HUNGARIAN JOURNAL
OF INDUSTRIAL CHEMISTRY
VESZPRÉM
Vol. 30. pp. 299 - 303 (2002)

HYDROTREATING OF FULL RANGE FCC GASOLINE

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Received: November 20, 2002

Sulphur content of engine gasoline must be reduced below 50 ppm in the European Union from 2005, and gasoline containing 10 ppm sulphur will have tax allowance [1,2]. FCC gasoline is one of the blend stocks being applied in largest amount (about 20-50%). The sulphur content of this is significant (about 50-2000 ppm), therefore 50-95% of the sulphur species of gasoline originates from this stream. Selective hydrotreating of FCC gasoline may be a favourable technique among the numerous new desulphurising methods. Achievements of a research work, made for hydrotreating a full range of FCC gasoline, are presented in this paper. The authors were able to find combinations of process parameters being suitable to produce gasoline blend stock of 11 ppm sulphur content with only 2 units loss of octane number.

Keywords: FCC gasoline, desulphurization, olefin saturation, octane loss

Introduction

Further reduction of the automotive emission can be achieved effectively with complex development of fuels, engine construction, lubricants and other parts of vehicles (catalytic converter, tyre etc.). Currently the sulphur specifications have dominant importance from the point of view of engine gasoline, because combustion products of sulphur species – beside air pollution – are poison the vehicle catalysts. Thus further significant reduction of sulphur content can be expected (*Table 1*) [3].

Three main long-run methods are offered for reducing sulphur content of gasoline, each of which results in lower sulphur content of FCC gasoline: reduction by hydrofining of FCC feed, application of new catalysts and catalyst additives in the FCC unit and desulphurisation of FCC gasoline [4, 5]. These strategies can be used either in themselves or in combination. Nevertheless, desulphurisation of FCC gasoline cannot generally be avoided to meet ultra low sulphur specifications of engine gasoline.

The loss of octane number can be very significant (up to 10-15 units) applying conventional hydrotreating of FCC gasoline. Accordingly, this process is not economical from two aspects: partly due to considerable loss of octane number, partly because significant hydrogen consumption. A number of desulphurising processes for FCC gasoline have been developed which can economically be used to produce low sulphur FCC gasoline with acceptable loss of octane number [6-17].

The new desulphurising processes are widely diversified in respect of their principle and technical configuration (selective hydrotreating, adsorption, extractive distillation, caustic extraction etc.). Options for desulphurisation of FCC gasoline are summarized in *Table 2* [18]. Some of these processes treat full range FCC gasoline, but others accomplish desulphurisation with only a portion of FCC gasoline. It is extremely important in the latter processes that the column for the distillation of gasoline has to be optimally designed and the cut point well selected [19].

Fig.1 illustrates the major optional pathways for post-treating of FCC gasoline. The main features of the processes indicated on this figure were already presented in *Table 2*. In some cases the light fraction of FCC gasoline is sent to an etherification or alkylation unit for boosting the octane number, while the heavier fraction is hydrotreated. This kind of combination reduces the overall octane loss of post-treating. These processes were not indicated on *Fig.1*.

During the research, the possibility of desulphurisation of a full range FCC gasoline on Pt,Pd/zeolite has been investigated. The aim of the study was to examine the effect of process parameters (primarily temperature and liquid hourly space velocity) on the yield and quality of liquid product and to determine the advantageous process parameters.

Table 1 Actual and planned motor gasoline specifications

Region, country, state	Maximum sulphur content ppm (actual)	Maximum sulphur content ppm (planned)	Maximum olefin content V/V % (actual)	Maximum olefin content V/V % (planned)
USA	500	30 (2006)	25	no change
California	30	15 (end of 2002)	4	no change
EU	150	50 (2005)	18	still not decided
Japan	100	10 (2008?)	not specified	still not decided

Table 2 Options for the desulphurisation of FCC gasoline

Process	Key feature	Industrial application	H_2-consumption	Octane loss	Name of process	Licensors
Naphtha hydro-treating (NHT)	conventional	yes	high	high	various	a number of firms
NHT+ octane increase	zeolite + isomerisation	yes	high	low	Octgain, Isal	ExxonMobil, UOP
Selective NHT	RT-225	yes	medium	low	SCANfining	ExxonMobil
	dual catalyst	yes	medium	low	Prime-G+	IFP
	catalytic distillation	yes	medium	low	CDHydro/ CDHDS	CDTech
Selective NHT + octane increase	combination	yes	medium	low	SCANfining II	ExxonMobil
Adsorption	Zn adsorbent	yes	low	low	S Zorb	Philips
	alumina adsorbent	pilot	low	low	Irvad	Alcoa
Extractive distillation	selective solvent sys.	yes	none	low	GT-DeSulf	GTC
Oxidation	peroxyacid	pilot	none	low	CED	Petrostar
	ultrasound	pilot	none	low	SulphCo	Bechtel
Alkylation	solid acid	pilot	low	low	OATS	BP
Bio processing	bio catalysis	no	none	low		Enchira

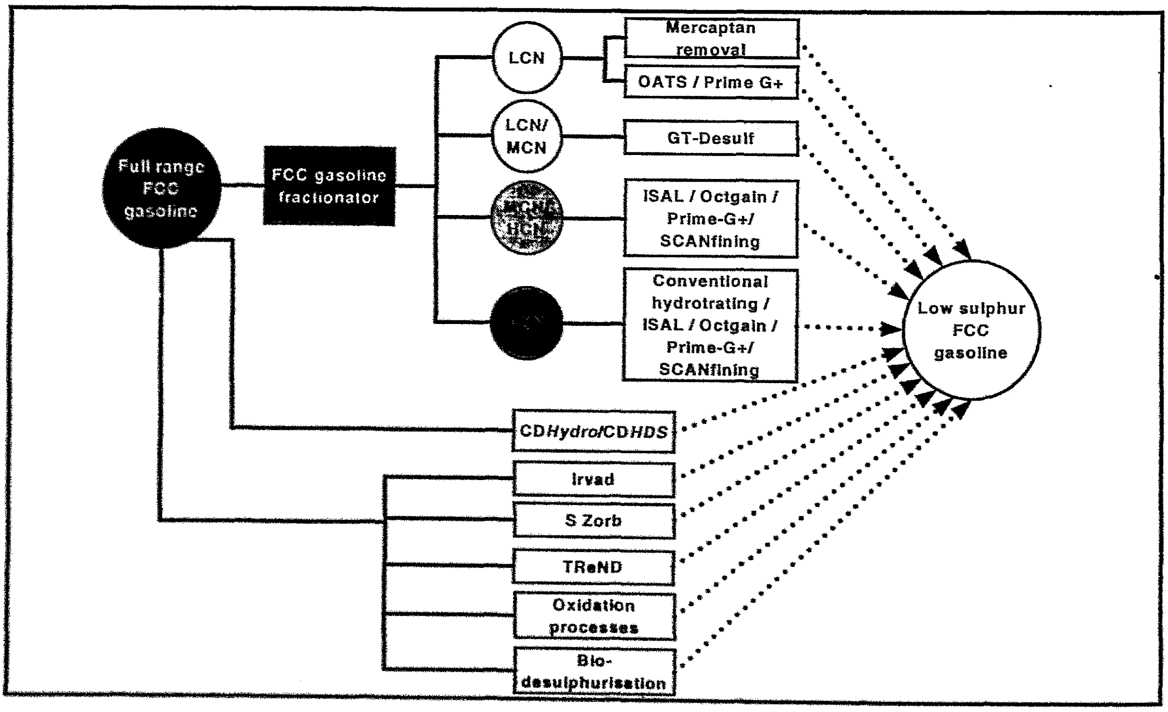

Fig. 1 Major optional pathways for the desulphurisation of FCC gasoline

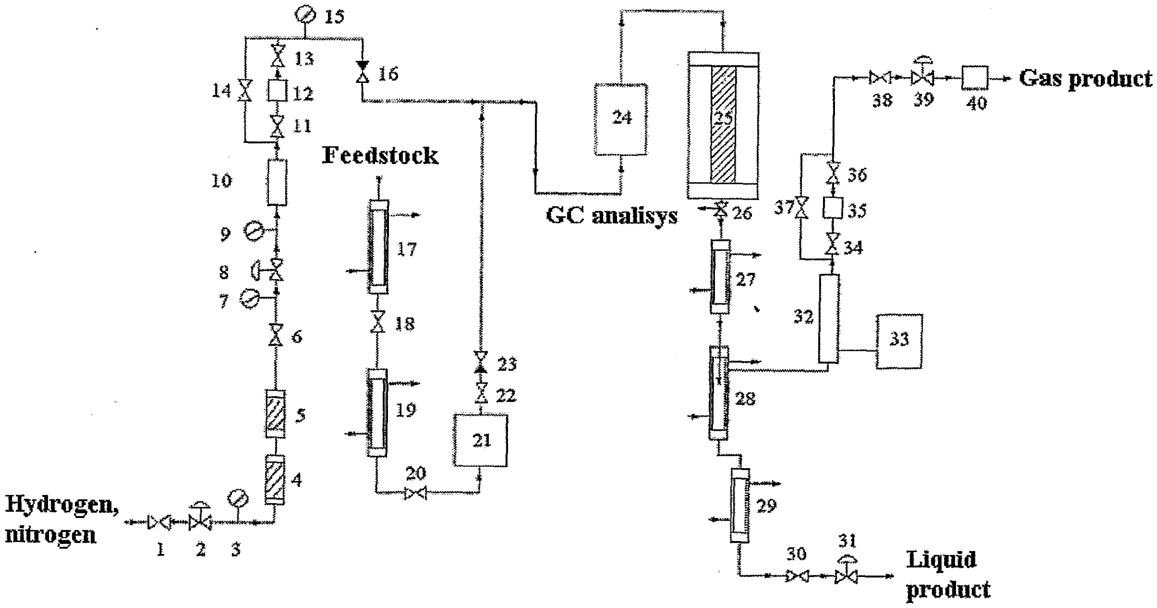

Fig.2 Simplified drawing of the test apparatus. Notations: 1, 6, 11, 13, 14, 18, 20, 22, 30, 34, 36, 37, 38: closing valves; 2, 8, 31, 39: control valves; 3, 7, 9, 15: manometers, 4: oxygen converter; 5: dryer; 10, 32: gas filter; 12: gas flow meter/controller; 16, 23: back valve; 17, 19: liquid feeds burettes; 21: liquid pump; 24: pre-heater; 25: reactor, 26: sampling valve, 27, 29: cooler, 28: separator; 33: pressure recorder; 35: pressure controller; 40: wet gas flow meter

Experimental

Apparatus

Desulphurisation of FCC gasoline has been carried out in a high-pressure reactor system (*Fig.2*) at the Department of Hydrocarbon and Coal Processing, University of Veszprém. This consists of a tubular reactor of 100 cm^3 efficient volume and is free of back mixing. It contains the same equipments and devices applied in the reactor system of desulphurising plants (pumps, separators, heat exchangers, as well as regulators of temperature, pressure and gas flow).

Catalysts

The hydrodesulphurising experiments were carried out on Pt,Pd/zeolite catalyst, applying 80 cm^3 of it.

Feedstock

As feedstock of the desulphurising experiments a full boiling range (data of simulated distillation: 6-228 °C) FCC gasoline were used. The major quality features are summarised in *Table 3*.

Methods

Compositions of feedstock and liquid products were analysed by gas chromatography (CHROMOCTANE) and the quality characteristics were calculated by a software from these compositions. Composition of gas products was determined, by gas chromatography (ASTM D 5134-90). Sulphur content was measured by pyro-fluorescence method (ASTM D 5453). The experiments were carried out on catalyst of steady-state activity, by continuous operation.

Results and discussion

Process parameters of the experiments (*Table 4*) were selected and based on literature data and on earlier results of the Department.

From the results of the experiments it can be stated that crack reactions – resulting in lighter hydrocarbons – have not proceeded in the investigated temperature range, because the yield of liquid products was high (>99.5 %) at every combination of process parameters.

The degree of desulphurisation of FCC gasoline depended on the process conditions. Sulphur content of the products (*Fig.3*) became lower with increasing temperature and decreasing LHSV. The highest level of desulphurisation (80 %) was reached at 280 °C and LHSV = 1.0 (*Fig.4*). Under these conditions the product contained 11 ppm sulphur.

Table 3 Main properties of the feedstock

Density (15,6°C), g/cm^3	0.7423
Sulphur, ppm	63
Nitrogen, ppm	13
Research octane number	93.4
Motor octane number	81.7
(RON + MON)/2	87.6
Composition, %	
n-paraffins	4.0
i-paraffins	31.8
olefins	24.9
aromatics	31.7
naphthenes	7.6

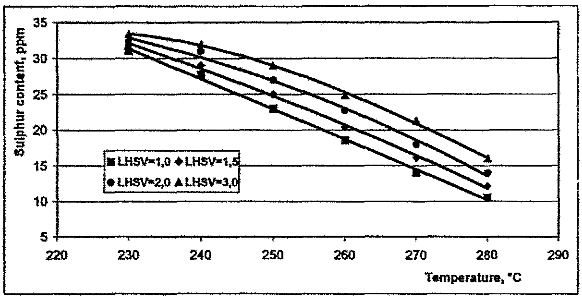

Fig.3 Sulphur content of products as function of temperature

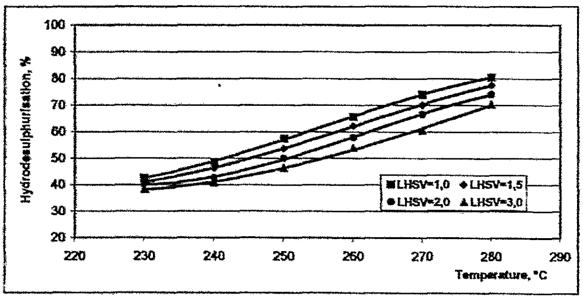

Fig.4 Hydrodesulphurisation as function of temperature

Taking into account the composition of the feedstock and products it can be stated that the olefin content of each product decreased in proportion to the feedstock. The degree of saturation of olefins as function of temperature is shown on *Fig.5*. Higher temperature and lower LHSV resulted in higher olefin saturation. The highest olefin saturation (approx. 50 %) occurred when desulphurisation was the lowest. Mainly paraffins have formed from the olefins, but in a less degree also aromatics and naphthenes. Evaluating the change of the concentration of paraffins it was stated that more n-paraffins than i-paraffins were formed from the olefins. Every product had lower iso/normal paraffin ratio than the feedstock (8.0). This ratio is presented on *Fig.6* as function of temperature. The ratio was lower at higher temperatures and lower LHSV. This can be attributed to thermodynamic reasons, because higher temperature hinders isomerisation.

Table 4 Applied process parameters

Parameter	Property
Reaction temperature, °C	230-280
Reaction pressure, bar	30
Liquid hourly space velocity, h^{-1}	1,0-3,0
H_2/hydrocarbon ratio, m^3/m^3	300

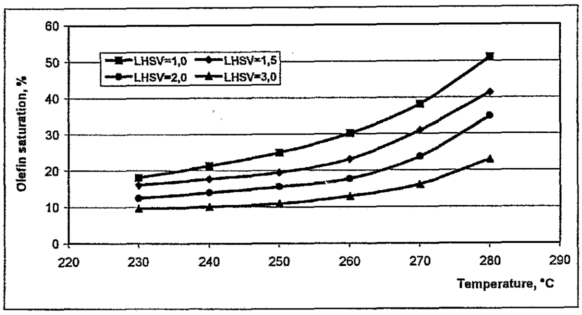

Fig.5 Olefin saturation as function of temperature

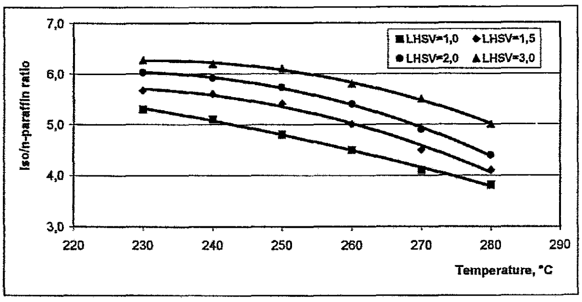

Fig.6 Iso/n-paraffin ratio as function of temperature

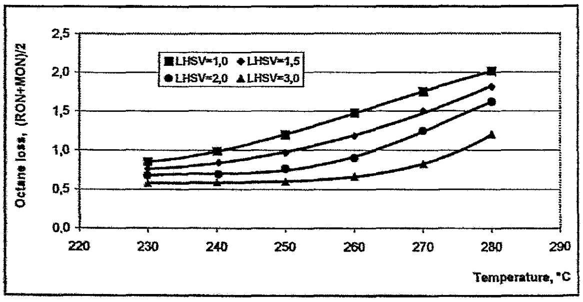

Fig.7 Loss of octane number as function of temperature

The outcome of the mentioned chemical changes was the lower octane number of the products. *Fig.7* illustrates the loss of octane number as function of temperature. The largest loss of octane number (2 units in [RON+MON]/2: the average of RON and MON) was observed at 280 °C, LHSV = 1.0 h^{-1}. Sensibility of every product became lower due to saturation of olefins. By desulphurisation to the same degree, the lowest loss of octane number could be reached with the largest LHSV (3.0 h^{-1}).

Removal of the light fraction of FCC gasoline could result in significant reduction of the loss of octane number, or lower sulphur content could be reached with the same loss of octane number.

Conclusions

From the results of the investigation carried out on Pt,Pd/zeolit catalyst with the use of full range FCC gasoline, having 63 ppm sulphur content it can be stated that at advantageous process conditions (280°C; 30 bar; LHSV=1,0; H_2/HC = 300) FCC gasoline of 11 ppm sulphur content can be produced with high yield and only 2 units decrease of octane number ([RON+MON]/2: average of RON and MON).

About 75 % of the olefins are in the light fraction of the feedstock (below 70 °C). This light fraction may contain very little sulphur, because it was passed through a Merox unit in the refinery, which extracts the mercaptans from the light fraction. Below 70 °C thiophenes are not present. This means that if we would cut the feedstock at 70 °C and we would only hydrotreat the heavier fraction, significant octane loss reduction could be reached, but only about 2 or 3 ppm of sulphur would bypass the desulphurisation with the light fraction. Furthermore, we can raise the temperature of the reactor, and we can reach higher level of desulphurisation without facing further significant octane loss. However, we have to confirm this with further experiments, and this is the aim of our next research work.

Nevertheless, our results confirm the opinion that hydrodesulphurisation of FCC gasoline can mainly be accomplished effectively and economically by expedient refinement of light and heavy fractions gained by fractionation.

ACRONYMS

FCC - fluid catalytic cracking
HCN - heavy cracked naphtha
LCN - light cracked naphtha
LHSV - liquid hourly space velocity
MCN - medium cracked naphtha
MON - motor octane number
RON - research octane number

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