End Point Reduction Of Diesel Using Zeolite Catalysts

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ABSTRACT

For most refiners, the overall availability of diesel has become less due to end point (T_{95}) lowering to meet fuel specifications, even though demand for diesel is on the rise. One way of increasing diesel output is by shifting the gas oil cut point to a higher temperature and reducing the end point of the deep cut diesel to the desired level by catalytic treatment. The present work summarizes the studies on the end point reduction of a straight run diesel feedstock (1.7 wt% S and 140 ppm N) over supported Ni-Mo formulations containing different zeolites. Three different zeolites and alumina were used for preparing the support material. The supports were then loaded with molybdenum and nickel. The end point reduction studies were carried out in a high-pressure reactor system at different operating conditions. The products were analyzed by a gas chromatographic simulated distillation method (ASTM D2887) and distillation (ASTM D86). A comparison of the performance of Ni-Mo catalysts containing different zeolites is presented in this work. Studies have confirmed that substantial end point (T_{95}) reduction of about 15-17°C can be achieved over zeolite catalysts.

Key words: Diesel end point, diesel specifications, zeolites, Ni-Mo-zeolite/alumina, hydrodesulfurization

1. Introduction

Global specifications for diesel are changing continuously to curtail hazardous emission from diesel vehicles. Sulfur content and end point (T_{95}) are the two important specifications targeted in diesel to improve its quality. In India, the sulfur content was decreased from 500 ppmw in 2000 (BS II) to 50 ppmw in 2010 (BS IV), and likewise, the T_{95} distillation temperature was reduced from 370 °C in BS II to 360 °C in BS IV specifications. The principal components of diesel emissions are particulate matter (soot), NOx and S-oxides. Though a reduction in S-content significantly reduces the amount of S-oxides and to a certain extent soot formation, substantial reduction of soot will be possible only if the amount of aromatic compounds, especially the large aromatic molecules, are decreased in the fuel. The content of these compounds increases with the end point of the diesel oil. Similarly, the refractory S-compounds, such as the dibetadialkyldibenzothiophenes that are difficult to desulfurize also increase with the end

point of the diesel [1]. Thus, there is a need to reduce the diesel end point to decrease both the aromatic components and the refractory S-compounds. As a consequence, along with the progressive decrease in the S-content of diesel fuel over the years, its end point (T_{95}) is also being lowered [2].

Lowering of the end point (EP) leads to a decreased availability of diesel. On the contrary, the refiner's diesel pool will be larger if the final cut point were higher, say 400°C. As the major components in the heavier end of diesel are the alkyl di- and poly-nuclear aromatics and long chain n-paraffins, it is possible to bring down the end point of the heavy diesel (T_{95} ~ 400°C) by dealkylation and ring hydrogenation of the aromatics and mild isomerization of the n-paraffins. This can be achieved by hydrotreating the heavy diesel over suitable catalysts. Essentially, the end point reduction process is similar to mild hydrocracking, but with a shift in focus with respect to the desired reactions. While hydrocracking essentially uses a

heavier feed (370 - 550°C) and aims at total hydrogenation of the multi-ring aromatics and subsequent ring opening of the naphthenic molecules and the hydrocracking of the long-chain n-paraffins [3], the end point reduction goals are rather modest as mentioned above, aimed only at end point reduction with minimal diesel yield loss. To date, no commercial process exists for the end point reduction of straight run diesel. However deep desulfurization processes incorporating additional reactors and catalysts to improve diesel quality and end point reduction are available [4,5]. A separate reactor with a different catalyst downstream of the HDS reactor(s) is generally used for diesel quality improvement.

The objective of the present work is to study the catalytic reduction of T_{95} distillation temperature with simultaneous desulphurization of a heavy straight run diesel fraction with a large S content under mild process conditions using zeolite containing catalysts. The aim is to achieve an EP decrease of ~ 20°C with minimal diesel yield loss.

The performance of the catalysts is evaluated in high-pressure bench-scale reactor set-up.

1.1. Diesel End Point Reduction – Important Reactions

The desired reactions that tend to lower the end point are: i) dealkylation of alkyl aromatics, ii) ring hydrogenation of the aromatics, iii) ring opening of naphthenes and hydrogenated aromatic rings, and iv) isomerization of n-paraffins. Important reactions that reduce the end point of diesel are shown below in reactions a to c. Dealkylation, hydrogenation and ring opening reactions can decrease the end point (and the pour point) and at the same time increase the cetane number. Since isomerization produces isoparaffins, which possess lower cetane numbers (CN) than the n-paraffins, only mild (and limited) isomerization is to be done to avoid significant CN loss. The overall effect of all these reactions is a decrease in diesel end point and improving diesel quality.
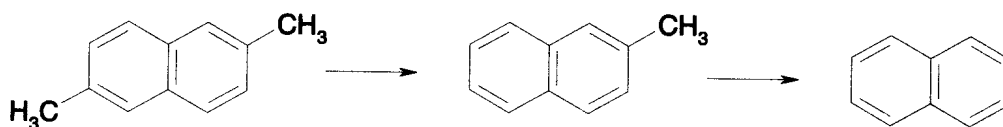
Typical reactions expected to occur during end point reduction:

a) <u>Dealkylation</u> (occurs on acid sites)

(2,6-dimethylnaphthalene)   (2-methylnaphthalene)   (naphthalene)

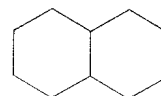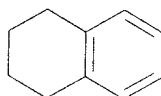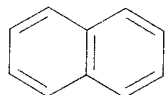B.p. (°C)   360   241   218

b) <u>Ring hydrogenation</u> (occurs on metal sites)

(naphthalene)   (tetralin)   (decalin)
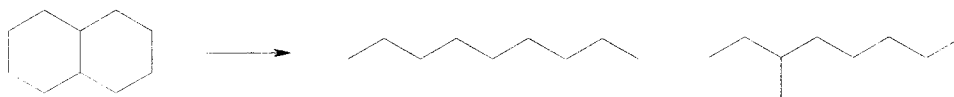
B.p. (°C)   218   207   193

c)   Ring opening and isomerization (require both metal and acid site)

(decalin)   (n-decane)   (3-methylnonane)

B.p. (°C)   193   174   165

d)   Cracking of paraffins (require mostly acid sites)

n-C_{20} paraffin (eicosane)   →   [lighter hydrocarbons, eg. n-decane, n-pentane etc.)]

B.p. (°C)   344   174   36

Besides the desired reactions (a – c), cracking reactions (d) that decrease the molecular weight of the hydrocarbons substantially can also occur. Such reactions cause a loss of diesel yield and are not desirable. The catalyst should minimize such cracking reactions to obtain reasonable yield of diesel. Besides the reactions shown above, HDS and HDN reactions will also take place. HDS reactions are also expected to make the feed lighter; for eg. HDS of 4,6-dimethyl dibenzothiophene (b.p. 365 °C) produces the lighter hydrocarbon, 4,4'-dimethylbiphenyl (b.p. 295 °C).

1.2 Requirement of end point reduction catalysts

The catalysts useful for end point reduction of diesel are dual functional catalysts that possess metallic and acidic functions. The metallic function takes part in hydrogenation-dehydrogenation, hydrogenolysis and ring opening reactions. The acid function is necessary for isomerization, ring opening and dealkylation reactions. In fact, some of the reactions like ring opening, isomerization and hydrocracking may require both acidic and metallic sites. The proposed catalyst is expected to possess the following components for its proper functionality to reduce end point of a high S straight run diesel fraction.

• Alumina support with required characteristics such as high surface area, large pores for easy diffusion of reactants and products. It is necessary for the dispersion of the Ni and Mo-components.

• Suitable metal component (either noble metals such as Pt or Pd, or mixed metal sulfides (Co-Mo, Ni-Mo or Ni-W))

• Acidic components for dealkylation / cracking / isomerization (silica-alumina; zeolites)

As noble metals are easily poisoned by S compounds in the feed, Pt or Pd containing catalysts are useful only when the feed S is low and are typically used to process desulfurized feeds. On the other hand, the mixed-metal sulfide catalysts operate well when the feed S-content is large. Over metal sulfide catalysts, hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions also take place.

In the present work, Ni-Mo mixed-metal sulfide was chosen as the metallic component in view of the high sulfur content of the diesel feed. In general, it is important that the activities of the acidic and hydrogenation functions are present in the right proportions (balanced) in the catalyst. An excess of either of the functions can lead to

substantial amounts of undesired reactions causing diesel yield loss.

2. Experimental

2.1. Catalysts used in the study:

The catalysts used in the present work were prepared at 200-250 g scale were essentially Ni-Mo-alumina, whose acidity was increased with the addition of different zeolites. The catalysts were prepared using different supports differing in the nature and amount of the acidic promoter. The general method of preparation of the catalysts was: i) blending of the acidic component (zeolite) with alumina hydrate (Plural SB, Sasol), peptizing and extruding into extrudates (1/16") followed by drying and calcination, and ii) loading of Mo (10-12% as oxide) and Ni (3- 4% as oxide) using suitable salts by a two step procedure with intermediate calcination. The final catalyst was calcined at 500 °C in air for 6 hours. The supports were characterized by different techniques, such as XRD, N_2 adsorption-desorption (for surface area and pore volume) and temperature programmed desorption (TPD) of NH_3 for acidity(AutoChem 2910, Micromeritics, USA). The standard procedure for the TPD measurements involved the activation of the sample in flowing He at 600 °C (1 h), cooling to 50 °C, adsorbing NH_3 from a He-NH_3 (10 %) mixture, desorbing in He at 50 °C for 30 min, and finally carrying out the TPD experiment by raising the temperature of the catalyst in a programmed manner (10 °/ min). The area under the TPD curve was converted into meq NH_3 desorbed per gram of catalyst based on injection of known volumes of the He-NH_3 mixture under similar conditions. The total amount of NH_3 desorbed is expected to be from acid sites of different strengths, the strength of the acid site depending on the temperature of desorption. The amount of NH_3 desorbing above 300 °C is treated as arising from strong acid centres.

The zeolites used in the studies were H-Y (SiO_2/Al_2O_3 (SAR) = 5.2), H-beta (β, BEA) (SAR = 25) and H-ZSM-5 (SAR = 30). All the samples were obtained from Zeolyst, USA.

2.2. Feeds used in the study:

Two different feeds (I and II) were used in the studies. The characteristics of the different feeds are presented in Tables 2 and 3. Feed I was a high S containing straight run (SR) diesel with a higher end point (S = 1.76 wt % and 90% distillation at 371 °C). Its aromatic content was 41.5 wt%. Feed II was a partially desulfurized feed containing 375 ppm S with a lower aromatic content of 35 wt%. Its distillation temperature (90%) was 359°C. The distillation characteristics of the two feeds are also presented as gas chromatograms in Tables 2 and 3. As seen from the tables, about 21% and 12% of the heavy ends of the feeds I and II have to be transformed to obtain a diesel T_{95} of 360°C.

2. 3. Evaluation of catalysts:

The performance of the catalysts was evaluated in a small high-pressure pilot-plant reactor using about 200 ml volume of the catalyst. Typical process flow diagram of the high-pressure reactor set-up used is presented in Figure 1.

The catalysts were evaluated using the following operating conditions:

Reactor temperature: 330 – 360 °C, pressure: 40 – 60 bars, H_2/oil ratio: 300 – 500 v/v and LHSV: 1-2 h^{-1}. All the catalysts were presulfided in-situ following standard procedures using a hydrocracker-diesel spiked with 2 wt % S (as DMDS).

The product distillation characteristics were obtained by ASTM distillation D-86 and by GC-Simulated Distillation method (Perkin-Elmer Clarus 500 with auto-sampler). The S-content of the product samples was measured by XRF (Model: Oxford Lab X 3500).

3. Results and Discussion

The physicochemical characteristics of the catalysts are presented in Table 1. The surface areas and pore volumes of the supports were, respectively, in the range of 229 – 328 m²/g and 0.33 – 0.41 ml/g. The acidity of the supports can be arranged in the order: β(60%)-Al_2O_3> ZSM-5(60%)- Al_2O_3> ZSM-5(30%)- Al_2O_3 ~ HY(50%)-Al_2O_3 (total acidity) and β(60%)-Al_2O_3> ZSM-5(60%)- Al_2O_3> ZSM-5(30%)- Al_2O_3> HY(50%)-Al_2O_3 (strong acidity).

The results of the activity studies obtained over catalysts prepared from the different zeolite containing supports are presented in Table 4 for the straight run feed and in Table 5 for the desulfurized feed (HDS). It is seen from Table 3 that both ZSM-5 and H-Y are able to reduce the EP substantially. However, the yield loss is more over ZSM-5 than over H-Y. This is understandable as ZSM-5 is known to possess stronger acidity leading to greater cracking activity. A similar observation can also be made in the case of the HDS feed (Table 4). Comparing the two feed-stocks, the end point lowering at similar process conditions is more for the HDS feed than for the SR feed. This is probably due to the presence of more N and refractory compounds in the heavier feed. The diesel yield is lower over the HDS feed due to its being easier to crack. Relationships between end point reduction and yield loss for the three zeolites and the two feeds are presented in Fig. 3. The separate plots observed for the three zeolites reveal that EP reduction depends mainly on the nature of the zeolite. The similarity of the slopes for the three zeolites may suggest that the reactions responsible for EP reduction are similar over the three zeolites. The order of superiority of the zeolites based on (lower) yield loss for a given EP reduction is H-Y > H-beta > H-ZSM-5. The fact that points for both the feeds lie on the same lines suggest that the reactions responsible for EP reduction are the same for both the feeds.

The relationship between end point reduction (ΔEP) and % HDS for SR Diesel is shown in Fig. 4. In the initial stages (up to about 6 -7 °C EP loss), there appears to be a linear relationship between % HDS and ΔEP. However, beyond this value, ΔEP does not depend on the extent of HDS. This is primarily due to the refractory nature of the residual S compounds.

The typical chromatograms of the products (B - D) obtained over the different zeolites (catalysts) are compared with that of the SR feed (A) in Fig. 5. The spikes in the chromatograms are due to the n-paraffins and the rest of the hydrocarbon types being present in the 'envelopes'. ZSM-5 is found to selectively convert the n-paraffins (shape-selectivity), while H-Y converts more of the compounds in the 'envelope', presumably the easy to crack naphthenes and iso-paraffins. Zeolite beta converts both the n-paraffins and other molecules to a similar extent. Also, the ΔEP of the product was only 6 °C in the case of beta suggesting a lower conversion of the feed. ΔEP was 15 °C and 17 °C for ZSM-5 and H-Y. Though the selective cracking of the n-paraffins by ZSM-5 is expected to decrease the pour point of the product, the cetane number is expected to be lower. Therefore, one would expect H-Y to be a better catalyst for EP reduction as it has a lower activity for cracking of n-paraffins. The studies reveal that it is possible to couple EP reduction with pour point lowering or cetane improvement based on the choice of the zeolite.

Conclusions

Pilot plant studies indicate that end point reduction of straight run diesel fraction with a large sulfur and nitrogen content is possible over zeolite containing Ni-Mo catalysts. The studies reveal that the extent of end point reduction and yield loss are related to the type of zeolite used. Though zeolite based catalysts are able to achieve significant end point reduction of diesel, the main concern is the level of yield loss, which will decide the usefulness of the process.

References

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Table 1.Textural and acidic properties of the supports.

Supports	Surface area (BET; m^2/g)	Pore volume (ml/g)	Acidity (mmol / g)	
			Strong[a]	Total[b]
30% ZSM5-70% Al_2O_3	229	0.37	0.092	0.127
60% ZSM5-40% Al_2O_3	279	0.33	0.166	0.185
60% H-Beta-40% Al	328	0.41	0.198	0.282
50% HY-50% Al_2O_3	291	0.34	0.035	0.131

[a]: NH_3 desorbed above 300 °C; [b]: total amount of NH_3 desorbed

Table 2. Properties of Diesel Feed I (Straight run; SR)

Property	Value
Density at 15 °C, gm/cc	0.8610
Viscosity at 40 °C, cSt	5.03
Pour point, °C	0
Aniline point, °C	74
Non-Aromatics	58.5
Aromatics, wt%	41.5
Sulphur (Nitrogen), ppmw	17,600 (140)

<u>ASTM D-86 Distillation</u>

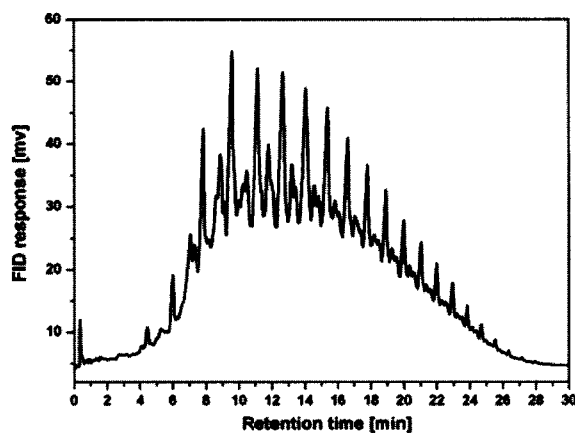|	
IBP	233
10%	271
30%	288
50%	306
70%	331
90%	371
92.8%	380

[Gas chromatogram of SR feed]

Table 3. Properties of Diesel Feed II (hydrodesulfurized; HDS)

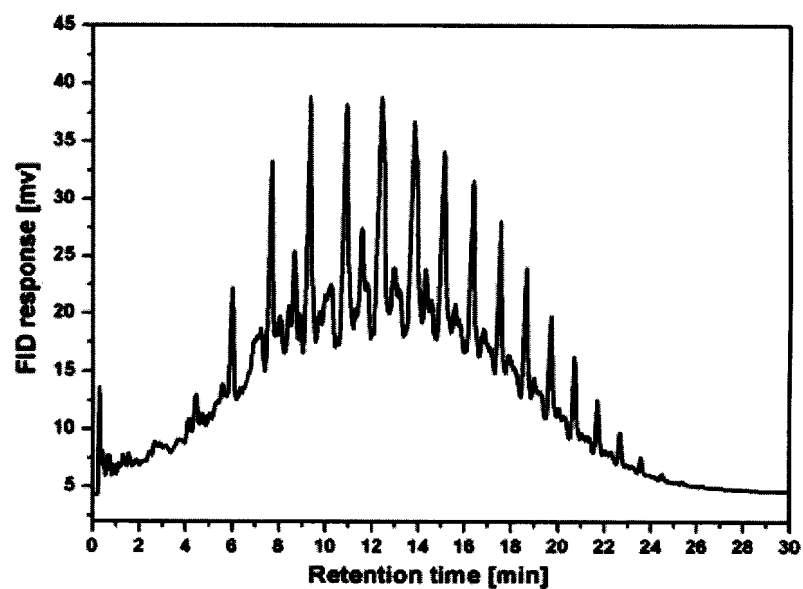| Property	Value
Density at 15 °C, gm/cc	0.8444
Viscosity at 40 °C, cSt	3.93
Aniline point, °C	79
Non-Aromatics	65.0
Aromatics, wt%	35.0
Sulphur (Nitrogen), ppmw	375 (XX)
ASTM D-86 Distillation	
IBP	222
10%	256
30%	280
50%	299
70%	322
90%	359
95%	383
FBP	385

[Gas chromatogram of HDS feed]

Table 4. Catalyst (Ni-Mo-) Evaluation using SR feed (Feed I)

Support (Zeolite, %)	Yield (%)	T90; -°C (ASTM D86)	S in product (ppm);(% HDS)	Temp (°C); Press (bars); H₂/oil (v/v)
Beta (60) – Al₂O₃	94	(365); 6	1500 (91)	360; 40; 400
ZSM-5 (60) – Al₂O₃	84.5	(359); 12	2900 (84)	340; 40; 400
-do-	80.5	(356); 15	1300 (93)	360; 40; 400
ZSM-5 (30) - Al₂O₃	92.5	(367); 4	3600 (80)	340; 40; 400
-do-	85.5	(361); 10	1500 (91)	360; 40; 400
HY (50) – Al₂O₃	96	(366); 5	2100 (88)	340; 40; 400
-do-	83	(354); 17	600 (97)	360; 40; 400

*: WHSV (h^{-1}) = 1.0

Table 5. Catalyst evaluation using HDS feed (Feed II)

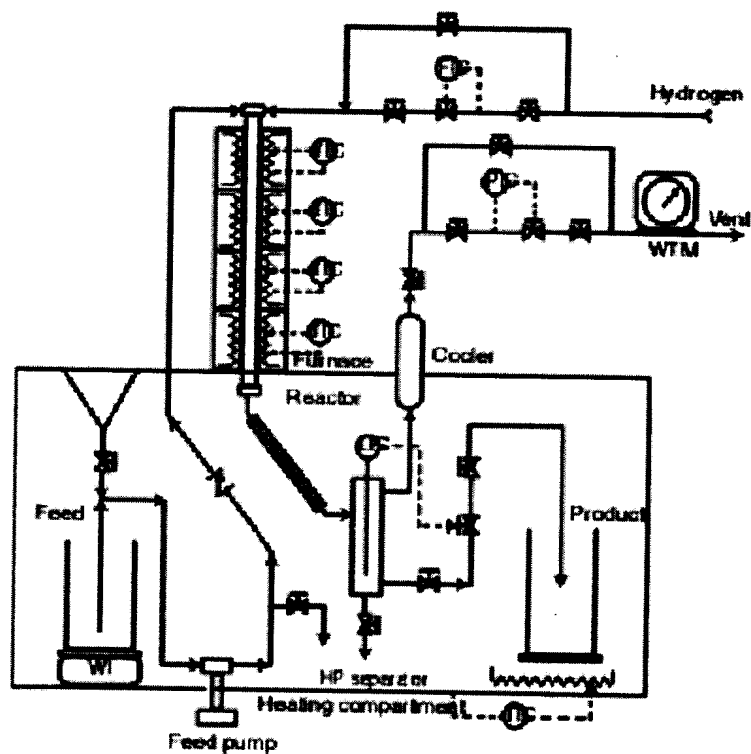| Catalyst	Yield (%)	T95; -°C (ASTM D86)	S in product (ppm);(% HDS)	Temp (°C); Press (bars); H₂/oil (v/v)*
Beta (60) - Al₂O₃	92	375; 8	110 (71)	340; 40; 400
-do-	88	373; 10	35 (91)	360; 40; 400
ZSM-5 (60)- Al₂O₃	80.5	370; 13	78 (79)	340; 40; 400
-do-	76	363; 20	26 (93)	360; 40; 400
ZSM-5 (30) - Al₂O₃	92	378; 5	98 (74)	340; 40; 400
-do-	81.5	371; 12	54 (86)	360; 40; 400
HY (50) - Al₂O₃	95	378; 5	87 (77)	340; 40; 400
-do-	82.5	364; 19	36 (90)	360; 40; 400

*: WHSV (h^{-1}) = 1.0

Legends for Figures

Fig. 1. Process flow diagram of high pressure reactor system
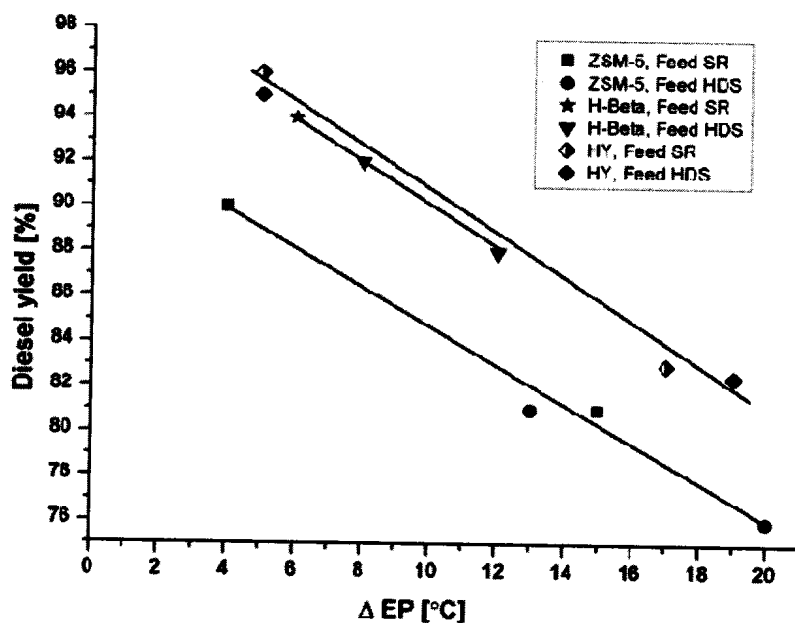

Fig. 2. Relationship between end point reduction and yield loss over the three zeolites for the two feeds
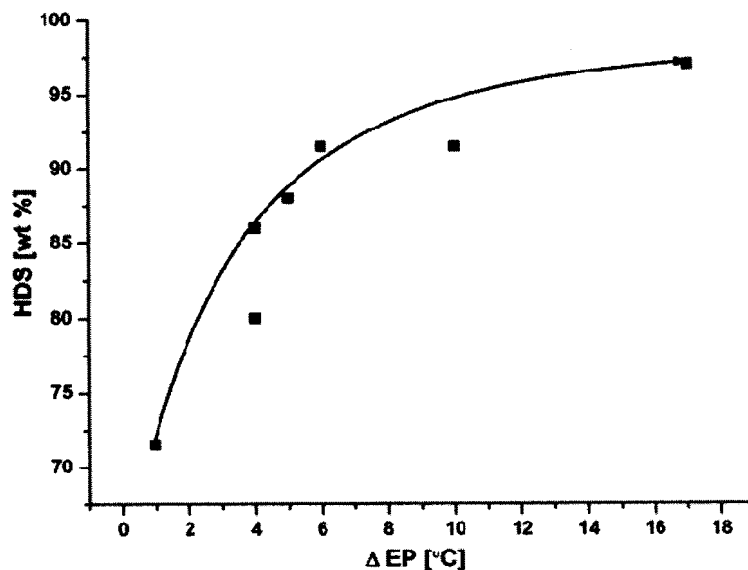
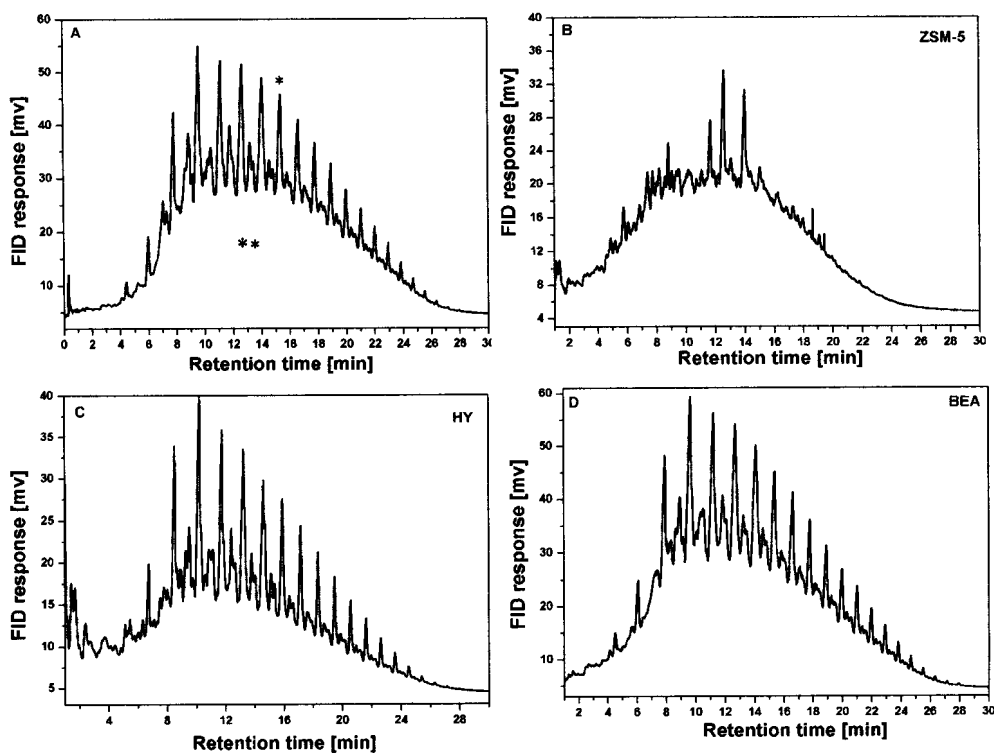Fig. 3. Relationship between end point reduction and % desulfurization of SR diesel

Fig. 4. Gas chromatograms of the SR feed (A) and the products obtained over different zeolites containing catalysts (B, ZSM-5; C, H-Y and D, H-beta). *: spikes correspond to n-paraffins, **: the envelope due to other components in the diesel