

**DIESEL AROMATICS SATURATION:
A COMPARATIVE STUDY OF FOUR CATALYST SYSTEMS**

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INTRODUCTION

It has previously been reported that a high aromatics content in diesel fuel both lowers the fuel quality and contributes significantly to the formation of undesired emissions in exhaust gases (1, 2). Because of the health hazards associated with these emissions, environmental regulations governing the composition of diesel fuels are being tightened in Europe and the USA (3, 4). There is, however, a large span in the stipulated maximum level of aromatics. The 1990 Amendments to the Clean Air Act will limit aromatics in the USA to 35%v or a minimum cetane number of 40 from 1993, whilst in California a maximum of 10%v will be enforced. In Sweden there are three diesel specifications in operation with a limit of 5%w aromatics in class 1, 20%w in class 2 and 25%w in class 3. In Denmark a minimum cetane number of 52 is likely to be required for city diesel.

At the same time the aromatics content of diesel feedstocks can vary widely: S.R. stocks typically contain 20-40%v aromatics and cracked stocks 40-70%v. Thus the requirements for aromatics saturation range from moderate to severe depending on refinery location and feedstock availability. Existing middle distillate hydrotreaters designed to reduce sulfur levels are capable of reducing aromatics content only marginally (5-7), and as such considerable attention has in recent years been paid to new catalysts and processes for aromatics saturation.

In this paper results obtained on four catalyst systems are reported. The systems investigated are:

- conventional hydrotreating catalysts in single-stage operation,
- NiMo/NiW in two-stage operation,
- Pt/Al₂O₃ in two-stage operation,
- sulfur-tolerant noble-metal catalyst in two-stage operation.

A comparison of the conditions necessary to obtain given aromatic specifications is made for all four systems.

EXPERIMENTAL

The hydrogenation runs were performed in a stainless steel tubular fixed-bed reactor (50 ml) operating in the down-flow mode. Once-through pure hydrogen gas was used. The feedstocks used in the present study and their properties are summarized in Table 1.

FEED CUT	A HGO	B Pretr. HGO	C Pretr. HGO	D Pretr. HGO	E LGO	F Pretr. LGO
SG	0.865	0.845	0.839	0.841	0.839	0.832
S, wppm	17,000	1400	1.5	300	1270	90
N, wppm	225	60	2	46	38	15
D86, °F						
IBP/10%	425/532	397/505	390/485	390/485	376/429	385/426
50/90%	624/710	600/703	600/689	597/689	480/547	478/545
EP	720	717	705	730	590	587
<u>Aromatics</u>						
FIA, %v	33.0	23.5	19.0	19.5	30.0	25.5
HPLC, %w						
total	36.0	25.0	20.0	21.0	32.5	28.0
mono-	20.5	19.0	16.5	17.0	17.5	17.0
di-	13.0	5.0	3.0	3.5	11.0	7.5
tri-	2.5	1.0	0.5	0.5	4.0	3.5
Aromatic carbon, %w	13.5	9.3	7.7	7.9	10.3	9.3

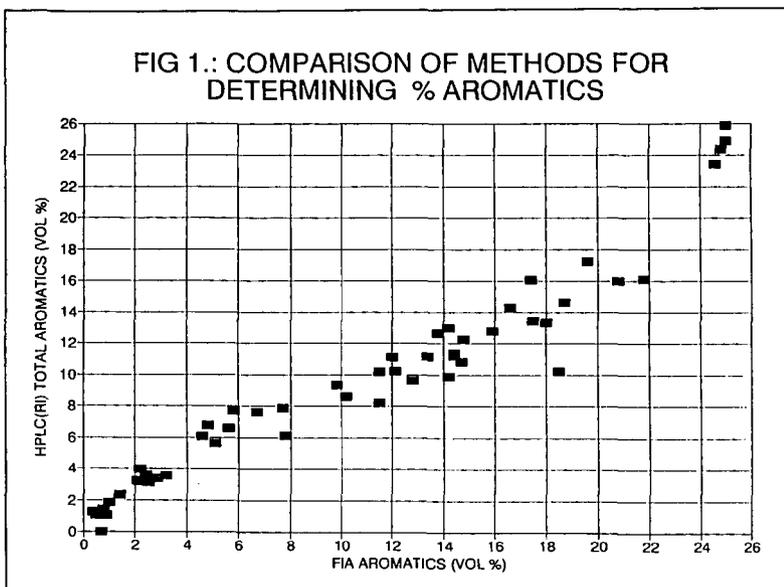
TABLE 1: Properties of Feedstocks.

Aromatics content in feed and products was measured by FIA, HPLC and Dhulesia's correlation (8). ¹³C NMR was used to check the results of Dhulesia's correlation. These two methods give the total content of aromatic carbon in wt%. The HPLC method uses two types of detectors, namely ultraviolet (UV) and refractive index (RI) to measure quantitatively different types of aromatics (i.e. mono-, di-, tri- and total aromatics) in feed and products. The FIA method (ASTM D1319) that has been prescribed by the EPA as a standard method for specifying aromatics levels in diesel fuels does not give any breakdown of aromatics type distribution, but gives the total aromatics content in vol%. Different methods usually give different absolute aromatics levels than those by FIA. Correlations between aromatics measured by FIA and other methods have been developed by several workers (5, 9). However, such correlations differ significantly with variations in feedstocks.

Among the various methods used in our laboratory for aromatics determination, the best agreement for total aromatics content was found between HPLC (RI) and FIA methods. A plot of total aromatics as measured by FIA and HPLC (RI) is shown in Figure 1.

The HPLC (RI) method is a standard IP method (IP 391/90). It can be used for routine aromatics analysis as well as a research tool to follow changes in concentration of different types of aromatics and reactions during hydrodearomatization.

FIG 1.: COMPARISON OF METHODS FOR DETERMINING % AROMATICS



RESULTS AND DISCUSSION

1. Conventional Catalysts in Single-Stage Operation

Tests were carried out on a commercial catalyst, TK 561, using a Kuwait HGO as feedstock. TK 561 is a catalyst containing Ni and Mo on alumina. The HGO is a straight run cut used as a feed to a commercial diesel hydrotreater with a high sulfur content and 36 wt% aromatic compounds (Feed A in Table 1). The tests were run at a wide range of conditions: hydrogen pressure 4.5-12.5 MPa (650-1815 psi); temperature 593-673K (608-752°F); LHSV 1-2.5 h⁻¹.

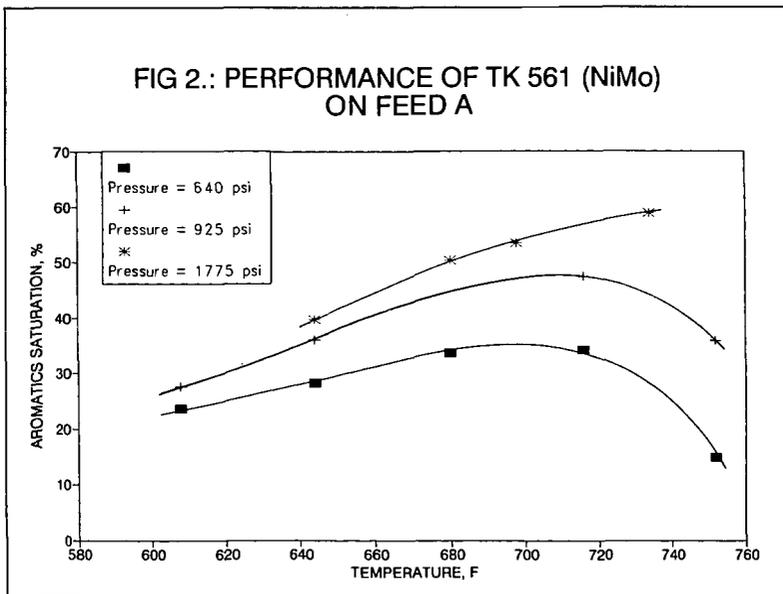
It was found that the degree of aromatics saturation increased with increase in reactor temperature up to a maximum level. The temperature at which the maximum conversion was obtained was a function of pressure and space velocity. Further increase in temperature resulted in a decrease in aromatics saturation. These results are illustrated in Fig. 2 in which the degree of aromatics saturation (as measured by ¹³C NMR) is plotted against temperature for three different pressure levels (LHSV held constant). The existence of a maximum conversion at a given pressure indicates a limitation imposed by thermodynamic equilibrium. This is supported by the HPLC aromatics analysis which shows that at high temperatures, the equilibrium between monoaromatic species and naphthenes is established. As seen in Figure 2, the maximum occurs at higher

temperatures as the pressure is increased, which is consistent with a shift in the equilibrium concentration.

A number of other catalysts were investigated over the same range of conditions, including CoMo and NiW (all on alumina) and TK 525, which is NiMo on a special carrier (the molar concentration of W and Mo is the same for the catalysts). Using only the data obtained at or below 633K (680°F) - below which temperature dehydrogenation reactions are negligible - and assuming first order kinetics, a comparison of the relative average activity of the catalysts was made (Table 2).

Catalyst Type	Relative Hydrogenation Activity
NiMo (TK 561)	100
NiW (TK 547)	90
CoMo	90
NiMo (TK 525)	125

TABLE 2: Traditional Hydrotreating Catalysts in Single-Stage Operation on Feed A.



It is seen that NiW gives lower activity than the NiMo catalysts in single-stage operation even though the difference in activity of the catalysts is not large.

The results show that when using these catalysts in single-stage operation it is necessary to operate at high pressures, which is in agreement with the conclusions of (10, 11).

2. NiMo/NiW Catalysts in Two-Stage Operation

Several workers (12, 13) have shown that H₂S inhibits aromatics saturation reactions. Our own studies indicated that the extent of inhibition depends on the catalyst system under investigation: NiW catalysts are more affected by H₂S than NiMo catalysts. This is illustrated by test runs on a pretreated HGO (Feed B, Table 1). This feedstock was obtained by hydrotreating a portion of Feed A using TK 561. Feed B contains about 10% of the sulfur and 70% of the aromatics in Feed A. Note, however, that the concentration of monoaromatics is about the same for the two feeds.

Using average first order rate constants, the performance of a NiW catalyst, TK 547, and TK 561 was compared. The results are shown in Table 3.

Catalyst Type	Relative Hydrogenation Activity	
	Feed A, S=1.7 wt%	Feed B, S=0.14 wt%
NiMo (TK 561)	100	100
NiW (TK 547)	90	225

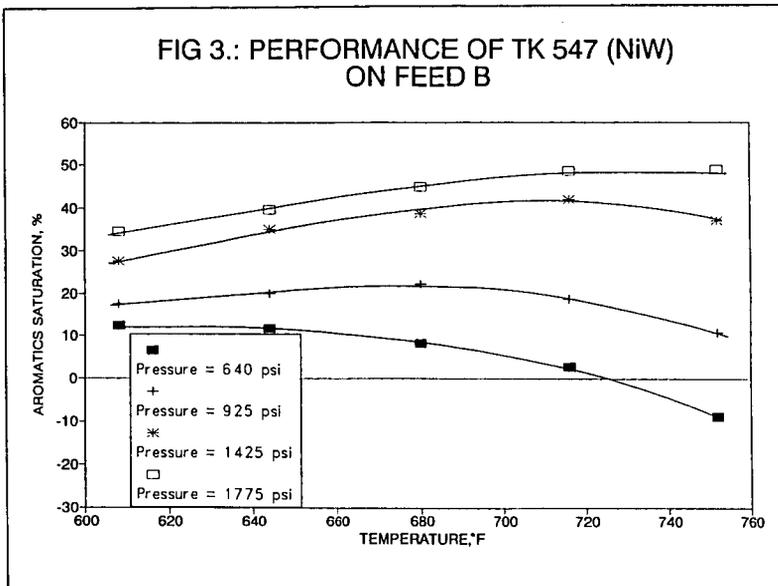
TABLE 3: Comparison of NiMo and NiW Catalyst Activity for Two Feed Sulfur Levels.

On Feed B, TK 547 is twice as active as TK 561. This opens up the possibility of a two-stage process with a NiMo-type catalyst in the first stage and NiW in the second with removal of H₂S between the stages.

The performance of TK 547 on Feed B at various temperatures and pressures is shown in Figure 3. Since there is a higher fraction of monoaromatics (the most refractive aromatic species) in Feed B, the overall levels of aromatics saturation are lower than those obtained with TK 561 on Feed A. It is seen that there is a maximum degree of saturation that can be achieved at a given pressure level and that the temperature at which the maximum occurs increases with increasing temperature.

It was found that it is possible to achieve higher levels of saturation at a given space velocity using NiMo + NiW in a two-stage process rather than NiMo in a single-stage process. However, high pressures or low space velocities are also needed with this catalyst system to obtain reasonable levels of aromatics reduction (see section entitled Comparison of Operating Conditions).

FIG 3.: PERFORMANCE OF TK 547 (NiW)
ON FEED B



3. Pt on Alumina in Two-Stage Operation

It is well known that catalysts based on Pt/Al₂O₃ exhibit excellent hydrogenation activity but are poisoned by quite small quantities of sulfur compounds in the feedstock (14). A severe pretreatment is therefore necessary to reduce the sulfur content to a level that does not affect the performance of the Pt/Al₂O₃ catalyst, which will normally mean reduction of sulfur content to below 2 ppm.

Feed C is a batch of Feed A that has been pretreated to give 1.5 ppm sulfur. The feed contains 20% aromatics which are almost all monoaromatics. A Pt/Al₂O₃ catalyst containing 0.6% Pt was tested on this feed at a variety of conditions. It was found that up to 60-70% reduction in aromatics content could be achieved at moderate conditions: pressure 4.5-6.0 MPa (650-870 psi); temperature 550-590K (530-600°F) and LHSV 0.75-1.5. However, as discussed later, the low space velocities that are required in the pretreatment stage to obtain sufficient reduction in sulfur content make this alternative economically unattractive for most applications.

4. Sulfur-Tolerant Noble Metal Catalyst in Two-Stage Operation

The sulfur tolerance of a noble metal can be increased e.g. by supporting it on zeolite as reported by (15, 16). It is therefore not necessary to pretreat so severely when using this type of catalyst. A process using TK 908, a noble-metal catalyst on a special carrier is described in (17). The sulfur tolerance of TK 908 is illustrated

by tests on two different feedstocks. The first test was made on Feed D which was obtained by hydrotreating a batch of Feed A. Feed D contains 300 ppm S and 21% aromatics (Table 1). Using this feed, 55% reduction in aromatics content (corresponding to 9% aromatics in the product) was achieved at 5.0 MPA (725 psi) and 600-620K (625-655°F)

The second feedstock Feed E (Table 1) is a hydrotreated diesel, the origin of which is a North Sea and Middle East LGO (Feed F, Table 1) The low end-point makes the cut suitable for class 1 Swedish diesel but the aromatics content needs to be reduced from 28%w to below 5%. Test results are shown in Figure 4 and it is seen that this goal can be achieved at a hydrogen pressure of 5.0 MPA (725 psi) and between 575-590K (580-600°F) depending on the H₂/oil recycle ratio.

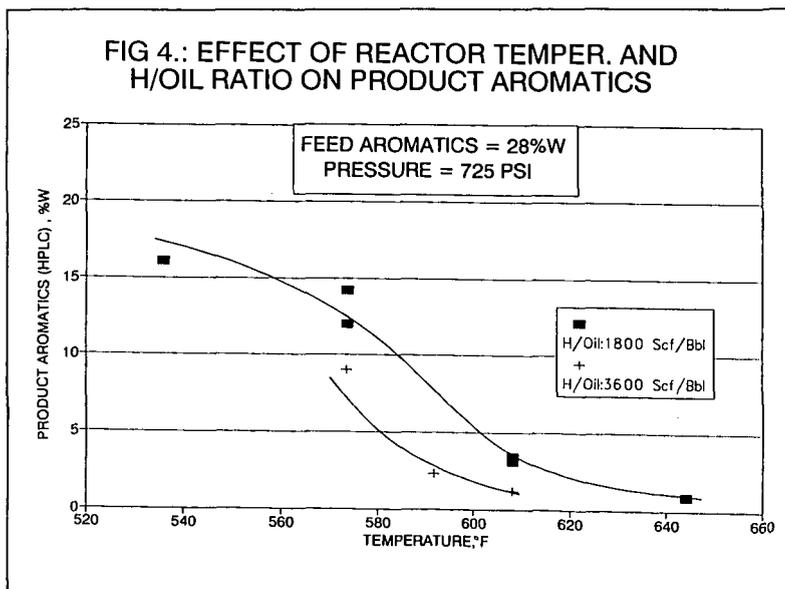
COMPARISON OF OPERATING CONDITIONS

Calculations have been made for each catalyst system to compare the relative reactor volumes needed to obtain a given product quality. The calculation basis was as follows:

Feedstock to first stage = Feed A (36%w aromatics).

Average reactor temperature = 625°F.

Product aromatics: for non-noble metal systems = 18%w, for noble metal systems = 10%w.



The results are presented in Table 4.

Catalyst System	NiMo	NiMo + NiW		CoMo+ Pt/Al ₂ O ₃	NiMo + TK 908	
No. of Stages	one	two		two	two	
Case	1	2	3	4	5	6
Feedstock	A	A	A	A	A	E
Aromatics in feed, %w	36	36	36	36	36	32.4
H ₂ pressure, psi	1450	1450	925	925	725	725
Average temp., °F	625	625	625	625	625	600
Aromatics in product, %w	18	18	18	10	10	5
Relative reactor volume NiMo=1.0	1.0	0.7	2.8	3.0	1.0	0.55

TABLE 4: Comparison of Operating Conditions.

The reactor volumes are relative to NiMo, single-stage operation = 1.0. In all other cases the relative reactor volume is for combined first and second stage. The size of the first-stage reactor is determined by the required level of sulfur in the feed to second stage.

It is seen that using NiMo + NiW in two stages results in a 30% reduction in reactor volume as compared with NiMo alone. This system is very sensitive to hydrogen pressure as is seen by comparing cases 2 and 3.

The use of a sulfur tolerant catalyst instead of a Pt/Al₂O₃ catalyst reduces the reactor volume by a factor of 3 (case 4 and 5) despite a lower operating pressure. It is also seen that the NiMo + TK 908 system results in 8% fewer aromatics in the product than NiMo alone at half the pressure and without increase in reactor volume. Furthermore, the feed used in this comparison has an unusually high sulfur content (1.7%w) and end boiling point (720°F). The NiMo + TK 908 system performs even better on lower sulfur feeds such as Feed E as seen in case 6.

Which of these systems should be used for a given service will depend on a large number of factors, but generally speaking, the NiMo + NiW system will be preferred at moderate levels of saturation, whilst for deep aromatics saturation the system employing the sulfur tolerant noble metal catalyst TK 908 will be preferred.

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