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(54) Title: GASOLINE UPGRADING PROCESS

(57) Abstract

Low sulfur gasoline of relatively high octane number is produced from a cracked, sulfur-containing olefinic naphthas by hydrodesulfurization followed by treatment over an acidic catalyst comprising an intermediate pore size zeolite such as zeolite ZSM-5 in combination with molybdenum. The use of the molybdenum in combination with the zeolite has been found to give improved catalytic activity coupled with lower coking, longer catalyst life and other advantages.

GASOLINE UPGRADING PROCESS

Field of the Invention

This invention relates to a process for the upgrading of hydrocarbon streams. It more particularly refers to a process for upgrading gasoline boiling range petroleum fractions containing substantial proportions of sulfur impurities. Another advantage of the present process is that it enables the end point of catalytically cracked gasolines to be maintained within the limits which are expected for Reformulated Gasoline (RFG) under the EPA Complex Model.

Background of the Invention

PCT/US 92/06537 and U.S.-A 5,346,609 and U.S.-A 5,409,596 describe a process for the upgrading of cracked naphthas, especially FCC naphtha, by sequential hydrotreating and selective cracking steps. In the first step of the process, the naphtha is desulfurized by hydrotreating and during this step some loss of octane results from the saturation of olefins. The octane loss is restored in the second step by a shape-selective cracking, preferably carried out in the presence of an acidic catalyst, usually an intermediate pore size zeolite such as ZSM-5. The product is a low-sulfur gasoline of good octane rating. PCT/US94/10548 and U.S. 5,411,658 describe a variant of that process using a molybdenum zeolite beta catalyst

Summary of the Invention

We have now found that molybdenum is extraordinarily effective when used in combination with ZSM-5 or another intermediate pore size zeolite as the acidic component of the catalyst. Not only is the catalyst more active but it is less subject to coking, with corresponding benefits in reduced catalyst aging and increased cycle lengths. The proportion of mercaptans is also lower and there is little

increase in hydrogen consumption. There is also an improvement in the quality of the treated gasoline product: at a constant product average octane rating (½(R+M)), the research octane number is about 1 number lower and the motor octane number about 1 number higher, indicating that the gasoline not only contains fewer olefins but is also less sensitive to driving conditions.

According to the present invention, therefore, a process for catalytically desulfurizing cracked fractions in the gasoline boiling range to acceptable levels uses an initial hydrotreating step to desulfurize the feed with some reduction in octane number, after which the desulfurized material is treated with a catalyst based on a molybdenum-containing intermediate pore size zeolite such as ZSM-5, to restore lost octane.

The process may be utilized to desulfurize catalytically and thermally cracked naphthas such as FCC naphtha as well as pyrolysis gasoline and coker naphthas, including light as well as full range naphtha fractions, while maintaining octane so as to reduce the requirement for alkylate and other high octane components in the gasoline blend.

The Drawings

Figures 1 to 4 of the accompanying drawings are graphs showing the results of comparative experiments described in the Examples.

Detailed Description

Feed

The feed to the process comprises a sulfur-containing petroleum fraction which boils in the gasoline boiling range, which can be regarded as extending from C_6 to about 500°F although lower end points below the 500°F end point are more typical. Feeds of this type include the naphthas described in PCT/US 92/06537, U.S.-A 5,346,609 and U.S.-A

5,409,596. Best results are obtained when, the process is operated with a gasoline boiling range fraction which has a 95 percent point (determined according to ASTM D 86) of at least about 163°C (325°F) and preferably at least about 177°C(350°F), for example, 95 percent points (T_{95}) of at least 193°C (380°F) or at least about 220°C(400°F). The process may be applied to thermally cracked naphthas such as pyrolysis gasoline, coker naphtha and visbreaker naphtha as well as catalytically cracked naphthas such as TCC or FCC naphtha since both types are usually characterized by the presence of olefinic unsaturation and the presence of sulfur. From the point of view of volume, however, the main application of the process is likely to be with catalytically cracked naphthas, especially FCC naphthas and for this reason, the process will be described with particular reference to the use of catalytically cracked naphthas.

The process may be operated with the entire gasoline fraction obtained from the catalytic cracking step or, alternatively, with part of it. Because the sulfur tends to be concentrated in the higher boiling fractions, it is preferable, particularly when unit capacity is limited, to separate the higher boiling fractions and process them through the steps of the present process without processing the lower boiling cut, as described in PCT/US 92/06537, U.S.-A 5,346,609 and U.S.-A 5,409,596.

The sulfur content of these cracked feed fractions will depend on the sulfur content of the feed to the cracker as well as on the boiling range of the selected fraction used as the feed in the process, as descibed in PCT/US 92/06537, U.S.-A 5,346,609 and U.S.-A 5,409,596.

Process Configuration

The selected sulfur-containing, gasoline boiling range feed is treated in two steps by first hydrotreating the feed by effective contact of the feed with a hydrotreating

catalyst, which is suitably a conventional hydrotreating catalyst, such as a combination of a Group VI and a Group VIII metal on a suitable refractory support such as alumina, under hydrotreating conditions. Under these conditions, at least some of the sulfur is separated from the feed molecules and converted to hydrogen sulfide, to produce a hydrotreated intermediate product comprising a normally liquid fraction boiling in substantially the same boiling range as the feed (gasoline boiling range), but which has a lower sulfur content and a lower octane number than the feed.

The hydrotreated intermediate product which also boils in the gasoline boiling range (and usually has a boiling range which is not substantially higher than the boiling range of the feed), is then treated by contact with the molybdenum-containing ZSM-5 catalyst under conditions which produce a second product comprising a fraction which boils in the gasoline boiling range which has a higher octane number than the portion of the hydrotreated intermediate product fed to this second step. The product from this second step usually has a boiling range which is not substantially higher than the boiling range of the feed to the hydrotreater, but it is of lower sulfur content while having a comparable octane rating as the result of the second stage treatment.

Hydrotreating

The hydrotreating step carried out in the manner described in PCT/US 92/06537, U.S.-A 5,346,609 and U.S.-A 5,409,596, using typical hydrotreating catalysts and the conditions disclosed there.

Octane Restoration - Second Step Processing

After the hydrotreating step, the hydrotreated intermediate product is passed to the second step of the process in which cracking takes place in the presence of

the acidic catalyst containing the molybdenum in addition to the intermediate pore size zeolite component. The effluent from the hydrotreating step may be subjected to an interstage separation in order to remove the inorganic sulfur and nitrogen as hydrogen sulfide and ammonia as well as light ends but this is not necessary and, in fact, it has been found that the first stage can be cascaded directly into the second stage. This can be done very conveniently in a down-flow, fixed-bed reactor by loading the hydrotreating catalyst directly on top of the second stage catalyst.

The conditions used in the second step of the process are selected to favor a number of reactions which restore the octane rating of the original, cracked feed at least to a partial degree. The reactions which take place during the second step which converts low octane paraffins to form higher octane products, both by the selective cracking of heavy paraffins to lighter paraffins and the cracking of low octane n-paraffins, in both cases with the generation of olefins. Ring-opening reactions may also take place, leading to the production of further quantities of high octane gasoline boiling range components. The molybdenum-containing zeolite catalyst may also function to improve product octane by dehydrocyclization/aromatization of paraffins to alkylbenzenes.

The conditions used in the second step are those which are appropriate to produce this controlled degree of cracking. Typical conditions are described in PCT/US 92/06537, U.S.-A 5,346,609 and U.S.-A 5,409,596. Typically, the temperature of the second step will be 150 to 480°C (300° to 900 °F), preferably 287° to about 220°C (550° to 800 °F). The pressure in the second reaction zone is not critical since hydrogenation will not contribute to product octane although a lower pressure in this stage will tend to favor olefin production with a consequent favorable effect on product octane. The pressure will therefore

depend mostly on operating convenience and will typically be comparable to that used in the first stage, particularly if cascade operation is used. Thus, the pressure will typically be about at least 170 kPaa (10 psig) and usually from 445 to 10445 kPaa (50 to 1500 psig), preferably about 2170 to 7000 kPaa (300 to 1000 psig) with comparable space velocities, typically from about 0.5 to 10 LHSV (hr^{-1}), normally about 1 to 6 LHSV (hr^{-1}). The present catalyst combination of molybdenum on ZSM-5 has been found to be effective at low pressures below about 1825 kPaa (250 psig) and even below 1480 kPaa (200 psig). Hydrogen to hydrocarbon ratios typically of about 0 to 890 $n.l.l^{-1}$. (0 to 5000 SCF/Bbl), preferably about 18 to 445 $n.l.l^{-1}$. (100 to 2500 SCF/Bbl) will be selected to minimize catalyst aging.

The use of relatively lower hydrogen pressures thermodynamically favors the increase in volume which occurs in the second step and for this reason, overall lower pressures are preferred if this can be accommodated by the constraints on the aging of the two catalysts. In the cascade mode, the pressure in the second step may be constrained by the requirements of the first but in the two-stage mode the possibility of recompression permits the pressure requirements to be individually selected, affording the potential for optimizing conditions in each stage.

Consistent with the objective of restoring lost octane while retaining overall product volume, the conversion to products boiling below the gasoline boiling range (C_5-) during the second stage is held to a minimum. However, because the cracking of the heavier portions of the feed may lead to the production of products still within the gasoline range, the conversion to C_5- products is at a low level, in fact, a net increase in the volume of C_5+ material may occur during this stage of the process, particularly if the feed includes significant amount of the

higher boiling fractions. It is for this reason that the use of the higher boiling naphthas is favored, especially the fractions with 95 percent points above 175°C (350°F) and even more preferably above 193°C (380°F) or higher, for instance, above 205°C (400°F). Normally, however, the 95 percent point (T_{95}) will not exceed 270°C (520°F) and usually will be not more than 260°C (500°F).

The acidic component of the catalyst used in the second step comprises an intermediate pore size zeolite. Zeolites of this type are characterized by a crystalline structure having rings of ten-membered rings of oxygen atoms through which molecules obtain access to the intracrystalline pore volume. These zeolites have a Constraint Index from 2 to 12, as defined in U.S. Patent No. 4,016,218. Zeolites of this class are well-known; typical members of this class are the zeolites having the structures of ZSM-5, ZSM-11, ZSM-22, ZSM-23, ZSM-35, ZSM-48 and MCM-22. ZSM-5 is the preferred zeolite for use in the present process. The aluminosilicate forms of these zeolites provide the requisite degree of acidic functionality and for this reason are the preferred compositional forms of the zeolites. Other isostructural forms of the intermdeiate pore size zeolites containing other metals instead of aluminum such as gallium, boron or iron may also be used.

The zeolite catalyst possesses sufficient acidic functionality to bring about the desired reactions to restore the octane lost in the hydrotreating step. The catalyst should have sufficient acid activity to have cracking activity with respect to the second stage feed (the intermediate fraction), that is sufficient to convert the appropriate portion of this material as feed, suitably with an alpha value of at least about 20, usually in the range of 20 to 800 and preferably at least about 50 to 200 (values measured prior to addition of the metal component). The alpha value is described in U.S. Patent 3,354,078 and

in J. Catalysis, 4, 527 (1965); 6, 278 (1966); and 61, 395 (1980). The experimental conditions of the test used to determine the alpha values referred to in this specification include a constant temperature of 538°C and a variable flow rate as described in J. Catalysis, 61, 395 (1980).

The zeolite component of the catalyst will usually be composited with a refractory binder or substrate such as silica, alumina, silica-zirconia, silica-titania or silica-alumina because the particle sizes of the pure zeolite are too small and lead to an excessive pressure drop in a catalyst bed.

The catalyst also contains molybdenum as a component which improves catalyst activity, stability as well as for improving product quality as described above. Typically, the molybdenum will be in the oxide or the sulfide form; it may readily be converted from the oxide form to the sulfide by conventional pre-sulfiding techniques. A molybdenum content of about 0.5 to about 5 weight percent, conventionally 1 or 2 to 5 weight percent, (as metal) is suitable although higher metal loadings typically up to about 10 or 15 weight percent may be used.

The molybdenum component may be incorporated into the catalyst by conventional procedures such as impregnation into an extrudate or by mulling with the zeolite and the binder. When the molybdenum is added in the form of an anionic complex such as molybdate, impregnation or addition to the muller will be appropriate methods.

The particle size and the nature of the catalyst will usually be determined by the type of conversion process which is being carried out with operation in a down-flow, fixed bed process being typical and preferred.

Examples

Examples showing the use of ZSM-5 without a metal component are given in PCT/US 92/06537, U.S.-A 5,346,609 and U.S.-A 5,409,596.

Examples 1 and 2 below illustrate the preparation of the ZSM-5 catalysts. Performance comparisons of these catalysts with different feeds and with a molybdenum-containing zeolite beta catalyst are given in subsequent Examples. In these examples, parts and percentages are by weight unless they are expressly stated to be on some other basis. Temperatures are in °C and pressures in kPaa, unless expressly stated to be on some other basis.

Example 1

Preparation of a Mo/ZSM-5 Catalyst

A physical mixture of 80 parts ZSM-5 and 20 parts pseudoboehmite alumina powder (Condea Pural™ alumina) was mulled to form a uniform mixture and formed into 1.5mm (1/16 inch) cylindrical shape extrudates using a standard augur extruder. All components were blended based on parts by weight on a 100% solids basis. The extrudates were dried on a belt drier at 127°C, and were then nitrogen calcined at 480°C for 3 hours followed by a 6 hour air calcination at 538°C. The catalyst was then steamed at 100% stream at 480°C for approximately 4 hours. The steamed extrudates were impregnated with 4 wt% Mo and 2 wt% P using an incipient wetness method with a solution of ammonium heptamolybdate and phosphoric acid. The impregnated extrudates were then dried at 120°C overnight and calcined at 500°C for 3 hours. The properties of the final catalyst are listed in Table 1 below together with the properties of the hydrotreating catalysts (CoMo, NiMo) used in the Examples.

Example 2

Preparation of HZSM-5 Catalyst

A physical mixture of 65 parts ZSM-5 and 35 parts pseudoboehmite alumina powder (LaRoche Versal™ alumina) was mulled to form a uniform mixture. All components were blended based on parts by weight on a 100% solids basis. Sufficient amount of deionized water was added to form an extrudable paste. The mixture was auger extruded to 1.5mm (1/16 inch) cylindrical extrudates and dried on a belt drier at 127°C. The extrudates were then nitrogen calcined at 480°C for 3 hours followed by a 6 hour air calcination at 538°C. Then catalyst was then steamed in 100% steam at 480°C for approximately 4 hours. The properties of the final catalyst are listed in Table 1 below.

TABLE 1

Properties of Catalysts

	CoMo HDS	NiMo HDS	Mo/ZSM-5	HZSM5
Zeolite	-	-	ZSM-5	ZSM-5
Zeolite, wt%	-	-	80	65
Alpha	-	-	132*	101
Surface area, m^2/g	260	160	289	337
n-Hex. srptn, cc/g	-	-	10.4	10.4
cy-Hex. srptn, cc/g	-	-	-	9.3
NiO, wt%	N/A	4	N/A	N/A
Co, wt%	3.4	N/A	N/A	N/A
Mo, wt%	10.2	16	3.6	N/A
P, wt%	-	-	1.7	N/A

* Before Mo impregnation
N/A Not applicable

Example 3

Performance comparison with a heavy FCC naphtha

This example illustrates performance advantages of a Mo-ZSM-5 catalyst (Example 1) over a H-ZSM-5 catalyst (Example 2) for producing low sulfur gasoline.

A dehexanized FCC gasoline derived from a fluid catalytic cracking process was treated to give a substantially desulfurized product with a minimum octane loss. The feedstock properties, together with those used in other experiments described below, are shown in Table 2 below.

Table 2
Properties of Naphtha Feeds

	Heavy Naphtha(I)	De-Hex Gaso.	Heavy Naphtha(II)
Nominal Boiling Range, °c	175-255	80-205	160-490
Specific Gravity, g/cc	0.916	0.805	0.896
Total Sulfur, wt%	2.0	0.23	1.2
Nitrogen, ppm	180	86	150
Bromine Number	10.4	54.3	22.1
Research Octane	96.4	92.3	92.7
Motor Octane	84.0	80.3	80.6
Distillation, °C(D-2887)			
IBP	58	57	134
5%	162	73	161
10%	182	88	171
30%	209	114	207
50%	228	142	228
70%	235	169	241
90%	255	207	257
95%	265	217	260
EP	296	245	271

The experiments were carried out in a fixed-bed pilot unit employing a commercial $CoMo/Al_2O_3$ hydrodesulfurization (HDS) catalyst and the Mo/ZSM-5 catalyst in equal volumes. The pilot unit was operated in a cascade mode where desulfurized effluent from the hydrotreating stage cascaded directly to the zeolite-containing catalyst to restore octane without removal of ammonia, hydrogen sulfide, and light hydrocarbon gases at the interstage. The conditions employed for the experiments included a hydrogen inlet pressure of 4240 kPaa (600 psig), a space velocity of 1.0

LHSV hr.$^{-1}$ (based on fresh feed relative to total catalysts) and 534 n.l.l.$^{-1}$ (3000 scf/bbl) of once-through hydrogen circulation.

Table 3 and Figure 1 compare the gasoline hydrofinishing performance of the (1) HDS and H-ZSM-5 catalyst combination and (2) HDS and Mo/ZSM-5 catalyst combination.

Table 3
Process Performance Comparison with Heavy FCC Naphtha(I)

	Heavy FCC Naphtha	CoMo HDS/ H-ZSM-5	CoMo HDS/ Mo/ZSM-5
Stage 1 Temp., °C	-	385	372
Stage 2 Temp., °C	-	405	400
Days on Stream	-	20.4	12.8
Product Analyses			
Sulfur, wt%	2.0	0.027*	0.006*
Nitrogen, ppmw	180	<1*	<1*
Research Octane	96.4	98.4	98.7
Motor Octane	84.0	85.4	86.2
Olefin Yield, wt%			
C_2=+C_3=+C_4=	-	0.19	0.14
C_5=+	-	0.40	0.09
C_5+ Gasoline Yields			
vol% 100	97.9	93.7	
wt%	100	94.5	90.2
Process Yields, wt%			
C_1+C_2	-	0.3	1.3
C_3	-	1.8	3.3
C_4	-	2.6	4.5
C_5-200°C	17.7	35.3	37.9
200-215°C	21.1	18.8	16.8
215°C+	61.2	40.4	35.5
Conversion, %			
200°C+	-	28	36
215°C+	-	34	42
Hydrogen Consumption (n.l.l.$^{-1}$)	-	130	155

* Measured with a H_2S stripped product
Conditions: 4240 kPaa, 1.0 hr.$^{-1}$ overall LHSV

The data contained in Table 3 and Figure 1 demonstrate the improvement in activity shown by the catalyst of the present invention. For example, in the temperature range from 345°C to 400°c, the Mo/ZSM-5 catalyst produces a gasoline with about 0.5 number higher road octane than the H-ZSM-5 catalyst. This octane advantage translates to approximately 6-8°C higher catalyst activity of Mo/ZSM-5 over H-ZSM-5 (Figure 1). The Mo/ZSM-5 catalyst achieves better back-end conversion than H-ZSM-5 (Table 3). The Mo/ZSM-5 catalyst also exhibits better desulfurization ability: the product sulfur level is substantially lower (270 ppm vs. 60 ppm, Table 3).

Example 4

Performance comparison for C_7+ FCC naphtha

This example illustrates the performance advantages of Mo/ZSM-5 catalyst (Example 1) over a HZSM-5 catalyst (Example 2) for producing low sulfur gasoline. This example uses a C_7+ naphtha fraction derived from a fluid catalytic cracking process (dehexanized FCC gasoline). The experiments were conducted at nearly identical conditions to Example 3.

The results are shown in Table 4 below and Figure 2; they demonstrate the improvement in activity of Mo/ZSM-5 catalyst over HZSM-5.

Table 4
Process Performance Comparison with C_7+ FCC Gasoline

	C_7+ FCC Gasoline Feed	CoMo HDS/ H-ZSM-5	CoMo HDS/ Mo/ZSM-5
Stage 1 Temp., °C	-	370	370
Stage 2 Temp., °C	-	400	401
Days on Stream	-	19.7	6.1
Product Analyses			
Sulfur, wt%	0.23	0.022*	0.004*
Nitrogen, ppmw	86	<1*	<1*
Research Octane	92.3	88.8	91.7
Motor Octane	80.3	80.3	82.7
Olefin Yield, wt%			
C_2=+C_3=+C_4=	-	0.93	0.50
C_5=+	-	0.52	0.12
C_5+ Gasoline Yields			
vol% 100	92.6	92.7	
wt%	100	92.8	92.7
Process Yields, wt%			
C_1+C_2	-	0.3	0.3
C_3	-	2.6	2.3
C_4	-	4.7	4.7
C_5-165°C	65.9	63.3	66.3
165-200°C	19.1	17.3	15.8
200°C+	15.0	12.1	10.5
Conversion, 165°C+, %	-	13	23
Hydrogen Consump.(n.l.l.$^{-1}$) ~62		-	57

* Measured with a H_2S stripped product

Conditions: 4240kPaa, 1.0 hr.$^{-1}$ overall LHSV

At 400°C, the H-ZSM-5 catalyst cannot recover the feed octane. The Mo/ZSM-5 catalyst exceeds the feed octane at 400°C. The CoMo HDS and Mo/ZSM-5 catalyst combination also exhibits better desulfurization ability, the product sulfur level being substantially lower (220 ppm vs. 40 ppm, Table

4). The Mo/ZSM-5 catalyst achieves much greater 165°C+ back-end conversion than H-ZSM-5 with only a slight increase in H_2 consumption (Table 4).

Example 5

Performance comparison at low pressure

This example illustrates improved stability of Mo/ZSM-5 at low pressure where catalyst aging phenomena are accelerated.

The performance of Mo/ZSM-5 catalyst (Example 1) in conjunction with NiMo hydrotreating catalyst is compared with that of H-ZSM-5 (Example 2) in conjunction with CoMo hydrotreating catalyst. This example used another heavy naphtha feed with a high bromine number of 25. The operating conditions were temperature in the range of 345°-425°C , 1310 kPaa (175 psia) H_2, 1 $hr.^{-1}$ LHSV, 356 $n.l.l^{-1}$ (2000 scf/bbl).

Table 5
Process Performance Comparison with Heavy FCC Naphtha(II)

	Heavy FCC Naphtha Feed	CoMo HDS/ H-ZSM-5[1]	NiMo HDS/ Mo/ZSM-5[2]
Stage 1 Temp., °C	-	400	345
Stage 2 Temp., °C	-	413	357
Days on stream, Rx1	-	87	7
Days on stream, Rx2	-	32	7
Product Analyses			
Sulfur, wt%	1.2		0.004*
Nitrogen, ppmw	150	6*	7*
Research Octane	92.7	93.5	95.5
Motor Octane	80.6	81.4	83.2
C_5+ Gasoline Yields			
vol% 100	97.0	96.9	
wt%	100	95.5	95.7
Process Yields, wt%			
C_1+C_2	-	0.3	0.2
C_3	-	1.5	1.5
C_4	-	2.0	3.0
C_5-165°C	6.9	20.5	17.3
165-200°C	15.9	20.1	16.4
200°C+	77.2	54.8	60.9
$C_2=+C_3=+C_4=$	-	2.2	0.9
C_5 Olefins wt%	-	1.0	0.5
165°C+ Conversion, %	-	19.6	17.1
Hydrogen Consump., N.L.L.$^{-1}$		-	53

* Measured with a H_2S stripped product

[1] Conditions 1690 kPaa, 0.95 hr.$^{-1}$ overall LHSV (1.9 over each catalyst bed), 390 n.l.l.$^{-1}$ hydrogen circulation

[2] Conditions 1790 kPaa, 0.78 hr.$^{-1}$ overall LHSV (2.5 over the first catalyst bed, and 1.1 over the second bed), 390 n.l.l.-^{1} hydrogen circulation.

The Mo/ZSM-5 catalyst exhibits good gasoline upgrading capability at low pressure in conjunction with a NiMo hydrotreating catalyst. As shown in Figure 3, NiMo HDS/Mo

ZSM-5 catalyst combination shows significantly higher activity than CoMo HDS/H-ZSM-5. The H-ZSM-5 catalyst was on stream for longer than the Mo-ZSM-5. Even allowing for the difference in time on stream, the NiMo/Mo-ZSM-5 system is 20-30°C more active. This activity advantage would increase the operating window for low pressure applications. An octane recovery at the feed level was observed at 350°C. Hydrogen consumption is higher with the new system, possibly because of the increased hydrogenation capabilities of NiMo vs CoMo HDS catalysts (Table 5).

At a given octane, the conversion with the Mo/ZSM-5 system is lower than with ZSM-5 due to the different reactor temperatures (Table 5). At constant reactor temperature, the conversion is higher, consistent with Examples 3 and 4. The C_5 olefin make is also lower with the NiMo/Mo-ZSM-5 system.

The data contained in Figure 4 show that the NiMo HDS/Mo-ZSM-5 catalyst system is substantially more stable. After one month on stream, this catalyst system has aged about 28°C while the CoMo/H-ZSM-5 system aged more than 55°C (data normalized to feed octane at 9°C/octane).

Example 6

Desulfurization performance comparison for a C_7+ FCC naphtha (dehexanized gasoline). This example illustrates the desulfurization advantage of the Mo/ZSM-5 catalyst (Example 1) over HDT alone or in combination with ZSM-5 catalyst (Example 2) for producing low sulfur gasoline.

A sulfur GC method was used to speciate and quantify the sulfur compounds present in the gasolines using a Hewlett-Packard gas chromatograph, Model HP-5890 Series II equipped with universal sulfur-selective chemiluminescence detector (USCD). The sulfur GC detection system was published by B. Chawla and F.P. DiSanzo in J. Chrom. 1992, 589, 271-279.

The data contained in Table 6 demonstrate the improvement in desulfurization and octane recovery activities shown by the catalyst of the present invention for this FCC naphtha.

Table 6
Catalyst Effect on Desulfurized Gasoline
For C_7+ FCC Naphtha

	Product from HDS only Base case	Product from HDS/H-ZSM-5 Cascade case	Product from HDS/Mo-ZSM-5 Cascade case
Av. Bed Temp Rx1(°C)	370	370	369
Av. Bed Temp Rx2(°C)	Nil	370	370
Research Octane	77.3	81.3	81.3
Motor Octane	71.5	74.7	75.2
Total RSH, ppm	0	24	5
Total Heavy S, ppm	172	194	65
Total HC Sulfur, ppm	172	218	70

Table 6 compares the sulfur level and octane of gasoline samples from the (1) HDT alone, (2) HDT and ZSM-5 catalyst combination, and (3) HDT and Mo/ZSM-5 catalyst combination. The HDT and Mo/ZSM-5 combination clearly exhibits superior desulfurization activity. For example, at 370°C, the Mo/ZSM-5 catalyst produces gasoline with 70 ppm total sulfur while HDT alone produces 172 ppm S and HDT/ZSM-5 produces 218 ppm S gasoline. The mercaptan level of Mo/ZSM-5 is much lower than that of ZSM-5 (24 vs. 5 ppm).

Example 7

Desulfurization performance comparison for a heavy FCC naphtha

This example illustrates the desulfurization advantage of the HDS/Mo-ZSM-5 catalyst combination over HDS/H-ZSM-5 catalyst combination for producing low sulfur gasoline for

the heavy FCC naphtha used in Example 3. The results are given in Table 7 below.

Table 7
Catalyst Effect on Desulfurized Gasoline
For Heavy FCC Naphtha(I)

	Product of HDS only Base	Product of HDS/ HZSM-5 Cascade	Product of HDS/ MoZSM-5 Cascade
Av. Bed Temp Rx1(°C)	370	370	370
ABT Rx2(°F)	Nil	370	371
Research Octane	91.3	96.8	97.2
Motor Octane	79.4	83.7	84.3
Total Mercaptans, ppm	0	252	31
Total Heavy S, ppm	174	155	179
Unknown S, ppm	2	12	4
Total HC Sulfur, ppm	176	419	214

The data in Table 7 demonstrate the improvement in desulfurization activity by the Mo/ZSM-5 catalyst. For example, at 700°F, the Mo/ZSM-5 catalyst produces gasoline with 214 ppm total sulfur while HDT alone produces 176 ppm S and HDT/ZSM-5 produces 419 ppm S gasoline. The mercaptan level of Mo/ZSM-5 is much lower than that of ZSM-5 (240 vs. 31 ppm).

The main mechanisms for the excellent desulfurization of Mo/ZSM-5 catalyst is believed to be by suppression of mercaptan formation and possibly by cracking of heavy sulfur species. The Mo in the Mo/ZSM-5 catalyst may saturate the olefins and hence hinders the recombination reactions which would tend to mercaptan formation.

Example 8

Performance comparison between zeolite beta and zeolite ZSM-5 with Coker Naphtha Feed

For this comparison, a nominal 40-180°C coker naphtha was used as the feed. Its properties are given in Table 8 below.

Table 8
PROPERTIES OF COKER NAPHTHA FEED

General Properties

Nominal Boiling Range, °C	40-180
Specific Gravity, g/cc	0.742
Total Sulfur, wt%	0.7
Nitrogen, ppm	71
Bromine Number	72.0
Research Octane	68.0
Motor Octane	60.6

Distillation, °C(D2887)

IBP	21
5%	37
10%	59
30%	96
50%	123
70%	147
90%	172
95%	177
EP	212

This coker naphtha was treated over the same CoMo hydrodesulfurization catalyst used in preceding examples in a cascade operation at 4240 kPaa (600 psig), 534 n.l.l.$^{-1}$ (3000 scf/bbl) H_2/oil ratio, 1.0 hr.$^{-1}$ overall LHSV, using temperatures at about 370°C in the hydrotreating stage and varying temperatures in the second (Mo/ZSM-5 stage). The same naphtha was also treated in the same way but using a Mo/zeolite beta catalyst in the second stage. The Mo/zeolite beta catalyst contained 4 weight percent Mo, based on the total catalyst weight. The operating conditions, comparable to those used for the runs with the ZSM-5 catalyst, are shown in Table 10 below, together with the results with this catalyst.

Table 9

Upgrading of Coker Naphtha with Mo/ZSM-5

	Feed	CoMoHDS/Mo/ZSM-5		
Stage 1 Temp., °C	-	372	370	371
Stage 2 Temp., °C	-	367	400	414
Days on Stream	-	5.0	8.2	9.2
Product Analyses				
Sulfur, wt%	0.7	0.020*	0.006*	0.012*
Nitrogen, ppmw	71	<1*	<1*	7*
Research Octane	68.0	42.8	68.7	78.4
Motor Octane	60.6	44.3	66.0	75.0
Olefin Yield, wt%				
C_2=+C_3=+C_4=	-	0.2	1.4	1.2
C_5=	-	0.2	0.6	0.4
C_5+ Gasoline Yields				
vol%	100	100.3	79.3	68.8
wt%	100	98.8	78.1	68.4
Process Yields, wt%				
C_1+C_2	-	0.1	1.1	2.2
C_3	-	0.4	9.0	13.8
C_4	-	1.0	12.4	16.4
C_5-150°C	71.3	71.4	61.7	52.0
150°C+	28.7	27.4	16.4	16.4
150°C+ Conversion,%	-	11	47	47
Hydrogen consump., n.l.l.$^{-1}$	-	71	107	142

* Measured with a H_2S stripped product

Conditions: 4240 kPaa, 534 n.l.l.$^{-1}$, 1.0 hr.$^{-1}$ overall LHSV

Table 10
Upgrading of Coker Naphtha with Mo/BETA

	Feed	CoMo HDS/ Mo/Beta			
Stage 1 Temp., °C	-	344	371	375	375
Stage 2 Temp., °C	-	344	370	400	413
Days on Stream	-	27.4	28.4	29.4	31.4
Product Analyses					
Sulfur, wt%	0.7	0.005*	0.005*	0.019*	0.009
Nitrogen, ppmw	71	1*	1*	2*	<1*
Research Octane	68.0	42.0	43.3	52.8	51.6
Motor Octane	60.6	43.8	46.0	52.9	52.9
Olefin Yield, wt%					
C_2=+C_3=+C_4=	-	0.2	0.6	0.6	0.6
C_5=+	39.9	0.1	0.3	0.3	0.3
C_5+ Gasoline Yields					
vol%	100	97.7	94.4	92.9	93.4
wt%	100	96.6	93.1	92.7	92.4
Process Yields, wt%					
C_1+C_2	-	0.1	0.2	0.2	0.2
C_3	-	0.6	1.3	1.3	1.4
C_4	-	2.9	5.6	5.7	6.1
C_5-150°C	71.3	71.4	71.3	69.7	71.9
150°C+	28.7	25.2	21.8	23.0	20.5
Conversion, %					
150°C+	-	19	30	26	34
Hydrogen consump., (n.l.l.$^{-1}$)	-	71	89	53	71

* Measured with a H_2S stripped product

Conditions: 4240 kPaa, 535 n.l.l.$^{-1}$, 1.0 hr.$^{-1}$ overall LHSV

The results in Tables 9 and 10 show that the combination of the hydrodesulfurization catalyst and the Mo/ZSM-5 can produce desulfurized gasoline with a road octane number of 77 at about 68 percent yield. By contrast, the zeolite beta catalyst can only improve the road octane number to 53 although both catalysts produce low sulfur gasoline range product.

Claims:

1. A process of upgrading a cracked, olefinic sulfur-containing feed fraction boiling in the gasoline boiling range by hydrodesulfurizing the sulfur-containing feed fraction to produce an intermediate product comprising a normally liquid fraction which has a reduced sulfur content and a reduced octane number as compared to the feed and contacting the gasoline boiling range portion of the intermediate product with an acidic catalyst comprising an intermediate pore size zeolite, to convert it to a gasoline boiling range product having a higher octane number than the gasoline boiling range fraction of the intermediate product, characterized in that
the intermediate pore size zeolite is used in combination with a molybdenum component.

2. The process as claimed in claim 1 in which the zeolite catalyst is a ZSM-5 catalyst comprising zeolite ZSM-5 in the aluminosilicate form.

3. The process as claimed in claim 1 or 2 in which the intermediate pore size zeolite catalyst includes from 1 to 15 weight percent molybdenum by weight of the catalyst.

4. The process as claimed in any of claims 1 to 3 in which the intermediate product is contacted with the intermediate pore size zeolite catalyst at a temperature of 150 to 480°C, a pressure of 170 to 10,445 kPaa, a space velocity of 0.5 to 10 $hr.^{-1}$ LHSV, and a hydrogen:hydrocarbon ratio of 0 to 890 $n.l.l.^{-1}$.

5. The process as claimed in nay of claims 1 to 4 in which the total sulfur content of the product fraction boiling in the gasoline boiling range is not more than 100 ppmw.

6. A process as claimed in any of claims 1 to 5 in which the feed has a sulfur content of at least 50 ppmw, an olefin content of at least 5 percent and a 95 percent point of at least 160°C.

7. The process as claimed in claim 6 in which the feed fraction has a 95 percent point of at least 175°C, an olefin content of 10 to 20 weight percent, a sulfur content from 100 to 5,000 ppmw and a nitrogen content of 5 to 250 ppmw.



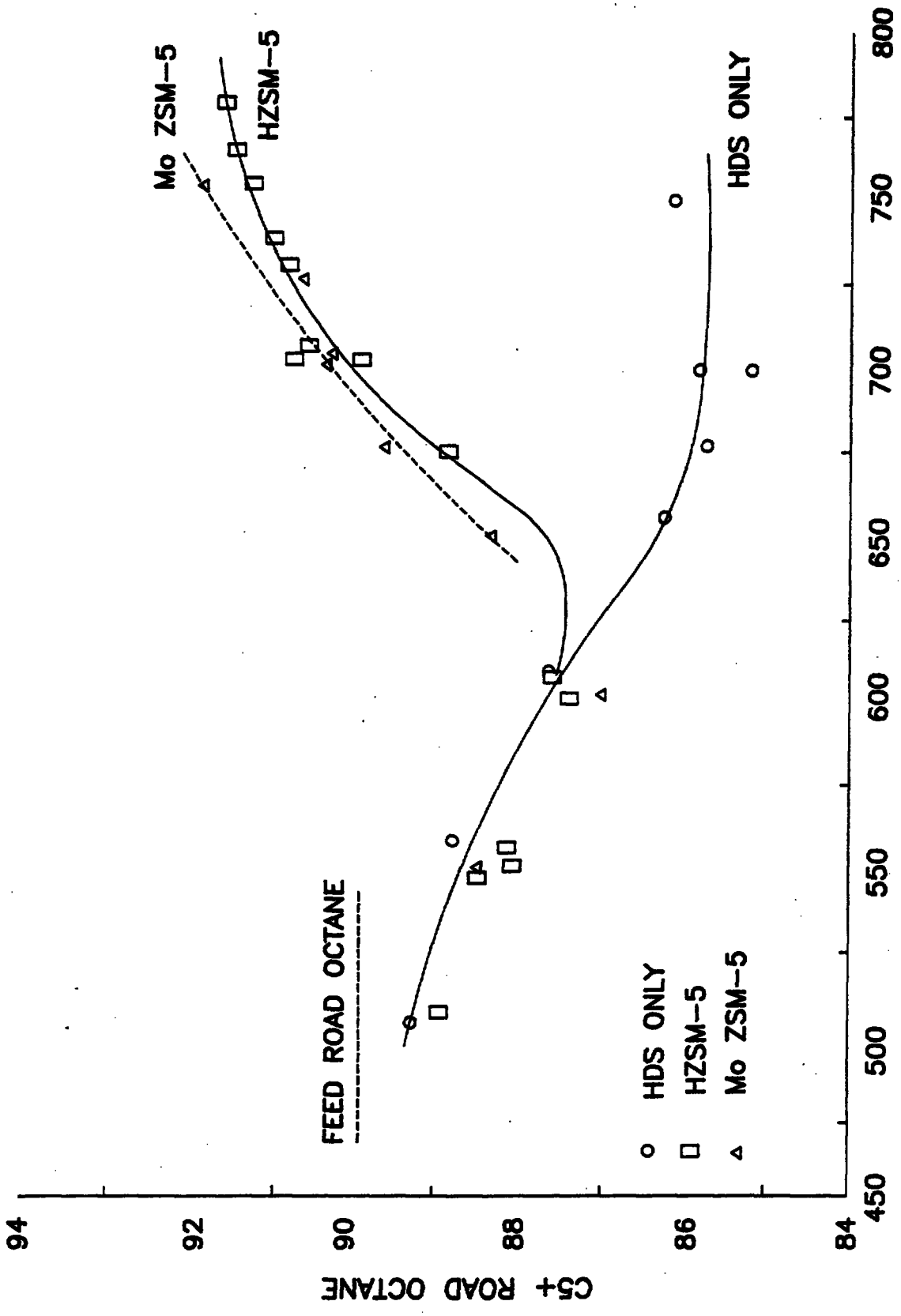

C5+ ROAD OCTANE
94
92
90
88
86
84
450
500
550
600
650
700
750
800
TEMPERATURE, F
Mo ZSM-5
HZSM-5
HDS ONLY
FEED ROAD OCTANE
HDS ONLY
HZSM-5
Mo ZSM-5

FIG. 1

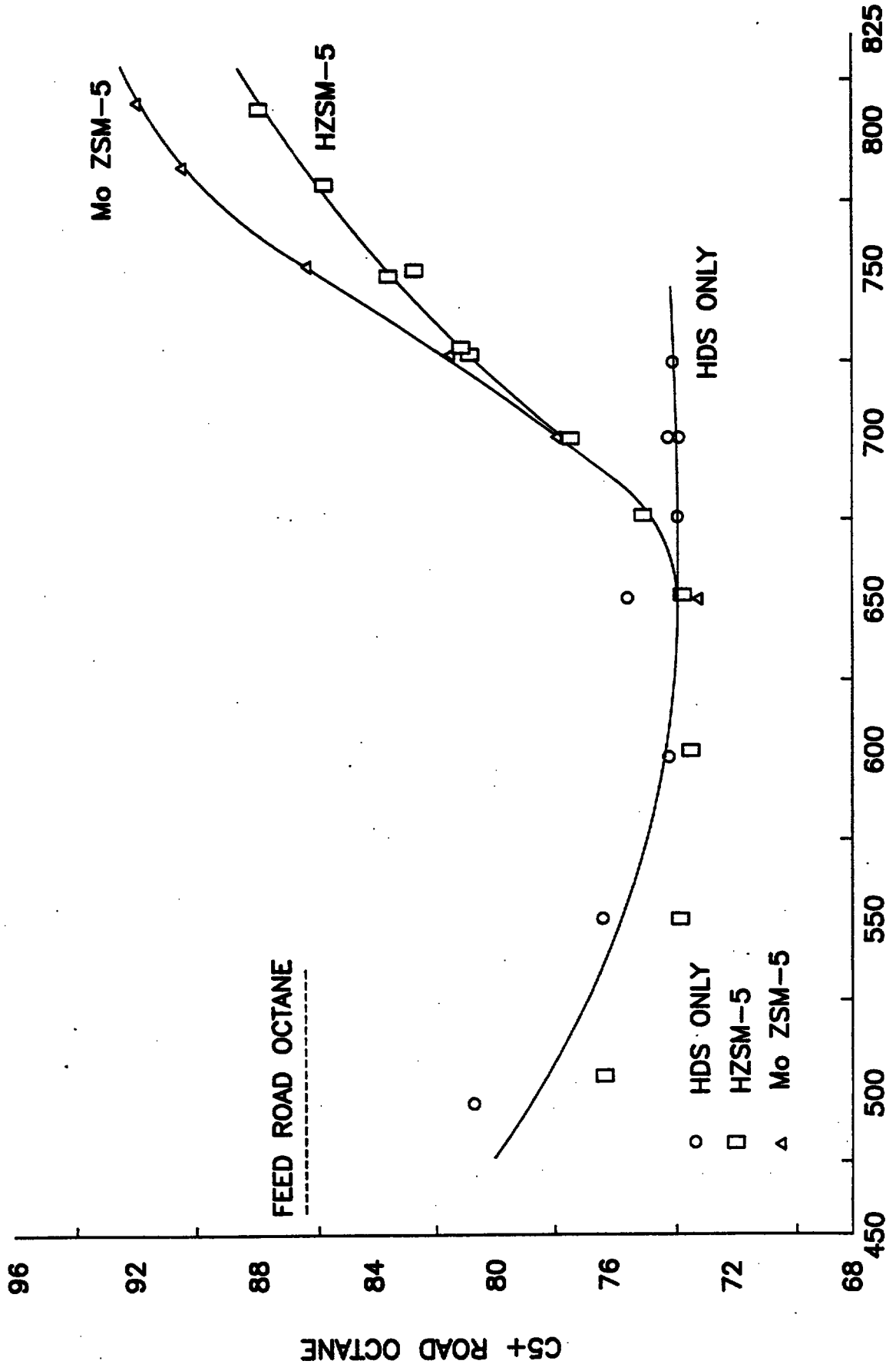

Mo ZSM-5
HZSM-5
HDS ONLY
FEED ROAD OCTANE
HDS ONLY
HZSM-5
Mo ZSM-5
C5+ ROAD OCTANE
96
92
88
84
80
76
72
68
450
500
550
600
650
700
750
800
825
TEMPERATURE, F

FIG. 2

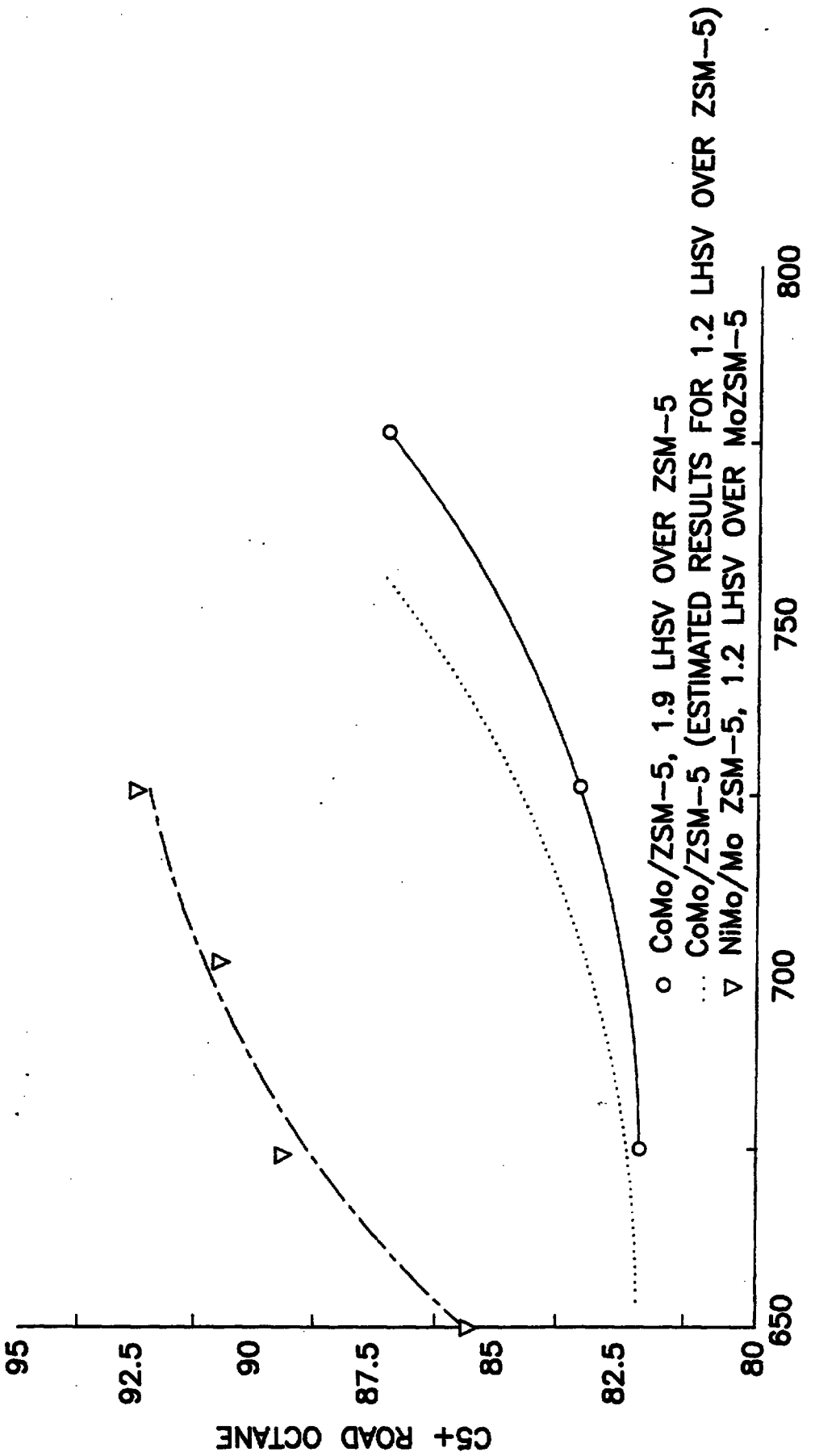

C5+ ROAD OCTANE
95
92.5
90
87.5
85
82.5
80
650
700
750
800
ZSM-5 TEMPERATURE, F
o CoMo/ZSM-5, 1.9 LHSV OVER ZSM-5
... CoMo/ZSM-5 (ESTIMATED RESULTS FOR 1.2 LHSV OVER ZSM-5)
▽ NiMo/Mo ZSM-5, 1.2 LHSV OVER MoZSM-5

FIG. 3

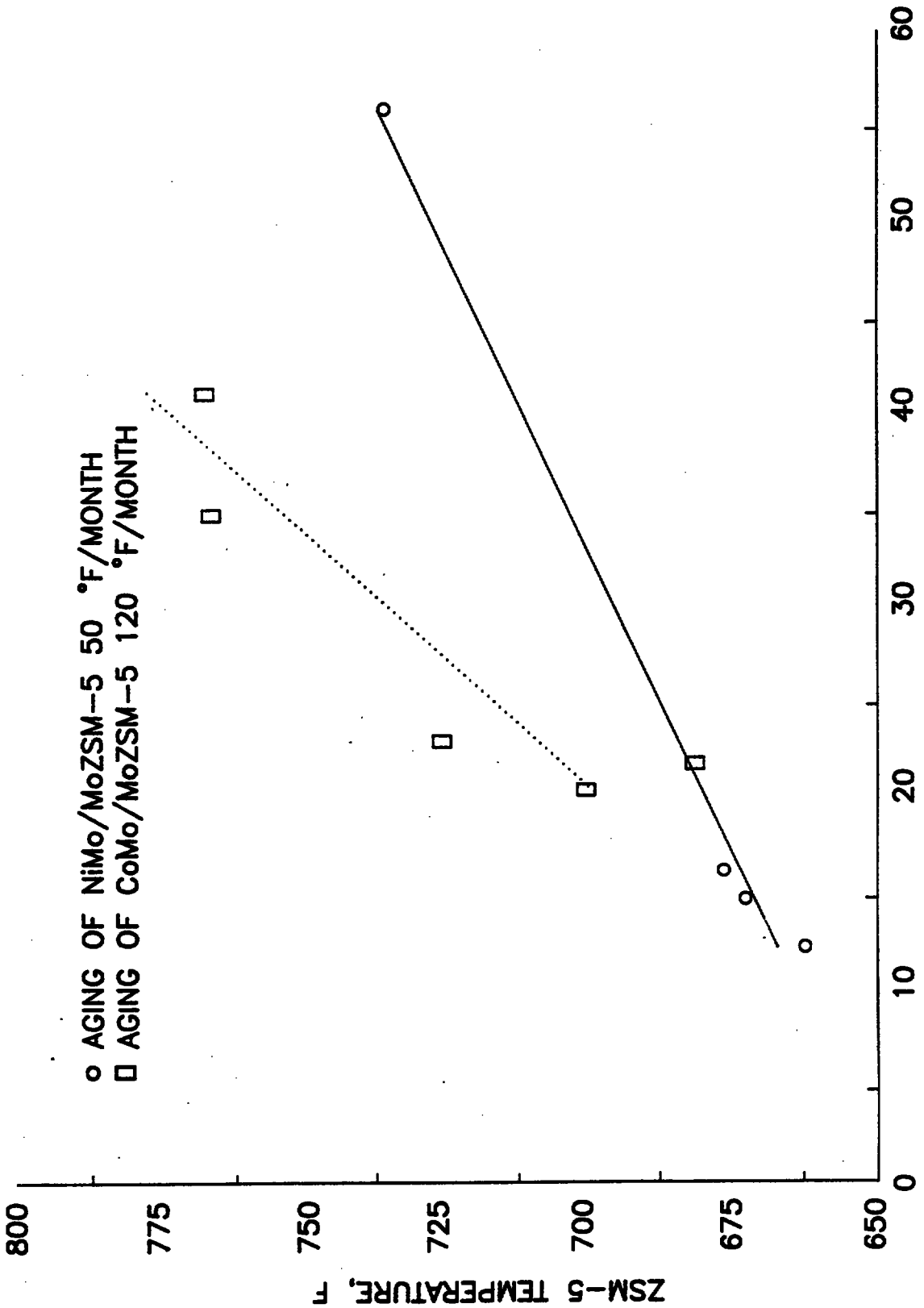

o AGING OF NiMo/MoZSM-5 50 °F/MONTH
□ AGING OF CoMo/MoZSM-5 120 °F/MONTH
ZSM-5 TEMPERATURE, F
800
775
750
725
700
675
650
0
10
20
30
40
50
60
DAYS ON STREAM

FIG. 4