

Deep Desulfurization of Fossil Fuels by Air in lactone solvent; the remarkable absence of a role for Catalysts

Xiaoding. Xu, Jacob A. Moulijn, and Michiel Makkee*

Catalysis Engineering, Delft University of Technology, Julianalaan 136, NL 2628 BL Delft, The Netherlands

* m.makkee@tudelft.nl

Introduction

Organic sulfur compounds (OSCs) in transportation fuels contribute to acid rain and cause deactivation of catalysts in automotive applications. The current technology to remove OSCs is so-called hydrodesulfurization (HDS). This process, however, requires severe reaction conditions (>350 °C, 50-100 bars of hydrogen, 0.5-2 kg_{oil}/(kg_{catalyst} h)), especially to remove alkyl-substituted DBTs to a 10 ppm level required by legislations for diesel fuel.

An alternative route reported to remove OSCs is oxidative desulfurization (ODS).^[1-4] ODS processes can be divided into two categories; those using a powerful oxidant, e.g. H₂O₂ or t-BuOOH, peracid, and those using air or oxygen.¹ The first category has the major disadvantage that the oxidants are expensive and not very selective, resulting in hydrocarbon oxidation. Unfortunately, air as such is not reactive enough and catalysts giving full conversion at high selectivity have not been reported. In this presentation, we describe a novel solvent system promoting sulfur oxidation with air in the absence of a catalyst that can be a base for a selective, simplified process for deep desulfurization

Experimental

Reactions were carried out in a batch reactor at 140 °C, 1 bar under continuous air flow. Analysis was done with gas chromatography equipped with a Flame Ionization Detector; occasionally a Sulfur Chemiluminescence Detector (GC/SCD) or GC/MS (mass spectrometer) were applied. The selection of the solvent was made on high polarity, accommodating a good solubility of the oxidized products, and on the boiling point range in the transportation fuels. Polar solvents applied in this study, were γ -butyrolactone (GBL), γ -valerolactone (GVL), δ -valerolactone (DVL), 1-methyl-2-pyrrolidinone (NMP) and ethyl heptanoate. As an inert fuel matrix, n-tetradecane, C₁₄ was used.

Results and Discussion

In C₁₄, some dibenzothiophene (DBT) conversion was observed. γ -butyrolactone (GBL) appeared to give striking results. Complete conversion of DBT at mild conditions was accomplished within 5 h. The addition of the best catalysts reported for air-ODS only led to reaction inhibition. Other OSCs studied, viz., thiophene, benzothiophene (BT), dimethyl-dibenzothiophene (DMDBT) and methyl-dibenzothiophene (MDBT) showed similar conversion behavior as DBT. Conversion rates of a mixture of those compounds in GBL are presented in Figure 1. The OSCs show satisfactory reactivity in the following order: thiophene >> DMDBT > MDBT > DBT > BT.

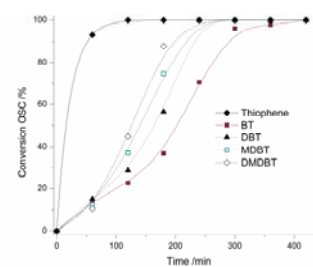


Figure 1. Conversion of thiophene (◆), BT (■), DBT (▲), MDBT (□), and DMDBT (◇), in a mixture containing equal molar amount (2.2 mM) OSCs in GBL by air at 140 °C as a function of reaction time

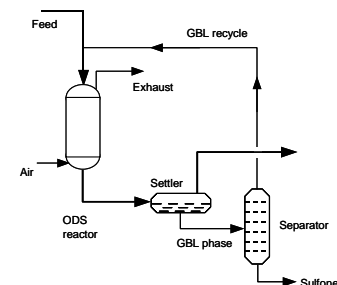


Figure 2 . Conceptual process scheme.

Based on our results we suggest a process scheme as illustrated in Figure 2. GBL is added to the feed and reaction takes place in air at 140 °C. In the settler, the GBL phase with the sulfones is separated. After separation, e.g., by distillation, GBL is recycled to the reactor. The scheme might be simplified further by application of a reactive separation, e.g., reactive extraction. For industrial applications, GBL consumption is a point of concern. We found that some GBL conversion (10 GBL molecules per OSC molecule converted) takes place due to some ring-oxidation. This calls for further mechanistic studies and process optimization and perhaps it is worthwhile to search for a more stable lactone.

Conclusions

OSCs present in the gasoline and diesel fuels can be converted to sulfones in lactones by air at 140 °C at atmospheric pressures in the absence of a catalyst at reasonable contact times (several hours). The solvent plays a decisive role. GBL, the cheapest lactone considered, is a good choice, and plays a catalytic role. This method can be used in the removal of sulfur compounds in oil fractions or as a post-treatment of fuels after a standard HDS operation. Compared to other ODSs the present system gives higher conversions and is very selective for oxidation of OSCs. The process scheme and operation is simplified due to absence of expensive catalyst and problems related to its deactivation and separation. .

References

- [1] I. V. Babich, J. A. Moulijn, *Fuel* **2003**, 82, 607.
- [2] C. Song, X. Ma, *Appl. Catal. B* **2003**, 41, 207.
- [3] C. Song, *Catal. Today* **2003**, 86, 211.
- [4] E. Ito, J. A. R. van Veen, *Catal. Today* **2006**, 116, 446.