

COS thermal decomposition as a step of e-CODUCT technology – simultaneous reduction of H₂S and CO₂

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Introduction

Modern refineries and petrochemical industries handle large amounts of CO₂ and H₂S in their waste streams. The acid gas is also formed as a by-product in biogas digesters and found in natural gas reservoirs. The existing acid gas treatment approach relies on the Claus process with elemental sulphur recovery, while CO₂ reduction demands high purity of the stock, which requires CO₂ separation from the acid gas.

Up to date there is no technology, which allows simultaneous reduction of H₂S and CO₂. Although a number of routes of CO₂ conversion exist, the main challenge remains in the composition of the streams, containing other acid gases. The Horizon Europe project e-CODUCT develops a new technology for the acid gas valorization. The e-CODUCT technology includes two steps – 1) conversion of CO₂ and H₂S into COS in a fixed bed reactor and 2) conversion of COS into CO and S_x in an electrothermal fluidized bed reactor. The products of the acid gas reduction are the platform molecule CO, which can be further converted into the useful chemicals or low-carbon fuels, and directly marketable Claus grade sulphur.

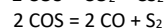
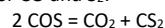
Materials and Methods

COS feedstock with certified purity of 99,9 % was supplied by Air Liquide (France). CO₂ with a certified purity > 99,998 % was supplied by Messer (Germany). CO with a certified purity > 99,997 % was supplied by Linde (Ireland).

Thermal decomposition of COS was being studied in commercial automated tubular reactor system FR 200 (Micromeritics, GA, USA). Outlet gases were analyzed by Agilent 490 micro GC (USA) and Fusion micro GC (Inficon, Switzerland). Chromatographic separation of outlet gases was done at two separated modules. Nitrogen and CO were separated on the Molsieve 5 Å column, while COS, CO₂ and CS₂ were separated on the polar PoraPLOT U column.

Results and Discussion

The process of COS thermal decomposition occurs via two dominant reaction routes leading to formation of CO₂ and CS₂, or CO and S₂:



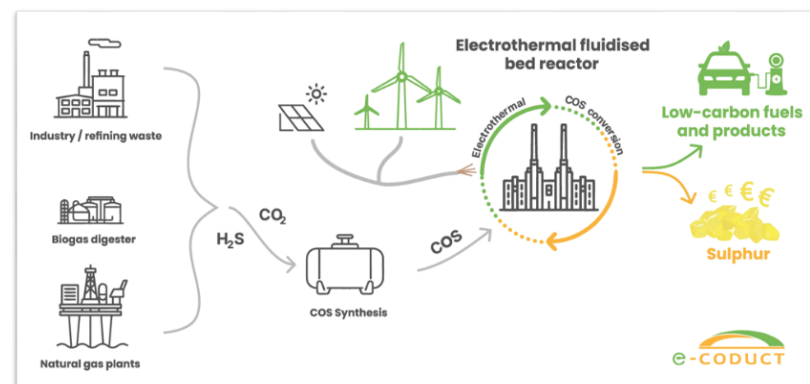
It has been shown experimentally, that formation of CO₂ and CS₂ upon COS thermal decomposition is dominant at temperatures below 650 °C¹. Higher temperatures (800 – 1200 °C) favor not only COS decomposition, but also lead to higher selectivity towards CO and S₂, which was demonstrated both experimentally and by thermodynamic calculations².

Although, literature data about COS thermal decomposition are very extensive, they give contradictory information about mechanism of the reaction. Herein we report the results of COS thermal decomposition, obtained in the laboratory tubular flow reactor under various conditions. Different COS concentration in the stream, residence time and influence of catalysts have been studied. With inlet COS concentration 4,5 mol% and residence time 5 s, COS conversion in empty Hastelloy X reactor was higher than 99 % with CO as the major (> 99 %) component of the gaseous phase at temperatures exceeding 950 °C.

Experimental data are utilized for development of microkinetic model of the system, which was further used for optimization of electrothermal fluidized bed reactor design for carrying out the process of COS thermal decomposition.

Significance

The results of the research are utilized in development of the e-CODUCT technology of simultaneous reduction of H₂S and CO₂, which are both produced as by-products in refineries and petrochemical industry. The mixture of gases is converted into COS, which is then converted into model molecule CO and marketable elemental sulphur. CO can be later on transferred into valuable chemicals or low-carbon fuels.



References

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2. K. Karan, A.K. Mehrotra, and L.A. Behie, *Chem. Eng. Commun.*, **2005**, 192, 370–385.