PRODUCTION OF LOW AROMATICS AND LOW SULPHUR DIESEL IN A HYDRODESULPHURIZATION (HDS) PILOT PLANT UNIT

A. A. LAPPAS[1]
R. BUDISTEANU[2]
K. DRAKAKI[1]
I. A. VASALOS[1]

1. Chemical Process Engineering Research Institute (CPERI)
and Department of Chemical Engineering
University of Thessaloniki, P.O. Box 361,
57001 Thermi, Thessaloniki
E-mail: angel@aliakmon.cperi.forth.gr
2. Politehnica University of Bucarest,
Bucarest Rumania

ABSTRACT

The present work investigates the hydrotreating process of a diesel in order to achieve lower sulphur and aromatics content. The entire work was performed in a Hydrodesulphurization (HDS) pilot plant unit located in Chemical Process Engineering Research Institute (CPERI). For the tests, a commercial HDS catalyst (CoMo) was used while the feed was provided by the deep desulphurization unit of a Greek refinery (Motor-Oil refinery). For the determination of diesel aromatics, a method based on the ASTM D-2549-85 was applied. The objective of the work was to investigate the ability of a typical HDS catalyst for aromatics saturation. The effect of the main hydrotreating operating parameters (T, P, WHSV, H_2/Oil ratio) on sulphur and aromatics removal was also investigated. In general, the data showed that the product density and the aromatic and sulphur content of diesel decreased as the temperature or pressure increased or space velocity decreased. It was concluded that with the present catalyst an aromatics saturation degree of up to 40% could be achieved, giving a diesel product with aromatics content of about 20-25% wt. However, high temperatures (>370°C) were required in order to achieve 500 ppmw sulphur in this feedstock.

INTRODUCTION

The demand for high quality transportation and heating diesel has grown significantly over the last years. Especially for EU, the transportation diesel demand is growing at a rate of about 5% per year which is higher than the corresponding one for gasoline (Anabtawi and Ali, 1991). In order to meet this increased demand, the refineries use heavy distillates as blending components into the diesel pool (Andari et al., 1996). One of these heavy components comes from the Fluid Catalytic Cracking unit (FCCU). This product, Light Cycle Oil (LCO), has high density and high content of heteroatoms (sulphur and nitrogen compounds) and of aromatics (Venuto and Habib, 1979). However, after some research projects carried out mainly in USA and Europe (Auto-Oil program), it is now acceptable

that some diesel compounds affect directly the emissions of the diesel engines exhausts (Concave review, 1996). It was proved that the sulphur compounds produce mainly SOx while the aromatics affect the NOx and the particulate emissions (Concave review, 1996; Roj and Karlsson, 1995).

For the above reasons, the refinery industry today faces on the one hand tighter specifications and on the other hand higher production demands for diesel. Stringent environmental legislation has already been introduced in Sweden (1991) and in California (1993) (Roj and Karlsson, 1995). In California, large refineries (over 50000 barrels per day-BPD capacity) are required to lower their diesel aromatics to 10% vol (determined by the Fluorescent Indicator Adsorption method-FIA) since October 1993. Small refineries (less than 50000 BPD) need to achieve 20% aromatics. In Sweden, the so-called Class I diesel has an aromatics limit of 5% vol and Class II of 20% vol. The corresponding limits for sulphur are 10 and 50 ppm (Cooper and Donnis, 1996). The Class II regulation is also expected to come into effect in the other Scandinavian countries as well. Stringent regulations in the diesel fuel quality are foreseen in the future for the EU countries. In addition to low sulphur levels, this also means a limitation of aromatics in diesel fuel and minimum cetane index. These two properties are interrelated, since by lowering the aromatics the fuel density also decreases, which in turn causes the cetane index to increase (Sugimoto, Tsuchiya and Sagara, 1992).

The rate of aromatics saturation is highly influenced by the distribution of aromatics among monocyclic, dicyclic and tricyclic compounds. Triaromatics are hydrogenated to diaromatics at rather mild conditions. Diaromatics are already less reactive than triaromatics, but still react at moderate conditions to form mono-aromatics. Triaromatics are hydrogenated at approximately 20-30% higher rate than diaromatics which, in turn react 10 to 20 times faster than single ring aromatics (Magnabosco, 1990). Therefore, the rate determining step in aromatics saturation is the hydrogenation of the mono-aromatic rings (Magnabosco, 1990, AKZO NOBEL Reports, 1993). Thus, the new technologies for extensive aromatics saturation require a two stage hydrotreating process to overcome thermodynamic limitations. In the first stage, the feedstock is treated over a NiMo catalyst at elevated tempera-

ture and pressure to remove sulphur and nitrogen compounds and also to saturate some aromatic compounds. In the second stage, the first stage product is treated at substantially lower temperatures over a higher hydrogenation activity noble metal catalyst (Pt/alumina) (Suchanek, 1990, Peries et al., 1991).

In Greece, since 1/1/97 the new specification for sulphur in diesel is 500 ppm (from 0.3 wt%). Moreover, although specifications for aromatics do not exist yet, the EU has set a minimum cetane index of 40 (for heating diesel) and 46 for transportation diesel and this requires a certain reduction of aromatics (35% max). It is probable that these limits will be even more stringent beyond 2000. For these reasons, Greek refineries, and especially those which have FCC units, have committed large investments for new deep desulphurization units. The work of this paper was performed in cooperation with two Greek refineries (Hellenic Aspropyrgos Refinery-HAR and Motor Oil-MOH refinery) in the HDS pilot plant of CPERI. The main objective of the work was to investigate the degree of aromatics saturation which can be achieved with a typical hydrodesulphurization commercial catalyst used now for sulphur reduction. Another aim of the study was to investigate the degree of diesel desulphurization and dearomatization achieved in the HDS pilot unit in relation to the Greek commercial units and to determine optimum operating variables for low sulphur and (especially) low aromatics diesel.

EXPERIMENTAL

Description of HDS pilot plant

The present work was conducted in a continuous flow, trickle bed hydrotreating pilot plant (HDS) located in CPERI laboratories. A schematic diagram of the unit is presented in Fig. 1.

The HDS unit consists of two fixed bed reactors (45.72 cm length x 2.8 cm ID) which can operate in series or independently one from the other, for up or down flow. The reactors can operate at temperatures up to 550 °C and pressures up to 150 atm. The feed system includes three independent gas feed modules and one liquid feed module with all the necessary equipment. The mass of catalyst fed in each reactor is 20 gr. For the better operation of the unit the catalyst is mixed (diluted), inside the reactor, with a non-active material (α-alumina). This dilution improves
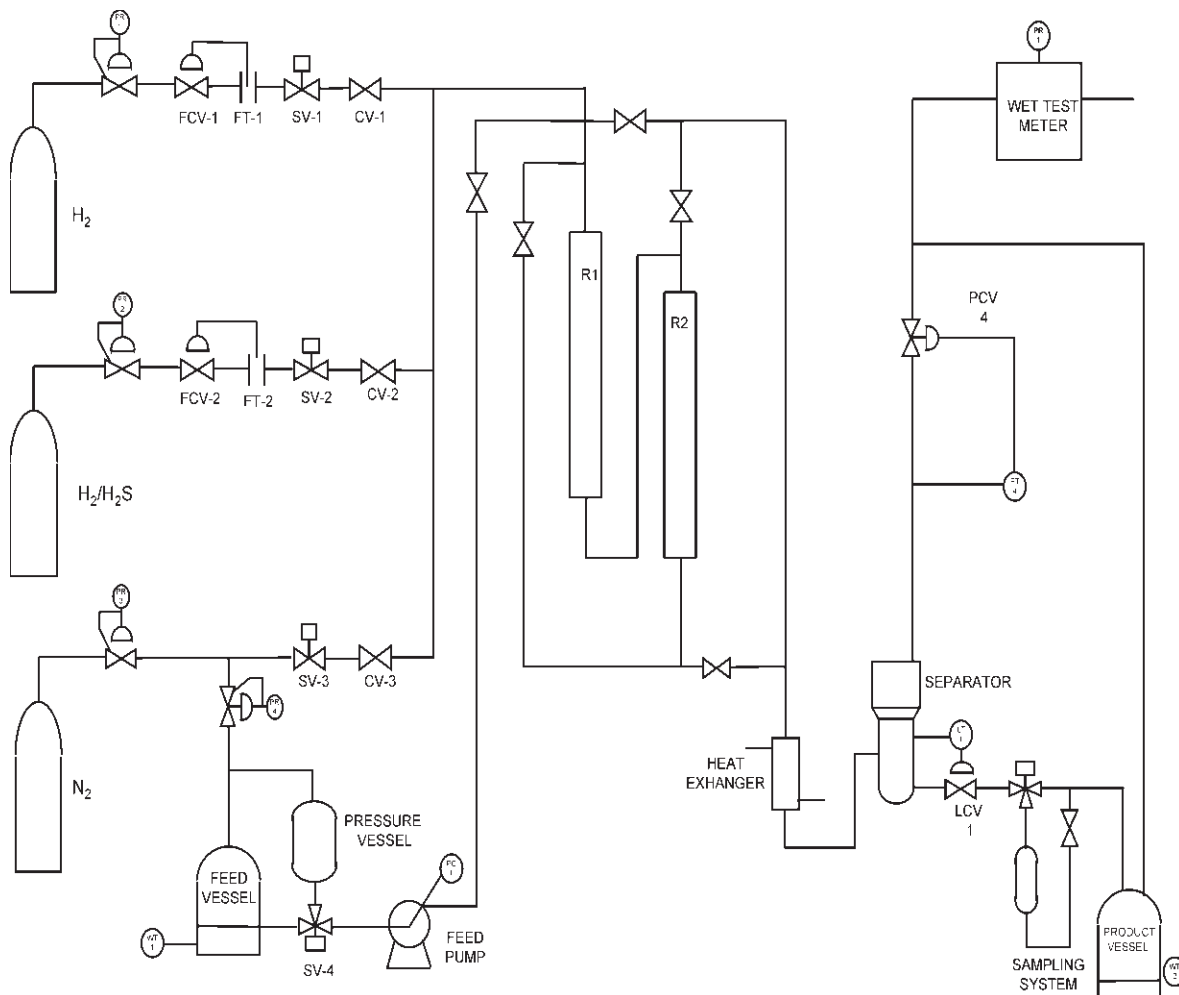
Figure 1. Schematic diagram of the HDS pilot plant unit

the flow pattern by increasing the liquid hold up and residence time distribution. Moreover, the inert material helps for achieving isothermal conditions in the two reactors during the experiments. According to the above, the loading of catalyst and α-alumina mixture is very important for the correct operation of the unit and it was performed with a special procedure developed in CPERI.

Before the start of the experiments, the catalyst is calcined for two hours at 425 °C and then is sulphidized by a H$_2$/H$_2$S gas mixture at 260 °C so that the catalyst metallic oxides convert to sulphide ones. For the tests, both reactors were used in down flow operation. The reactors outlet is cooled and led to a separator where the gas and liquid parts are separated. The level of the liquid product in the separator is automatically regulated. The gases exiting

the separator pass through a NaOH trap so that the produced H$_2$S is removed and then through a wet test meter. The pilot plant unit is fully automated and functions by means of a computer connected with an automatic control system. The computer receives all the plant signals and executes all the control and adjustment actions, so that the unit can operate for a long period of time at unattended operation.

The diesel oil treated in the pilot unit was the real feedstock from the deep hydrodesulphurisation unit of MOH refinery. This diesel was a mixture of a diesel from the atmospheric tower of the refinery and of a diesel from the FCCU (LCO). The catalyst was a commercial CoMo type catalyst, supplied by Criterion Company. The properties of the diesel and the catalyst used are given in Tables 1 and 2, respectively.

Table 1. HDS feedstock properties

Type	Diesel MOH	
Density, g cm^{-3}	0.8676	
Sulphur content, %wt	1.894	
Aromatic content, %wt	36.91	
Refractive Index (20 $^{\circ}$C)	1.4898	
Viscosity, cst	37.78 $^{\circ}$C	98.89 $^{\circ}$C
	4.357	1.518
ASTM D-86 ($^{\circ}$C)		
IBP:172.3, 5%:234.5, 10%:250.8, 50%:302, 90%:358.5, FBP:385		

Table 2. Catalyst properties (Criterion 448)

Extrude shape	Trilobe
Nominal size, mm	1.2
Loss of ignition (482.22 $^{\circ}$C), % wt	< 2.0
Cobalt,% wt dry basis	3.1
Molybdenum,% wt dry basis	12.4
Surface area, m^2 g^{-1}	250
Pore volume, cm^3 g^{-1}	0.53
Side plate crush strength, lb (kg)	15 (7)
Bulk crushing strength, kg cm^{-2}	11
Attrition Index	98+
Reactor loading density, lb ft^{-3} (kg l^{-1})	38 (0.61)
Compacted bulk density, lb ft^{-3} (kg l^{-1})	44 (0.70)

Aromatics determination

A very important point in the works of diesel dearomatization is the analytical techniques used to measure the aromatics. Thus, different methods have been proposed in literature (UV aromatics, FIA, HPLC etc.) (Nash, 1989). Among them, FIA (ASTM D-1319) (ASTM methods, 1993) is the most standard method. However, most diesel have end points higher than that proposed by FIA. For this reason, in the present study, a more general procedure was applied for aromatics determination. The method covers the separation and determination of representative aromatics and non-aromatics fractions from hydrocarbon mixtures with boiling point range between 232 and 538 $^{\circ}$C. According to this, the amount of aromatics in the products (and in the feed as well) was determined by Elution Chromatography. The entire process is based on a modification of a standard ASTM method, ASTM

D-2549-85 (ASTM methods, 1985). For the procedure, a weighed amount of sample is charged at the top of a chromatographic column packed with activated alumina oxide and silica gel. N-pentane is added to the column to elute the non-aromatics fraction. The non-aromatics fraction is a mixture of paraffinic and naphthenic hydrocarbons if sample is a straight-run material. If the sample is a cracked stock, the non-aromatics fraction will also contain aliphatic and cyclic olefins. When all the non-aromatics are separated, the aromatics fraction is eluted by addition of diethyl-ether, dichloro-methane and methanol. The aromatics fraction may contain aromatics, condensed naphtheno-aromatics, aromatic olefins and compounds containing sulphur, nitrogen and oxygen atoms. The solvents are completely removed by evaporation and the residues are weighed and calculated as the non-aromatics and aromatics fractions of the sample. Full details for this method are given in the literature (Lappas et al., 1997a, Lappas et al., 1997b).

RESULTS AND DISCUSSION

As it was previously pointed out, a very important part of this work concerns the correct determination of aromatics content in the hydrogenated products. For this reason, the repeatability of the method ASTM D-2549-85 was tested by running the procedure many times for some random samples. The repeatability was found to be satisfactory. Moreover, the quality of separation was verified by a gas chromatography mass spectroscopy procedure using a GC/MS apparatus (HP GC/MS 5859 MS ENGINE). According to this procedure, the aromatics which were separated by the ASTM D-2549-85 method, were analyzed in the GC/MS and their separation was found satisfactory (Lappas et al., 1997a; Lappas et al., 1997b).

The independent operating parameters which affect the hydrogenation procedure are: Temperature (T), Pressure (P), Weight Hourly Space Velocity (WHSV), H$_2$/oil ratio. The effect of these parameters was studied using the following range of values: WHSV= 1.5, 2, 3, 4, 6 hr^{-1}, T= 280, 310, 340, 370°C, P= 20, 25, 30, 35, 40, 50, 60 bar, H$_2$/oil ratio = 800, 1000, 1200, 1800, 2000 SCFB (Standard Cubic Feet Hydrogen per Barrel Diesel, 1 SCFB = 0.166 NL gas / L feed).

Effect of space velocity

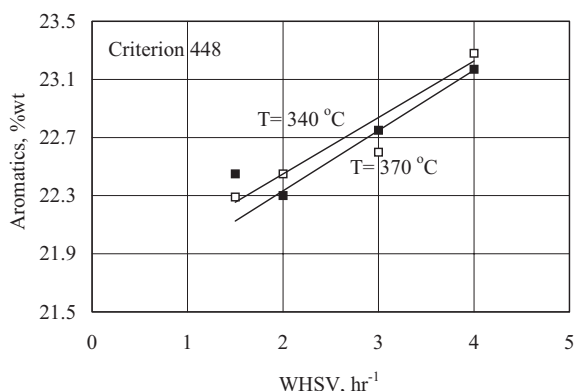The influence of the space velocity on diesel dearomatisation is given in Fig. 2.

Figure 2. Effect of WHSV on product aromatics (P= 40 bar, H_2/Oil= 1800 SCFB)

It is observed that the decrease of space velocity results in an improved product quality. The aromatic content decreases and inversely the saturation degree increases. This increase seems to be almost linear (Fig. 2). The maximum dearomatisation degree was 39.6 % (22.3 %wt aromatics in the product), achieved in the following conditions: WHSV=2 hr^{-1}, T= 370°C, P= 40 bar and H_2/oil= 1800 SCFB. These results are in agreement with those reported in literature on similar catalysts (Anabtawi and Ali, 1991; Andari et al., 1996).

Effect of temperature

The effect of temperature on dearomatisation was studied at the temperature range 280-380 °C at 30 bar, at WHSV of 4 h^{-1} and hydrogen flow rate of 1000 SCFB. The results are presented in Fig. 3.

As it can be seen, at constant space velocity pressure and H_2/oil ratio, the product aromatics content decreases as temperature increases. The decrease of aromatics is rapid up to a temperature of about 340 °C. Beyond this temperature the decrease is very slow. As it is known from literature, at high temperatures, the dehydrogenation reactions rate increases substantially and chemical equilibrium is achieved. The maximum dearomatisation degree was 34% (24.35 %wt aromatics in the product) and was achieved at the following optimum operating conditions: T= 340 °C, WHSV= =4 hr^{-1}, P= 30 bar and H_2/oil ratio= 1000 SCFB.
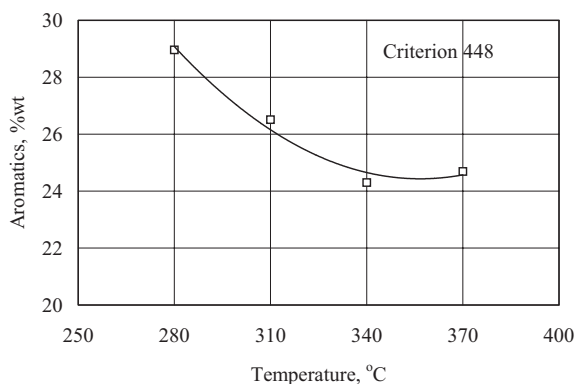

Figure 3. Effect of temperature on product aromatics (P= 30 bar, H_2/Oil= 1000 SCFB, WHSV= 4 hr^{-1})

Effect of pressure

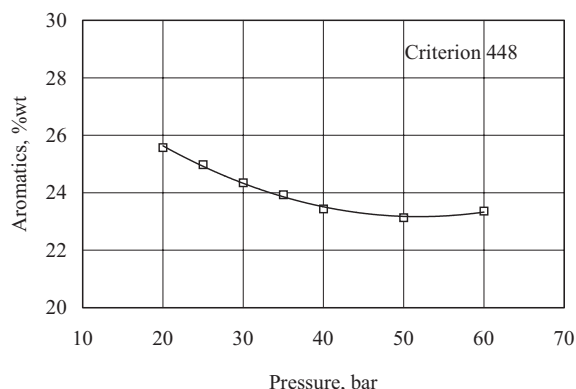The effect of pressure on the aromatics content is given in Fig. 4.

Figure 4. Effect of pressure on the aromatics content (T= 340°C, H_2/Oil= 1000SCFB, WHSV= 4 hr^{-1})

It is obvious that the trends are similar to those of temperature, i.e. by increasing the pressure the product quality improves since the aromatics content decreases. Moreover, the effect of pressure on the aromatics reduction is stronger up to a value of about 50 bar. After this value the effect of pressure is almost negligible. The maximum dearomatisation degree was 37.3% (23.13 %wt aromatics content) and was achieved at the following optimum operating conditions: WHSV= 4 hr^{-1}, T= 340 °C, P= 50 bar and H_2/oil= 1000 SCFB.

Effect of H_2/oil ratio

The effect of the H_2/oil ratio on the aromatics content in the hydrogenated products is given in Fig. 5.

The results of Fig. 5 are referred to a constant temperature (340 °C) and to two different values of space velocities and pressures.
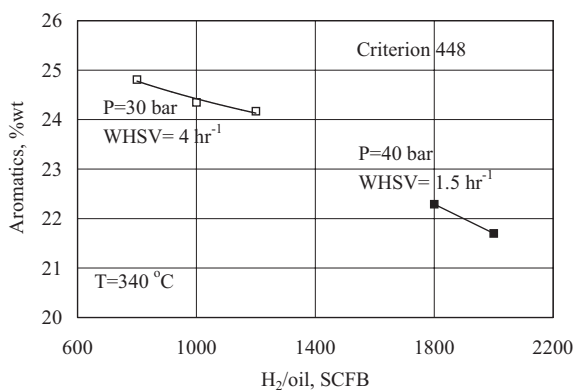

Figure 5. Effect of H$_2$/Oil ratio on product aromatics

It is observed that at the milder conditions (P= 30 bar, WHSV= 4 hr^{-1}), and at the more severe ones (P= 40 bar, WHSV= 1.5 hr^{-1}), a higher H$_2$/oil ratio causes a higher degree of dearomatisation. The maximum dearomatisation degree was 41.2 % (21.7%wt aromatics content) and was achieved at the following conditions: WHSV= 1.5 hr^{-1}, T= 340ºC, P= 40 bar and H$_2$/oil= 2000 SCFB.

The change of the operating parameters also affects the physical properties of the products, especially the density and the refractive index. It was concluded that their variation is similar to the aromatics content one. Data showed that, in general, the product density and refractive index decreased as the temperature (Fig. 6) and pressure increased, or space velocity decreased. These variations can affect the refinery profitability since diesel products are available in a volume basis. In any case, hydrogenated diesel fuel is of excellent quality, high cetane index, very low sulphur level, practically nitrogen free, very good color and color stability.

All the experimental results described above are in accordance with literature. It is known (Cooper and Donnis, 1996; Yoes and Asim, 1987; Suchanek, 1990), that the rate of hydrogenation increases with the temperature or the partial pressure increasing. Thus, in order to maximize the saturation rate, hydrotreating is carried out at elevated hydrogen partial pressures, in presence of a high hydrogenation activity, non-noble metal catalyst such as nickel
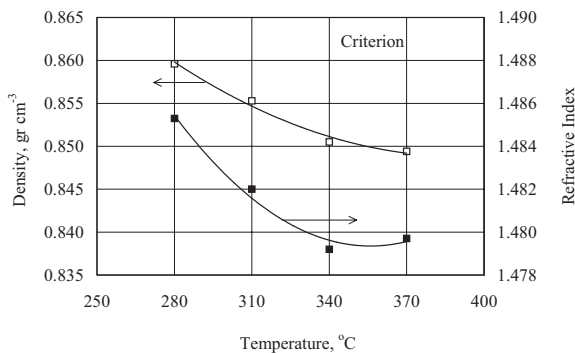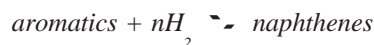

Figure 6. Effect of temperature on product density and refractive index (P= 30 bar, H$_2$/Oil= 1000 SCFB, WHSV= 4 hr^{-1})

or cobalt-molybdenum supported on alumina. Of course, an increase in the reactor temperature increases the rate of hydrogenation reactions, but affects the equilibrium as well. Thermodynamic equilibrium is expected to shift toward aromatics with temperature increasing (or hydrogen partial pressures increasing) as follows:

$$aromatics + nH_2 \rightleftharpoons naphthenes$$

Effect of operating variables on sulphur removal

In literature, NiMo or NiW catalysts are considered as highly active for aromatics saturation (Marchal et al., 1996). The catalyst used in this study is more appropriate for sulphur removal than aromatics saturation. For this reason, it is also important to have an indication of the sulphur removal achieved with this commercial CoMo catalyst. Thus, simultaneously with the aromatics content, the sulphur content of the hydrotreated samples was also determined. This measurement was performed using an XRF apparatus (Horriba 800). The effect of WHSV on sulphur removal is presented in Fig. 7.

This figure gives the % remaining sulphur in the product as a function of inverse WHSV. Figures of this type can reveal the reaction order kinetics for sulphur removal. However, it is clear that the limit of 500 ppm can not be achieved at 340 °C, in any WHSV (P= 40 bar and H$_2$/oil= 1800 SCFB). Increasing the temperature to 370 °C, the limit of 500 ppm can be achieved even at WHSV= 4 hr^{-1}. Fig. 8 shows that temperature is the most important parameter for the desulphurization of this feed.

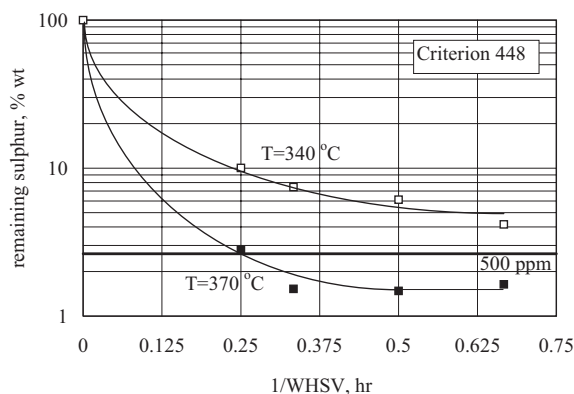Experimental results (not presented in this paper)

Figure 7. Effect of WHSV on product remaining sulphur (P= 40 bar, H$_2$/Oil= 1800 SCFB)

Figure 8. Effect of temperature on product sulphur content (P= 30 bar, H$_2$/Oil= 1000 SCFB, WHSV= 4 hr^{-1})

show that the H$_2$/Oil ratio has a marked influence on diesel desulphurization. In contrast, the experimental results showed that an increase in pressure beyond 40 bar, leads to a marginal improvement in sulphur removal. The present results are in accordance with literature (Andari et al., 1996; Shih et al., 1992).

CONCLUSIONS

The various hydrotreatment operating parameters have a different influence on the aromatics and sulphur content of diesel. Thus, by decreasing the space velocity and increasing the temperature, the pressure and the H$_2$/Oil ratio, the aromatics and sulphur contents decrease and inversely, the saturation degree increases. Although aromatics saturation

is limited by chemical equilibrium at high temperatures (>350 °C) and pressures (>50 bar), an aromatics saturation degree of up to 40% can be achieved using a typical HDS catalyst. The hydrotreating procedure can give a diesel product with aromatics content of about 20-25 %wt. However, very high temperatures (>370 °C) are required in order to achieve the 500 ppmw sulphur in this feedstock at a WHSV of 4 hr^{-1}.

Acknowledgments

REFERENCES

AKZO NOBEL Technical Reports (1993). *Ketjenfine 853*, February.

Anabtawi, J.A., Ali, S.A.(1991). Effects of Catalytic hydrotreating on Light Cycle oil Fuel quality. *Ind. Eng. Chem. Res.*, **30**, pp. 2586.

Andari, M.K., Seedo, A., Stanislaus, A., Qabazard, H.M. (1996). Kinetics of individual sulfur compounds in deep hydrodesulfurization of Kuwait diesel oil. *Fuel*, **75**, pp.1664.

Concave review (1996). Auto-Oil, the Commission's proposal on transport fuels, 29/11/1996.

Cooper, B.H., Donnis, B.B.L.(1996). Aromatic saturation of distillates: an overview. *App. Catalysis A: General*, **137**, pp. 203.

Lappas, A.A., Patiaka, D.K., Ikonomou, D., Vasalos, I.A.(1997b). Separation Characterization and Catalytic Cracking kinetics of Aromatic Fractions obtained from FCC Feedstocks. *Ind. Eng. Chem. Res.*, **36**, pp. 3110-3115.

Lappas, A.A., Patiaka, D.K., Dimitriadis, B.D., Vasalos, I.A. (1997a). Separation and Characterization of Paraffins and Naphthenes from an FCC Feedstock. *Applied Catalysis: A General*, **152**, pp. 7-26.

Magnabosco, L.M. (1990). Principles of Hydroprocessing in Petroleum Refining. *Stud. Surf. Sci. Catal.*, **53**, pp. 481-496.

Marchal, N., Mignard, S., Kasztelan, S. (1996). Aromatics saturation by sulfided Nickel-Molybdenum hydrotreating catalysts, *Catalysis today*, **29**, pp. 203-207.
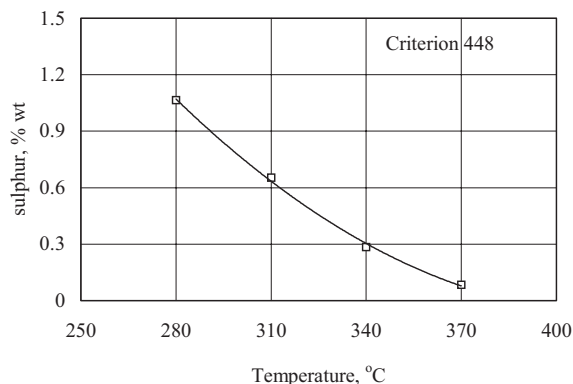
Nash, R.M. (1989). Meeting the challenges of low aromatics diesel, presented at the *NPRA Annual Meeting*, San Francisco, California, March 19-21.

Peries, J. P., Billon, A., Hennico, A., Kressmann, S. (1991). IFP Deep Hydrodesulfurization and Aromatics Hydrogenation on Straight Run and Pyrolysis Middle Distillates, presented at the *NPRA Annual Meeting*, San Antonio, Texas, March 17-19.

Roj, A., Karlsson, K. (1995). High quality diesel fuel reduces emissions. *Fuel Reformulation*, September/October.

Shih, S.S, Mizrahi, S., Green, L.A., Sarli, M.S. (1992). Deep desulfurization of distillates. *Ind. Eng. Chem. Res.*, **31**, pp. 1232.

Standard Test Method D-2549-85 (1985). Separation of representative Aromatics and Non aromatics fractions of highly boiling points by elution chromatography. *Annual book of ASTM standards.*

Standard Test Method D-1319-93 (1993). Hydrocarbon types in liquid petroleum products by fluorescent indicator, *Annual book of ASTM standards.*

Suchanek, A. J. (1990). Catalytic routes to low-aromatics diesel look promising. *Oil & Gas Journal*, May 7, pp. 109-119.

Sugimoto, A., Tsuchiya, F., Sagara, H. (1992). Deep Hydrodesulfurization of Light Gas Oil, presented at the *NPRA Annual Meeting*, New Orleans, Louisiana, March 22-24.

Venuto, J., Habib, E.T. (1979). Fluid Catalytic Cracking with Zeolite Catalysts, Marcel Dekker (Eds), New York.

Yoes, J. R., Asim, M. Y. (1987). Diesel aromatics difficult to reduce. *Technology, Oil & Gas Journal*, May 11, pp.54-58.