Supporting Information

The role of MoS_2 nano-slabs in the protection of the heterogeneous cracking catalyst for the total conversion of heavy oils to good quality distillates.

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1. Evolution of the average molecular weight of Asphaltenes during a long test run of the EST technology

The evolution of the average molecular weight of the asphaltenes during a long test run performed on the EST Commercial Demonstration Plant (1250 barrel/day capacity) was determined as follows. The asphaltenes are firstly separated from the samples periodically collected on the recycled stream by using *n*-pentane (ASPH-C5). Each sample is then subjected to the following analyses:

1) Determination of the average molecular weight by Gel Permeation Chromatography (GPC) using a Water System controller 600-MS equipped with autosampler Waters 717 and a refractometer Waters 410 as detector. The Waters Millenium rel. 3.20 software package was used for data collections and elaborations. The calibration was performed using polystyrene samples with different declared molecular weights (42900-17500 – 9580-2560 – 947-510 Da) and for lighter products with samples of dialkylbenzenes with molecular weights between 470 and 358 Da.
2) ^{1}H and ^{13}C NMR analyses, performed with, respectively, a Bruker AMX (resonance frequency: 300 MHz) and a Varian (resonance frequency: 500 MHz); ca. 809 mg of asphaltenes are dissolved in $CDCl_3$, for a total weight of ca. 1 g. the following molecular parameters are directly derived from the NMR spectra:

   from ^{1}H NMR:
   H_{aro} = mole% of H bonded to aromatic C
   H_{α} = mole% of H bonded to C atoms in α respect to aromatic C
   H_{β} = mole% of H bonded to C atoms in β respect to aromatic C and more distant from the aromatic C
   H_{γ} = mole% of H bonded in methyl groups in γ and more distant from the aromatic C

   from ^{13}C NMR:
   C_{aro} = mole% of aromatic C
   C_{ali} = mole% of aliphatic C
   n = average number of C in the aliphatic chains
3) Determination of C, H, N and S content. C, H and N analyses were performed following the standard method ASTM D5192-02 using a LECO CHN1000 analyzer, using EDTA for its calibration.S content was determined with the LECO SC432 analyzer, following the standard method ASTM 1552-03.

For selected samples, the different analytical data were elaborated generating an "average molecule", which describe the main characteristics of the asphaltenes fraction in terms of: number of condensed aromatic rings, degree of substitution of the peripheral aromatic C, average length of the aliphatic chains, S and N content.
The evolution of the average molecular weight during the long test run on the EST Commercial Demonstration Plant and the characteristics of the "average asphaltenes molecule" at three different T.O.S. are reported in Fig. S1.

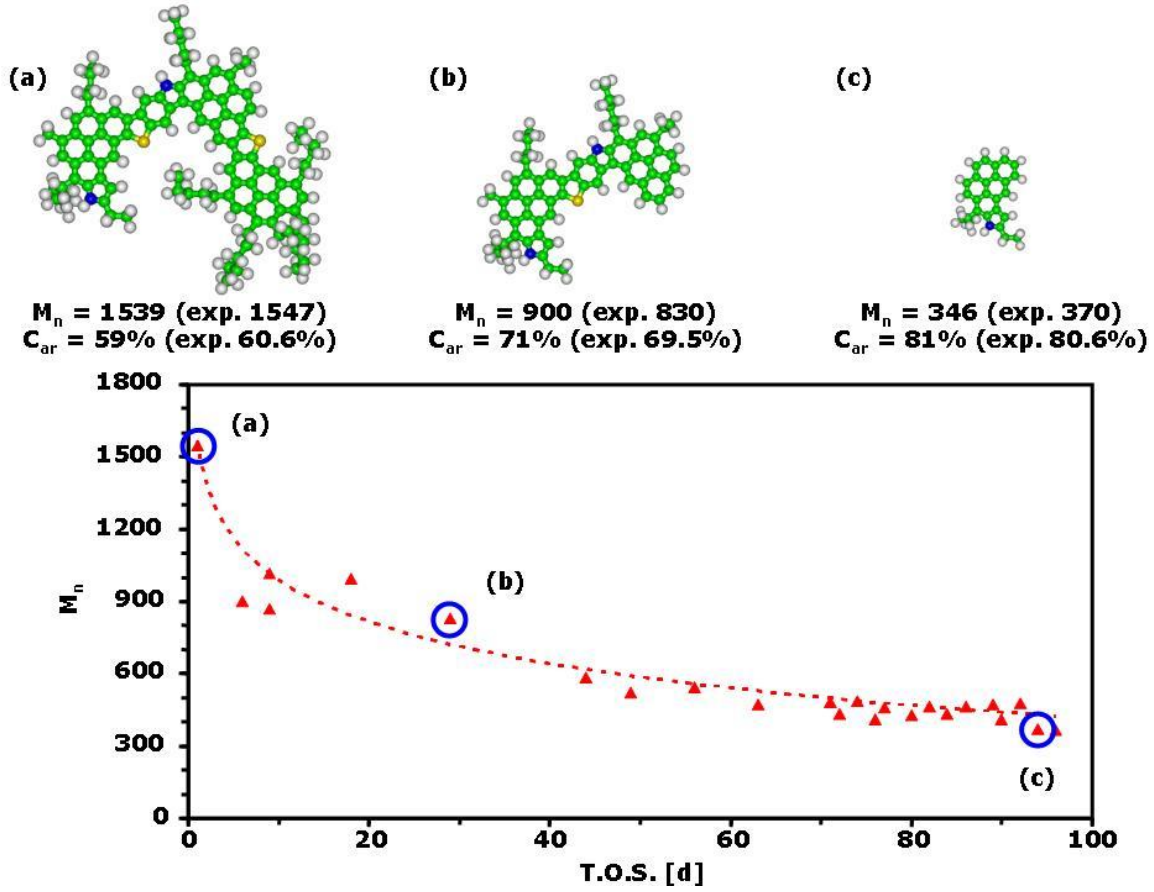

Fig. S1. Evolution of the average molecular weight of the asphaltenes separated from the recycle of the EST process. The average molecular weight of each sample was determined by Gel Permeation Chromatography (GPC). The models reported above represent the hypothetical average molecules at the three different T.O.S. indicated by the blue circles, built according to the chemical (C, H, N, S content) and spectroscopic (^{1}H and ^{13}C NMR) evidences.

2. Catalytic tests

Ebullated bed pilot plant test

The pilot plant includes a 7.5 L ebullated bed reactor, equipped with a pump that carries out the external recirculation of the liquid phase through a special recovery system and a check valve (Fig. S2). The hydrotreating catalyst (1800 g in 1.5 mm pellets, Tab. S1) is confined inside the reactor by proper grids and ebullated by the liquid flow. Average reaction temperature was 430°C. The feed (Ural Vacuum Residue) is mixed with hydrogen at 130 bar pressure bar and fed to the reactor. Typical fresh feed flowrate is 800-1000 g/h.
The product stream exits from the reactor and enters the separation section, equipped with HP/LP separators and a vacuum distillation column. The main separator operates at a temperature between 320 and 350°C and it separates the effluent into a gas phase and into a heavy liquid. The gas stream is cooled by water and it is fed to the cold separator operating at temperatures around 50 – 60°C. Under these conditions, hydrogen and condensable hydrocarbons separate from distillates and water. The liquid heavy products are sent to the vacuum column, from which a distillate (vacuum gasoil, VGO) from the head and a bottom fraction are obtained. The bottom is recycled, mixed with the fresh feed and fed to the reactor. The tests with MoS_2 were performed by adding an oil-soluble molybdenum precursor to the fresh feed in order to obtain Mo concentration of 2000 ppmw.

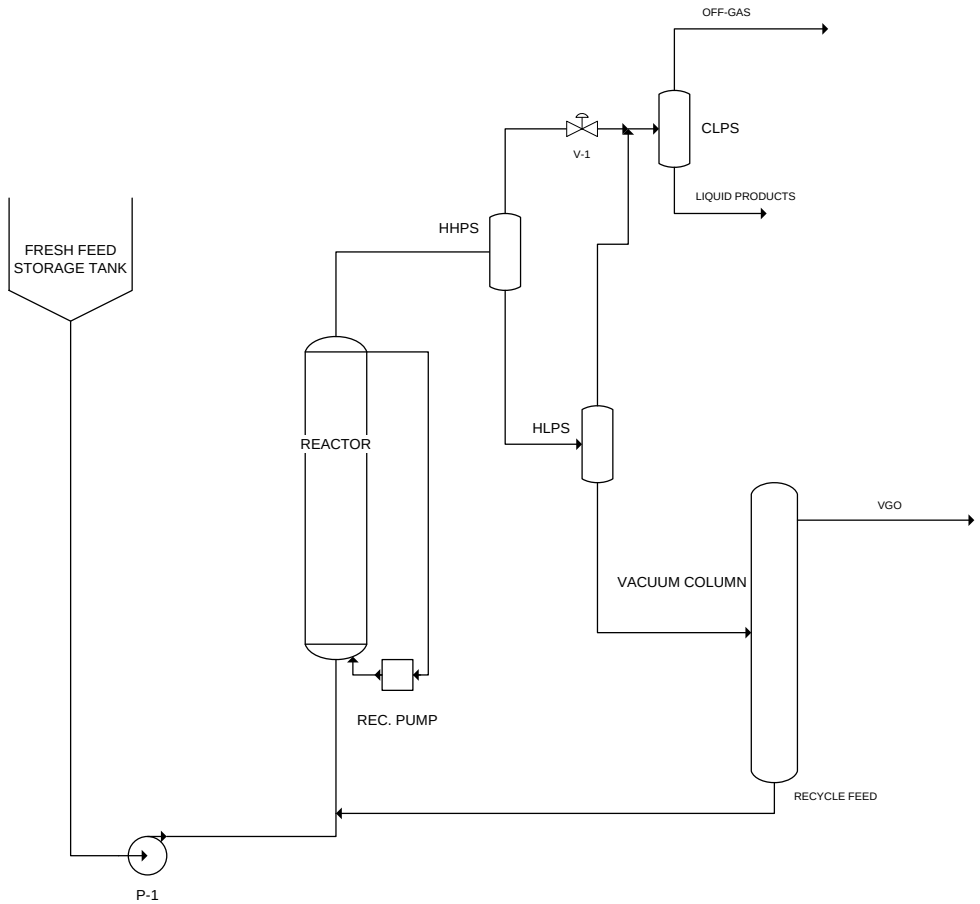

Fig. S2 Schematic representation of the ebullated bed pilot plant.

Table S1 Characteristics of the hydrotreating catalyst used in the ebullated bed pilot plant tests

Mo	wt%	10.1
Ni	wt%	3.9
P	wt%	2.4
γ-Al_2O_3	wt%	balance
Specific Surface Area	m^2/g	294
Specific Pore Volume	ml/g	0.72
Pellet Diameter	mm	1.5

Bench-scale slurry hydrocracking plant test

The reactor is a 600 cm^3 volume mechanically stirred autoclave. Liquid feedstock (Ural Vacuum Residue) and hydrogen are continuously fed to the reactor. Vapor products are extracted from the top of the reactor and condensed at room temperature (Fig. S3)
The feed flowrate is regulated in order to maintain a constant volume of liquid in reactor and it is usually in the range 20-30 g/h.
The purge of the liquid and fresh catalyst make-up are made through a system of pneumatic valves. Typical operating conditions are 430°C temperature and 130 bar pressure. Mo-precursor is mixed with the feedstock and fed to the reactor at the beginning of the test until about 2000 ppmw concentration is reached. The cracking catalyst in dual catalyst tests is added and removed in a batch-wise mode, in order to maintain a 30-40 % amount referred to the reaction holdup.

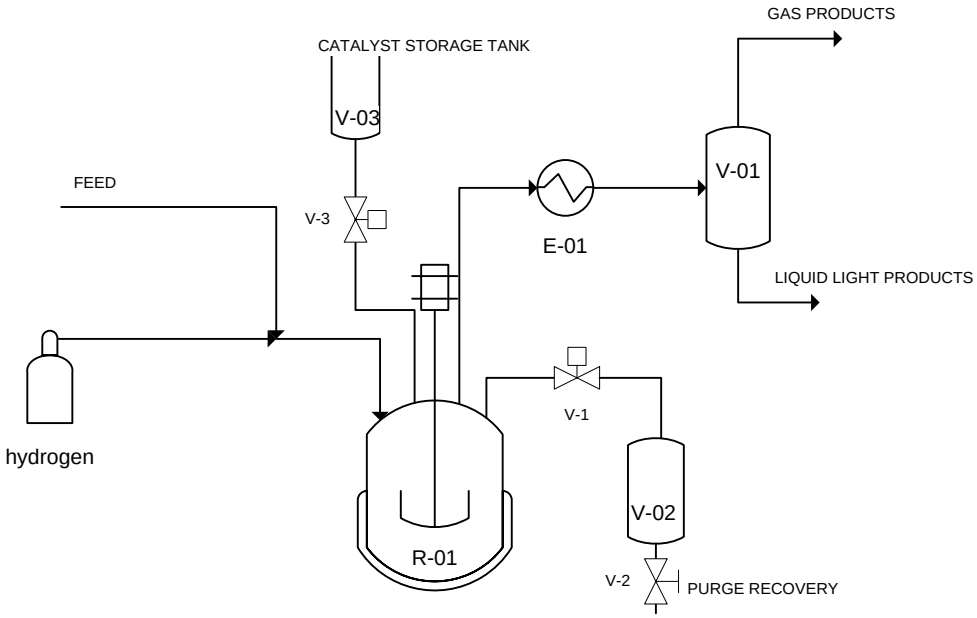

Fig. S3 Schematic representation of the bench-scale slurry hydrocracking plant

Tab. S2 Characteristics of the cracking catalyst used in the Bench-scale slurry hydrocracking plant test

Al	wt%	20.1
Si	wt%	28.1
La	wt%	1.7
O	wt%	balance
Specific Surface Area	m^2/g	261
Specific Pore Volume	ml/g	0.16
Bulk Density	g/cm^3	2.52
Particle Average Diameter	μm	70

3. Ebullated bed pilot plant test

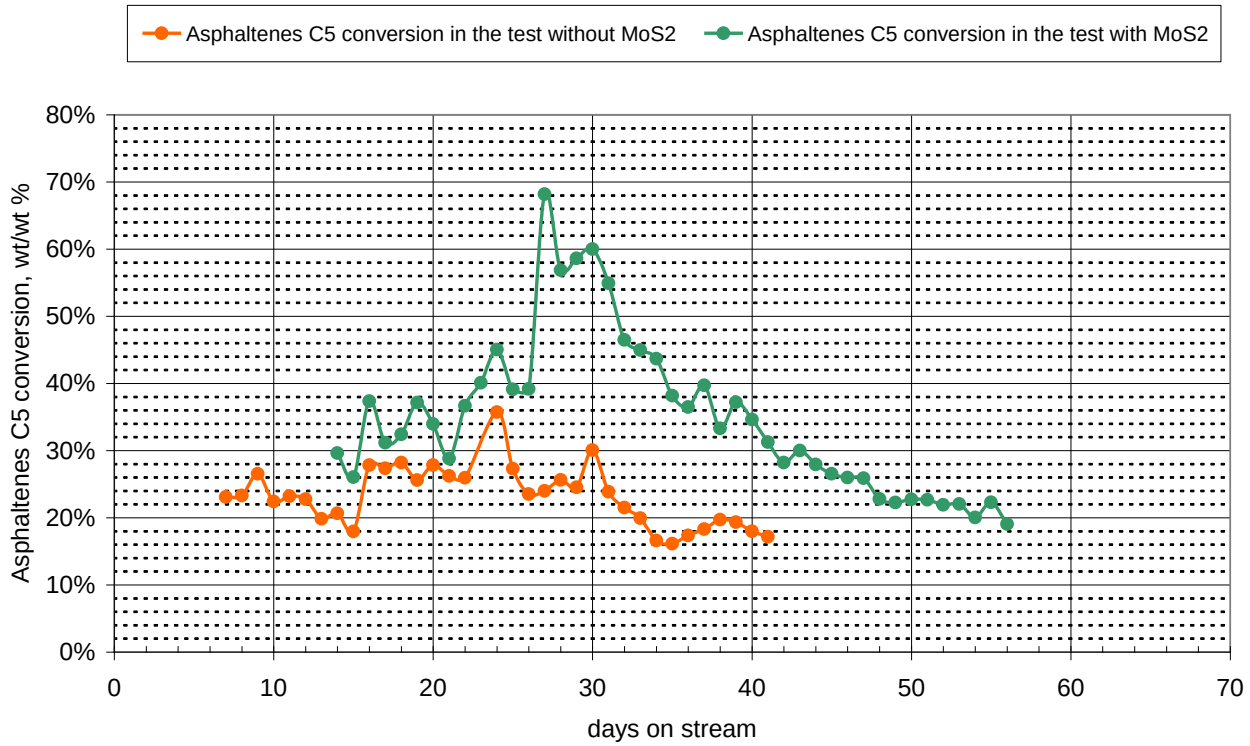

Fig. S4 Conversion of the heavy fraction (500C°+) of the feedstock in ebullated bed test: reference test (orange curve); dual catalyst test (green curve).

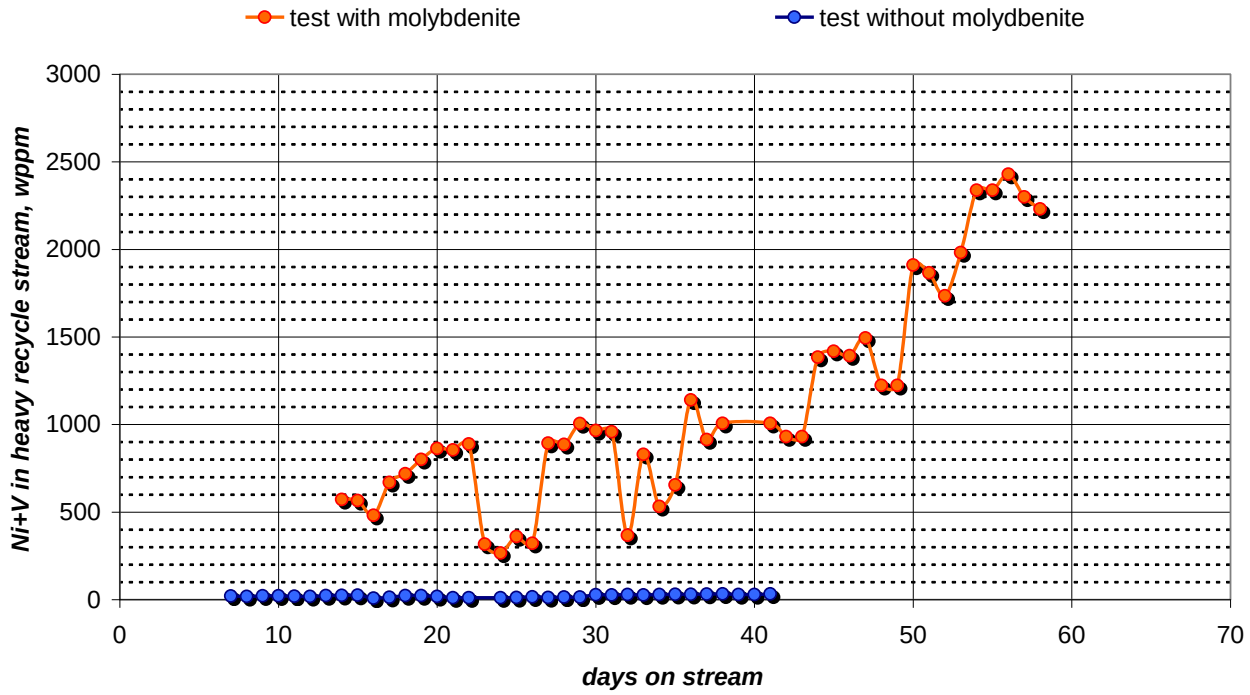

Fig. S5 Metals content in the heavy fraction obtained in pilot plant test with hydrocracking catalyst only (orange curve) and dual catalyst system (blue curve).

4. Bench-scale slurry hydrocracking plant tests

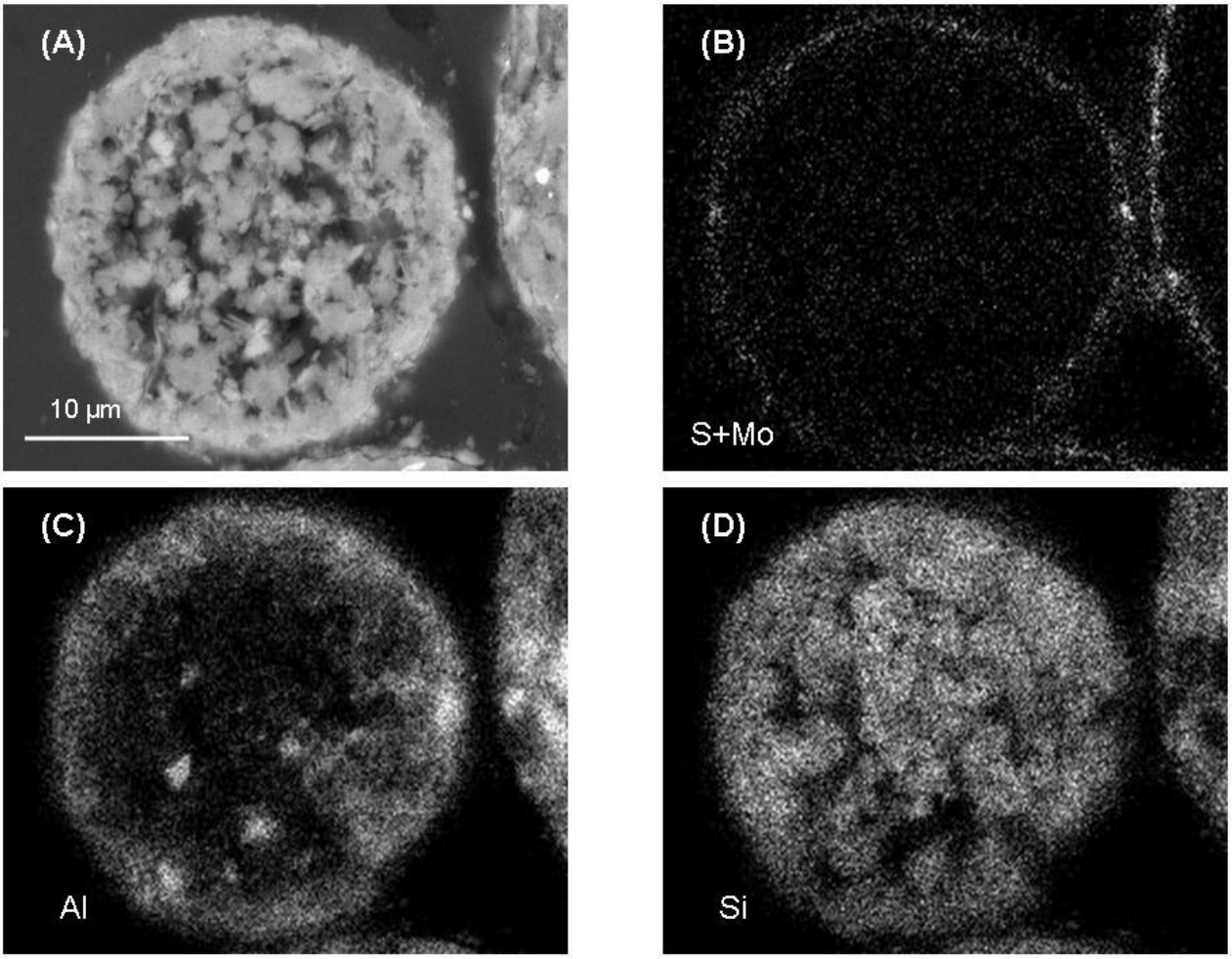

Fig. S6 SEM micrograph of an internal section of a cracking catalyst particle (A) and X-ray maps showing the distribution of S-Mo (B), Al (C) and Si (D).