

Complementary information for E&F (PARAGON)

Pilot plant operation with 15% of LCO + 85% of LGO. The performance of the pilot plant unit operating over a period of 10 weeks using 15% of LCO + 85% of LGO to produce a low sulfur diesel component was followed by full analysis of the feed and product after 1, 6 and 10 weeks (SOR, MOR, EOR). The temperature was increased from 350°C as a function of time in order to maintain constant sulfur content of 15 ppm in the product. Other operating conditions were 0.1 h⁻¹, 10.1 MPa, and an H₂/HC molar ratio of 4. Test runs were carried out to check all the all operating variables and be able to proceed with a reconciliation procedure for the data obtained. At the end of the run, the unit was shut down under hydrogen flows, and large samples of catalyst (WNPd/TiO₂Al₂O₃) were taken from the upper, middle, and bottom of the reactor beds using a device specifically built for this purpose. The samples were then analyzed by several techniques. Other tests were performed using 100% LCO (Feed II) for three months and under the same operating conditions as those given above. Table 1 shows the properties of Feed 1 (left-hand columns) and the products obtained after one week, after 1.5 months, and after 3 months in operation to produce 15 ppm of low-sulfur diesel. The rightmost column presents the results obtained in the pilot plant with the same catalyst and operating conditions but using pure LCO for 3 months. The temperature was also increased to keep the sulfur content at ~15 ppm in the products. Processing both feeds clearly led to catalyst deactivation, and increasing the temperature during operation was essential to maintain the sulfur content constant in the product. Detailed analysis of the sulfur present as DBT and naphtho-thiophene (NT) can be seen in the third and fourth rows. The results show a progressive increase in DBT content and the concomitant decrease of sulfur present in other products due the differences in activation energy of these compounds and the different reaction mechanisms involved. Indeed, desulfurization occurred via both direct and indirect paths. Detailed analysis of the type of DBT compounds present in the products of both catalysts indicates a progressive increase in poly-alkylate-dibenzothiophene.

Table 1. Analysis of the products obtained in a pilot plant as a function of time on stream.

Properties wt%	Feed I	SOR	MOR	EOR	Feed II	NiMo.
Time on stream months	-	0.1	1.5	3	-	3
MWA Temperature °C	-	340	355	367	354	380
DBT type of Sulfur ppm	10080	10	13	15	15400	12
Napht-Arom Sulfur ppm	986	5	2	0	1300	3
Diaromatics	5	8	12	17	5	8
Monoaromatics	13	14	15	20	13	14
Naphtheno-Aromatic	10	12	14	16	10	12
Tricycloparaffins	1.8	2	2.2	6	1.8	2
Di cycloparaffins	16	16	14	12	16	16
Mono-cycloparaffins.	25	22	18	14	25	22
Paraffins wt	29.2	26	24.8	15	29.2	26
C ₅ -C ₁₀ wt%	0	4.3	5.2	6.1	0	6.2
C ₁ -C ₄ wt%	0	1.8	2.3	2.6	0	2.3
Cetane Number (-)	-	47	44	42	-	40

Table 1 shows a significant change in hydrogenation and cracking reactions as a function of time on stream. The metal and acid sites on the catalytic surface deactivated at different rates. Deactivation of metallic sites was responsible for some reduction in hydrogenation capabilities, while that of acid

sites produced a large decrease in isomerization and ring opening, leading to an increase in paraffin content. Table 2 shows an increase in the weight % of diaromatics and naphthenic-aromatic molecules and a small reduction in the content of mono-aromatics, mono-naphthenes, and C_{10}^+ paraffins, despite the temperature increase along the operating cycle. These phenomena contribute to the decrease of the cetane number (an indicator of diesel quality) along the cycle length at quasi-constant hydrogen consumption. Over time, the isomerization and naphthenic ring opening sites became gradually less efficient at producing poly-alkyl-benzene and poly-alkyl-cyclohexane type compounds. This improved the proportion of paraffin to aromatic rings in the molecules, because cracking and dealkylation reactions of aromatic branches continued to occur during the cycle. As a result, an increase in intermediary compounds (naphtheno-aromatic) was observed. It is interesting to note that commercially deactivated catalyst that had been used for 14 months on stream performed similarly to the catalyst deactivated after 2 years without LCO in the commercial plant. The increase in C_1 - C_4 paraffins with time on stream due to the increase in temperature reflects the survival of the cracking and dealkylation active sites. The “passivation” of the surface was not proportional to the amount of carbonaceous deposit, or to the decline in total acidity of the sample. The deactivation seems to be more associated with the selective elimination of some isomerization-type acid sites by the polyaromatics of the LCO.