



Article

Removal of Organic Sulfur Pollutants from Gasification Gases at Intermediate Temperature by Means of a Zinc–Nickel-Oxide Sorbent for Integration in Biofuel Production

Josemaria Sánchez-Hervás ^{1,*} , Isabel Ortiz ¹ , Veronica Martí ¹ and Alberto Andray ²

¹ CIEMAT, Sustainable Thermochemical Valorization Unit, Energy Department, 28040 Madrid, Spain; isabel.ortiz@ciemat.es (I.O.); veronica.marti@ciemat.es (V.M.)

² Faculty of Chemical Engineering, University Complutense of Madrid, 28040 Madrid, Spain; aandray@ucm.es

* Correspondence: josemaria.sanchez@ciemat.es; Tel.: +34-686254241

Abstract: Production of renewable fuels from gasification is based on catalytic processes. Deep desulfurization is required to avoid the poisoning of the catalysts. It means the removal of H₂S but also of organic sulfur species. Conventional cleaning consists of a several-step complex approach comprising catalytic hydro-treating followed by H₂S removal. In this work, a single-stage process using a zinc and nickel oxide sorbent has been investigated for the removal of organic sulfur species present in syngas. The process is called reactive adsorption and comes from the refinery industry. The challenge investigated by CIEMAT was to prove for the first time that the concept is also valid for syngas. We have studied the process at a lab scale. Thiophene and benzothiophene, two of the main syngas organic sulfur compounds, were selected as target species to remove. The experimental study comprised the analysis of the effect of temperature (250–450 °C), pressure (1–10 bar), space velocity (2000–3500 h^{−1}), tar components (toluene), sulfur species (H₂S), and syngas components (H₂, CO, and full syngas CO/CO₂/CH₄/H₂). Operating conditions for removal of thiophene and benzothiophene were determined. Increasing pressure and temperature had a positive effect, and full conversion was achieved at 450 °C, 10 bar and 3500 h^{−1}, accompanied by simultaneous hydrogen sulfide capture by the sorbent in accordance with the reactive adsorption desulfurization (RADS) process. Space velocity and hydrogen content in the syngas had little effect on desulfurization. Thiophene conversions from 39% to 75% were obtained when feeding synthetic syngas mimicking different compositions, spanning from air to steam-oxygen-blown gasification. Toluene, as a model tar component present in syngas, did not strongly affect the removal of thiophene and benzothiophene. H₂S inhibited their conversion, falling, respectively, to 2% and 69% at 350 °C and 30% and 80% at 400 °C under full syngas blends.

Keywords: desulfurization; organic sulfur; thiophene; benzothiophene; reactive adsorption; ZnO–NiO sorbent; gasification; biofuels



Citation: Sánchez-Hervás, J.; Ortiz, I.; Martí, V.; Andray, A. Removal of Organic Sulfur Pollutants from Gasification Gases at Intermediate Temperature by Means of a Zinc–Nickel-Oxide Sorbent for Integration in Biofuel Production. *Catalysts* **2023**, *13*, 1089. <https://doi.org/10.3390/catal13071089>

Academic Editor: Gang Li

Received: 26 May 2023

Revised: 24 June 2023

Accepted: 29 June 2023

Published: 11 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Nowadays, gasification of biomass and waste is becoming increasingly relevant for the production of gaseous biofuels such as synthetic natural gas and hydrogen, liquid biofuels, e.g., sustainable aviation fuels and naphtha via Fischer Tropsch, FT, or for the generation of chemicals, for instance, methanol or hydrocarbons to be used in chemical platforms [1].

Raw gasification gas must undergo a number of purification steps prior to its final use. Of all the pollutants, tars have historically been the bottleneck for the large-scale implementation of gasification [2]. However, when the produced gas is to be used for any of the chemical synthesis processes mentioned above, the rest of the contaminants present in the gas are equally critical. The presence of sulfur species is particularly an issue. The vast majority of catalysts used in the stages of adjustment of the composition of the

gasification gas and in the chemical synthesis processes themselves are extremely sensitive to sulfur, undergoing deactivation processes [3].

While the formation and concentration of tars is related to the operating conditions and not so much to the composition of the biomass or waste, the concentration of sulfur is considered to depend more on it [4]. As shown in Table 1 (own data), the variation of sulfur in biomass and waste feedstock is significant; particularly those most available worldwide contain appreciable amounts of sulfur. It is generally considered that between 30 and 50% of the sulfur present in the fuel is released into the gas phase.

Table 1. Sulfur content of different feedstock often used for gasification (own data).

Feedstock	Sulfur (wt% daf) ¹
Pine pellets	0.03
Straw	0.15
Beer bagasse	0.26
Cattle manure	0.95
Municipal Solid Waste	0.55
Sewage Sludge	0.40

¹ dry-ash-free weight.

Within the advanced applications of gasification, the production of biomethane, often called SNG, Substitute Natural Gas, has reached a great potential [5], with high expectations for 2030 and 2050 [6]. A good number of examples have demonstrated technologies for its production [7–9]. Sulfur removal showed to be a relevant stage, and complex systems were used.

Regarding syngas purity for SNG production, sulfur content should be as low as 0.1 ppmv in order to avoid poisoning the nickel catalysts used in methanation reactors [3]. When the critical sulfur load is reached at the active sites, the catalyst becomes passive and is not able to convert the gasification gas to CO₂ and CH₄. The poisoning of nickel catalysts by sulfur is considered irreversible. Studies of oxidation at programmed temperatures [10] show that sulfur desorbs from 800 °C. However, at this temperature, the catalyst undergoes thermal deactivation.

For many years, removal of sulfur compounds from gasification gases has focused mainly on their inorganic forms, H₂S (and COS). Comprehensive reviews of gasification gas cleaning processes [11–13] show that mid- to high-temperature cleaning using regenerable sorbents based on metal oxides of iron and zinc and zinc titanates is the most appropriate route when the gas is intended for chemical synthesis and biofuel production. Novel sorbents derived from recycled materials [14] or based on innovative supports such as graphene are being investigated [15].

Nevertheless, in the recent years, attention has started to be paid to the elimination of organic sulfur species. PSI has studied the high temperature catalytic reforming of tars and organic sulfur species [16], finding that at T = 740 °C and GHSV = 9000 h^{−1}, thiophene and benzothiophene were eliminated, leaving only a 20% benzothiophene (<1 ppmv) so that the system can be used in chemical synthesis processes from gasification.

Agnion and the University of Graz are also very active in this subject [17–19]. Their approach is based on the use of a hydrodesulfurization Co-Mo catalyst, HDS (5000 h^{−1}, T = 300–510 °C) and/or Ni for the reforming of tars and organic sulfur species, followed by adsorption in a fixed bed with ZnO (1000 h^{−1}, 300 °C).

In the ESME process [20], a three-fixed-bed reactor system is used, the first with an HDS catalyst at 280 °C, followed by an H₂S adsorption reactor with ZnO at 420 °C and an unspecified guard bed at 460 °C. The process is carried out at low space velocity, 200–250 h^{−1}, gas flow 11–12 NI/min (0.6–0.7 Nm³/h) and at a 6-bar pressure. Sulfur reduction concentration below 0.1 ppmv in campaigns of 500 h was demonstrated. The authors also studied other adsorbents such as activated carbon.

The literature shows that the removal of organic compounds in gasification gases is based on the transfer of technology from the hydrotreatment processes of refinery products.

Hydrodesulfurization (HDS) is the most widely used and oldest desulfurization technology where the conversion of organic sulfides (thiophene, mercaptans, etc.) into H_2S occurs through Co/Mo or Ni/W sulfide catalysts on alumina (Al_2O_3) [21]. Other alternatives such as extractive desulfurization (EDS), oxidative desulfurization (ODS), reactive adsorption desulfurization (RADS) and adsorption desulfurization (ADS) are being investigated [22,23]. The latter two options are claimed to provide the best results [24].

According to Bartholomew and Farrauto [25], during hydrodesulfurization, aromatic sulfur compounds are hydrogenated to produce hydrogen sulfide and mixtures of butene isomers in the case of thiophene, alkylbenzenes (benzothiophene), and biphenyls (dibenzothiophene). Reactivity decreases with an increasing number of benzene rings. As HDS catalysts, sulfides of CoMo/ Al_2O_3 and NiMo/ Al_2O_3 , Ru, are mainly used in fixed-bed reactors at 300–400 °C and 30–130 atm. The removal of H_2S is carried out in washing towers with amines at a low temperature, 35 °C, and 3–6 atm.

The use of different catalysts or adsorbents that have a greater sulfur retention capacity with good yields and which are economical is being investigated. Zeolite Y was tested by several scientists due to its huge adsorption sites and excellent thermal stability [21,26–28]. However, adsorption (ADS) with said zeolite provides low sulfide adsorption capacity and selectivity due to competitive adsorption between olefins and sulfide aromatics. The selectivity towards the elimination of thiophene with the zeolite improved after the temperature and the Si/Al ratio increased.

In gasification gases, thiophene is one of the most abundant organic sulfur compounds, and therefore its removal is one of the main targets. As reported in the literature, first, the use of activated carbon was studied, and other adsorbents (transition metals) were used later [29–31]. There is research employing reactive adsorption desulfurization (RADS) of thiophene using a Cu/ZnO adsorbent on coke oven gas (COG). The coke oven gas used (COG) is a mixture of H_2 , CH_4 , CO and CO_2 , etc., from the coke industry and with multiple uses (production of ammonia, methanol, etc.) [32]. Cu^0 nanoparticles in the Cu/ZnO adsorbent dissociate H_2 and break the C-S bond of thiophene so that sulfur is transferred to ZnO and converted to ZnS. During thiophene removal, C_4H_6 and C_4H_{10} are generated due to the presence of H_2 [33–36]. Hydrogenation is essential to remove thiophene. The desulfurization activity and the selectivity of the Cu/ZnO sorbent for thiophene removal have been studied in a fixed bed reactor and under various space velocity conditions (2000–6000 h^{-1}). For the desulfurization of FCC gasoline, Ni/ZnO has also been used; however, its selectivity decreases too much at high space velocities. The mechanism of action of this adsorbent is similar to that of CuO. In the presence of H_2 , NiO in the adsorbent can convert to Ni^0 , adsorbs thiophene, breaks the C-S bond releasing Ni_3S_2 and C_4 hydrocarbons, and generates ZnS from ZnO [33]. This RADS technology with these metal oxides as adsorbents makes it possible to obtain high-octane gasoline with high sulfur retention capacities, good yields and using mild operating conditions (intermediate temperature and pressure). Cu/ZnO and Ni/ZnO adsorbents are useful not only in thiophene removal. In addition, they are useful in benzothiophene and dibenzothiophene removal, as well as inorganic sulfur (H_2S) removal. Apart from the Ni/ZnO- Al_2O_3 - SiO_2 adsorbent, there is a similar one ($\text{NiSO}_4/\text{ZnO-Al}_2\text{O}_3\text{-SiO}_2$) that improves the selectivity of dibenzothiophene desulfurization and has been used at temperatures between 350 and 420 °C in the presence of hydrogen [21].

In the case of benzothiophene, desulfurization directly to biphenyl is being investigated on the one hand and hydrodesulfurization to cyclohexylbenzene and cyclohexyl on the other hand [37]. It has been observed that water is an impurity that can catalyze hydrogen transfer reactions and form H_2S from organic sulfur to be removed [38]. Various oxides on graphene are being investigated to remove benzothiophene from fuel [39]. Molecularly imprinted polymers on the surface of carbon microstructures have also been used to remove both benzothiophene and dibenzothiophene from gasoline [40]. However, the use of transition metal oxides is more effective in the case of benzothiophene and dibenzothiophene removal coming from or mixed with gasification gases.

For adsorption, fixed-bed reactors have been mostly used. Nevertheless, for the removal of sulfur compounds (H_2S , mercaptans, thiophenes, etc.) present in gases from biomass gasification, fluidized bed reactors have been tested as well. For the measurement of the compounds to be studied, gas chromatography (GC) or the gravimetric method were used [4,41]. Other possible techniques are Fourier Transform Infrared Spectroscopy (FTIR), GC analysis of liquid samples with flame ionization detector (FID) or mass spectrometry (MS).

As discussed above, a great deal of experience in organic sulfur removal relies on transfer of technology from the petrochemical sector. In that sense, since the 1990s, ConocoPhillips (formerly Phillips Petroleum) has been developing sorbents for the removal of sulfur species, initially inorganic, for refinery products. The families of Z-Sorb and S-Zorb adsorbents are based on zinc and nickel oxides, the first being indicated for fixed-bed reactors and the second for fluidized-bed ones. Studies [42,43] have shown that these adsorbents have the ability to remove organic sulfur species in refinery products, with lower consumption of low-purity hydrogen. In addition, compared to conventional hydrodesulfurization, it has the advantage that hydrogenation and adsorption of hydrogen sulfide take place in a single step.

Different formulations of these products have been patented and studied for other uses, such as the removal of hydrogen sulfide in gasification gases [44,45]. Particularly, the results of pilot scale studies with the sorbent designated as Z-SorbIIITM demonstrated the extraordinary capacity of desulfurization (removal of H_2S) applied to gasification gases [46,47].

Based on the discussion above, the objective of this paper is to make contribution to R&D in deep desulfurization technologies of biomass and waste gasification gases at high temperature (300–500 °C) for integration in renewable fuel production (SNG, biofuels) and thus reduce the use of and dependence on fossil fuels.

Specifically, the present work focuses on the assessment of a sorbent based on zinc and nickel oxide for the removal of organic sulfur species from gasification gases (thiophene, benzothiophene) in a single stage by means of reactive adsorption. The technology has been successfully proven for gasoline sulfur removal. The use of the sorbent for H_2S removal in gasification gases at 300–500 °C and 1–20 bar was similarly demonstrated by the authors. Both facts mean a sound assumption for evaluating its feasibility for removal of organic sulfur compounds present in gasification gases.

2. Results and Discussion

For the removal of organic sulfur species using the ZnO–NiO sorbent, thiophene (TF), and benzothiophene (BTF) were selected as target species. A base case test was set, for which the operating conditions were as follows: thiophene, 500 ppmv, 20% H_2 in N_2 ; 350 °C; 10 bar; 3500 h^{-1} . From the reference case test, the effect of temperature, pressure, space velocity, and presence of tar components with toluene as the model compound were determined under simplified reaction conditions. This was addressed by systematically changing the operating conditions of the given parameter, the effect of which was being studied, and by adding different components. Then, the effect of the co-existence of other sulfur species (H_2S , and benzothiophene) and of full syngas was established in order to determine performance under more realistic conditions. The experiment series are summarized: tests under simplified atmosphere in Table 2 and under complex atmosphere in Table 3.

To the best of our knowledge, there is no specific literature on reactive adsorption desulfurization using ZnO–NiO sorbents for thiophene and benzothiophene removal from syngas. For that reason, the base case scenario operating conditions were taken from other applications.

Table 2. Experimental tests for the assessment of organic sulfur compound (thiophene) removal using the zinc-oxide, nickel-oxide Z Sorb IIITM sorbent under simplified syngas atmospheres.

Test Series	Objective	Operating Conditions ¹
1	Reference case	350 °C, 3500 h ⁻¹ , 10 bar, TF (500 ppmv), H ₂ (20% v/v), N ₂ makeup
2	Effect of T	200, 250, 300, 350, 375, 400, 450 °C, 3500 h ⁻¹ , 10 bar, TF (500 ppmv), H ₂ (20% v/v), N ₂ makeup
3	Effect of P	350 °C, 3500 h ⁻¹ , 0.5, 1, 5, 8, 10 bar, TF (500 ppmv), H ₂ (20% v/v), N ₂ makeup
4	Effect of GHSV	350 °C, 2000, 2500, 3000, 3500 h ⁻¹ , 10 bar, TF (500 ppmv), H ₂ (20% v/v), N ₂ makeup
5	Effect of H ₂	350 °C, 3500 h ⁻¹ , 10 bar, TF (500 ppmv), 10, 15, 20, 30, 40, 50% v/v H ₂ , N ₂ makeup
6	Effect of thiophene	400 °C, 3500 h ⁻¹ , 10 bar, 500, 1000 ppmv TF, H ₂ (20% v/v), N ₂ makeup
7	Effect of Toluene	350 °C, 3500 h ⁻¹ , 10 bar, TF (500 ppmv), 1.5, 3, 4, 6 µL/min TOL, 20% v/v H ₂ , N ₂ makeup

¹ TF: thiophene, TOL: toluene.**Table 3.** Experimental tests for the assessment of thiophene and benzothiophene removal using the zinc-oxide, nickel-oxide Z Sorb IIITM sorbent under complex atmospheres.

Test Series	Objective	Operating Conditions ¹
8	Effect of CO	350 °C, 3500 h ⁻¹ , 10 bar, TF (0.08%), 4 µL/min TOL, 20%, 40% v/v H ₂ , 40% v/v CO (syngas C)
9	Effect of full syngas	350 °C, 3500 h ⁻¹ , 10 bar, TF (500 ppmv), 4 µL/min TOL, syngas A, CO/CO ₂ /CH ₄ /H ₂ (32.9/11.2/0.7/29.9% v/v), syngas B CO/CO ₂ /CH ₄ /H ₂ (24.2/8.2/0.5/22% v/v)
10	BTF removal	350 °C, 3500 h ⁻¹ , 10 bar, BTF (1, 3 ppmv), 5850 ppmv TOL, 20%, H ₂ , 40% v/v CO, N ₂ makeup
11	TF & BTF combined removal	350, 400 °C, 3500 h ⁻¹ , 10 bar, 800 ppv TF, 100 ppmv BTF, 5850 ppmv TOL, 20%, H ₂ , 40% v/v CO, N ₂ makeup
12	Effect of H ₂ S	350, 400 °C, 3500 h ⁻¹ , 10 bar, 1000 ppv TF, 100 ppmv BTF, 0.36% v/v H ₂ S, 5850 ppmv TOL, 20%, H ₂ , 40% v/v CO, N ₂ makeup

¹ TF: thiophene, BTF: benzothiophene, TOL: toluene.

Temperature and pressure were specifically set according to studies dealing with thiophene and benzothiophene removal from gasoline and using the Ni/ZnO S-Zorb process [48,49] or sorbents containing Ni/ZnO in their formulations [30,50], with NiO content similar to that of the sorbent used in our study (5 wt% NiO) [48]. It must be noted that the reaction atmosphere is very different. For instance, in the work of Kong et al. [50], thiophene at a sulfur concentration of 100 ppmw was added to sulfur-free n-heptane used as a model gasoline A. Model gasoline B contained a 100 ppmw sulfur as thiophene and 35 wt% of isopentene as olefins, 15 wt% toluene as aromatic compounds. The model gasoline B also contained 10 wt% of cyclohexane to mimic the cycloalkane.

Gas space velocity was selected in accordance with previous studies carried out by the authors using the same sorbent for H₂S removal [15].

Even focusing on a completely different application which is organic sulfur removal from gasoline, all the available studies show that a large ratio of hydrogen to organic sulfur compound is used. For our study, hydrogen content was set as that typically found in gasification gases [51].

In the following subsections, the main findings and results are presented and discussed.

2.1. Removal of Thiophene, Effect on Main Operating Parameters

2.1.1. Effect of Temperature

The effect of temperature on thiophene conversion is shown in Figure 1. The other parameters were maintained constant: 10 bar of pressure, a 3500 h⁻¹ space velocity, using a gas mixture containing 500 ppmv of thiophene, a 20% hydrogen and nitrogen balance. The amount of hydrogen is typical of air–steam gasification. It can be observed that below 300 °C, hydrogenation of thiophene is very small. At high temperatures, the elimination of thiophene is favored, displaying an inflection point in the graph at 350 °C and reaching full conversion (100%) at 450 °C. The justification for using high temperatures to achieve a high conversion in the elimination of thiophene is the fact that at these temperatures, the weakening of its bonds is favored. The results are in agreement with those obtained by

Kong et al. [50], which concluded that Ni/ZnO does not adsorb the thiophene effectively at 300 °C.

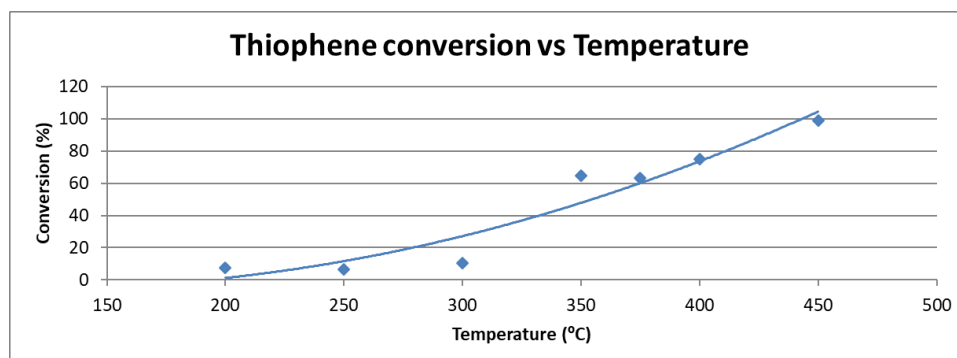


Figure 1. Effect of temperature on thiophene conversion (thiophene, 500 ppmv; 20% H₂ in N₂; 10 bar; 3500 h^{−1}).

Despite the fact that some studies, e.g., the one by Zhang and co-workers [34], claim that a pre-reduction of the sorbent under H₂ flow at 360 °C for 6 h was necessary prior to the desulfurization activity test, in our case, the sorbent seems to have been activated in situ in accordance with the study of Bezverkhyy and co-workers [36].

2.1.2. Effect of Pressure

The effect of pressure was studied keeping constant the other parameters as indicated in Figure 2. Temperature was 350 °C, space velocity was 3500 h^{−1}, the gas mixture contained 500 ppmv of thiophene and a 20% hydrogen and nitrogen balance.

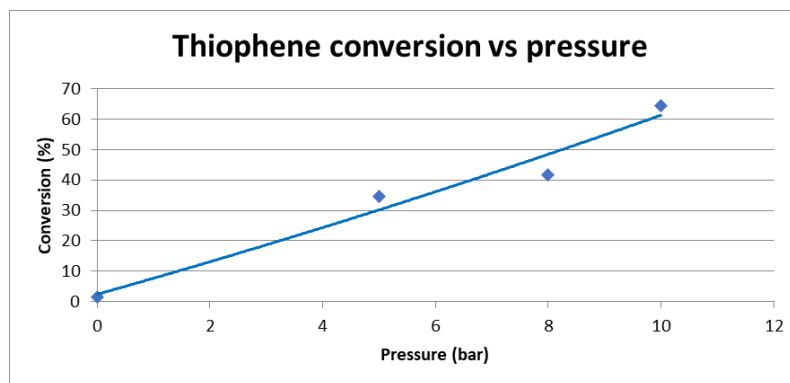


Figure 2. Effect of pressure on thiophene conversion (thiophene, 500 ppmv, 20% H₂ in N₂; 350 °C; 3500 h^{−1}).

Looking at the effect of pressure, it can be observed that its increase leads to a higher conversion of thiophene, following an almost linear trend. This is in agreement with the effect of pressure on thiophene removal by reactive adsorption observed by others. Most reported studies on removal of organic sulfur compounds were conducted under high-pressure conditions, which was found to favor desulfurization. Thus, Fan and co-workers in their studies using Ni/ZnO as adsorbent concluded that the optimal operating pressure was 15 bar [52]. Also, as reported by Zhang et al. [48], the S-Zorb process for the production of low-sulfur gasoline by reactive adsorption of sulfur compounds using a solid sorbent was carried out under H₂ pressures in the range of 3–35 bar.

A positive effect of increasing pressure can be expected looking at the reactive adsorption desulfurization concept. The ConocoPhillips S Zorb SRT, Houston, TX, USA, uses a Ni/ZnO sorbent, and so does our Z-SorbIIITM sorbent that specifically adsorbs sulfur-containing molecules and removes the sulfur atom from the molecule. The sulfur atom is

retained on the sorbent while the hydrocarbon portion of the molecule is released back into the process stream. The chemistry involved is reported to be as follows: The Ni atoms are the active centers for adsorption of sulfur-containing molecules by forming a Ni–S bond. The sulfur is then removed via breakage of C–S bonds, producing NiS_x and sulfur-free hydrocarbons. Finally, the NiS_x is recovered to metallic nickel under hydrogen flow with ZnO acting as sulfur acceptor by forming ZnS species [49,53]. Adsorption and cleavage of C–S bonds are processes which are favored by pressure; therefore, an enhancement in conversion can be expected on raising operating pressure.

2.1.3. Product Distribution

Chromatographic data revealed that thiophene was the only sulfur species detected. Hydrogen sulfide was not present in the gas leaving the reactor. This proves that the reactive adsorption process was taking place. According to the idea proposed by Ito and Van Veen [54] based on the previous findings by Babich et al. [55] and Tawara et al. [56] for the Ni on ZnO sorbent, Ni functions as hydrodesulfurization sites, while ZnO takes up the resulting H₂S, converting into ZnS in the process. Li et al. [21] who prepared a Ni/ZnO adsorbent by homogeneous precipitation and applied it successfully to the deep desulfurization of gasoline also observed that the active metal (Ni) reacts with the sulfur-containing compound under an H₂ atmosphere to form metal sulfides. Subsequently, the metal sulfides react with ZnO to form ZnS.

According to Babich and Moulinj [55], HDS of thiophenic compounds proceeds via two reaction pathways as shown in Figure 3. In the first one, hydrogenation, the aromatic ring is hydrogenated to convert into tetrahydrothiophene and sulfur is subsequently removed as H₂S, forming 1-butene and butane upon further hydrogenation. The second one is the hydrogenolysis pathway, by which the sulfur atom is directly removed from the molecule opening the ring to yield hydrogen sulfide and 1,3-butadiene. Further hydrogenation of the hydrocarbon produces butene and butane as in the first case. Both pathways occur in parallel, employing different active sites of the catalyst surface. The pre-dominating type of reaction pathway depends on the nature of the sulfur compounds, the reaction conditions, and the catalyst used.

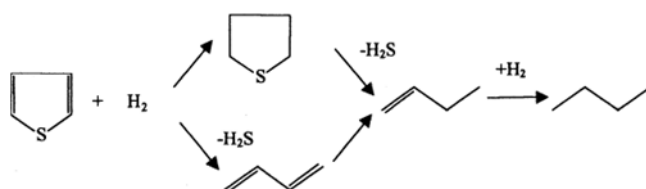


Figure 3. Typical thiophene hydrotreating pathway (as extracted from Babich et al. [55]).

In our case, hydrogenolysis seems to be the main pathway, judging by the nature of the desulfurization pattern. However, as shown in Figures 4 and 5, the number of hydrocarbon products and their distribution is quite complex, much more so than the hydrodesulfurization pathways reported by Babich et al.

Regarding product distribution, 1-butene was the main species shown by GC, which is in accordance with the hydrogenolysis pathway by which the ring is opened, releasing H₂S. However, in our studies, other compounds appeared, including 2-butene, isobutene, cyclopentene, 1-pentene and lower C-carbon molecules such as propene. Upon increasing the temperature, a more complex mixture containing hydrocarbons with four to six carbon atoms, and linear alifatic compounds were formed from thiophene hydrogenation; in addition, growing amounts of C₂ compounds were detected. Also, formation of butane took place, which was a clear indication of further hydrogenation of the unsaturated aliphatic species. Changes in temperature produced a higher number of products and less arranged distribution compared to the effect of pressure. At 350 °C, an increase in system pressure led to higher selectivity to 1-butene, followed by butane, 2-butene and iso-butene.

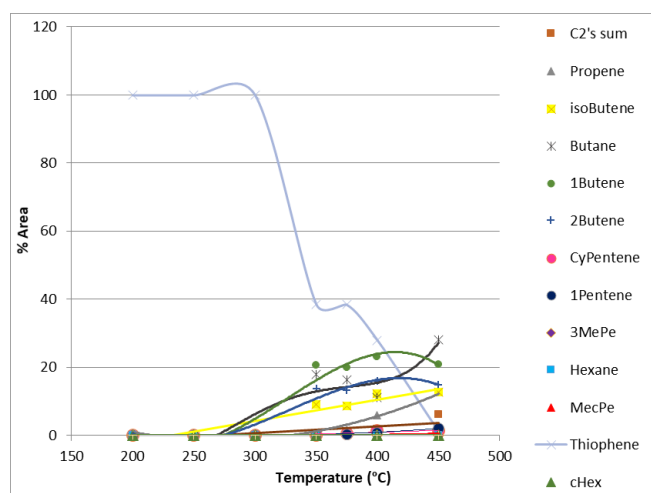


Figure 4. Product distribution during thiophene conversion as a function of temperature (thiophene, 500 ppmv; 20% H₂ in N₂; 10 bar, 3500 h^{−1}).

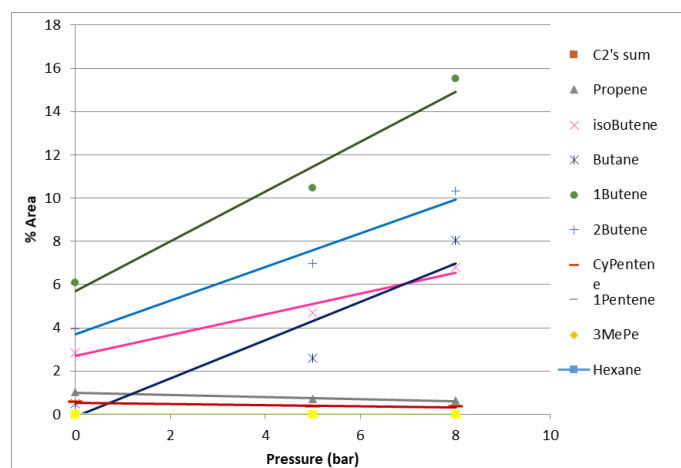


Figure 5. Product distribution during thiophene conversion as a function of pressure (thiophene, 500 ppmv; 20% H₂ in N₂; 350 °C, 3500 h^{−1}).

2.1.4. Effect of Gas Hourly Space Velocity

Gas hourly space velocity, GHSV, is the ratio of gas flow rate in standard condition to the volume of the sorbent loaded into the reactor. Its effect on thiophene conversion was evaluated. From 2000 to 3000 h^{−1}, raising gas space velocity yielded overall lower conversion as Figure 6 shows, decreasing from 72.8% to 47.6%. Sorbent–gas reaction kinetics are usually diffusion limited; thus, the amount of sulfur absorbed is affected by the velocity of the gas stream. The thiophene molecules need to access the active sites of the sorbent and decompose, and the resulting H₂S is captured by the sorbent. An increase in space velocity means a decrease in the contact time, what leads to a lower performance in gas–solid sorption systems. However, in this particular case, further increase in gas velocity showed that the conversion was slightly enhanced again reaching 64.7%. In any case, the effect is smaller than that of temperature and pressure. It must be noticed that this non-definitive trend on the effect of this parameter might be because of the narrow window of velocities tested.

2.1.5. Effect of Hydrogen

As depicted in Figure 7, hydrogen concentration seems to have little effect on conversion, most likely due to the large amount of hydrogen available. The rationale behind using those hydrogen contents (from 10% v/v to 50% v/v) was to evaluate how the desul-

furization process would perform over a wide range of syngas compositions. It must be taken into account that a large content of hydrogen might have led to partial reduction in the sorbent, nickel oxide and zinc oxide to the corresponding metals, which in turn might have meant that the reactive adsorption process would have not proceeded.

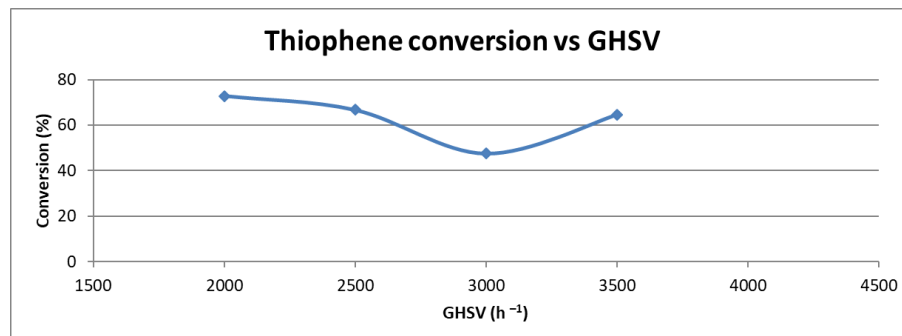


Figure 6. Effect of gas hourly space velocity on thiophene conversion (thiophene, 500 ppmv; 20% H₂ in N₂; 350 °C; 10 bar).

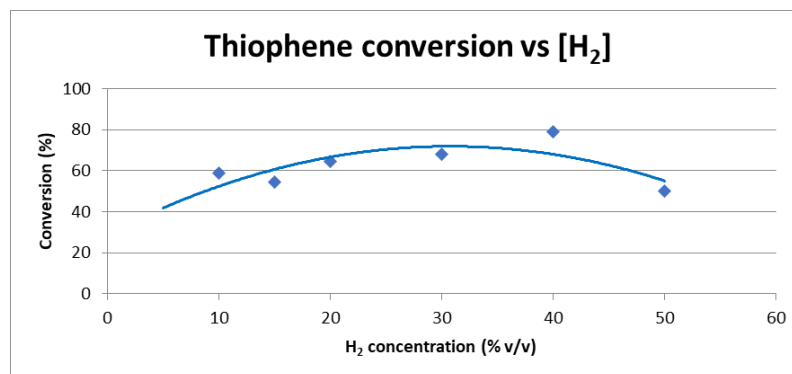


Figure 7. Effect of hydrogen content on thiophene conversion (thiophene, 500 ppmv; 10 to 50% H₂ in N₂; 350 °C; 10 bar; 3500 h⁻¹).

Thiophene conversion reached values from 60 to 80%. It should be noted that when the hydrogen content in the gas mixture was set as high as 50% *v/v*, thiophene conversion decreased to 50%, the lowest of the series, which might indicate that the active components, zinc oxide, responsible for H₂S capture, and especially nickel oxide, responsible for hydrogenolysis, might be suffering some reduction. Despite this loss in performance, it can be concluded that the process would work for a wide range of syngas compositions, from air gasification, which typically contains hydrogen content in the 10–15% *v/v* range, to hydrogen-rich syngas as that produced by air–oxygen–steam and steam gasification for which the water–gas–shift is favored and hydrogen can reach 50% *v/v*.

Our findings are consistent with those of other studies found in the literature. For nickel–zinc oxide sorbents, it was observed by Babich and Moulijn [55] that with an excess of hydrogen, thiophene decomposition is thermodynamically feasible over a large temperature range, e.g., up to 625 °C; the equilibrium composition contains less than 50 ppm S and all sulfur is fixed in the sorbent as ZnS. The role of hydrogen in reactive adsorption desulfurization has been clarified from thermodynamic modeling as well. Only when hydrogen is in excess (H₂ to thiophene ratio above stoichiometric) is thiophene desulfurized completely, and the kinetics are fast [57], whereas with a stoichiometric ratio of hydrogen to thiophene in the reacting mixture, the process does not result in a high desulfurization level.

2.1.6. Effect of Aromatic Inorganic Pollutants

Co-existence of aromatic hydrocarbons together with organic sulfur compounds might mean competition for hydrogenation or that aromatics might deactivate the sorbent. To study a potential detrimental effect, the influence of adding toluene as a tar model compound has been determined.

As presented in Figure 8, adding toluene at different concentrations to the thiophene–hydrogen–nitrogen gas mixture had some effect on thiophene conversion. Adding the tar model compound in a low concentration of 1.5 $\mu\text{L}/\text{min}$ led to a decrease in thiophene conversion from 64.6% (toluene free case) to 37.9%. However, increase in toluene addition to 6 $\mu\text{L}/\text{min}$ resulted in a recovery of thiophene conversion to 59.2%. Despite not showing a clear trend, what can be concluded is that toluene did not affect thiophene conversion very strongly.

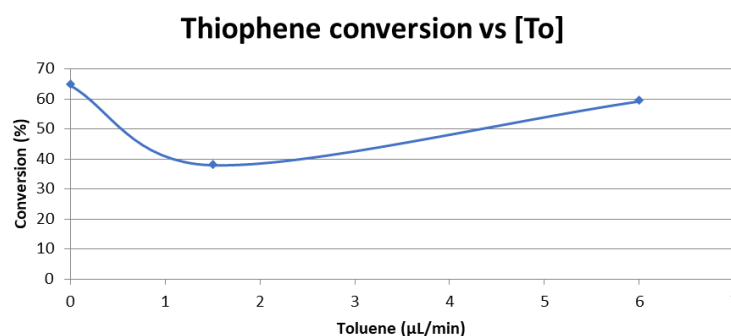


Figure 8. Effect of toluene addition on thiophene conversion (thiophene, 500 ppmv; 20% H_2 in N_2 ; 350 $^\circ\text{C}$; 10 bar; 3500 h^{-1}).

It must be taken into account once again that all the previous studies on thiophene and organic sulfur species removal with this type of sorbent originate from the gasoline desulfurization sector. Therefore, the effect of compounds such as toluene is hardly ever studied in those papers. The only reference found is in the work by Kong and co-workers [50]. They evaluated the reactive adsorption desulfurization over a Ni/ZnO adsorbent preparing a synthetic gasoline blend which had a 15 wt% toluene as an aromatic compound. Its concentration remained close to the initial value, which implies that toluene did not react on the Ni/ZnO adsorbent. Moreover, the inventors of the ConocoPhillips S Zorb gasoline sulfur removal technology [53] claim that their process substantially lowers the sulfur concentration in FCC gasoline without loss of aromatics. From our results, it can be suggested that the Z-Sorb sorbent, close in composition to the S Zorb sorbent, could be used for organic sulfur compound removal from syngas in the presence of tar components without loss of performance.

2.2. Removal of Organic Sulfur Species under Synthetic Syngas

After having proven the reactive adsorption desulfurization concept for thiophene and having determined the effect of temperature, pressure, space velocity, hydrogen content and presence of tar component, toluene, on thiophene removal under simplified reaction conditions, a more realistic study campaign was carried out. The effect of gas blends mimicking full syngas (syngas A and syngas B) on the removal of thiophene as well as that of $\text{CO}-\text{H}_2$ blends (syngas C) was studied. Tar aromatics (toluene) were added. Finally, co-existence of other sulfur species (H_2S , benzo thiophene) under synthetic full syngas conditions was determined.

Three different syngas compositions were prepared from bottled gases. Major syngas compositions were as follows: syngas A: $\text{CO}/\text{CO}_2/\text{CH}_4/\text{H}_2/\text{N}_2$ (32.9/11.2/0.7/29.9/25.3% v/v), syngas B: $\text{CO}/\text{CO}_2/\text{CH}_4/\text{H}_2/\text{N}_2$ (24.2/8.2/0.5/22/45.1% v/v), syngas C: $\text{CO}/\text{H}_2/\text{N}_2$ (40/40/20% v/v). Looking at Figure 9, it can be observed that significant thiophene removal was achieved (conversion from 39% to 75%) using different syngas compositions. None of

the main syngas components, carbon monoxide, hydrogen, carbon dioxide, or methane, seem to have a strong deleterious effect on the performance.

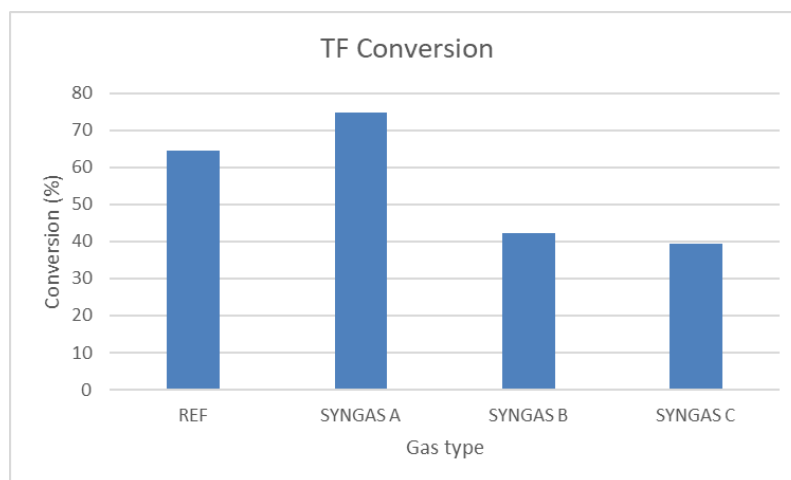


Figure 9. Thiophene conversion under full syngas composition (test series 8 and 9) (350 °C, 3500 h^{−1}, 10 bar, TF 800 ppm, 4 µL/min TOL).

Finally, the combined removal of thiophene, benzothiophene and hydrogen sulfide was studied at 350 °C and 400 °C. The conversion efficiency is plotted in Figure 10. On the horizontal axis, the different cases are presented according to the following legend: thiophene, TF or benzothiophene BTF in the N₂ + H₂ + CO blend; m: simultaneous feeding of thiophene and benzothiophene in the N₂ + H₂ + CO blend; c: simultaneous feeding of H₂S + thiophene + benzothiophene in the N₂ + H₂ + CO blend. Toluene (5850 ppmv) was also added in all tests.

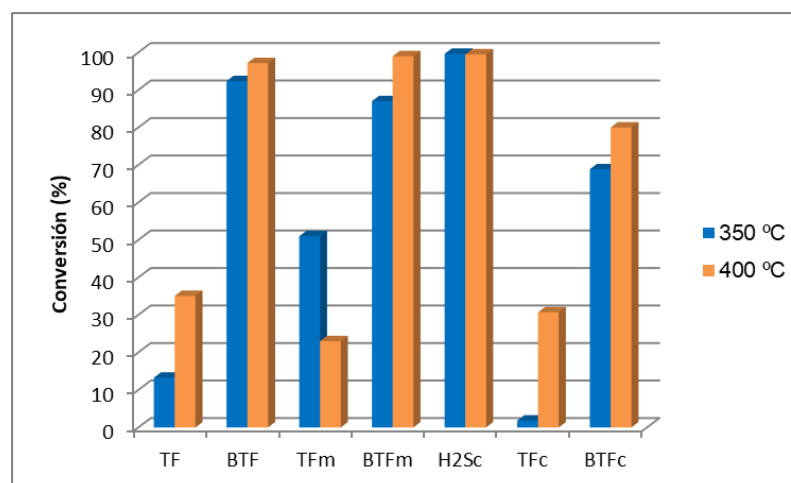


Figure 10. Sulfur organic compound removal under full syngas composition, test series 10, 11 and 12. Operating conditions: 3500 h^{−1}, 10 bar, 5850 ppmv Tol, 20%, H₂, 40% v/v CO, N₂ makeup.

As depicted in Figure 10, better removal efficiencies of organic sulfur compounds were generally achieved on increasing temperature. Upon examination of the removal of the different sulfur species, the following conclusions can be drawn: Hydrogen sulfide was completely removed, both at 350 °C and 400 °C. This result was expected and proceeded via sulfidation of zinc oxide, as shown in previous studies by the authors using the Z-Sorb IIITM sorbent [46,47]. Regarding benzothiophene, almost complete removal at 350 °C and complete removal at 400 °C was achieved when fed as single organic sulfur species (the BTF case). In the presence of thiophene, the BTFm case, the conversion of

benzothiophene decreased at 350 °C (87%) but complete conversion was maintained at 400 °C. In the combined presence of hydrogen sulfide and thiophene, the BTFC case, the removal of benzothiophene was 69% at 350 °C and 80% at 400 °C. Therefore, the presence of H₂S inhibited, to some extent, the abatement of benzothiophene. As for thiophene, the presence of other sulfur species affected its removal. However, no conclusive trends can be established. Thus, at 350 °C, the presence of benzothiophene seems to have a positive effect on thiophene removal, increasing from 13% (TF case) to 51% (TFm case), whereas the presence of hydrogen sulfide (TFc case) inhibits almost completely the removal of thiophene (2%). On the contrary, at 400 °C, the presence of benzothiophene has a negative effect on thiophene conversion, decreasing from 35% for the TF case to 23% for the BTFC case. At that temperature, the presence of H₂S, TFC, has only a slight negative effect on thiophene conversion, which was 30% in the simultaneous presence of H₂S and benzothiophene.

The main conclusion from this study on the combined removal of organic and inorganic sulfur species with the ZnO-NiO sorbent is that the sorbent is capable of removing the different compounds. Inorganic hydrogen sulfide is completely removed, whereas its presence has some impact on the removal of organic sulfur species, benzothiophene and thiophene. Also, benzothiophene affects, to some extent, the removal of thiophene, which might mean a competition for the active sites. For the future, further studies are necessary, including a detailed characterization of the products to establish the desulfurization reactions, the pathways and potential interactions among the different compounds.

3. Materials and Methods

3.1. Experimental Facility

The lab-scale equipment used for the study is a MicroActivity Pro unit, which can be seen schematically in Figure 11. Maximum gas flowrate is 4.5 NL/min and the system allows studying reactions at up to 600 °C and 30 bar. The core of this experimental unit is the interchangeable tubular reactor of 9.2 mm in diameter and 0.3 m in length that is housed in a cylindrical furnace. In this case, a Hastelloy C reactor was used to avoid corrosion problems due to the presence of sulfur compounds. The whole system is housed inside an electrically heated hot box which preheats the gases, vaporizes the liquids and avoids undesirable condensation downstream the reactor. Gases are injected and blended using mass flow controllers, MFCs, while liquids are fed by means of a high performance metering pump, HPLC and syringe pump for organic sulfur and tar compounds. Temperature and pressure are precisely controlled by TIC and PIC devices. A cooling Peltier type (COOL) allows separation of gas and liquids downstream the reactor controlled by a level indicator controller (LIC). A more detailed description of this facility can be found in previous papers published by the authors [14,15].

For the current study, hydrogen and carbon monoxide were fed from pure component bottles. Thiophene was fed as gas diluted in N₂ (2000 ppmv TF). Toluene was fed as liquid. Dibenzothiophene was dissolved in toluene. Also, thiophene was dissolved for some experiments (series 11 and 12). Hydrogen sulfide was fed as bottled gas (9000 ppmv H₂S, nitrogen balance). In addition, bottled gas containing the main compounds present in syngas was used to assess the desulfurization process under gasification gas conditions (44% v/v CO/15% v/v CO₂/1% v/v CH₄/40% v/v H₂).

A computerized system commanded and controlled the process stages: (1) pressurisation and heating to the process temperature under inert atmosphere, (2) desulfurization under the established process conditions including adjusting the composition to the desired values set in Tables 2 and 3 and (3) cooling down and depressurization again under inert atmosphere.

Gas compositions of the reactor inlet and outlet streams were measured online. To that aim, a 7890 A-5975C Agilent GC-FID-SCD, Agilent, Santa Clara, CA, USA, was calibrated and used for monitoring. The gas chromatograph has two channels in parallel consisting of a Flame Ionization Detector, FID for hydrocarbon measurement and a Sulfur Chemiluminescence Detector for selective and accurate sulfur species determination. Channel 1

with the FID detector has a DB-Petro column ($50\text{ m} \times 0.2\text{ mm} \times 0.5\text{ }\mu\text{m}$), and the injector works in a split mode, He: 1 mL/min . Channel 2 with an SCD detector has a DB-Sulfur column ($60\text{ m} \times 0.32\text{ mm} \times 4.2\text{ }\mu\text{m}$). For the analysis, a specific chromatographic method was developed. The injector was kept at $300\text{ }^{\circ}\text{C}$ using a 10:1 split ratio in both channels. Method duration was 21 min, with two temperature ramps, from $50\text{ }^{\circ}\text{C}$, $5\text{ }^{\circ}\text{C/min}$, to $120\text{ }^{\circ}\text{C}$, $10\text{ }^{\circ}\text{C/min}$, up to $180\text{ }^{\circ}\text{C}$; holdup time 1 min.

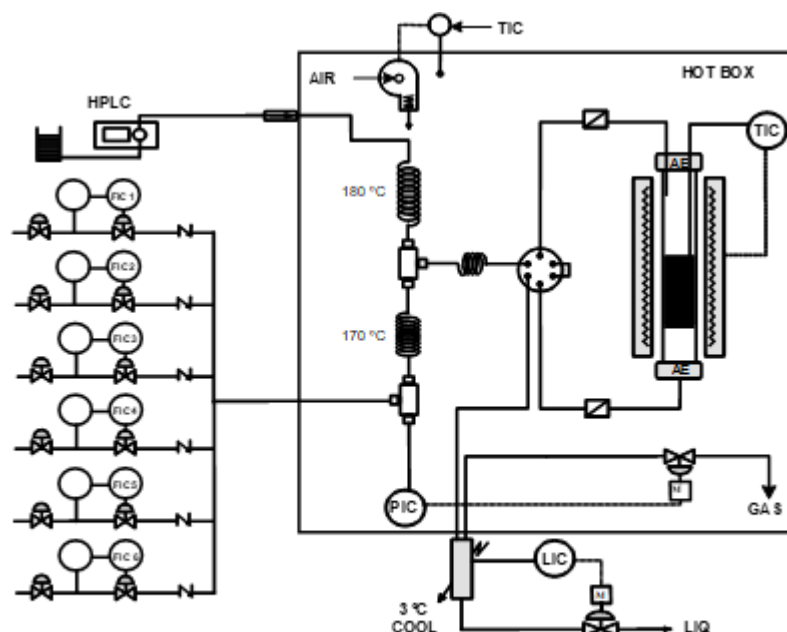


Figure 11. Diagram of the MicroActivity unit used for the experimental tests.

To follow permanent gases, an HP5890 Series II GC, Hewlett-Packard Co., Spring, TX, USA was used. It has a thermal conductivity detector and two columns, a Porapak Q $2\text{ m} \times 1/8''$, Agilent, Santa Clara, CA, USA, and a Molecular Sieve 3 FT, Agilent, Santa Clara, CA, USA, which can be isolated and bypassed. The injector was maintained at $100\text{ }^{\circ}\text{C}$, running an isothermal method at $35\text{ }^{\circ}\text{C}$ for 6 min.

Sampling lines were kept at $200\text{ }^{\circ}\text{C}$ and heated samples were fed directly into the analysis equipment. Injection was carried out in automatic mode by means of gas valves.

3.2. Sorbent

As stated in the introduction section, the scientific goal of this work was to demonstrate that a metal oxide sorbent, comprising zinc oxide and nickel oxide in its formulation, initially manufactured for hydrogen sulfide removal in refinery streams and later from gasification gases, is also capable of removing organic sulfur compounds.

The sorbent was manufactured and provided by Phillips Petroleum Company, later ConocoPhillips under the trade name Z-Sorb IIITM. Currently, novel formulations are commercialized as S-Zorb. The Z-Sorb IIITM sorbent consists of zinc oxide and nickel oxide as a promoter supported on a proprietary matrix designed to provide stability and prolong the sorbent life. According to the Material Safety Data Sheet, it contains a $<50\text{ wt\%}$ zinc oxide and a $<10\text{ wt\%}$ nickel oxide [46]. The sorbent was supplied in pellets of $1/8$ inches (0.32 cm) in diameter and $1/4$ – $3/8$ inches (0.64 – 0.95 cm) in length. The bulk density of the sorbent was 0.88 g/cm^3 . For testing, the sorbent was crushed in an agate mortar and then re-pelletized to 0.5 – 1 mm size using a Specac 15T manual hydraulic press, Orpington, United Kingdom. For each test, the amount of sorbent loaded into the reactor was typically 4.5 g .

4. Conclusions

Designing catalytic deep desulfurization processes to prepare clean fuels is of paramount importance. In order to convert raw gasification gases into gaseous and liquid biofuels, the sulfur content in the feed gas to the dedicated catalytic reactors must usually be around 1 ppmv and sometimes even as low as 0.1 ppmv. Not only inorganic sulfur but also organic sulfur must be reduced to such low levels.

In this work, a zinc–nickel-oxide sorbent originally designed for hydrogen sulfide removal from refinery streams and adapted to syngas treatment has been studied for the first time for thiophene and benzothiophene removal. One major advantage of the designed desulfurization process is that it is a one-stage process compared to the complex several-stage systems used industrially.

By systematically studying the effect of process parameters, operating conditions for complete removal of thiophene and benzothiophene have been determined.

Removal of thiophene and benzothiophene occurred through reactive adsorption consisting of hydrogenation of the organic species and simultaneous capture of hydrogen sulfide. Temperature was found to be the parameter with the strongest effect on desulfurization. Below 300 °C, very little thiophene conversion activity happened, whereas full conversion was achieved at 450 °C. In the case of benzothiophene, 400 °C was enough. Pressure enhanced thiophene removal linearly. Space velocity and available hydrogen showed to have little effect on desulfurization. Other pollutants present in syngas such as tar (toluene as model compound) did not affect removal of thiophene and benzothiophene. Good thiophene conversion was obtained when feeding synthetic syngas mimicking different compositions ranging from air to steam-oxygen-blown gasification. The performance and efficiency of the sorbent in syngas blends containing hydrogen sulfide, thiophene and benzothiophene was acceptable as well.

In summary, this novel process for organic sulfur compound removal from gasification gases holds promise for implementation in biofuel generation.

Author Contributions: Conceptualization, J.S.-H. and I.O.; methodology, I.O. and V.M. investigation, I.O., V.M. and A.A.; writing—original draft preparation, J.S.-H. and A.A.; writing—review and editing, J.S.-H. and I.O.; supervision, J.S.-H.; project administration, J.S.-H.; funding acquisition, J.S.-H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Spanish Ministry of Economy, Industry and Competitiveness, ECOSGAS project, grant number (ENE2016-75811-R) and the Spanish Ministry of Science and Innovation, GONDOLA project, grant number PDC2021-120799-I00.

Data Availability Statement: Data available on request from the authors.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jayakumar, M.; Bizuneh Gebeyehu, K.; Deso Abo, L.; Wondimu Tadesse, A.; Vivekanandan, B.; Prabhu Sundramurthy, V.; Bacha, W.; Ashokkumar, V.; Baskar, G. A comprehensive outlook on topical processing methods for biofuel production and its thermal applications: Current advances, sustainability and challenges. *Fuel* **2023**, *349*, 128690. [\[CrossRef\]](#)
2. Cortazar, M.; Santamaria, L.; Lopez, G.; Alvarez, J.; Zhang, L.; Wang, R.; Bi, X.; Olazar, M. A comprehensive review of primary strategies for tar removal in biomass gasification. *Energy Convers. Manag.* **2023**, *276*, 116496. [\[CrossRef\]](#)
3. Molino, A.; Larocca, V.; Chianese, S.; Musmarra, D. Biofuels production by biomass gasification: A review. *Energies* **2018**, *11*, 811. [\[CrossRef\]](#)
4. Materazzi, M.; Lettieri, P.; Mazzei, L.; Taylor, R.; Chapman, C. Reforming of tars and organic sulphur compounds in a plasma-assisted process for waste gasification. *Fuel Process. Technol.* **2015**, *137*, 259–268. [\[CrossRef\]](#)
5. Held, J. Gasification-Status and technology. *Rapp. SGC* **2012**, *240*, 1102–7371.
6. Peters, D.; Van der Leun, K.; Terlouw, W.; Van Tilburg, J.; Berg, T.; Schimmel, M.; Van der Hoorn, I.; Buseman, M.; Maarten Staats, M.; Mark Schenkel, M.; et al. *Gas Decarbonisation Pathways 2020–2050: Gas for Climate Guidehouse*; Stadsplateau 15: Utrecht, The Netherlands, 2020.
7. Seiffert, M.; Rönsch, S.; Schmiersahl, R.; Zeymer, M.; Majer, S.; Pätz, C.; Kaltschmitt, M.; Rauch, R.; Rehling, B.; Harald Tremmel, H.; et al. *Bio-SNG—Demonstration of the Production and Utilization of Synthetic Natural Gas (SNG) from Solid Biofuels; D 1.4 Finla*

- Project Report, TREN/05/FP6EN/S07.56632/019895 6th Framework Programme; DBFZ German Biomass Research Centre: Leipzig, Germany, 2009; pp. 1–46.
8. Rabou, L.; van Egmond, B.F.; Vreugdenhil, B.J.; van der Drift, A. *Measurement of Organic Sulphur and Nitrogen Compounds in Biomass Producer Gas by SPA Sampling*; ECN: Petten, The Netherlands, 2014.
 9. Hedenskog, M. Experiences of operating the world's first industrial scale bio-SNG facility, GoBiGas. In Proceedings of the 2nd International Conference on Renewable Energy Gas Technology, Barcelona, Spain, 7–8 May 2015.
 10. Struis, R.; Schildhauer, T.J.; Czekaj, I.; Janousch, M.; Biollaz, S.M.A.; Ludwig, C. Sulphur poisoning of Ni catalysts in the SNG production from biomass: A TPO/XPS/XAS study. *Appl. Catal. A Gen.* **2009**, *362*, 121–128. [\[CrossRef\]](#)
 11. Woolcock, P.J.; Brown, R.C. A review of cleaning technologies for biomass-derived syngas. *Biomass Bioenergy* **2013**, *52*, 54–84. [\[CrossRef\]](#)
 12. Aravind, P.V.; De Jong, W. Evaluation of high temperature gas cleaning options for biomass gasification product gas for Solid Oxide Fuel Cells. *Prog. Energy Combust. Sci.* **2012**, *38*, 737–764. [\[CrossRef\]](#)
 13. Prabhansu; Karmakar, M.K.; Chandra, P.; Chatterjee, P.K. A review on the fuel gas cleaning technologies in gasification process. *J. Environ. Chem. Eng.* **2015**, *3*, 689–702. [\[CrossRef\]](#)
 14. Maroño, M.; Ortiz, I.; Sánchez, J.M.; Alcaraz, L.; Alguacil, F.J.; López, F.A. Effective removal of hydrogen sulfide using Mn-based recovered oxides from recycled batteries. *Chem. Eng. J.* **2021**, *419*, 129669. [\[CrossRef\]](#)
 15. Sánchez-Hervás, J.M.; Maroño, M.; Fernández-Martínez, R.; Ortiz, I.; Ortiz, R.; Gómez-Mancebo, M.B. Novel ZnO-NiO-graphene-based sorbents for removal of hydrogen sulfide at intermediate temperature. *Fuel* **2022**, *314*, 122724. [\[CrossRef\]](#)
 16. Rhyner, U.; Edinger, P.; Schildhauer, T.J.; Biollaz, S.M.A. Experimental study on high temperature catalytic conversion of tars and organic sulfur compounds. *Int. J. Hydrogen Energy* **2014**, *39*, 4926–4937. [\[CrossRef\]](#)
 17. Kienberger, T.; Zuber, C.; Novosel, K.; Baumhagl, C.; Karl, J. Desulfurization and in situ tar reduction within catalytic methanation of biogenous synthesis gas. *Fuel* **2013**, *107*, 102–112. [\[CrossRef\]](#)
 18. Zuber, C.; Hochenauer, C.; Kienberger, T. Test of a hydrodesulfurization catalyst in a biomass tar removal process with catalytic steam reforming. *Appl. Catal. B Environ.* **2014**, *156–157*, 62–71. [\[CrossRef\]](#)
 19. Zuber, C.; Husmann, M.; Hochenauer, C.; Kienberger, T. Optimization of the desulfurization step in a catalytic gas cleaning process. In Proceedings of the 23rd European Biomass Conference and Exhibition, Wien, Austria, 1–4 June 2015.
 20. Rabou, L.; Aranda, G. *500 Hours Producing bio-SNG from MILENA Gasification Using the ESME System*; ECN: Petten, The Netherlands, 2015; pp. 1–49.
 21. Li, L.; Ju, F.; Sun, Y.; Pan, H.; Ling, H. Self-sulfidation adsorbent for reactive adsorption desulfurization. *Fuel* **2022**, *313*, 122696. [\[CrossRef\]](#)
 22. Zhang, G.; Xue, P.; Wei, J.; Zhang, Y.; Zhao, L.; Gao, J.; Xu, C. Competitive adsorption mechanism of thiophene with diethyl sulfide in Y zeolite: Displacement and migration. *Chem. Eng. J.* **2022**, *435*, 135141. [\[CrossRef\]](#)
 23. Chen, M.; Chen, J.; Liu, Y.; Liu, J.; Li, L.; Yang, B.; Ma, L. Enhanced adsorption of thiophene with the GO-modified bimetallic organic framework Ni-MOF-199. *Colloids Surf. A Physicochem. Eng. Asp.* **2019**, *578*, 123553. [\[CrossRef\]](#)
 24. Vafaei, F.; Jahangiri, M.; Salavati-Niasari, M. Adsorptive desulfurization of model fuels using ferrite nickel-silica in continuous system: Modelling of breakthrough curves, thermodynamic study and experimental design. *Fuel* **2022**, *327*, 124999. [\[CrossRef\]](#)
 25. Bartholomew, C.H.; Farrauto, R.J. Chapter 9: Petroleum Refining and Processing, Hydrotreating. In *Fundamentals of Industrial Catalytic Processes*, 2nd ed.; Wiley Interscience; John Wiley & Sons Inc. Publisher: Hoboken, NJ, USA, 2006; Volume 2, p. 639.
 26. Sun, H.Y.; Sun, L.P.; Li, F.; Zhang, L. Adsorption of benzothiophene from fuels on modified NaY zeolites. *Fuel Process. Technol.* **2015**, *134*, 284–289. [\[CrossRef\]](#)
 27. Wei, F.; Guo, X.; Liao, J.; Bao, W.; Chang, L. Ultra-deep removal of thiophene in coke oven gas over Y zeolite: Effect of acid modification on adsorption desulfurization. *Fuel Process. Technol.* **2021**, *213*, 106632. [\[CrossRef\]](#)
 28. Shi, Y.; Yang, X.; Tian, F.; Jia, C.; Chen, Y. Effects of toluene on thiophene adsorption over NaY and Ce(IV)Y zeolites. *J. Nat. Gas Chem.* **2012**, *21*, 421–425. [\[CrossRef\]](#)
 29. Edinger, P.; Grimekis, D.; Panopoulos, K.; Karellas, S.; Ludwig, C. Adsorption of thiophene by activated carbon: A global sensitivity analysis. *J. Environ. Chem. Eng.* **2017**, *5*, 4173–4184. [\[CrossRef\]](#)
 30. Saleh, T.A.; Sulaiman, K.O.; Al-Hammadi, S.A.; Dafalla, H.; Danmaliki, G.I. Adsorptive desulfurization of thiophene, benzothiophene and dibenzothiophene over activated carbon manganese oxide nanocomposite: With column system evaluation. *J. Clean. Prod.* **2017**, *154*, 401–412. [\[CrossRef\]](#)
 31. Malone, W.; Kaden, W.; Kara, A. Exploring thiophene desulfurization: The adsorption of thiophene on transition metal surfaces. *Surf. Sci.* **2019**, *686*, 30–38. [\[CrossRef\]](#)
 32. Hernandez, A.D.; Kaisalo, N.; Simell, P.; Scarsella, M. Effect of H₂S and thiophene on the steam reforming activity of nickel and rhodium catalysts in a simulated coke oven gas stream. *Appl. Catal. B Environ.* **2019**, *258*, 117977. [\[CrossRef\]](#)
 33. Wei, F.; Zhang, X.; Liao, J.; Guo, J.; Bao, W.; Chang, L. Desulfurization mechanism of an excellent Cu/ZnO sorbent for ultra-deep removal of thiophene in simulated coke oven gas. *Chem. Eng. J.* **2022**, *446*, 137140. [\[CrossRef\]](#)
 34. Zhang, J.; Liu, Y.; Tian, S.; Chai, Y.; Liu, C. Reactive adsorption of thiophene on Ni/ZnO adsorbent: Effect of ZnO textural structure on the desulfurization activity. *J. Nat. Gas Chem.* **2010**, *19*, 327–332. [\[CrossRef\]](#)
 35. Ryzhikov, A.; Bezverkhy, I.; Bellat, J.P. Reactive adsorption of thiophene on Ni/ZnO: Role of hydrogen pretreatment and nature of the rate determining step. *Appl. Catal. B Environ.* **2008**, *84*, 766–772. [\[CrossRef\]](#)

36. Bezverkhyy, I.; Ryzhikov, A.; Gadacz, G.; Bellat, J.P. Kinetics of thiophene reactive adsorption on Ni/SiO₂ and Ni/ZnO. *Catal. Today* **2008**, *130*, 199–205. [CrossRef]
37. Sun, Y.; Li, L.; Ju, F.; Ling, H. Evolution of nickel species in reactive adsorption desulfurization of benzothiophene. *Sep. Purif. Technol.* **2022**, *283*, 120204. [CrossRef]
38. Liu, J.; Fan, X.-r.; Zhao, W.; Yang, S.-w.; Hu, B.; Yang, S.-g.; Lu, Q. Mechanical insight into the formation of H₂S from thiophene pyrolysis: The influence of H₂O. *Chemosphere* **2021**, *279*, 130628. [CrossRef]
39. Mohseni, E.; Rahmani, A.; Hamdi, Z. Poly (4,4'-methylenedianiline)-graphene oxide nanocomposite: Synthesize and application in removal of benzothiophene from model liquid fuel. *Environ. Monit. Assess.* **2014**, *193*, 737. [CrossRef]
40. Liu, W.; Liu, X.; Yang, Y.; Zhang, Y.; Xu, B. Selective removal of benzothiophene and dibenzothiophene from gasoline using double-template molecularly imprinted polymers on the surface of carbon microspheres. *Fuel* **2014**, *117*, 184–190. [CrossRef]
41. Anca-Couce, A.; von Berg, L.; Pongratz, G.; Scharler, R.; Hochenauer, C.; Geusebroek, M.; Kuipers, J.; Vilela, C.M.; Kraia, T.; Panopoulos, K.; et al. Assessment of measurement methods to characterize the producer gas from biomass gasification with steam in a fluidized bed. *Biomass Bioenergy* **2022**, *163*, 106527. [CrossRef]
42. Hydrocarbon Online. S Zorb Sulfur Removal Technology for Gasoline. Available online: <http://www.hydrocarbononline.com/doc/s-zorb-sulfur-removal-technology-for-gasoline-0001> (accessed on 12 May 2023).
43. Sinopec Tech S ZorbTM Sulfur Removal Technology. Available online: <http://www.sinopectech.com/en/index.php?m=Product&a=show&id=35#:~:text=S%20Zorb%20sulfur%20removal%20technology,the%20dominant%20technology%20applied%20in> (accessed on 25 May 2023).
44. Schmidt, R.; Tsang, A.; Cross, J.; Summers, C.; Kornosky, B. Laboratory simulated slipstream testing of novel sulfur removal processes for gasification application. *Fuel Process. Technol.* **2008**, *89*, 589–594. [CrossRef]
45. Qiu, L.; Zou, K.; Xu, G. Investigation on the sulfur state and phase transformation of spent and regenerated S zorb sorbents using XPS and XRD. *Surf. Sci.* **2013**, *266*, 230–234. [CrossRef]
46. Sánchez, J.M.; Ruiz, E.; Otero, J. Selective removal of hydrogen sulfide from gaseous streams using a zinc-based sorbent. *Ind. Eng. Chem. Res.* **2005**, *44*, 241–249. [CrossRef]
47. Sánchez-Hervás, J.M.; Otero, J.; Ruiz, E. A Study on Sulfidation and Regeneration of Z-Sorb III Sorbent for H₂S Removal from Simulated ELCOGAS IGCC Syngas. *Chem. Eng. Sci.* **2005**, *60*, 2977–2989. [CrossRef]
48. Zhang, Y.; Yang, Y.; Han, H.; Yang, M.; Wang, L.; Zhang, Y.; Jiang, Z.; Li, C. Ultra-deep desulfurization via reactive adsorption on Ni/ZnO: The effect of ZnO particle size on the adsorption performance. *Appl. Catal. B Environ.* **2012**, *119–120*, 13–19. [CrossRef]
49. Lyu, Y.; Sun, Z.; Meng, X.; Wu, Y.; Liu, X.; Hu, Y. Scale-up reactivation of spent S-Zorb adsorbents for gasoline desulfurization. *J. Hazard. Mater.* **2022**, *423*, 126903. [CrossRef]
50. Kong, A.; Wei, Y.; Li, Y. Reactive adsorption desulfurization over a Ni/ZnO adsorbent prepared by homogeneous precipitation. *Front. Chem. Sci. Eng.* **2013**, *7*, 170–176. [CrossRef]
51. Hofbauer, H.; Rauch, R.; Ripfel-Nitsche, K. *Report on Gas Cleaning for Synthesis Applications Work Package 2E: Gas Treatment*; Thermal Net: University of Technology Institute of Chemical Engineering Viena: Vienna, Austria, 2007; pp. 1–75.
52. Fan, J.; Wang, G.; Sun, Y.; Xu, C.; Zhou, H.; Zhou, G.; Gao, J. Research on reactive adsorption desulfurization over Ni/ZnO–SiO₂–Al₂O₃ adsorbent in a fixed-fluidized bed reactor. *Ind. Eng. Chem. Res.* **2010**, *49*, 8450–8460. [CrossRef]
53. Vander Laan, J. ConocoPhillips S Zorb Gasoline Sulfur Removal Technology: Unique Chemistry, Proven Performance, and Optimized Design, ConocoPhillips. Available online: <https://www.yumpu.com/en/document/view/51243737/1-conocophillips-s-zorb-gasoline-sulfur-removal-technology-> (accessed on 22 May 2023).
54. Ito, E.; van Veen, J.A.R. On novel processes for removing sulphur from refinery streams. *Catal. Today* **2006**, *116*, 446–460. [CrossRef]
55. Babich, I.V.; Moulijn, J.A. Science and technology of novel processes for deep desulfurization of oil refinery streams: A review. *Fuel* **2003**, *82*, 607–631. [CrossRef]
56. Tawara, K.; Nishimura, T.; Iwanami, H.; Nishimoto, T.; Hasuike, T. New hydrodesulfurization catalyst for petroleum-fed fuel cell vehicles and cogenerations. *Ind. Eng. Chem. Res.* **2001**, *40*, 2367–2370. [CrossRef]
57. Poels, E.K.; van Beek, W.P.; den Hoed, W.; Visser, C. Deactivation of fixed-bed nickel hydrogenation catalysts by sulfur. *Fuel* **1995**, *74*, 1800–1805. [CrossRef]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.