



# The Modeling of Industrial Scale Desulfurization Using the P-Cube™ Flow Reactor

## ABSTRACT

ThalesNano's P-Cube™ was used to model desulfurization reactions that have been previously carried out on a 100 mL and a kiloton plant reactor. The P-Cube™ showed that it could reproducibly replicate the reaction results of these larger reactors to within 2 ppm for sulfur content and 0.06% for diaromatic content. Only 5 cm<sup>3</sup> of catalyst was needed and the reaction time was a period of hours instead of typical reaction times of days.

This translates to significant cost savings in terms of time and chemical resources enabling products to be brought faster to market. The results validate that the P-Cube™ can be used to accurately predict catalyst activity in kiloton scale reactors. All work was carried out by MOL group, which was recently voted number 1 in Europe for performance in exploration and processing (upstream).<sup>1</sup>



## INTRODUCTION

Sulfur is a naturally occurring component of crude oil and is found in both gasoline and diesel. To reduce the air pollution from the transportation sector it is essential to reduce the amount of sulfur in fuels. Not only because it is an air pollutant, but more importantly, sulfur prevents the adoption of all major pollution control technologies. This application note is an example of how reaction parameters were optimized for the production of an ultra-low-sulfur (< 10 ppm) middle distillate (kerosene, gasoil) using catalytic hydrogenation.

## CATALYST

The catalyst used for the experiment was a broadly used industrial catalyst. This CoMo catalyst shows a superior activity in units with hydrogen partial pressure at 30 bar and is best applied in conditions of less than 20 ppm of product nitrogen.

## FILLING THE REACTOR WITH CATALYST

To appropriately test preformed industrial catalyst pellets in a small reactor it is crucial to ensure the adequate flow of materials through the catalyst bed. The widely accepted rule-of-thumb is that the inner diameter of the reactor ( $D_{\text{rea}}$ ) should be over 20 times larger than the particle diameter of the catalyst ( $D_{\text{cat}}$ ).

<sup>1</sup>[http://www.mol.hu/en/about\\_mol/news\\_media\\_centre/news\\_releases/2010/mol\\_is\\_still\\_the\\_best\\_european\\_company\\_in\\_the\\_field\\_of\\_gas\\_and\\_oil\\_operation/](http://www.mol.hu/en/about_mol/news_media_centre/news_releases/2010/mol_is_still_the_best_european_company_in_the_field_of_gas_and_oil_operation/)

In this case  $D_{rea}/D_{cat} < 7$ . It is feasible to overcome this problem through the addition of an inert material with the proper shape and physical properties. With such a solution in place it is possible to ensure ideal flow without having to chop or crush the catalyst pellets. The size of catalyst particles has a strong effect on reactivity. In order to reduce the number of variables during scale-up it is better to use the same catalyst that is used in production. In the current case, SiC with a 0.15 mm average diameter was applied in a 2 times excess volume. The cross section of the reactor with the filled catalyst is shown in Figure 1. The full volume of the catalyst bed was about 10 mL. The fill consisted of (from top to bottom): 1 mL SiC of a 0.25 mm particle size; mixture of 5 mL catalyst and 5.5 mL of SiC (0.15 mm); 2 mL of SiC (0.25 mm) and 3.9 mL of SiC with 0.5 mm particle size. The total length of the reactor column was 30 cm with the top 8.5 cm containing a metal pre-heater. The temperature of the reactor was measured with a thermocouple as shown in Figure 1.

### CATALYST PRE-TREATMENT

The catalysts tested had been supplied by the maker as (inactive) metal oxides. The first step was the conversion of oxides into the active sulfide form through the use of sulfidizing materials. Such freshly formed sulfides usually bear a high initial activity, which has to be reduced in order to accurately measure the long term catalyst activity (months or years). This was achieved by flowing the sample gasoline through the reactor for 168 hours at 290°C.

### EXPERIMENTAL PROCEDURE

The undiluted oil sample (26.2 g) was flowed through the reactor three times at 270°C, and three times at 290°C at a flow of 0.2 mL/min. A 30 min interval was inserted between the two reaction series, so the reactor could be heated from 270°C to 290°C. The total residence time for each run was 3 hours. It can be seen in Table 1 that all the temperature, pressure and the flow rate values could be well controlled within a narrow range. This effective control of the parameters ensures the reproducibility of the results and the homogenous, superior quality of the product. These are crucial for an effective scalable process. The rate of heating also proved to be a very important factor to achieve the afore mentioned predictability of product qualities.

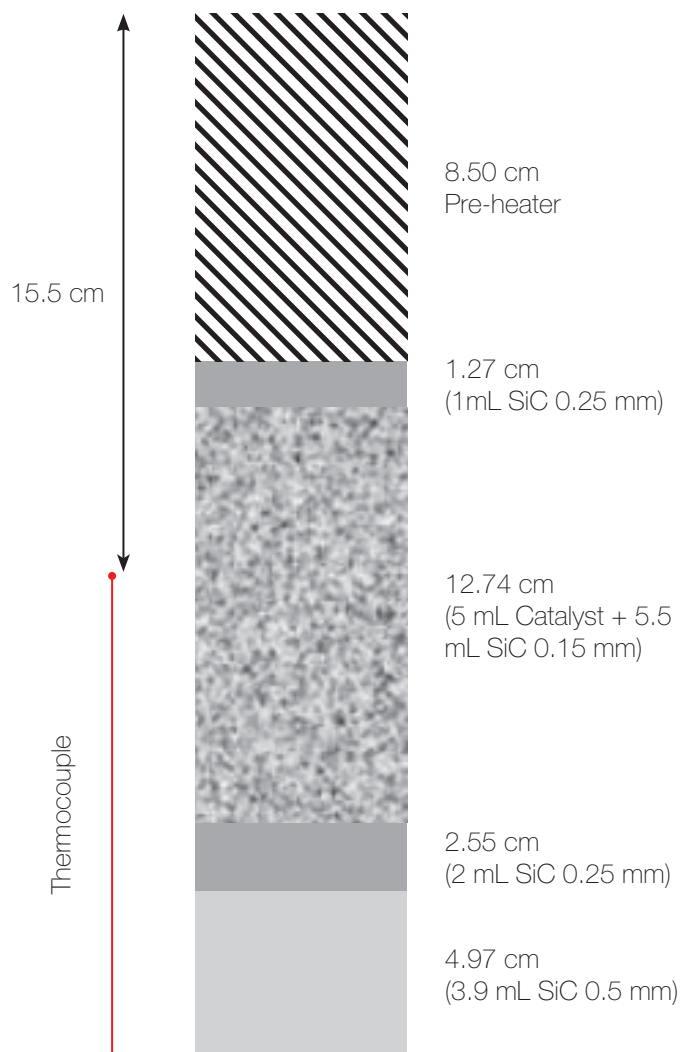


Figure 1: Cross section of reactor with catalyst bed composition

The same experiment was carried out using a different raw material in terms of sulfur and diaromatic content on a proprietary Test Reactor 20 times as large with a catalyst bed of 100 mL. This equipment successfully simulated the same application on large scale production facilities of up to 200 m<sup>3</sup>, capable of producing petroleum products in megatons annually.



Sample ID	Elapsed time (min)	Temperature (°C)	Pressure (bar)	H <sub>2</sub> flow (mL/min)	Petrol flow (mL/min)	Strip N <sub>2</sub> flow (mL/min)
2PET1M1	360	269.9	31.1	40	0.2	33
2PET1M2	540	269.8	30.9	40	0.2	33
2PET1M3	720	269.9	31.4	40	0.2	33
2PET2M1	930	290.6	31.4	40	0.2	33
2PET2M2	1110	290.5	31.2	40	0.2	33
2PET2M3	1290	290.7	31.4	40	0.2	33

Table 1: Summary of the reaction parameters of the kerosene desulfurization process

## RESULTS

The chemical composition of the samples during the reactions were followed by a broad range of analytical methods including classical industry methods and modern gas chromatography measurements.

The change of sulfur and diaromatic contents in a typical representative experiment series is summarized in Table 2 and Figure 2. It is clearly seen that the required product could not be obtained at 270°C and had to be raised to 290°C. The sulfur content could be decreased to the targeted value (8.4 ppm) by the end of the last run.

Sample ID	Elapsed time (min)	Sulfur content (ppm)	Diaromatic content (%)
Raw material (petroleum)	0	1326.0	1.48
2PET1M1	360	224.0	1.29
2PET1M2	540	91.0	1.03
2PET1M3	720	83.0	0.98
2PET2M1	930	36.0	0.66
2PET2M2	1110	11.0	0.34
2PET2M3	1290	8.4	0.36

Table 2: Result summary of reactions performed detailed above

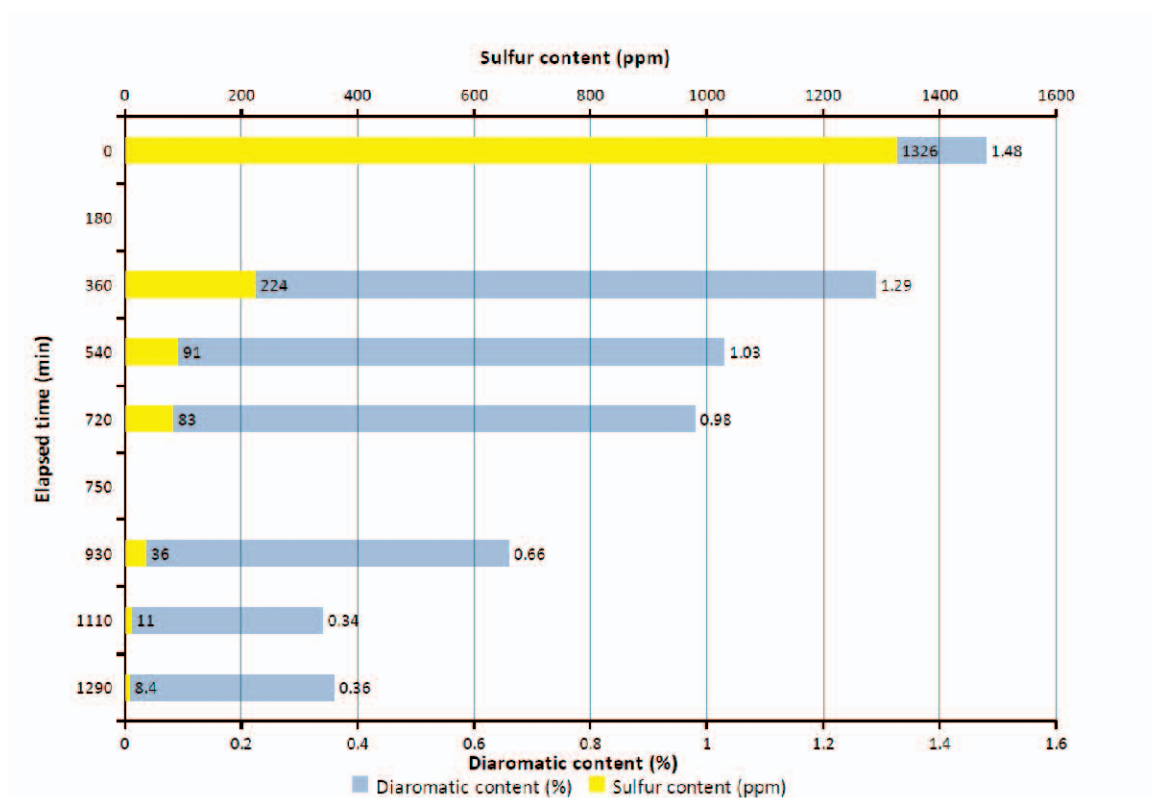


Figure 2: Sulfur and diaromatic contents of the samples as a function of reaction time

	<b>Sulfur content (ppm)</b>	<b>Diaromatic content (%)</b>
Raw Material (petroleum)	1660	1.26
----- 270°C -----		
100 mL Test Reactor	72	0.84
P-Cube™	83	0.98
----- 290°C -----		
100 mL Test Reactor	6	0.3
P-Cube™	8	0.36

Table 3: Comparison of the constituents of the products in P-Cube™ and a proprietary 100 mL Test Reactor

The results, summarized in Table 3, of comparison reactions between the Test Reactor and P-Cube™, show the maximum purity achieved on both reactors. The values were within such a narrow margin that we can conclude the P-Cube™ could also be used to simulate results on the megaton reactor.

## CONCLUSIONS

It was shown that the P-Cube™ is capable of performing desulfurization reactions effectively, reaching the desired content of sulfur. This proves that the system is suitable to mimic reactors of a much larger scale. This is extremely advantageous because substantial time and resources can be saved. The P-Cube™ is flexible and can be adapted rapidly to the clients needs. It requires less catalyst and it significantly reduces the time necessary to perform experiments. Another advantage is the smaller footprint and the smaller - thus safer - amount of hydrogen used.

For further information please contact us at [flowchemistry@thalesnano.com](mailto:flowchemistry@thalesnano.com) or visit our website: [www.thalesnano.com](http://www.thalesnano.com)

### ThalesNano Nanotechnology Inc.

Zahony u. 7.  
H-1031 Budapest  
Hungary  
Tel.: +36 1 880 8500  
Fax.: +36 1 880 8501  
E-mail: [sales@thalesnano.com](mailto:sales@thalesnano.com)

### US Office ThalesNano

50 S. Penn St. Suite B-2  
Hatboro  
PA. 19040  
USA  
Tel.: +1 732 274 3388  
E-mail: [USAsales@thalesnano.com](mailto:USAsales@thalesnano.com)

### UK Office

Carl Jones  
Head of Global Sales  
Tel.: +44 (0) 7868 843 819  
E-mail: [UKsales@thalesnano.com](mailto:UKsales@thalesnano.com)

Finally, the experiment highlights an advantage of flow reactors unparalleled by batch reactors, which is the ease of scale-up. Reaction conditions optimized in gram-scale (pressure, temperature, catalyst-reagent contact time, etc.) could be adopted to reactors million times larger.

## ACKNOWLEDGEMENT

ThalesNano Inc. would like to thank to MOL DS Development who performed the above reactions.