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TRANSPORTATION FUELS: Desulfurizing diesel

Carole Lamonier

Transportation fuels such as diesel contain organosulfur molecules that, when combusted, form sulfur oxides, which are toxic and poison vehicles' catalytic converters. Now, a method is demonstrated that can reduce the sulfur concentration of diesel fuel to very low levels at low temperatures and pressures.

With the global demand for energy rising, fossil fuels remain the bedrock of energy use with a total oil demand of about 94 million barrels per day in 2015, which is expected to continue to grow until 2040, according to International Energy Agency forecasts¹. *As part of this growth*, demand for transportation fuels for trucking, aviation and shipping, is expected to increase. Transportation fuels contain sulfur-containing compounds, which, when combusted, lead to formation of sulfur oxides (SO_x) that are strong poisons of the catalysts used in vehicles' exhaust gas converters and are responsible for a degradation of air quality. To address this issue, environmental regulations have been introduced in many countries to drastically reduce the sulfur content of transportation fuels to 15 ppm or less². Hydrodesulfurization, using transition metal sulfide catalysts and performed under high hydrogen pressure (> 30 bar) and temperature (320-380°C), is the conventional catalytic process used by the petroleum industry for sulfur removal and is the subject of significant research^{3,4}. The increasingly stringent sulfur specifications for transportation fuels, beneficial from an environmental point of view, present a major technical and economic challenge for petroleum refining. In particular, the development of processes that require less hydrogen, whilst lowering pressures and temperatures is very challenging. Now, writing in *Nature Energy*, John Shabaker, Kendall Houk, Robert Grubbs and co-workers from across the US, Switzerland and China have developed a non-catalytic desulfurization method that does not directly require hydrogen, to obtain diesel with ultra-low sulfur content, which is performed at atmospheric pressure and a temperature below 200°C⁵.

Shabaker, Houk, Grubbs and colleagues first demonstrate the desulfurization of isolated sulfur-containing molecules that can be found in petroleum streams. One such compound, dibenzothiophene, is treated with a stoichiometric mixture of potassium alkoxide and hydrosilane (the method is thus termed the *KOSi* method), using mesitylene as a solvent, leading to cleavage of the C-S bonds. In this case no H₂S formed and sulfur is removed by formation of Si-S-Si species that can be separated by filtration. The researchers find that the optimized conditions require three equivalents of potassium *tert*-butoxide and three equivalents of triethylsilane for every one equivalent of sulfur, with the reaction performed under nitrogen. The same method is also successfully applied – and with the same efficiency – to the desulfurization of 4,6 dimethyldibenzothiophene (4,6-Me₂DBT, Figure 1). The two methyl groups close to the sulfur atom in 4,6-Me₂DBT create steric hindrance, making it known as a particularly refractory-sulfur compound in the classical hydrodesulfurization process and one that mainly requires hydrogenation of one aromatic ring before C-S bond breaking. However, using the researchers' *KOSi* method, desulfurization occurs without significant reduction of aromatic rings. Interestingly, for the even more bulky 4,6 diethyldibenzothiophene, with which the classical hydrodesulfurization process typically struggles, the desulfurization capacity (involving direct C-S cleavage to form 4,6 diethylbiphenyl) was maintained.

The researchers propose mechanistic details, investigated by density functional theory (DFT), which give the free energy profile for the desulfurization of 4,6-Me₂DBT. Applying the same hydrosilane/potassium alkoxide treatment to the oxygen-containing analogue of 4,6-Me₂DBT, 4,6 dimethyldibenzofuran, no deoxygenation product was formed and only one C-O bond cleavage was observed with formation of hydroxyl-compound, in agreement with DFT calculations.

Next, Shabaker, Houk, Grubbs and colleagues mimic a diesel cut of petroleum fuel oil by introducing 10000 ppm of sulfur in the form of 4,6-Me₂DBT into an ultra-low-sulfur diesel (ULSD). After subjecting the mimic to the desulfurization treatment, the resulting fuel has a sulfur content equal to 2.3 ppm – a value lower than even the most stringent environmental regulations mandate. Investigating the process further, with a view to potential industrial applications, the researchers verify that the method can operate under air and with ULSD as a solvent for 4,6-Me₂DBT desulfurization without significant loss of efficiency. While the reaction was much more sensitive to the presence of water, the removal of water from hydrocarbon mixtures is relatively straightforward and is unlikely to constitute a blocking point for refining applications. Despite the relatively long reaction time, reducing the time on stream may be possible through optimization of engineering parameters. Furthermore, the researchers suggest that triethylsilane could be replaced by a common, inexpensive and non-

toxic polymeric hydrosiloxane, which would bring additional environmental as well as economic benefits.

Even if there is still work before industrialization of this chemical desulfurization process, especially because it takes place in a batch reactor with a rather long reaction time, the proof-of-concept of the desulfurization reactivity is clear. The method may be adaptable to a continuous-flow process for refining applications, especially if it is considered as a polishing treatment for the removal of the refractory sulfur compounds such as 4,6-Me₂DBT that are not removed in classical hydrodesulfurization processes. Moreover, compared to alternative technologies to decrease sulfur content, such as oxidative desulfurization, which produce sulfones that need to be further removed from the feed by extraction⁶, this new chemical treatment leads to the removal of sulfur by C-S bond cleavage, leaving intact the initial hydrocarbon structure in the feed. That is, the removal of the whole sulfone – with the attached hydrocarbon structure, leading to the loss of C_xH_y molecules from the initial feed – is avoided. It is also worth noting that reducing the amount of hydrogen required in petroleum refining could also reduce the environmental impact of upgrading heavy oils by decreasing the quantity of CO₂ generated by current hydrogen production technologies.

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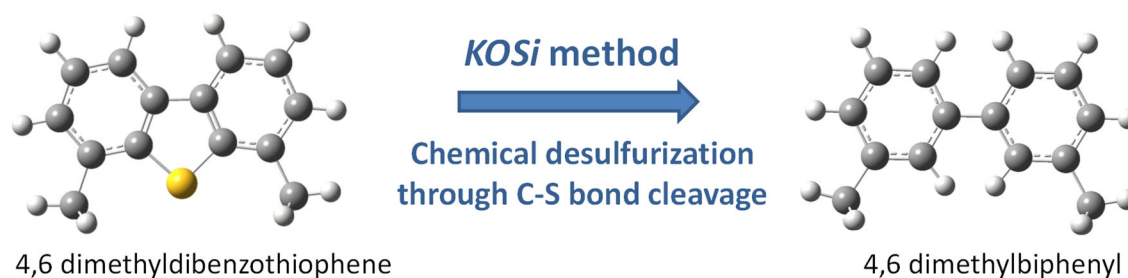


Figure 1. Desulfurization using the *KOSi* method. Using a non-catalytic process based on potassium *tert*-butoxide and hydrosilane, refractory sulfur-containing molecules found in petroleum feeds, such as 4,6 dimethyldibenzothiophene (4,6-Me₂DBT) can be desulfurized. Grey, yellow, and white represent carbon, sulfur, and hydrogen atoms, respectively.

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