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Importance of Isoparaffins in the Crude Oil Refining Industry

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The requirements against various crude oil-based fuels (e.g. gasoline, diesel fuel) and engine oils are increasing throughout the world due to the environmental and performance regulations. Beside the sulphur content, aromatics and olefins are getting more and more unwanted compounds in the mentioned petroleum products (Dixson-Decléve, 2007). Among the different types of hydrocarbons (n-paraffins, i-paraffins, olefins, naphthenes, aromatics), isoparaffins have the most advantageous performance properties in gasolines, diesel fuels and even in base oils. Therefore, these hydrocarbon compounds have a great importance in the refining industry. New processes for low and medium temperature benzene saturating isomerization, which was developed by the authors, for catalytic hydrodewaxing of gas oils as well as for selective isomerization of lubricating base oils are presented in the paper, together with the excellent analytical and performance properties of the corresponding products.

1. Production of benzene-free light naphtha fractions rich in isoparaffins

Recently, hydrocarbon fractions rich in isoparaffins are one of the most important components of modern engine gasolines, because they have high octane numbers (ca. 85-100) with low sensitivity (difference of research and motor octane number). They also improve the octane number distribution (high octane number in the front end of the distillation curve). They are practically free of sulfur, olefins and aromatics, they are non-toxic and no harmful products are formed during their combustion. There are a number of cost-effective possibilities for the production of isoparaffin fractions in the refinery. These include separation of suitable gasoline fractions to iso- and n-paraffins, direct and indirect alkylation (dimerization of olefins followed by hydrogenation) and isomerization of n-paraffins.

Engine gasoline blending components rich in isoparaffins are mostly produced with the catalytic isomerization of C_5-C_7 paraffin hydrocarbons. Among the potential catalysts almost only the bi-functional hydroisomerization catalysts, active at low (<200°C) and medium temperatures (200°C-300°C), are industrially applied by now. This is caused the fact that the equilibrium concentration of high octane number isopentane and 2,2-dimetyl-butane decreases nearly exponentially with the temperature (Figure 1).

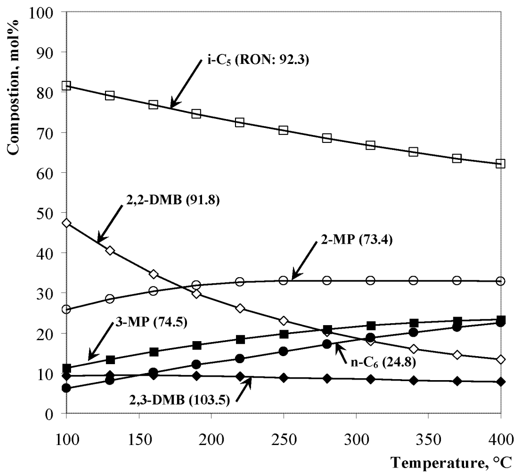

Figure 1: Equilibrium concentration of acyclic C_5 and C_6 paraffins at different temperatures

With a once-through operation, $Pt/Al_2O_3/Cl$ catalysts still provide the best octane number and highest yield of the isomerate product (Figure 2) (Anderson, et al., 2004). The reduction of benzene content in engine gasolines (≤ 1.0 v/v%) made the benzene reduction in light naphthas necessary. Out of the several possibilities for benzene reduction (extraction, alkylation, hydrogenation, etc.) our Department has developed the so-called benzene-saturating isomerization processes. These processes are the upgraded versions of the low and medium temperature light naphtha isomerization processes. The modified catalysts (new generation Pt/H-mordenite; combination of Pt/Al_2O_3 catalysts of different chlorine content) of these processes are able to simultaneously carry out the saturation of benzene (up to 4% in the feed) and isomerization of C_5-C_7 paraffins.

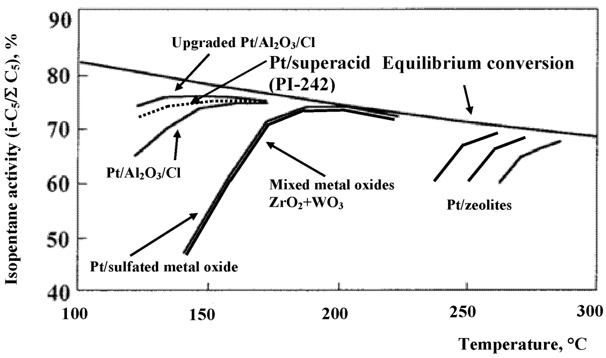

Figure 2: Comparison of the isomerization activity of several commercial isomerization catalysts.

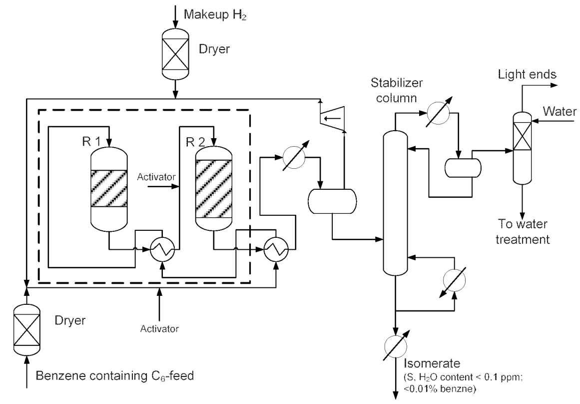

Figure 3. Simplified flow sheet of the new isomerising process for benzene containing n-hexane fraction

The simplified scheme of the new, low temperature benzene-saturating isomerization process developed by us is illustrated in Fig. 3. The main features of the process are given in Table 1 (Hancsók et al., 2007). In addition, for comparability reasons, Table 1 also contains the corresponding data for the medium temperature benzene-saturating isomerization process. This indicates well that the octane number of the isomerates produced in the one-step benzene-saturating isomerization process, which applies two reactors

Table 1. Comparison of the results of low temperature and medium temperature benzene saturating isomerization

Characteristics	Low temp. process	Medium temp. process
Catalyst	Pt/Al_2O_3/chlorine	Pt/H-mordenite
chlorine content, %		
reactor I.	3.0-4.1	-
reactor II.	7.1-9.1	-
Benzene in feed, %	0.0-4.6	0.0-4.6
Temperature, °C	120-190	260-265
LHSV, h^{-1}	1.5	1.0-1.5
Pressure, bar	25-30	25-30
H_2/HC molar ratio	1.5:1.0 (mean)	2.0:1.0
Stabilized isomerate		
yield, %	99.4-98.6	96.2-93.7
benzene content, %	<0.01	<0.01
After separating practically 100% of n-hexane		
yield, %	84.6-77.6	75.8-71.9
RON	86.0-86.4	82.4-84.6
MON	86.8-86.6	82.9-84.4
$\Delta RON_{(product-feed)}$	52.1-49.0	49.0-47.1

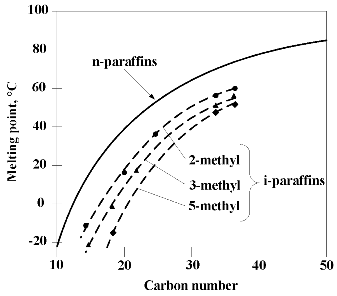

Figure 4. Melting point of paraffins C_{14}-C_{38} paraffins vs. carbon number

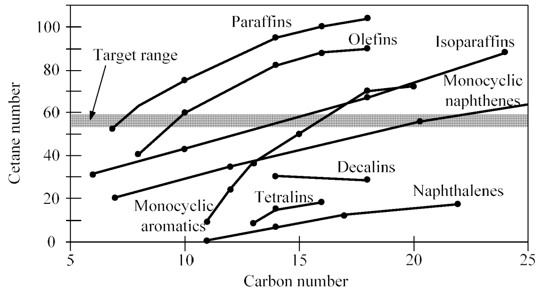

Figure 5. Cetane number of hydrocarbon types vs. carbon number

loaded with catalysts of different chlorine content (i.e. different ratios of hydrogenating / isomerizing activity) and operated at different process parameters, is about 2-5 units higher compared to those obtained in the medium temperature benzene-saturating isomerization beside the significant energy saving.

2. Production of diesel fuels rich in isoparaffins

In case of the diesel fuels, n-paraffins have the highest cetane numbers. On the other hand, melting point of these n-paraffins in the gas oil boiling range (230-370°C) can be well above the ambient temperature that worsens the cold flow properties (cold filter plugging point, pour point) of diesel fuels. Branched paraffins (especially C_{13}-C_{24} metil-paraffins), however, have both high cetane numbers and excellent cold flow properties (Figure 4 and 5) (Coutinho, 2000; Coutinho et a., 2002).
Main characteristics of a product mixture obtained through the hyrodewaxing of a previously deeply hydrodesulphurized gas oil fraction over a novel composition $Pt/SAPO\text{-}11/Al_2O_3$ catalyst, which was prepared by a new method, are summarized in Table 3.

Table 3. Characteristics of a gas oil product, hydrodewaxed over a novel $Pt/SAPO\text{-}11/Al_2O_3$ catalyst

Characteristics	Feedstock	Product
Density, g/cm^3	0.875	0.839
Boiling range, °C	230-378	225-362
CFPP, °C	+26	-7
Sulphur content, ppmw	131	37
Ratio of i/n-paraffins	0.37	3.2
Yields		
<220°C	-	6.7
gas oil	-	93.3
Cetane number	56	55

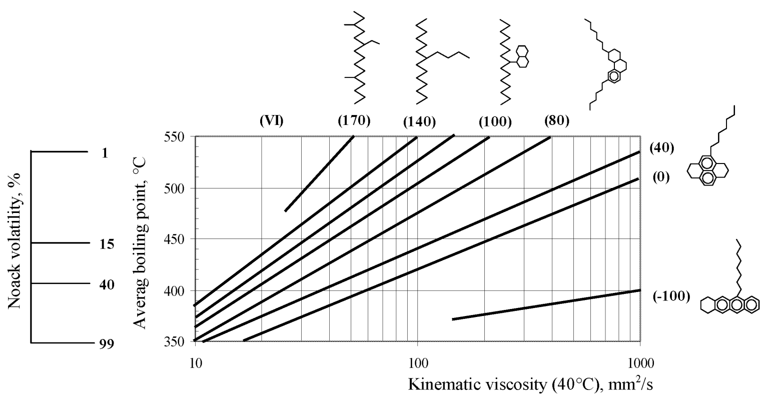

Figure 6. Relationship between the kinematic viscosity, Noack volatility and average boiling point of lubricating base oils

The data clearly demonstrate that in contrast with the conventional hydrodewaxing catalyst, the yield of gas oil is about 15-20 absolute % higher over Pt//SAPO-11/Al_2O_3, that is specially important in the European Union because of the increasing demand on diesel fuel. The characteristics of this product even fulfill the requirements of the valid EN 590:2004 standard for diesel fuels, except for CFPP. However CFPP can be adjusted to the required level with small concentration of cold flow improving additive.

3. Production of modern base oils rich in isoparaffins

As for the lubricant base oils, also isoparaffins have the most beneficial characteristics from lubrication aspects (Sivasanker, 2003). Isoparaffin molecules containing only one or a few side chains have high viscosity index (>140), low pour point, low Noack volatility and high oxidation stability at the same time (Figure 6) (Martin, 2005).
By modifying the Pt/SAPO-11/Al_2O_3 catalyst, which was mentioned in the previous section, for the isomerization of feeds rich in higher molecular weight (C_{20}-C_{40}) n-paraffins, results given in Table 4 were obtained.

Table 4. Results of hydrodewaxing of a wax feed over Pt/SAPO-11/Al_2O_3
(T: 320-360°C; P_{H2}:40-80 bar; LHSV:0.75 h^{-1}; H_2/HC: 320 $m^3/m^{3)}$

Characteristics	Feedstock	Base oil product
Content of C_{20-} hydrocarbons, wt%	9.8	16.9-14.6
Content of $C_{20+,}$ hydrocarbons wt%	90.2	83.1-86.4
Mass ratio of i-/n-paraffins	0.41	3.29-3.94
Kinematic viscosity (100°C), mm^2/s	-	3.9-4.15
Viscosity index	-	136-142
(pour point) , °C	+39	-17 (-) -12
Volatility, (Noack), %	-	14-10
Sulphur content, mg/kg	94	<10
Aromatics content	8.5	1.0-3.8

The data in Table 4 suggests that practically sulphur-free (<10 mg/kg), base oils of high viscosity index (136-142), low pour point (-17 to -12 °C) and very low aromatics content (1.2-3.8 wt%) can be produced with the selective isomerization of the solid product having high pour point.
These so-called Group III base oils (API categorization) are excellent blend stocks in the formulation of high performance engine oils, which are suitable for the reduction of fuel consumption (Infineum Trends, 2006).

Summary

In the petroleum refining industry (downstream and marketing division), the availability of practically sulphur-free blend stocks having very low aromatics content and high isoparaffin content is an essential criteria for maximizing profit in the production process of engine gasolines, diesel fuels and lube base oils. These blend stocks can be produced from suitable feedstocks by using hydroisomerization catalyst (e.g., with the benzene-saturating isomerization of benzeneous light naphtha feeds or with the selective isomerization of the n-paraffins contained in gas oil and lube base oils, over a tailor made Pt/SAPO-11/Al_2O_3, for instance).

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