Understanding the decomposition of TBPS for efficient catalyst sulphiding

Identifying optimal operating conditions for sulphiding without negatively impacting the performance of hydroprocessing catalysts

Jennifer A Jackson **The Lubrizol Corporation**
Tiago Vilela **Avantium R&D Solutions**

Hydroprocessing plays a crucial role in the refining industry. To ensure the catalytic activity of hydrotreating catalysts, sulphiding is employed. Sulphiding involves the conversion of initially inactive metal oxides present in the catalysts into active metal sulphides, significantly enhancing their performance in hydroprocessing. However, achieving efficient catalyst activation through sulphiding is not without challenges.

The sulphiding process requires careful selection of sulphiding agents that can effectively convert metal oxides into sulphides under specific operating conditions. One notable sulphiding agent is tert-butyl polysulphide (TBPS), a commercially available compound provided by The Lubrizol Corporation and under the proprietary tradename SulfrZol 54.

In contrast to traditional sulphiding agents like dimethyl disulphide (DMDS), TBPS offers several advantages. It has more ideal health and safety characteristics, a higher flash point (DMDS: 16°C vs TBPS: 100°C), reduced odour (DMDS: foul, TBPS: diesel-like), and improved emissions profile. When TBPS is used as a sulphiding agent, it produces butane and hydrogen sulphide (H_2S) as by-products, while DMDS yields methane (and methylmercaptan) and H_2S. This distinction is significant as it contributes to a safer, cleaner, and more effective catalyst activation process in refineries.

Decomposition profile

The primary objective of this study is to investigate and illustrate the decomposition profile of TBPS as a sulphiding agent. To achieve this objective, an experimental programme was conducted involving the sulphiding of three commercial catalysts commonly used in diesel and naphtha hydrotreating processes: CoMo, NiMo, and NiW.

The experimental tests covered a wide range of operating conditions, including varying temperatures, pressures, space velocities, and gas-to-oil ratios. These conditions were carefully selected to simulate real-world hydrotreating processes and to evaluate the impact of different parameters on the sulphiding process. By exposing the catalysts to TBPS under selected operating conditions, we aimed to facilitate the decomposition of the sulphiding agent into H_2S and isobutane, with intermediary components consisting of butyl mercaptans and iso-butene.

Relatively low temperatures used in this study (ranging from 150°C to 240°C) were chosen to reflect typical operating conditions in sulphiding hydrotreating processes. At these temperatures, only a fraction of the surface metals on the catalysts are likely to convert into sulphides. The transformation from metal oxides to sulphides typically occurs sequentially as operating temperature increases. Therefore, understanding the TBPS decomposition profile is crucial for optimising the sulphiding process.

This investigation focused on determining the decomposition profile of TBPS under different operating conditions. The aim was to identify the temperature at which TBPS starts decomposing and the influence of catalysts on its decomposition. Additionally, we analysed the formation and consumption rates of the intermediate components (isobutene and C_4 mercaptans) and the final products (H_2S and isobutane), considering factors such as temperature, catalyst type, H_2 partial pressure, gas-to-oil ratio, and liquid hourly space velocity (LHSV).

By comprehensively studying the decomposition profile of TBPS and its effects on catalysts, the sulphiding process can be optimised to ensure efficient activation without compromising catalyst performance. Results of this study will provide valuable insights for refiners, helping advance hydroprocessing techniques and contributing to the development of cleaner and more sustainable refining practices.

Experimental

This study was conducted in a 16-parallel fixed-bed reactor system with stainless-steel reactors with a diameter of 2mm and a total length of 561mm, including an isothermal section of 300mm. The gaseous product was analysed using an online gas chromatograph (GC), while the liquid reaction product from each reactor was collected in individual sample vials for subsequent offline analyses.

Two liquid samples per 24 hours were collected, and two were selected for offline analysis. To maintain stable conditions during gas-liquid separation, the sample vials were temperature-controlled. Gas exiting the vials was analysed using the online GC, which provided measurements of hydrocarbons, H_2, He, and H_2S.

Avantium's Flowrence technology relies on the use of single-string reactors, wherein catalyst particles are arranged in
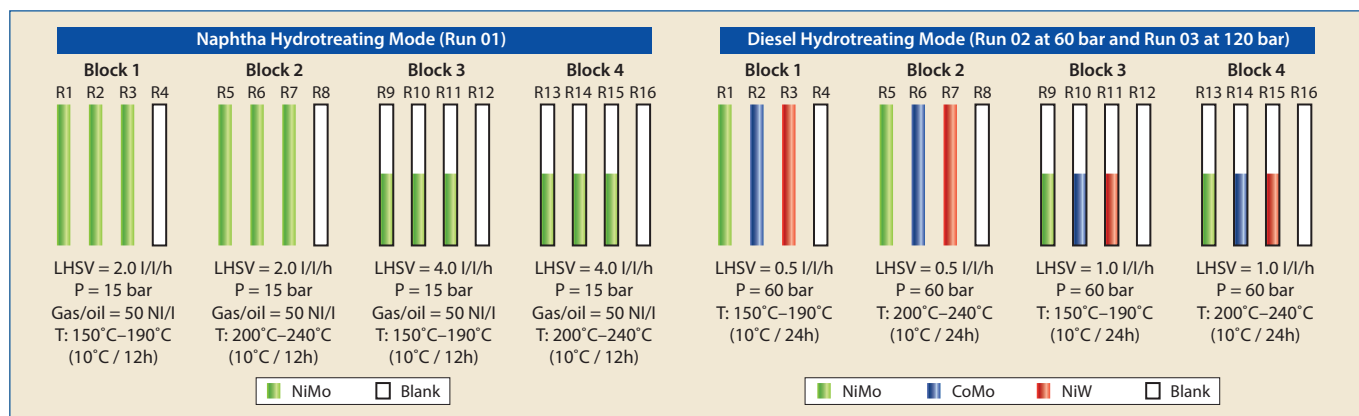
Figure 1 Experimental design

a specific order. This arrangement allows for the decoupling of axial dispersion phenomena from fluid dynamics, facilitating ideal plug flow reaction conditions near the reactor inlet.

For a more detailed understanding of the theory supporting the use of single-pellet-string reactors, refer to the publications by Moonen et al[1] and Ortega et al.[2]

Test design

The experimental programme aimed to evaluate the decomposition profile (by-products yield vs temperature) of the sulphiding agent TBPS at typical operating conditions used for the sulphiding of hydroprocessing catalysts. By studying the presence of the different by-products formed during the catalyst sulphiding, the objective was to identify the operating conditions that favour the use of TBPS as a sulphiding agent without affecting the catalyst's performance. The experimental programme for studying the decomposition of TBPS was conducted in three different runs performed at a testing unit with 16 reactors in parallel.

The catalyst loading was carried out using three commercial catalysts: CoMo, NiMo, and NiW 1/16in trilobe extrudates obtained from Topsoe. Before loading, no crushing, sieving, or other structural changes were performed on the catalyst particles.

In all three runs, the reactors were operated under constant conditions for a duration of 12 hours. Following four hours of operation at each condition, the analysis of gas effluent commenced, proceeding sequentially from reactor 1 to 16. This sequential analysis spanned a total duration of four hours, allowing approximately 15 minutes per reactor. During this time, a single cumulative liquid sample was collected. This sampling procedure was repeated during the final four hours of operation for each testing condition, with the second sampling phase considered more representative due to the longer stabilisation time.

Run01 focused on simulating the sulphiding of a NiMo catalyst used in naphtha hydrotreatment. Each reactor block contained triplicate NiMo catalysts, along with a blank reactor filled with Zirblast. The reactor setup is illustrated in **Figure 1**. Throughout Run01, a fixed pressure of 15 barg and a gas-to-oil ratio of 50 Nl/l were maintained. Sequential temperature changes occurred every 12 hours. In addition, the LHSV was varied by loading a smaller amount of catalyst in reactors 9 to 16 (blocks 3 and 4).

The test designs for Run02 and Run03 are also illustrated in Figure 1. Run02 and Run03 had identical testing protocols, except for the partial pressure of H_2 (60 bar in Run02, and 120 bar in Run03). Prior to introducing the liquid feed, the catalyst was heated from 50°C to 120°C at a constant heating rate of 15°C/h, with H_2 flowing at a rate of 4.7 NmL/min/reactor. The temperature was then held constant at 120°C for two hours to ensure proper drying. Following drying, the gas flow rate was reduced to 2.5 NmL/min/reactor, and the liquid feed was introduced at a flow rate of 16.7 mg/min. This soaking step aimed to prepare the catalyst and was performed at a constant temperature of 120°C for five hours. Once soaked, the reactor's pressure was increased to 60 bar of H_2 partial pressure for Run02 and 120 bar for Run03. The temperature was then adjusted to the setpoint for Condition 1 (150 and 200°C) at a rate of 15°C/h, which was maintained for all subsequent temperature adjustments.

The reactors were maintained at a constant operating condition for 12 hours, similar to Run01. After four hours of operation at each condition, the gas effluent analysis was performed sequentially, starting with reactor 1 and concluding with reactor 16. The total duration of the sequence for analysing all 16 reactors was four hours, with 15 minutes allocated for each reactor. Additionally, to assess the influence of TBPS thermal decomposition, a set of four reactors (one per block) was filled with Zirblast (without catalyst) and treated and analysed under the same conditions as the reactors loaded with NiMo, CoMo, or NiW catalysts.

These tests aimed to simulate the sulphiding of three different catalysts (NiMo, CoMo, and NiW) used in the production of ultra-low sulphur diesel (ULSD) under varying operating conditions. During the test, each reactor block maintained a fixed temperature for a period of 24 hours. For the first 12 hours, the gas-to-oil ratio was kept at 500 Nl/l, and then it was reduced to 250 Nl/l for the subsequent 12 hours, while all other operating conditions remained unchanged. Gas effluent samples were collected at each testing condition, and two consecutive samples were analysed using the online GC. Liquid effluent samples were also collected during this period for the analysis of total sulphur content.

TBPS by-product distribution online GC analysis

The gas chromatography online analysis was conducted to identify and quantify various components in the gas effluent.

The following components were analysed using specific detectors:
- Hydrogen (TCD detector)
- Nitrogen (TCD detector)
- Helium (TCD detector)
- Hydrogen sulphide (TCD detector)
- Methane, ethane, and propane (FID detector)
- n-butane and isobutane (FID detector)
- 1-butene and isobutene (FID detector)

Helium was used as an internal standard in the GC analysis and was supplied at a constant flow rate along with hydrogen as the gas feed to the reactors. The concentration of helium, being an inert gas, was utilised to calculate the total mass flow rate of the effluent gas. The gas chromatography analysis had a total duration of 15 minutes, allowing sequential sampling of the gas effluent from the 16 parallel reactors over a span of four hours. The liquid product from each reactor was accumulated during this four-hour period. Sampling of the gas and liquid started after four hours of stabilisation under each testing condition.

The first sampling occurred between four to eight hours, followed by a second sampling between eight to 12 hours while operating under fixed conditions. To estimate the amount of unconverted TBPS in the product effluent, the total sulphur concentration of each liquid sample was measured. It was assumed that no other sulphur-containing species remained in the liquid product for calculation purposes. This was possible since the total amount of sulphur in the feed and products (unconverted TBPS and H_2S) was known.

The amount of organic sulphur present in the non-spiked solvent (Table 1) was assumed to be inert in the reactors at the tested operating conditions. Direct analysis of butyl mercaptans in the GC was not feasible due to limitations in the setup, such as the total duration of the GC method and the availability of a calibration gas for this component. Instead, the total mass flow rate of butyl mercaptan in the gas effluent was calculated by performing an elemental sulphur balance.

The estimation of hydrogen consumption at each testing condition was done by weight difference. This involved using the gas flow rate fed into each reactor (measured by the mass flow controller) and the concentration of hydrogen in the gas effluent measured through the GC analysis. Further information on the calculations is provided in the reference section. A graphic representation of the distribution of the different products formed in the TBPS decomposition is presented in **Figure 2**. This scheme already considers the assumptions made for the estimation of the different by-product yields:
- No vaporisation of the solvent, and TBPS only present in the liquid product.
- No conversion of organic sulphur across the reactors.
- No dissolution of H_2S and butyl mercaptans in the liquid product.

Although an ideal gas-liquid separation of the different by-products is not possible in the testing setup, the effect of the small amount of gases dissolved in the liquid product and the heavy components 'carried' away in the gas stream has a minimal impact on the estimation of the by-product yields.
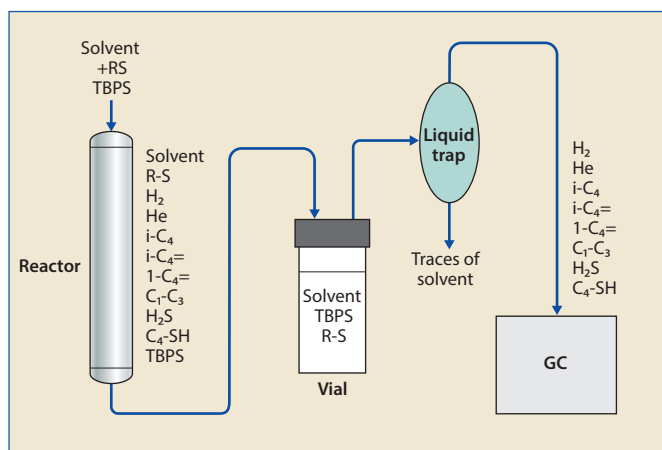

Figure 2 TBPS by-product distribution in the testing unit

Results

Thermal decomposition of TBPS without catalyst present

The thermal decomposition of TBPS with no catalyst present was examined in duplicate reactors using two LHSV. The LHSV was adjusted by loading a smaller amount of catalyst in reactors 9 to 16 (blocks 3 and 4). Key components, including H_2S, isobutane, isobutene, C_4 mercaptans, and TBPS, were analysed in the online GC for their product yields. Each marker in **Figure 3** represents a specific component, while different colours indicate varying space velocities. The experimental conditions typical for naphtha hydrotreating were sustained for a duration of 12 hours. Gas effluent samples were sequentially analysed through gas chromatography, and liquid effluent samples were collected and assessed for total sulphur content. Throughout Run01, a fixed pressure of 15 barg and a gas-to-oil ratio of 50 Nl/l were maintained. Sequential temperature changes occurred every 12 hours.

After analysing the reactors without the presence of a catalyst, it was observed that temperatures below 200°C showed negligible amounts of H_2S and isobutene. This suggests that most of the TBPS remains unconverted or decomposes into non-volatile sulphur components that remain in the liquid phase and cannot be distinguished from TBPS itself.

Additionally, prior research by Heller and Roberts[3] reported a decomposition temperature of approximately 160°C for TBPS, suggesting that the extent of thermal decomposition into highly volatile components would likely be negligible. In the same temperature range (below 200°C), the trends in yields indicate the formation of some volatile sulphur components. However, these fluctuations may be attributed to intrinsic variations in sample analysis and deviations from

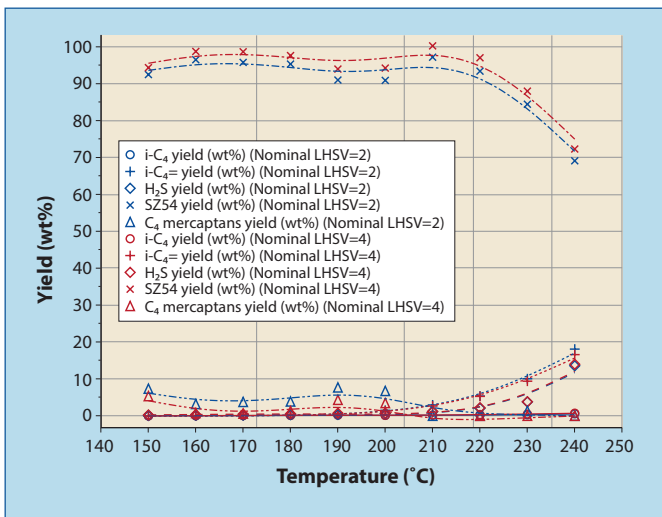| Solvent feeds properties		
Properties	**Naptha**	**Diesel**
Density @ 15°C, g/ml	0.7549	0.8342
Sulphur before spiking, ppmwt	100	2,915
Sulphur after spiking, ppmwt	20,675	23,407
SufrZol 54 added, wt%	37,034	3,834
IBP, °C	65	133
FBP, °C	196	437

Table 1

Figure 3 Product yields resulting from the thermal decomposition of TBPS without catalyst (Run01)

Figure 4 Product yields resulting from the thermal decomposition of TBPS without catalyst (Run02)

the assumptions described in the Experimental section. Between 200°C and 210°C, noticeable amounts of H_2S and isobutene are produced in the absence of a catalyst, indicating partial decomposition of TBPS. Beyond this temperature range, the decomposition rate of TBPS significantly increases, as evidenced by the rapid changes in the yields of H_2S, isobutene, and unconverted TBPS. This observation aligns with findings reported in the literature, where the exclusive formation of H_2S and isobutene as decomposition products has been reported.[4]
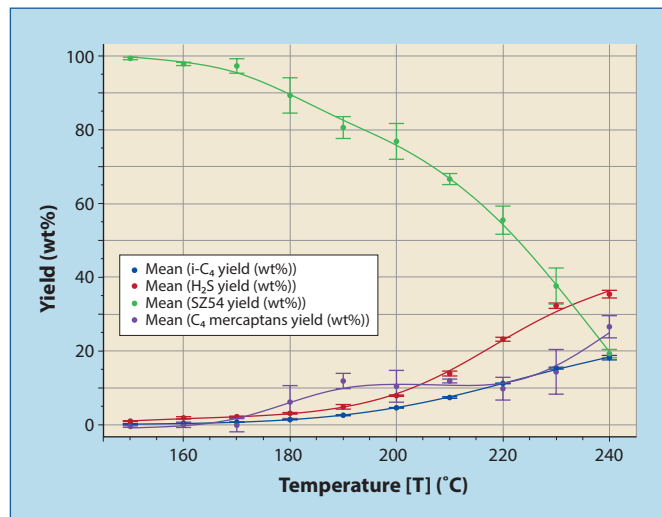
The thermal decomposition of TBPS was also investigated in Run02 and Run03 in the absence of catalyst, with identical testing protocols except for the partial pressure of H_2. The results from Run02, presented in **Figure 4** in the absence of catalyst, exhibited concentration profiles that followed similar trends to those observed in Run01 without catalyst. However, TBPS started to decompose at a lower temperature of around 170°C, likely due to the lower space velocity employed in the experiment. At this temperature, clear formation of H_2S and isobutene was observed, consistent with the findings of Heller and Roberts,[2] who reported a decomposition temperature of approximately 160°C for TBPS. The results of the thermal decomposition in Run03 were similar to those of Run02.

Figure 5 compares the yields of three key components (H_2S, isobutene, and isobutane) between the two runs. Differences mainly manifested in the H_2S and isobutene yields. At a higher partial pressure of hydrogen (120 bar in Run03), the formation rate of H_2S appeared slightly higher compared to the test using 60 bar of H_2. Additionally, at any given temperature, the content of isobutene was consistently lower, while the content of isobutane was higher when the partial pressure of H_2 was increased. This indicates that the hydrogenation reaction of isobutane is favoured at higher partial pressures of H_2, aligning with the expected behaviour as hydrogenation reactions typically exhibit positive reaction rate orders with respect to the hydrogen partial pressure.

Decomposition of TBPS over NiMo used in naphtha hydrotreating

The decomposition of TBPS over NiMo catalysts was investigated in Run01, designed to simulate the sulphiding in naphtha hydrotreating. The resulting product distribution of sulphur species and non-sulphur species vs temperature is presented in **Figure 6**. The results are grouped by LHSV, with LHSV=2 displayed on the left in blue and LHSV=4 on the right in red. The data represents the mean values obtained from duplicate reactors operating under the same reaction conditions.

Unlike the behaviour observed in the reactors without a

catalyst, the presence of a catalyst promotes the decomposition of TBPS into sulphur-containing and non-sulphur-containing species. Even under the mildest testing conditions (T=150°C and LHSV=4 L/L/h), approximately 50% of the TBPS is decomposed into a range of products. The relatively weak S-S bonds can easily break, resulting in the formation of tert-butyl mercaptan species. In both subplots, it is evident that TBPS is progressively decomposed as the temperature increases, reaching complete conversion above approximately 230°C.

Furthermore, H_2S is the primary by-product of TPBS decomposition at temperatures above 200°C, with a maximum yield of 54-57% observed around 230°C. The slightly higher maximum H_2S content vs the theoretical 54% can be explained by the fluctuations that may be attributed to intrinsic variations in sample analysis and deviations from the assumptions described in the Experimental section. The influence of temperature and LHSV on the product distribution follows the expected behaviour. For instance, at a given temperature, the fraction of unconverted TBPS is higher at the highest LHSV (shortest contact time).

Similarly, the trends observed in the evolution of products shift to higher temperatures in reactors operating at LHSV=4 compared to those at LHSV=2. The plot for LHSV=4 demonstrates that C_4 mercaptans and isobutene act as intermediate reaction products in a series of reactions involving TBPS as the reactant and H_2S and isobutane as the final products. Notably, the maximum yield of C_4 mercaptans is achieved at a lower temperature than isobutene, suggesting that C_4 mercaptans likely serve as intermediates in the formation of isobutene. Additionally, isobutane is only formed once a substantial concentration of isobutene is present in the system, indicating that isobutane is formed through the hydrogenation of isobutene. It is important to note that the observed species evolution is partially observed at LHSV=2; however, starting the test at

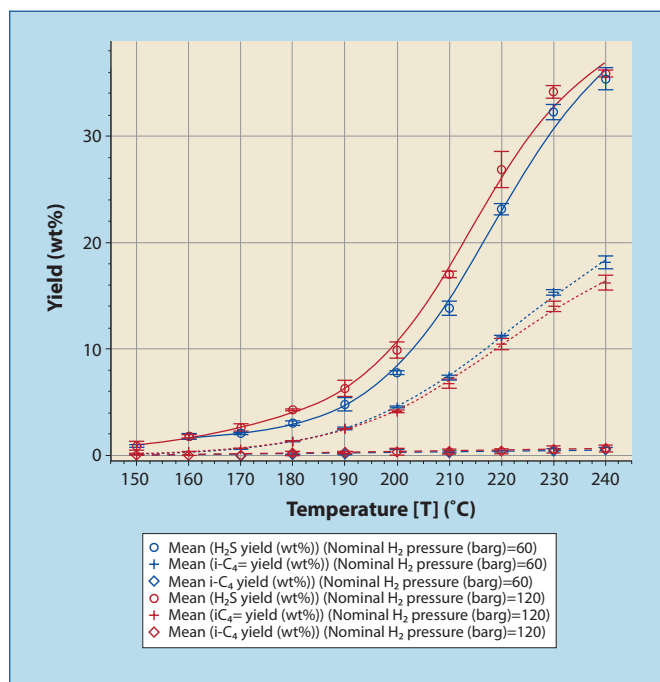**Figure 5** Key components yields resulting from the thermal decomposition of TBPS without catalyst at PH2 = 60 bar (Run02, blue) and PH2 = 120 bar (Run03, red)

lower temperatures would be necessary to obtain a similar profile as the one shown at LHSV=4.

The thermal decomposition of TBPS investigated in Run01 without catalyst present showed that at temperatures below 200°C, TBPS remained mostly unconverted or decomposed into non-volatile sulphur components. The presence of a NiMo catalyst facilitated the decomposition of TBPS, resulting in the formation of sulphur-containing and non-sulphur-containing species.

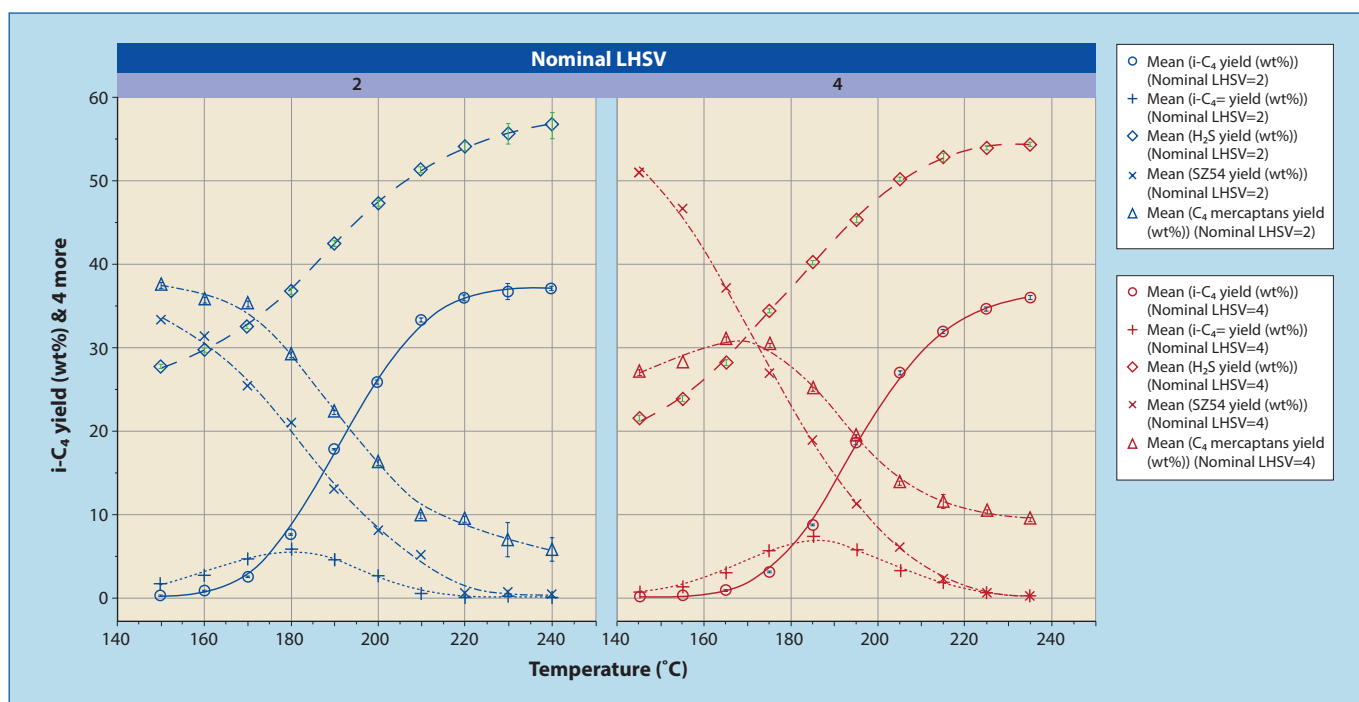Higher temperatures led to increased decomposition rates, with H_2S being the primary by-product. The

Figure 6 Product yields resulting from the decomposition of TBPS over NiMo catalysts (Run 01)
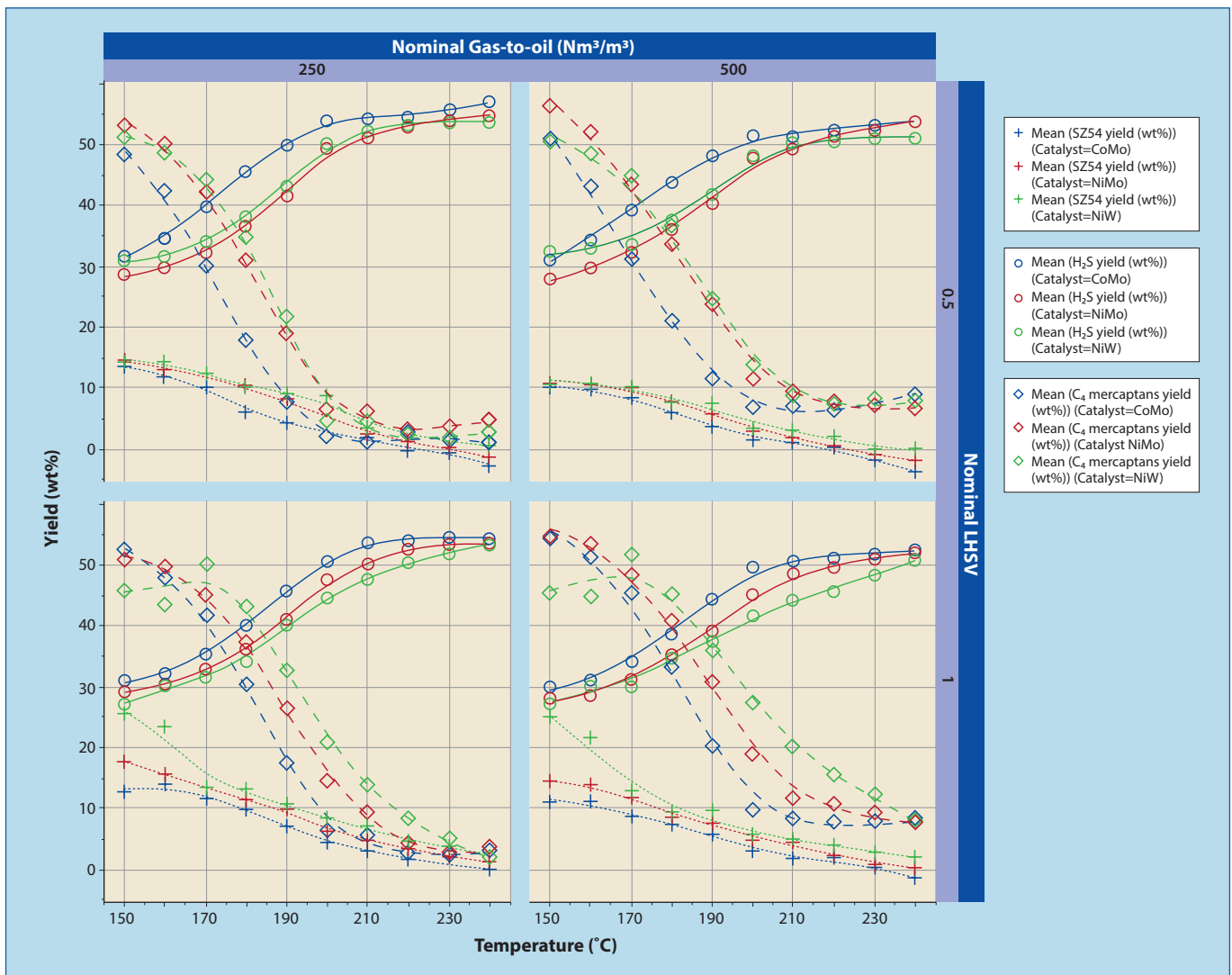
Figure 7 Product yields resulting from the decomposition of TBPS over CoMo, NiMo, and NiW catalysts at PH2 = 60 bar (Run02)

influence of temperature and LHSV on product distribution followed expected trends. The results also indicated that C_4 mercaptans and isobutene acted as intermediate reaction products, with C_4 mercaptans likely serving as intermediates in the formation of isobutene. Overall, the findings provided valuable insights into the decomposition behaviour of TBPS and its interaction with NiMo catalysts in naphtha hydrotreatment processes.

Decomposition of TBPS over CoMo, NiMo, and NiW catalysts used in diesel hydrotreating

Decomposition of TBPS over CoMo, NiMo, and NiW catalysts was investigated in Run02 and Run03, and the resulting product distribution of sulphur and non-sulphur species vs temperature is illustrated in **Figure 7**. The data is grouped by LHSV and gas-to-oil ratio, with a specific focus on the condition at LHSV = 0.5 and gas-to-oil ratio = 500 in the first quadrant from Run02. Notably, the observed trends were consistent across various LHSV and gas-to-oil ratios, allowing us to concentrate on this representative condition.

The presence of a catalyst significantly facilitated the decomposition of TBPS into both sulphur-containing and non-sulphur-containing species, confirming the findings

from Run01 and closely aligning with those of Run03. In the first quadrant, at the lowest temperature of 150°C, approximately 85% of TBPS decomposed, with tert-butyl mercaptan constituting around 55% of the product yields and H_2S accounting for approximately 30%. The notable abundance of C_4 mercaptans can be attributed to the relatively weak S-S bonds present in TBPS, which easily break under the test conditions.

Consistent with the results obtained in Run01, the decomposition of TBPS increased as the temperature rose, with nearly complete conversion observed at 240°C. Within the temperature range of 150-210°C, C_4 mercaptans underwent rapid decomposition, leading to the formation of H_2S, which reached its peak concentration above 220°C. Similar to the findings in Run01, C_4 mercaptans acted as intermediate reaction products in the decomposition of TBPS to H_2S.

Interestingly, the LHSV and gas-to-oil ratio had a mild impact on product distribution. Regardless of catalyst type, at fixed temperature and LHSV, an increase in the gas-to-oil ratio from 250 to 500 resulted in a minor effect on the yield of unconverted TBPS but had a more pronounced influence on the C_4 mercaptans yield. This observation can be attributed to the larger volumetric flow rate of gas, leading to shorter
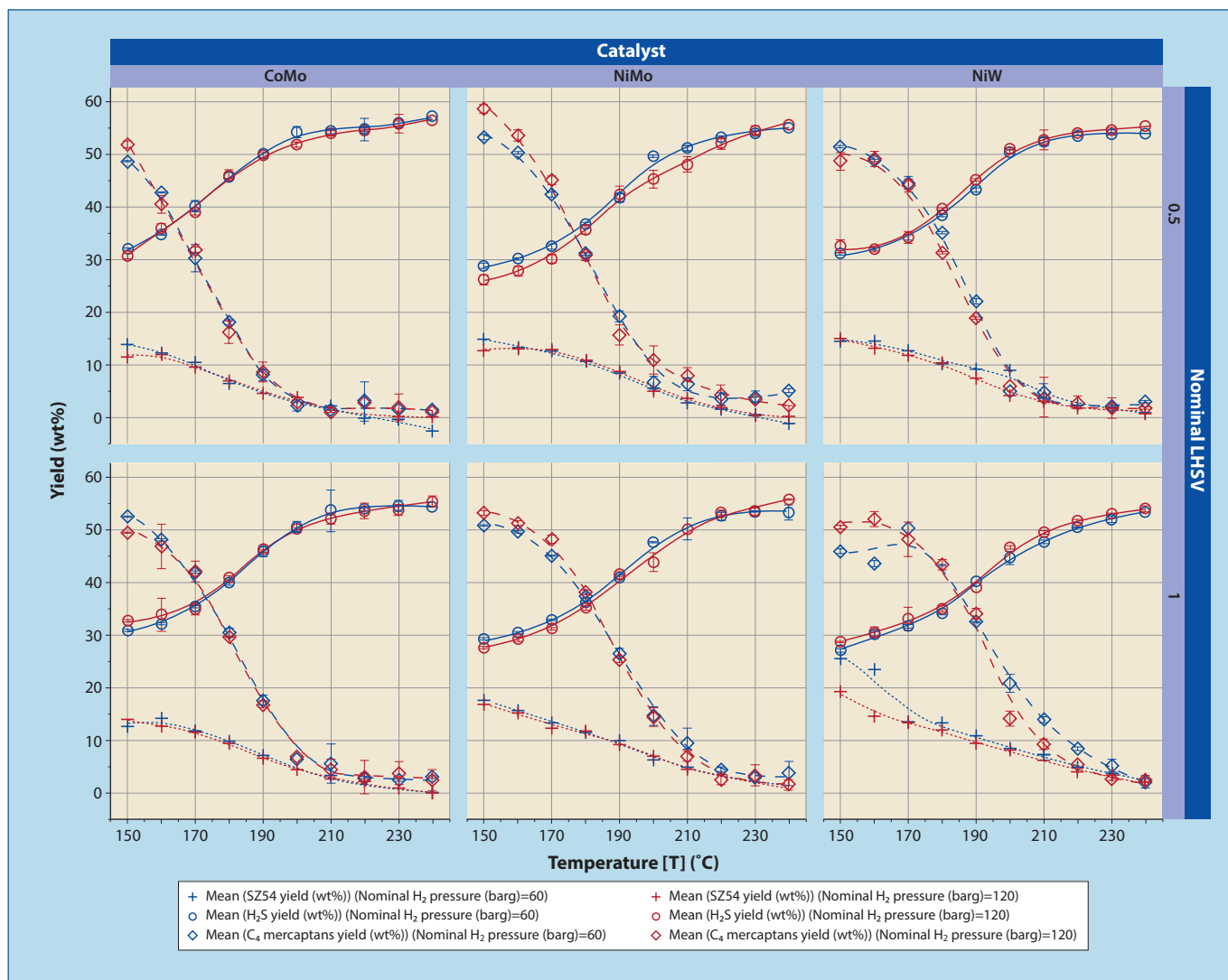
Figure 8 TBPS product yields, H₂S, and C₄ mercaptans obtained at 60 bar and 120 bar hydrogen pressure, Run02 (blue colour) and Run03 (red colour)

contact times for the reaction to progress from C₄ mercaptan to H₂S. Consistent with the results observed in Run01, the influence of LHSV adhered to expectations. At a given temperature, the fraction of unconverted TBPS was greater at higher LHSV (shorter contact times), while trends in product evolution shifted to higher temperatures in reactors operating at LHSV = 1.0 compared to those at LHSV = 0.5.

Moreover, the type of catalyst employed exhibited a discernible impact on the decomposition of TBPS. The data presented in **Figure 8** revealed that the CoMo catalyst facilitated a faster decomposition of TBPS compared to the NiMo and NiW catalysts. Notably, significant differences were observed in the decomposition of C₄ mercaptans and H₂S, suggesting that the catalyst type played a crucial role in the C-S bond cleavage step, leading to the formation of isobutene and H₂S species.

Figure 9 displays the evolution of isobutene and isobutane species during the TBPS decomposition. Like Figure 8, the results are presented in quadrants based on the LHSV and gas-to-oil ratio used in the tests. It is important to note that species such as C₁-C₃ and n-butane were excluded from the plot due to their yields falling below 0.5 wt%. At the lowest space velocity, it was observed that isobutane

reached its maximum yield at temperatures above ~220°C, while the yield of isobutene remained almost negligible under these conditions. In contrast, at LHSV = 1 and gas-to-oil ratio = 500 (fourth quadrant), even at higher temperatures, isobutene was not entirely converted, resulting in the isobutane yield not reaching its maximum. This discrepancy can be attributed to gas contact time, as explained earlier in relation to the evolution of C₄ mercaptans.

Notably, the CoMo catalyst exhibited a faster isobutene hydrogenation rate compared to the other catalysts, while the NiW catalyst displayed the lowest hydrogenation activity. Nonetheless, due to the lack of physicochemical characteristics of the catalysts, a more comprehensive analysis of the results was not possible.

In summary, in Run02 and Run03, the decomposition of TBPS over CoMo, NiMo, and NiW catalysts showcased distinct product distributions. The presence of catalysts facilitated the decomposition, with temperature playing a significant role. The LHSV and gas-to-oil ratio had mild effects on the product distribution, primarily impacting the yield of C₄ mercaptans. Furthermore, the type of catalyst employed influenced the decomposition process, with the CoMo catalyst demonstrating a faster decomposition rate.
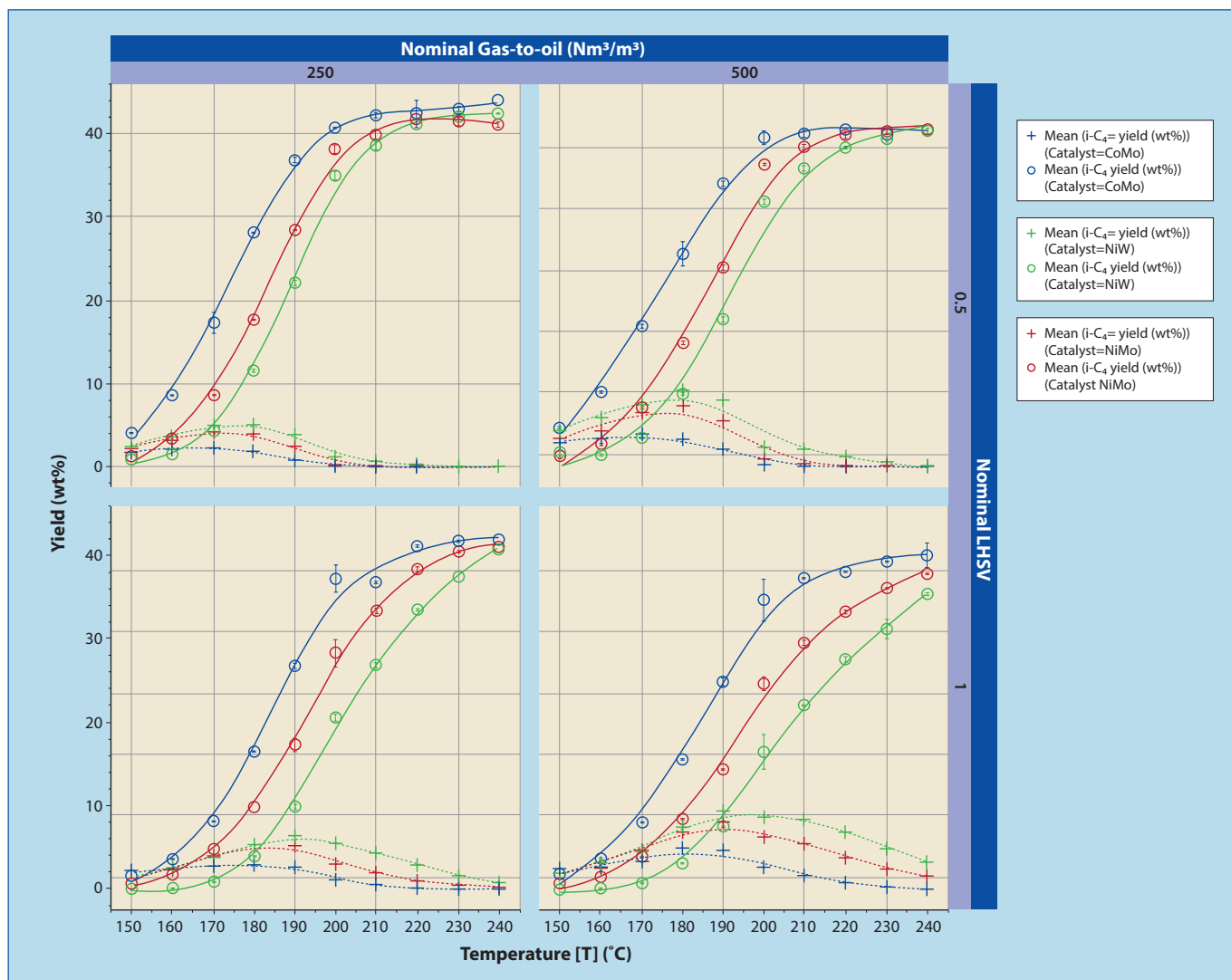
Figure 9 Product yields of isobutene and isobutane resulting from the decomposition of TBPS over CoMo, NiMo, and NiW catalysts at PH2 = 60 bar (Run02)

Conclusion

The study aimed to investigate the decomposition profile of TBPS, a sulphiding agent, in hydroprocessing catalysts. The presence of a catalyst significantly facilitated the decomposition of TBPS into sulphur-containing and non-sulphur-containing species. The type of catalyst employed exhibited a discernible impact on the decomposition of TBPS. The CoMo catalyst facilitated a faster decomposition rate compared to the NiMo and NiW catalysts. Notably, significant differences were observed in the decomposition of C_4 mercaptans and H_2S, indicating that the catalyst type played a crucial role in the C-S bond cleavage step, leading to the formation of isobutene and H_2S species.

The thermal decomposition of TBPS started at around 170°C and increased with temperature. At temperatures below 200°C, TBPS remained mostly unconverted or decomposed into non-volatile sulphur components. However, in the presence of a catalyst, TBPS began to decompose at lower temperatures, indicating the catalytic effect on its decomposition. The relatively weak S-S bonds in TBPS facilitated its breakdown, leading to the formation of tert-butyl mercaptan, which then underwent further decomposition into H_2S and isobutene. These findings align with previous studies that reported a decomposition temperature of approximately 160°C for TBPS.

The decomposition of TBPS increased as the temperature rose, with nearly complete conversion observed at 240°C. H_2S was the primary by-product of TBPS decomposition, with a maximum yield observed around 230°C. The influence of temperature and LHSV on the product distribution followed expected trends. At a given temperature, the fraction of unconverted TBPS was higher at higher LHSV (shorter contact times), while the trends in product evolution shifted to higher temperatures in reactors operating at higher LHSV.

Furthermore, various factors were found to influence the decomposition of TBPS and the formation of H_2S, C_4 mercaptans, isobutene, and isobutane. The H_2 partial pressure, gas-to-oil ratio, LHSV, and temperature all exhibited varying degrees of influence on the product distribution. The H_2 partial pressure showed a weak effect on TBPS decomposition and the formation of H_2S, C_4 mercaptans, isobutene, and isobutane, with some dependence on the catalyst type.

The gas-to-oil ratio also had a weak effect on TBPS decomposition and the formation of H_2S and C_4 mercaptans, except for the NiW catalyst at PH2 = 60 bar and temperatures above 200°C. The LHSV demonstrated a weak

effect on TBPS decomposition and the formation of H_2S and C_4 mercaptans, with an exception for the NiW catalyst at PH2 = 60 bar. Temperature exhibited a strong influence on all aspects, including TBPS decomposition, H_2S formation, C_4 mercaptan formation, isobutene formation, and isobutane formation.

The findings from this study provide valuable insights for optimising the sulphiding process in hydroprocessing and refining practices. By understanding the decomposition profile of TBPS and its interaction with different catalysts, refineries can enhance the efficiency and effectiveness of the sulphiding process, leading to improved catalyst activation and overall performance in hydroprocessing. Further research and investigation may be necessary to explore the behaviour and performance of other sulphiding agents and their interactions with different catalyst types under various operating conditions. The knowledge gained from this research can contribute to the development of cleaner and more sustainable refining practices, aligning with the industry's goals for environmental responsibility.

In summary, the investigation of the decomposition profile of TBPS in hydroprocessing catalysts provided valuable insights into the sulphiding process. The presence of a catalyst significantly facilitated the decomposition of TBPS, with H_2S as the primary by-product. The type of catalyst, temperature, LHSV, and gas-to-oil ratio influenced the product distribution.

SulfrZol 54 is a mark of Lubrizol.

References
1 Moonen R, Alles J, Ras E-J, Harvey C, Moulijn J A, Performance testing of hydrodesulfurization catalysts using a single-pellet-string reactor, *Chem. Eng. Technol.*, 40 (11), pp.2,025-2,034, 2017.
2 Ortega C, et al, *Can. J. of Chem. Eng.*, 99, pp.1,288-1,306, 2021.
3 Heller F E, Roberts C D, Atomized polysulfide used in ethylene stream cracker, Patent 7 154 016 B2, 2006.
4 Fabuss M, Duncan D A, Smith J O, Satterfield C N, Effect of Organosulfur Compounds on Rate of Thermal Decomposition of Selected Saturated Hydrocarbons, *Industrial & Engineering Chemistry Process Design and Development*, Vol. 4, pp.117-122, January 1965.

Jennifer A Jackson is Innovation Technology Manager at Lubrizol, overseeing product line innovation and R&D for upstream oilfield and refinery chemistry. With 18 years of experience in specialty oilfield chemicals and R&D leadership, she develops growth strategies with a focus on innovative technologies. She holds a PhD in inorganic chemistry from the University of Texas at Austin and a BS in chemistry from Wichita State University. She has numerous publications and patents in corrosion science and oilfield chemistry. *Email: Jennifer.Pate@lubrizol.com*

Tiago Vilela leads the Refinery Catalyst Testing (RCT) global services for Avantium Catalysis is responsible for the overall performance of the business line. He has more than 20 years of experience in engineering, project management, management consultancy, and business development. He holds an MSc degree in chemical engineering from the University of Aveiro, Portugal, and a Professional Doctorate in Engineering degree from Delft University of Technology, the Netherlands. *Email: Tiago.Vilela@avantium.com*