

PRODUCTION OF ENVIRONMENTALLY FRIENDLY GASOLINE BLENDING COMPONENTS

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Our paper describes and evaluates the environmentally friendly possibilities to satisfy some new regulations for motor gasolines. During the research work the hydroisomerization of n-heptane containing n-hexane fractions was investigated on platinum/H-mordenite catalyst. The effect of temperature and liquid hourly space velocity on the yield of liquid and gas products, as well as their composition and properties were examined. The gained and our previous results indicated that the used catalyst with suitably chosen process conditions is applicable to upgrade a hexane fraction containing a few percents of n-heptane. With gasoline blending and emission predicting calculations we proved the advantageous properties of isoparaffin rich fractions. Thus we pointed out that the production of a gasoline containing more isoparaffins, less aromatics, olefins and MTBE decreases its potential harmful effects.

Keywords: environmentally friendly gasoline; hydroisomerization; reduction of emission

Introduction

As a by-product of the fast industrial development and motorization, our Earth suffers from serious environmental harms and damages. Among others one of the most significant is air pollution, the major part of which originates from the use of motor vehicles, as well as from the production, transportation and storage of their fuels. Besides the carbon dioxide causing greenhouse effect, the emissions of nitrogen-oxides, carbon monoxide and various hydrocarbons are significant.

Because of human biological aspects, the aromatic compounds getting to the atmosphere and – within these – the light aromatics as benzene and toluene are especially dangerous. The carcinogen benzene causes reversible depression of bone marrow activity and acute myeloid monocytic leukaemia, while toluene can generate nerve system damage [1]. The disadvantageous property of heavy aromatics is that they have the largest photochemical activity besides olefins in motor gasoline. Thus they greatly contribute to the formation of ozone and photochemical smog [2-4]. In turn ozone, even in low concentration, can cause lung damage. Nevertheless according to the car manufacturers

aromatic hydrocarbons are not only dangerous for biological organisms, but they also have a harmful effect on the catalysts of motor vehicles. These compounds are blamed for the deposits forming on the surface on the catalysts, and thus for their reduced activity.

However, gasoline blending components containing significant amount of aromatic compounds (e.g. reformate, pyrolysis gasoline, etc.) largely contribute to the gasoline pool even nowadays, since their high research octane number greatly helps in the production of unleaded motor gasoline having excellent anti-knock property.

Because of the preceding the benzene content, and later on possibly the total aromatic content of motor gasoline will be limited in the developed world [5]. The elimination of aromatic compounds like benzene decreases the octane number, especially the front octane number. The originating quantitative and qualitative demands have to be satisfied with the use of other gasoline blending components.

One possible, widely used solution is the application of oxygenates (MTBE, ETBE, TAME, ethanol, methanol, etc.) having high octane number and volatility. Due to their oxygen content these compounds

Table 1 Main feed properties

Properties	Feed type				
	A	B	C	D	E
Composition, %					
2,3-Dimethylbutane	0.1	-	-	-	-
2-Methylpentane	0.4	0.5	0.3	0.3	0.3
3-Methylpentane	0.4	1.0	0.6	0.3	0.5
n-Hexane	98.7	96.5	95.8	93.2	89.5
Methylcyclopentane	0.4	0.9	0.3	0.4	0.5
n-Heptane	-	1.1	3.0	5.8	9.2
Sulphur content, ppm			24-28		
Water content, ppm			37-48		
Research octane number	31.7	31.8	30.7	29.7	27.9
Motor octane number	30.6	30.8	29.7	28.8	27.9

promote the perfect burning, although their thermal values are lower than those of the commonly used gasoline blending components containing hydrocarbons. On the other hand oxygenates are soluble in water, therefore in case of leakage they can go further into water like other blending components, endangering seriously the animal world and flora [6]. It implies further dangers that their atmospheric reactivity (TAME, ETBE) and ozone producing activity are high, too [2-4]. Furthermore, animal evidence suggests that MTBE may be a weak carcinogen. The U.S. petrochemical industry and U.S. EPA reviewed the results of a 3.5 million USD study on mice and rats exposed by inhalation to MTBE. At high concentrations, rats exhibited kidney lesions and tumours, and mice developed liver tumours [6,7]. On the basis of these results, MTBE-free gasoline was put into market in California. Instead of MTBE the less harmful ethanol was used [8].

In addition to oxygenates numerous, environmentally more friendly motor gasoline blending components (e.g. alkylate, isomerate) are at the refineries disposal to satisfy quality and quantity demands originating from the reduction of benzene and total aromatic content of motor gasolines. However, their production in larger quantity is not possible, because the availability of their raw materials is limited, or their production is too expensive. Thus the economic and combined way to produce motor gasoline with reduced benzene and total aromatic content is the reduction of concentration of aromatic hydrocarbons in blending components having large aromatic content, and their use in lower quantity.

Since one of the most significant benzene and aromatic sources is reformate, a possible way to produce gasolines with less aromatics is the use of reformate with reduced aromatic content. One possible solution is the increase of the initial boiling point of feeds of reforming units. In this way benzene, its precursors and partly the precursors of toluene (the heptanes) are removed from the feed. Thus these compounds go to the light gasoline [9,10].

This light fraction has low octane number, thus it cannot be used as gasoline blending component without any conversion. This could be the catalytic isomerisation. However, there is little information on

the isomerisation of heptanes containing hexane fractions (especially n-heptane having RON of 0) [11]. Thus during our research work the isomerisation of n-heptane containing hexane fractions was studied on an isomerisation catalyst active at middle-temperature. With gasoline blending calculations we proved the advantageous properties of isoparaffin rich fractions. Furthermore we pointed out that the connection of isomerisation and reforming units will become more important in the refineries.

Experimental

Materials

Experiments were carried out with different n-heptane containing hexane fractions. Table 1 shows the main properties of feeds. Hydrogen was purified by passing through an oxygen converter containing Pd/alumina catalyst, followed by a molecular sieve LINDE 4A trap at room temperature. A 0.4 % Pt/H-mordenite/alumina was applied as catalyst.

Apparatus

Experiments were performed in a continuous tubular reactor free of back mixing which made possible pre-treatments (drying, reduction) of the catalyst and the study of its activity. The description of the apparatus is given elsewhere [12].

Method

The catalyst was packed in the isothermal zone of the reactor between two layers of Raschig rings and activated in situ, in flowing hydrogen as described according to the following. The temperature of catalyst bed was increased from room temperature to $300 \pm 2^\circ\text{C}$ with a rate of $25\text{-}30^\circ\text{C h}^{-1}$ in $40 \pm 1 \text{ dm}^3 \text{ h}^{-1}$ dry hydrogen flow at atmospheric pressure. The catalyst was kept at this temperature for 5 h in hydrogen flow, then it was heated to $450 \pm 2^\circ\text{C}$ as before kept at this temperature for 2 h, and cooled to the reaction temperature with a rate of $25\text{-}30^\circ\text{C h}^{-1}$ in hydrogen flow.

The composition of feeds and products was determined according to the ASTM-D 5134-90 standard.

The research and motor octane numbers (RON and MON) were calculated on the basis of the blending octane numbers of the components and their volume percent.

The applicability of the high quality products as favourable gasoline blending components was proven by a product blend optimisation program run under HPI Gasoline Blending Optimizer (Model-MG) software package for the case of achieving maximum profitability and limiting benzene, aromatics and MTBE.

Table 2 Process parameters

Parameters	
Temperature, °C	210-270
Pressure, bar	20-40
Liquid hourly space velocity (LHSV), h ⁻¹	1.0-3.0
Hydrogen/Hydrocarbon molar ratio	1:1-3:1

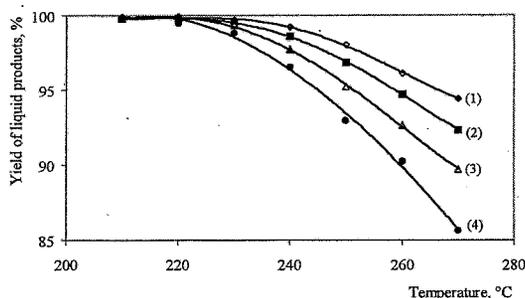


Fig. 1 The yield of liquid products as a function of temperature, n-heptane in feed: 3.0 %: 1) LHSV: 3.0 h⁻¹, 2) LHSV: 2.0 h⁻¹, 3) LHSV: 1.5 h⁻¹, 4) LHSV: 1.0 h⁻¹

Results and Discussion

During our research work the effect of process conditions and n-heptane content on the yield of liquid (C₅+) and gas products (C₄-), their quality and octane number were examined. Process parameters applied in the reactor system are shown in Table 2. In the following, the favourable results in respect of isomerisation of n-hexane are discussed.

The yield of liquid products decreased with increasing temperature in all cases, as Fig. 1 shows for 3.0 % n-heptane containing feed. Of course the yield of gas products changed inversely containing mainly isobutane and propane. On the other hand the amount of liquid products almost linearly decreased with n-heptane content of feeds, and as Fig. 2 indicates these lines become more precipitous as temperature increased.

The isomerisation reactions of n-hexane were characterised by the approach of equilibrium concentration of 2,2-dimethylbutane at the given temperature, since the reaction rate of 2,2-dimethylbutane formation is the lowest during the isomerisation of n-hexane. Therefore, all the other components in the product approach their equilibrium concentrations to greater degrees than 2,2-dimethylbutane. This is well proven as an example by the data reported for 2- and 3-methylpentane in Table 3.

The DATEC values for 2,2-dimethylbutane decreased on increasing n-heptane content in the feed (Table 3). n-Heptane inhibited the isomerisation of n-hexane and this inhibition was most pronounced for the slowest isomerisation conversion, i.e. for the formation of 2,2-dimethylbutane.

The yield of the mixture of isoparaffins also decreased with increasing n-heptane content in the feed because of reasons discussed before. The RON of isoparaffin mixtures is nearly the same for all feeds (82.6-83.2, Table 3). n-Heptane slows down to some

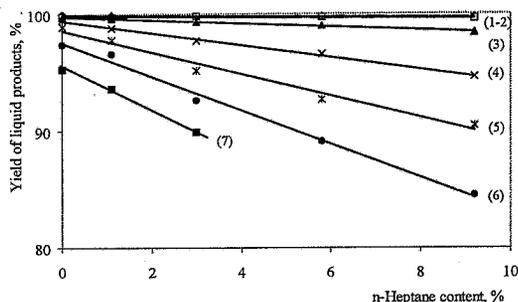


Fig. 2 The yield of liquid products as a function of n-heptane in feeds, LHSV: 1.5 h⁻¹: 1) 210°C, 2) 220°C, 3) 230°C, 4) 240°C, 5) 250°C, 6) 260°C, 7) 270°C

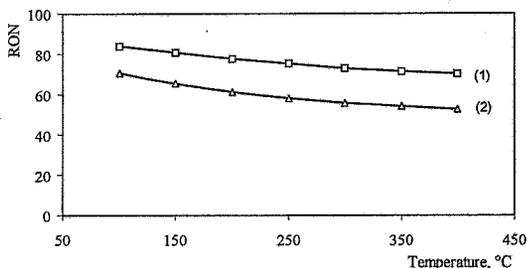


Fig. 3 The equilibrium octane number of 1) hexanes and 2) heptanes

extent the isomerisation of n-hexane, but simultaneously it isomerises to isoheptanes. However, as Fig. 3 shows, the RON of hexanes is higher than that of heptanes at equilibrium composition.

The advantageous properties of isomerate were proved by blend optimisation runs (HPI Gasoline Blending Optimizer, Model-MG) performed with the use of other gasoline blending components (MTBE, n-butane, light straight run gasoline, alkylate, FCC gasoline, reformat, hydrocrackate, raffinate, aromatics). The addition of isomerate helps to satisfy the new regulations by decreasing the total aromatic, olefin, benzene and MTBE content (Table 4). The sulphur content of the blended gasoline also decreased from 0.0199 % to 0.0175 % applying isomerate. But gasoline with less than 1 vol. % benzene can only be produced, if the reformat has less benzene content, i.e. its precursors are eliminated before the reforming unit [10]. The light gasoline can be upgraded in the isomerisation unit together with its original feed rich in C₅/C₆ n-paraffins.

In Table 4 we also summarised the predicted emissions gained by the use of calculated gasoline properties. To predict the emissions the following equations, developed by AUTO/OIL Programme and CONCAWE, were used [13,14].

Emission of carbon monoxide, g km⁻¹:

$$E_{CO} = [2459 - 0.05513 E_{100} + 0.0005345 E_{100}^2 + 0.009226 C_A - 0.0003103(97 - C_S)] \cdot [1 - 0.37 \cdot (C_{O_2} - 17.5)] \cdot [1 - 0.008 \cdot (E_{150} - 902)]$$

Table 3 Summary of the most important isomerisation results

Feed type	A	B	C	D	E
n-Heptane in feed, %	0.0	1.1	3.0	5.8	9.2
Temperature, °C	260-270	260-270	260-270	260	260
Hydrogen/hydrocarbon molar ratio			2:1		
LHSV, h ⁻¹	1.0-1.5	1.0-1.5	1.0-1.5	1.0	1.5
Liquid (C ₅ +) product characteristics					
Yield, %	96.5-94.9	93.5-3.6	90.2-89.9	86.4	84.5
DATEC of 2,2-DMB, %	77.4-68.2	73.3-63.2	64.0-63.2	60.8	43.0
DATEC of 2-MP and 3-MP, %	99.8-99.9	99.8-99.7	99.8-99.6	98.5	89.2
iso- and cycloparaffins					
Yield, %	76.4-72.9	72.9-70.7	68.4-67.7	64.3	55.0
RON	82.4-82.2	82.4-82.0	82.1-82.0	82.1	81.6
MON	82.9-82.7	82.9-82.4	82.6-82.5	82.6	82.1

Table 4 Summary of the gasoline blending and emission predicting calculations

	Number of blending calculation			
	1	2	3	4
Some specifications of gasoline				
RON at least			95	
Limit of E _A max., vol. %			40	
Limit of E _B max., vol. %	2.0	2.0	1.0	1.0
Benzene content of reformat, vol. %	4.0	4.0	4.0	2.0
Blended gasoline at maximum profit				
Use of isomerate	no	yes	yes	yes
aromatic content, vol. %	34.9	32.8	32.6	31.5
benzene content, vol. %	2.0	1.8	1.7	1.0
olefin content, vol. %	9.3	9.3	8.6	7.9
MTBE content, vol. %	0.9	0.5	0.9	0.5
sulphur content, %	0.0199	0.0204	0.0188	0.0175
Calculated emissions, g km ⁻¹				
CO	1.25	1.18	1.18	1.16
HC	0.18	0.17	0.17	0.17
NO _x	0.15	0.16	0.16	0.16
Benzene	0.063	0.059	0.058	0.050

Emission of hydrocarbons, g km⁻¹:

$$E_{CH} = [0.1347 - 0.000548E_A + 257C_A e^{-(0.2642E_{100})} - 0.000040(97 - C_S)] [1 - 0.004(C_{O1} - 4.97)] [1 - 0.022(C_{O2} - 1.75)] [1 - 0.01(E_{150} - 90.2)]$$

Emission of nitrogen oxides, g km⁻¹:

$$E_{NO_x} = [0.1884 - 0.001438C_A + 0.00001959E_{100} \cdot C_A - 0.00005302(97 - C_S)] \cdot [1 + 0.004(C_{O1} - 4.97)] \cdot [1 + 0.001 \cdot (C_{O2} - 1.75)] \cdot [1 + 0.008(E_{150} - 90.2)]$$

Emission of benzene, g km⁻¹:

$$E_B = [15.74 + 11.711C_B + 0.7289(C_A - C_B)]$$

The emission predicting results confirm that the use of isomerate highly decreased the emission of CO and benzene. The emission of hydrocarbons did not decreased significantly, though that of NO_x slightly increased.

Conclusions

Hexane fractions containing few percents (1-2 %) n-heptane can be upgraded resulting in high octane number increase on Pt/H-mordenite/alumina catalyst, under suitably chosen process parameters and recycling of components having low octane number. Naturally the application of isomerisation of light gasoline fractions containing n-heptane strongly depends on the availability of technologies of a given refinery, needs of petrochemicals and the environmental protection regulations. However, based on our gasoline blending calculation data we proved the advantageous properties of isoparaffin rich fractions. Furthermore, we pointed out that the connection of isomerisation and reforming units will become more important in the future.

Moreover, emission-predicting results confirm that the use of isomerate decreases the emission of carbon monoxide, hydrocarbons, benzene, though that of NO_x slightly increases.

SYMBOLS

MTBE	methyl tertiary butyl ether
ETBE	ethyl tertiary butyl ether
TAME	tertiary amyl methyl ether
U.S.EPA	United States Environmental Protection Agency
RON	research octane number
MON	motor octane number
LHSV	liquid hourly space velocity
2-MP	2-methylpentane
3-MP	3-methylpentane
2,2-DMB	2,2-dimethylbutane
DATEC	degree of approach of thermodynamical equilibrium concentration
FCC	fluid catalytic cracking
CONCAWE	Conservation of Clean Air and Water - Europe

E_{CO}	emission of carbon monoxide, $g\ km^{-1}$
E_{CH}	emission of hydrocarbons, $g\ km^{-1}$
E_{NO_x}	emission of nitrogen oxides, $g\ km^{-1}$
E_B	emission of benzene, $g\ km^{-1}$
E_{100}	volume percent distilled at $100^\circ C$, %
E_{150}	volume percent distilled at $150^\circ C$, %
C_A	total aromatics content, vol. %
C_{Ol}	total olefin content vol. %
C_{O_2}	oxygen content, %
C_B	benzene content, vol. %
C_S	sulphur content, %

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