalin owing to their rapid deactivation due to coking. A significant amount of hydrocarbons with more than 10 carbon atoms are formed, while the selectivity to ring opening products is very low.

On monofunctional metal catalysts lacking Brønsted acid sites ring opening occurs by hydrogenolysis of endocyclic C–C bonds on the metal. Among the various metals utilized iridium and platinum are the most widely investigated and present the best performances in terms of activity and selectivity. Differently from monofunctional acidic catalysts, monofunctional metal catalysts are relatively stable, but the selectivity is still low with maximum yields of Open Chain Decanes (OCDs) of ca. 10 wt% [30] and 20 wt% [46]. Bifunctional catalysts based on a metal with a high hydrogenolytic activity coupled with a good selectivity for ring opening appear to be best suited for the SRO of naphthenic structures. The best performance as for the selectivity of ring opening has

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