

Article

Catalyst Screening for Low-Temperature Stabilization of Furfural: Effects of Sulfur Poisoning

Amalie Paarup Krebs ¹, Rui Pedro da Cruz ¹, Martin Høj ¹, Magnus Zingler Stummann ², Lived Yegres Lemus-Olsen ² and Anker Degn Jensen ^{1,*}

¹ DTU Department of Chemical and Biochemical Engineering, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

² Topsoe A/S, 2800 Kongens Lyngby, Denmark

* Correspondence: aj@kt.dtu.dk

Abstract

Biomass-derived fast pyrolysis oil (PO) represents a promising alternative fuel for aviation and heavy transport. However, its high content of oxygenated organic molecules necessitates catalytic hydrodeoxygenation (HDO) before it is viable to be sent to a refinery. Single-step upgrading processes have encountered significant challenges, particularly reactor plugging and catalyst deactivation. To address these issues, an initial stabilization step at lower temperatures has been proposed to stabilize the most reactive compounds in the oil prior to hydrodeoxygenation. In this study, a range of different carbon- and Al₂O₃-supported catalysts (Ni/Al₂O₃, sulfided NiMo/Al₂O₃, Ru/C, Pd/C, Pd/Al₂O₃, Pt/C, and Pt/Al₂O₃) were evaluated for furfural stabilization in a batch reactor for 1 h with an initial pressure of 90 bar H₂ and 180 °C with and without sulfur present. Sulfur tolerance was assessed by repeating all experiments with the addition of 1170 wt-ppm sulfur to the feedstock. The most active catalysts—Ni/Al₂O₃, Ru/C, Pd/C, and Pd/Al₂O₃—also exhibited the highest susceptibility to sulfur poisoning. Although Pt/C did not demonstrate the highest overall activity, sulfur addition appeared to enhance its performance, both in terms of furfural conversion and liquid yield of desired products.

Keywords: stabilization; pyrolysis oil upgrading; sulfur poisoning; model compounds; catalyst deactivation; batch experiments; catalyst screening

1. Introduction

Climate change presents a significant challenge to the long-term sustainability of human society. To meet the targets outlined in the Paris Agreement, substantial reductions in greenhouse gas emissions are required across all sectors [1]. According to Eurostat, the transportation sector accounted for approximately 31% of total energy consumption within the European Union in 2022 [2]. While electrification has gained traction in the light-duty vehicle segment, the aviation and heavy-duty transport sectors continue to rely on fossil-based fuels. In these areas, the development of sustainable, energy-dense alternatives is essential to reducing dependence on fossil resources [3].

Sustainably sourced liquid hydrocarbons are viable alternatives for sectors such as aviation and heavy-duty transport due to their high energy density and compatibility with existing infrastructure. Biomass offers a renewable carbon source, and one promising conversion route is pyrolysis. In particular, fast pyrolysis enables the optimal production of a liquid bio-oil by rapidly heating biomass in the absence of oxygen, thereby maximizing



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liquid yield and minimizing char and gas formation [4,5]. Nevertheless, the resulting pyrolysis oil (PO) is a complex mixture containing a wide array of different organic compounds, most of which are oxygenated. The high oxygen content—reaching up to 45 wt% on a wet basis—contributes to several undesirable properties, including reduced heating value, elevated acidity, and poor thermal stability. These properties pose challenges for direct utilization and necessitate further upgrading to make POs viable for fuel purposes.

There are different methods of upgrading biomass-derived fast POs to lower the oxygen content and improve fuel properties. One approach is hydrodeoxygenation (HDO), a process where oxygen is removed from the oil with hydrogen over a catalyst at elevated temperatures and pressures (up to 400 °C and 200 bar, respectively) [6,7]. However, many have reported issues with the upgrading process when conducting it in a single step, including catalyst deactivation and reactor plugging due to coke formation [8,9]. The high content of carbonyl compounds in these oils has been reported to be a major factor in coke formation during heating, due to their tendency to polymerize [6]. Therefore, a two-step process has been proposed, where the pyrolysis oil is stabilized by hydrogenation (HYD) during the first step at temperatures below 200 °C before the actual HDO in the second step [10]. Despite many years of research on the subject, suitable catalysts have not yet been commercialized [3,11,12].

Different types of catalysts have been studied for the stabilization step. In general, they can be divided into three different categories: sulfided conventional hydrotreating catalysts, reduced base metal catalysts (in particular Ni), and reduced noble metal catalysts. Sulfided NiMo and CoMo catalysts are well-established in fossil fuel refining, particularly for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) processes [3,13]. Their proven ability to remove sulfur and nitrogen from petroleum fractions makes them logical candidates for hydrodeoxygenation of biomass-derived pyrolysis oils (POs). While these catalysts do exhibit activity towards HDO, studies suggest that such catalysts require higher temperatures than the mild conditions required during the stabilization step [14]. Additionally, continuous operation over extended periods of time has revealed operational challenges, including significant coke formation and catalyst deactivation [15]. Furthermore, sulfided catalysts require a minimum sulfur content in the feed to maintain catalytic activity over time. Since bio-based pyrolysis oils typically contain sulfur levels below this threshold [3,16,17], sulfur must be externally introduced to sustain catalyst performance. This requirement, however, does not pose a major practical limitation, as sulfur can be added directly to the feed or recovered and recycled from the product gas stream to achieve the necessary concentration in the feed.

Due to the abundance and low price of nickel, metallic Ni catalysts have gained interest for the stabilization of PO [15,18–25]. Furthermore, they are active at relatively low temperatures and can catalyze both HYD and HDO, as shown by numerous studies over the last decades [22,23,26,27]. Han et al. [27] investigated the mild catalytic hydrotreatment of PO over a Ni/SiO₂ catalyst using a mix of three different model compounds: hydroxyacetone, furfural, and phenol. The Ni/SiO₂ catalyst was successful in converting all model compounds; however, the experiments revealed that furfural had an inhibitory effect on the conversion of both hydroxyacetone and especially phenol.

Noble metal catalysts such as ruthenium, palladium, and platinum, on various support materials, have been investigated for the stabilization of PO [28,29]. Their primary advantage lies in their high catalytic activity for both HYD and HDO at low temperatures [21,30], making them attractive for mild upgrading processes. However, these catalysts are susceptible to poisoning by sulfur compounds, which are present in bio-derived PO at concentrations ranging from 45 to 1153 ppm [17]. In addition to this sensitivity, the scarcity and high cost of noble metals further limit the feasibility of using noble metal catalysts

in large-scale PO stabilization. As a result, despite their excellent activity, noble metal catalysts are considered less viable for industrial implementation in bio-oil upgrading.

Although model compound experiments are not able to fully replicate the complexity of real PO, they offer unique and valuable insight into the reaction mechanisms that may occur during hydrotreatment. Consequently, numerous studies have employed model compounds to investigate catalytic upgrading pathways and inform the design of more effective processes for real bio-oil feeds [22,27,31].

In this work, we study the impact of sulfur on catalyst activity for the conversion of furfural in a batch reactor for a wide array of catalysts. Furfural was chosen as the model compound since it is important to convert it during the stabilization step, due to its high propensity for polymerization. The chosen catalysts span all three mentioned categories for active materials, i.e., reduced noble metals, reduced base metals, and sulfided metals. Both Al_2O_3 and carbon were employed as support materials to assess the influence of the support on catalytic performance.

2. Materials and Methods

2.1. Materials

Furfural and dodecanethiol (used as a sulfur source) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Noble metal catalysts were purchased from Sigma-Aldrich and pre-reduced high-loaded (>25 wt%) Ni/ Al_2O_3 (quadrilobed extrudates) and pre-sulfided NiMo/ Al_2O_3 catalysts (trilobed extrudates) were supplied by Topsoe A/S (Kongens Lyngby, Denmark, previously described in [14,32]). A list of all catalysts can be seen in Table 1.

Table 1. List of catalysts used in the experiments.

Catalyst	Loading	Supplier
Ni/ Al_2O_3	>25 wt%	Topsoe
Sulfided NiMo/ Al_2O_3	-	Topsoe
Ru/C	5 wt%	Sigma-Aldrich
Pd/C	5 wt%	Sigma-Aldrich
Pd/ Al_2O_3	5 wt%	Sigma-Aldrich
Pt/C	5 wt%	Sigma-Aldrich
Pt/ Al_2O_3	5 wt%	Sigma-Aldrich

2.2. Experimental Setup

The experiments were performed in a lab-scale batch reactor setup (500 mL autoclave, Parr 4575 HP/HT pressure reactor with a Parr 4848 reactor controller) as previously described [14,32] (see photograph in Figure S1). The reactor was loaded with 50 g of furfural and 2 g of the catalyst. For the experiments with sulfur addition, 0.37 g of dodecanethiol (corresponding to 1170 wt-ppm S) was added (see Table S1 for overview of experiments). The reactor was flushed with nitrogen to remove air and then pressurized to 90 bar with hydrogen gas. Under stirring, the reactor was heated to the reaction temperature (180 °C, heating rate on average 6.3 °C/min), where it was kept for 1 h. Afterward, it was externally quenched in an ice bath. The stirrer was turned off, the pressure reduced to 20 bar, and a gas sample was taken for GC analysis. The reactor was unloaded, weighed, and the liquid and catalyst were separated by gravity filtration. The retrieved catalyst was subsequently washed with acetone and dried in air.

2.3. Analysis Methods

2.3.1. Gas Chromatography

Both gas and liquid samples were analyzed using gas chromatography. The gas phase was analyzed with a Global Analyzer Solutions (GAS) (Breda, Holland) assembled Thermo

Fisher Trace 1300 GC (Thermo Fisher, Waltham, MA, USA) with three detectors: two TCDs and one FID. One TCD was used to quantify H_2 , the other to quantify CO , CO_2 , and N_2 (both using micro-packed columns). An Agilent (Santa Clara, CA, USA) J&W HP-PLOT Al_2O_3 S column (25 m long, inner diameter of 0.53 mm, and a layer thickness of 10 μm) was used for hydrocarbon analysis on the FID together with a backflush column Restek Rtx–1.5 m long, 0.53 mm ID, and 4 μm layer (as described in [33]). The FID was used to quantify C_1 to C_5 hydrocarbons individually and C_{6+} as a combined group. The GC was calibrated using certified calibration gases as external standards.

The liquid phase was analyzed using an Agilent 7890B GC (Agilent, Santa Clara, CA, USA) with FID and a 5977B MSD (Agilent, Santa Clara, CA, USA). Each sample was diluted in ethyl acetate (1:9) prior to injection. The carrier gas was Helium, the split ratio was 20.5:1, and the injection volume was 1 μL . Compound identification was done on the basis of the GC-MS, while the GC-FID was used for quantification. Calibration was done with the following chemical standards: furfural, furfuryl alcohol, and 2-methylfuran. The quantification of other compounds was done using the FID response factors calculated based on ref. [34].

2.3.2. XRF

The catalyst compositions were analyzed by XRF on a Series 2 Puma from Bruker, with a silver anode and an energy dispersive HighSense XP detector. The spot size was limited to 18 mm with a collimating mask and the samples were loaded in 20 mm plastic sample cups with 4 μm polypropylene foil. Quantification was done using Bruker's standardless methods in the Spectra Elements software (v3.2.42.0).

2.3.3. Elemental Analysis

Elemental analysis of the carbon content of the Al_2O_3 -supported catalysts was performed on a Thermo Scientific FlashSmart CHNS/O Elemental Analyzer (Thermo Scientific, Waltham, MA, USA). For each measurement, 2–3 mg of sample was weighed into tin capsules, sealed, and deposited in the autosampler. The combustion was carried out at 950 $^{\circ}C$ in an oxygen-rich environment, followed by reduction in the combustion gases in a separate reactor held at 530 $^{\circ}C$. Helium was used as the carrier gas at a flow rate of 140 mL/min. All spent catalysts were analyzed in triplicate and compared to the fresh catalysts. Quantification of C, H, N, and S was performed using 2,5-bis(5-tert-butyl-2-benzoxazolyl)thiophene (BBOT STD, Thermo Scientific, Waltham, MA, USA) as calibration standard. The gases CO_2 , H_2O , SO_2 , and N_2 were separated on the chromatographic column prior to detection via TCD. Elemental analysis was calculated based on the peak areas relative to the BBOT standard and subsequently reported as weight percentages.

2.3.4. X-Ray Diffraction

The structural changes in the catalysts and the formation of metal sulfides were investigated by X-ray diffraction (XRD), using a Panalytical X'Pert Pro instrument (Worcestershire, UK) in Bragg–Brentano geometry working in reflectance mode, using CuK_{α} radiation ($\lambda = 1.541 \text{ \AA}$), as previously described in [32]. The instrument is equipped with a monochromator, soller-, divergence- and anti-scatter slits. The analysis was conducted at Topsoe A/S. A portion of a powder sample was mounted in a standard XRD holder. The sample was measured in a horizontal spinning sample stage over the 2θ scan range from 5° to 70° , with a 0.017° step size in ambient air. The resulting diffraction pattern was analyzed using the X'Pert Highscore Plus software (v5.2) from Panalytical. The measured pattern matched the reference lines from a powder diffraction database file (PDF4+). Rietveld analyses were performed using the Topas Software (v6).

2.3.5. BET Surface Area

For the alumina-supported catalysts, BET surface areas were determined by the multipoint method on a 3P Instruments Sync440 (3P Instruments GmbH & Co. KG, Odelzhausen, Bayern, Germany) employing N₂. For the carbon-supported catalysts, surface areas were determined by multipoint N₂ adsorption/desorption on a Quantachrome Autosorb iQ2 (Quantachrome Instruments, Boynton Beach, Florida, USA) with the ASiQwin software (v5.23).

2.4. Calculations

Hydrogen consumption (in mmol/g feed) was calculated based on the change in pressure before and after each experiment (at room temperature) and the fraction of H₂ gas in the gas sample taken at the end of the experiment:

$$\text{H}_2 \text{ consumption} = \frac{(p_{i,\text{room T}} - p_{f,\text{room T}} \cdot x_{\text{H}_2,f}) \cdot V_{\text{gas,reactor}}}{R \cdot T_{\text{room}}} \cdot \frac{1}{m_{\text{FU}}} \quad (1)$$

where $p_{i,\text{room T}}$ is the initial pressure at room temperature, $p_{f,\text{room T}}$ is the final pressure at room temperature, $x_{\text{H}_2,f}$ is the H₂ fraction of the final gas phase, $V_{\text{gas,reactor}}$ is the volume of gas in the reactor, m_{FU} is the mass of furfural, R is the gas constant, and T_{room} is the room temperature.

The yield of each gas product in C% of the feed was calculated from the final pressure and gas analysis:

$$Y_{\text{gas prod}} [\text{C}\%] = x_{\text{prod}} \cdot \frac{p_{f,\text{room T}} \cdot V_{\text{gas,reactor}}}{R \cdot T_{\text{room}}} \cdot \frac{N_{\text{C}}}{n_{\text{C,FU}}} \cdot 100\% \quad (2)$$

where x_{prod} is the molar fraction of the product gas in the gas phase, $p_{f,\text{room T}}$ is the final pressure at room temperature, $V_{\text{gas,reactor}}$ is the volume of gas in the reactor, R is the gas constant, T_{room} is the room temperature, N_{C} is the number of carbon atoms in the product molecule, and $n_{\text{C,FU}}$ is the amount of C in the feed.

The conversion was calculated from the furfural concentration determined by GC-FID:

$$X_{\text{FU}} [\%] = \frac{c_{\text{FU},f}}{c_{\text{FU},i}} \cdot 100\% \quad (3)$$

The yield of a liquid phase product was likewise calculated from the concentrations determined by GC-FID and the calculated FID response factors, calculated based on ref. [34]:

$$Y_{\text{liq prod}} [\text{C}\%] = c_{\text{prod}} \cdot V_{\text{liq},f} \cdot M_{\text{prod}} \cdot \frac{N_{\text{C}}}{n_{\text{C,FU}}} \cdot 100\% \quad (4)$$

where c_{prod} is the concentration of the product, $V_{\text{liq},f}$ is the volume of the liquid product, M_{prod} is the molar mass of the product, N_{C} is the number of carbon atoms in the product molecule, and $n_{\text{C,FU}}$ is the amount of C in the feed.

Mears' criterion, the Weisz–Prater number, and the effectiveness factor were calculated as well to address mass transfer limitations, and can be seen in Supplementary Section S1 [35–39].

3. Results and Discussion

3.1. Conversion of Furfural

All catalysts listed in Table 1 were evaluated according to the conditions outlined in Table S1 (see Figure S2 for mass balances). Figure 1 (see data in Tables S2 and S3) presents the hydrogen consumption plotted against furfural conversion for each catalyst, comparing experiments without sulfur addition (Figure 1A) and with sulfur present in the

feed (Figure 1B). The theoretical hydrogen consumption for the conversion of furfural to furfuryl alcohol (indicated in blue in Figure 2) and to tetrahydrofurfuryl alcohol (red) is plotted as reference lines in Figure 1, relative to furfural conversion. These lines are shown alongside the experimental data to facilitate comparison between observed and expected hydrogen uptake. As shown in Figure 2, furfuryl alcohol is a product that can be considered as an intermediate compound in polymerization reactions, and, therefore, it was deemed advantageous to not only reduce the carbonyl group to an alcohol but also hydrogenate the furan ring to mitigate these polymerizations. The apparent reaction rates were calculated based on the initial and final amount of furfural in each experiment (see Table S8) and used to investigate mass-transfer limitations (Supplementary Section S1), since the Ni/Al₂O₃ and sulfided NiMo/Al₂O₃ catalysts were in extruded form, while all other catalysts were powders. The calculations revealed Ni/Al₂O₃ to be the most affected by mass-transfer limitations (effectiveness factor of 0.76 for the experiment without sulfur and 0.93 with sulfur) and the sulfided NiMo/Al₂O₃ to only be slightly more affected (effectiveness factor ~0.97 regardless of sulfur addition) than the powder catalysts (effectiveness factors ~1 regardless of sulfur addition; see all results in Table S10).

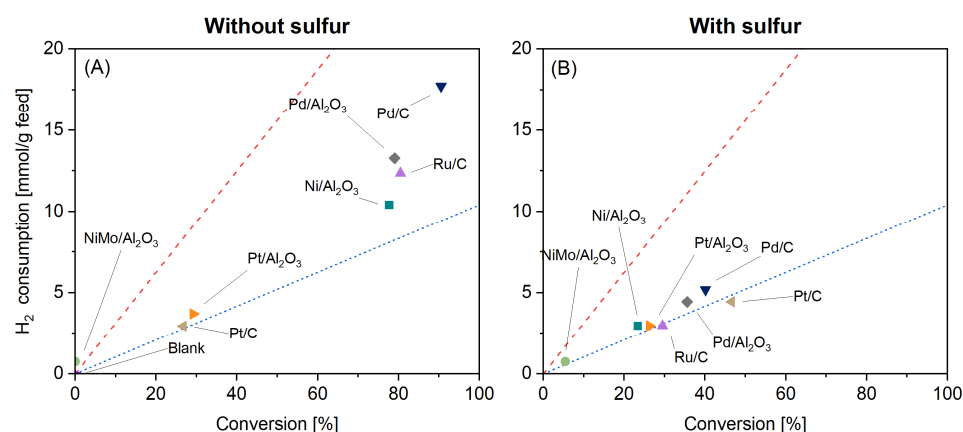


Figure 1. Hydrogen consumption plotted against the conversion of furfural for all experiments (A) without sulfur, and (B) with 1170 wt-ppm sulfur added to the feed. The theoretical H₂ consumption is plotted as lines for the following reactions: furfural to furfuryl alcohol (blue, 100% conv. = 20.8 mmol H₂/g furfural) and to tetrahydrofurfuryl alcohol (red, 100% conv. = 31.2 mmol H₂/g furfural).

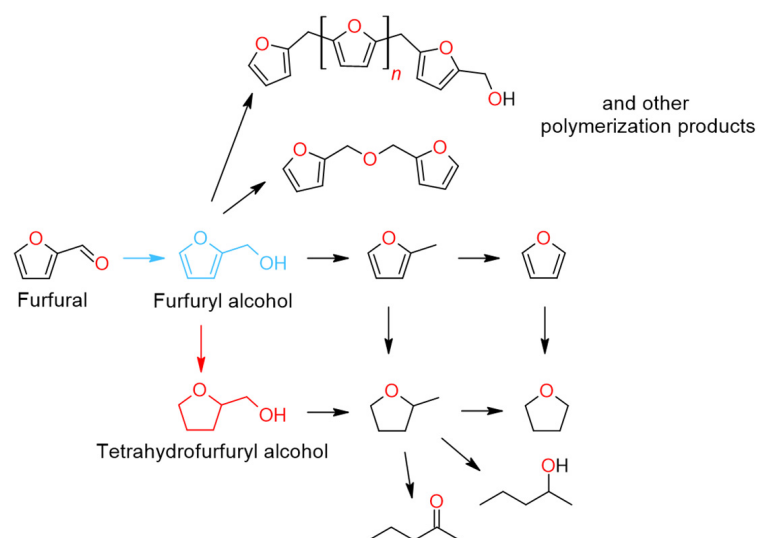


Figure 2. Overview of furfural and some of the possible products that can be formed during stabilization based on GC-MS results and previous studies [27,33,40]. The colored structures correspond to

the theoretical hydrogen consumption plotted as lines in Figure 1 for the hydrogenation of furfural to furfuryl alcohol (blue, dotted) and tetrahydrofurfuryl alcohol (red, dashed).

The blank experiment had a hydrogen consumption of 0 mmol/g feed and no conversion. The experiment with the sulfided NiMo/Al₂O₃ catalyst without sulfur addition showed a slightly higher hydrogen consumption (0.7 mmol/g feed) but no measurable conversion of furfural. However, in the case of sulfur addition, the conversion increased to 5.4% while the hydrogen consumption stayed the same, thus indicating that a small amount of sulfur in the feed was beneficial for the sulfided NiMo/Al₂O₃ catalyst. Similarly, Bouvier et al. [41] observed that an increase in the partial pressure of H₂S resulted in an increase in hydrogenation (HYD) and acid-catalyzed activity, although direct deoxygenation (DDO) remained relatively consistent regardless of the partial pressure of H₂S. Those experiments were, however, performed at a higher temperature (340 °C), and as the conversion from these experiments was not high in either of the experiments in this study, the most evident conclusion was that the sulfided NiMo/Al₂O₃ was not active at the used conditions, regardless of sulfur addition. This is in line with previous studies, where sulfided NiMo/Al₂O₃ is usually employed at higher operating temperatures [14,32,42].

Among the tested catalysts, the two platinum catalysts (Pt/C and Pt/Al₂O₃) exhibited intermediate levels of furfural conversion. The Pt/Al₂O₃ catalyst showed slightly higher conversion and hydrogen consumption compared to Pt/C, with values of 29% vs. 27% conversion, and 3.69 mmol/g feed versus 2.94 mmol/g feed, respectively. For both catalysts, the observed hydrogen consumption aligned with the theoretical hydrogen consumption for the hydrogenation of furfural to furfuryl alcohol. When sulfur was introduced into the feed, the Pt/Al₂O₃ catalyst exhibited only a slight decrease in furfural conversion (26% compared to 29%), while hydrogen consumption dropped by approximately 20%, from 3.69 to 2.95 mmol/g feed. This suggests partial inhibition of hydrogenation activity, likely due to sulfur poisoning. In contrast to the Al₂O₃-supported Pt catalyst, the Pt/C catalyst responded positively to sulfur addition, with furfural conversion increasing from 27% to 47% and hydrogen consumption rising to 4.43 mmol/g feed. This unexpected positive effect may indicate a promoting effect of sulfur on the carbon support surface interaction with Pt. This should be further investigated, preferably on a continuous setup to study whether this possibly promoting effect could be sustained long-term.

The Ni/Al₂O₃ catalyst demonstrated relatively high activity in the absence of sulfur, achieving a furfural conversion of 78% and a hydrogen consumption of 10.4 mmol/g feed. The level of hydrogen uptake at this conversion corresponds to partial hydrogenation beyond furfuryl alcohol, by comparison with theoretical hydrogen consumption lines. Upon sulfur addition to the feed, the catalyst performance declined significantly. Furfural conversion dropped to 23%, and hydrogen consumption decreased by approximately 72%, reaching 2.95 mmol/g feed. This significant reduction in activity and hydrogen uptake indicates strong sulfur-induced deactivation, likely due to poisoning of active sites on the nickel surface [32,43,44].

Two different palladium catalysts were tested (Pd/C and Pd/Al₂O₃) and both exhibited excellent activity towards converting furfural, with the Pd/C catalyst being the best (91% vs. 79%). The two highest hydrogen consumptions were achieved using the two palladium catalysts without sulfur added to the feed (17.7 and 13.3 mmol/g for Pd/C and Pd/Al₂O₃, respectively), showing that these catalysts were exceptionally good at facilitating the hydrogenation of furfural. However, the addition of sulfur vastly reduced the hydrogen consumption (5.17 and 4.43 mmol/g furfural for Pd/C and Pd/Al₂O₃, respectively) as well as the conversion (40% and 36% for Pd/C and Pd/Al₂O₃, respectively). This is in agreement with the literature on palladium catalysts, which not only supports

the excellent hydrogenation activity of the catalyst [21] but also the observed susceptibility to sulfur poisoning [45,46].

Lastly, the Ru/C catalyst, a type of catalyst often used as a benchmark in similar studies [23–25,47], showed a high conversion (81%) and hydrogen consumption (12.4 mmol/g feed) with no sulfur in the feed. However, the addition of sulfur significantly diminished both of these measures of activity to 30% and 2.96 mmol/g feed, respectively. As with the palladium catalysts, this is in agreement with the literature on the topic, as Ru/C is known to facilitate high conversions but also deactivate in the presence of sulfur [12,40].

3.2. Products

Figure 3 and Table S4 show the gas yield and product distribution for all experiments without (left columns) and with sulfur (right columns) added to the feed. In general, the loss of carbon to the gas phase was very low (below 0.5 C%), except for the sulfur-free experiment with the Ru/C catalyst, where over 1 C% was lost to the gas phase, primarily as methane. This is likely in relation to the high activity of the catalyst and serves to show that a high conversion may lead to unwanted reactions, such as loss of carbon to the gas phase. Furthermore, the Ru/C catalyst is a known methanation catalyst and it should therefore be expected to produce a higher amount of methane compared to the other tested catalysts [48]. The distribution of gas products varied slightly depending on both catalyst and the presence of sulfur, but, in general, only CO₂, C₁ to C₃ paraffins, and low amounts of heavier volatile hydrocarbons (denoted C₆₊) were detected. C₂ to C₅ olefins and C₄ to C₅ paraffins were not detected, and CO was only detected in the case of the sulfur-free experiment with Ni/Al₂O₃ (0.091 C%), where it was also the main product, followed by methane (0.070 C%) and C₆₊ (0.067 C%). With the addition of sulfur, the total gas yield decreased from 0.28 C% to 0.17 C%, which correlates well with the lower activity. Furthermore, the main gas product changed to CO₂ (0.097 C%), followed by C₆₊ (0.063 C%). The experiments conducted with the sulfided NiMo/Al₂O₃ resulted in very low gas yields in general, though the experiment with sulfur addition did result in a slightly larger yield (0.048 and 0.52 C% without and with sulfur, respectively). Of the two palladium catalysts, the Pd/C produced the most gas in the sulfur-free experiments (0.085 C% vs. 0.054 C%), with the majority being CO₂ (0.083 C%). However, the addition of sulfur resulted in an increased gas production for both Pd catalysts in spite of the lower furfural conversion and hydrogen consumption. While the main gas product for Pd/C remained CO₂ (0.076 and 0.064 C% without and with sulfur, respectively), a shift in main gas product was observed from C₆₊ (remained at 0.031 C%) to CO₂ (increased from 0.022 to 0.059 C% with the addition of sulfur) for Pd/Al₂O₃.

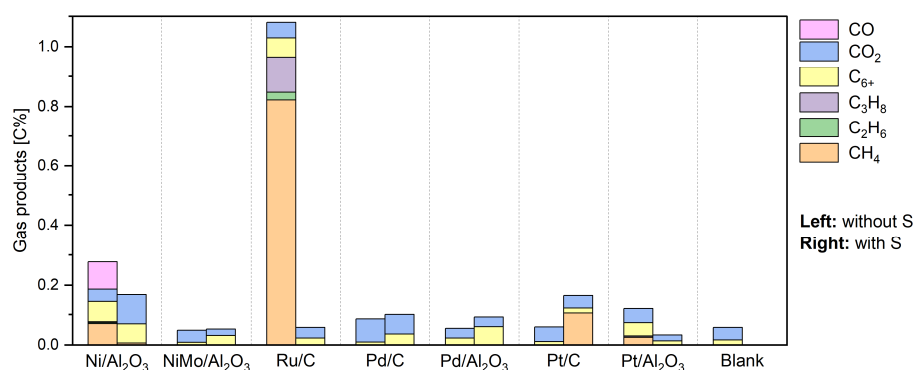


Figure 3. Gas products for all experiments without sulfur (left columns), and with sulfur (right columns) added to the feed. Calculated from gas analysis and change in pressure before and after the experiment. All experiments were conducted with 2 g of catalyst and 50 g of furfural with an initial pressure of 90 bar H₂ (at room temperature), at 180 °C for 1 h.

Similarly, the sulfur experiment with the Pt/C catalyst also had a higher gas production compared to the sulfur-free experiment (0.16 vs. 0.059 C%, respectively). However, for this catalyst, the increase in gas production correlates with an increase in furfural conversion (see Figure 1). This may also explain the shift from CO₂ to methane as the primary gas product. The gas yield was likewise low for both experiments with Pt/Al₂O₃, though higher for the sulfur-free experiment (0.12 vs. 0.033 C%), which was in agreement with the slightly higher conversion for the sulfur-free experiment shown in Figure 1. The main gas products in both the experiment without and with sulfur added were C₆₊ (0.044 and 0.016 C%, respectively), and CO₂ (0.046 and 0.020 C%, respectively). Finally, for the blank experiment, only a small amount of C₆₊ (0.016 C%) and CO₂ (0.042 C%) was detected.

In Figure 4, the GC detected liquid yield for all experiments is shown, with the full data set given in Tables S5 and S7. Even though the conversion for the different experiments spanned from 0 to 90.5%, the total liquid yield never exceeded 35 C%. This can be partially attributed to the formation of larger non-volatile products not detectable by GC (see GC detected mass balance in Figure S3). For all sulfur-free experiments (except for the sulfided NiMo/Al₂O₃), the main product is furfuryl alcohol. For the experiments with the noble metal (Pd, Pt and Ru) catalysts in the presence of sulfur, the main product remained furfuryl alcohol. For the sulfur-free experiment with Ni/Al₂O₃, the total GC-detected liquid yield amounted to 31.6 C% of the carbon in the feed. Furfuryl alcohol was the main product (21 C%) with 2-methyl furan (4.2 C%) and tetrahydrofurfuryl alcohol (2.5 C%) as the secondary and tertiary products. A significant amount of furfural-derived dimers was also produced (3.0 C%). Along with the smaller amount of trimers (0.93 C%), this shows that some polymerization occurred alongside the hydrogenation. The addition of sulfur significantly reduced the GC-detected liquid yields. This was expected, since the much lower conversion (Figure 1B) resulted in low overall yield. Furthermore, the lower total yield of GC-detectable products may also be a consequence of the formation of larger polymerization molecules due to a lower catalyst activity. While the product selectivity did not change much, the amount of products did, with the GC detected total liquid yield only amounting to 6.8 C% when sulfur was present in the feed.

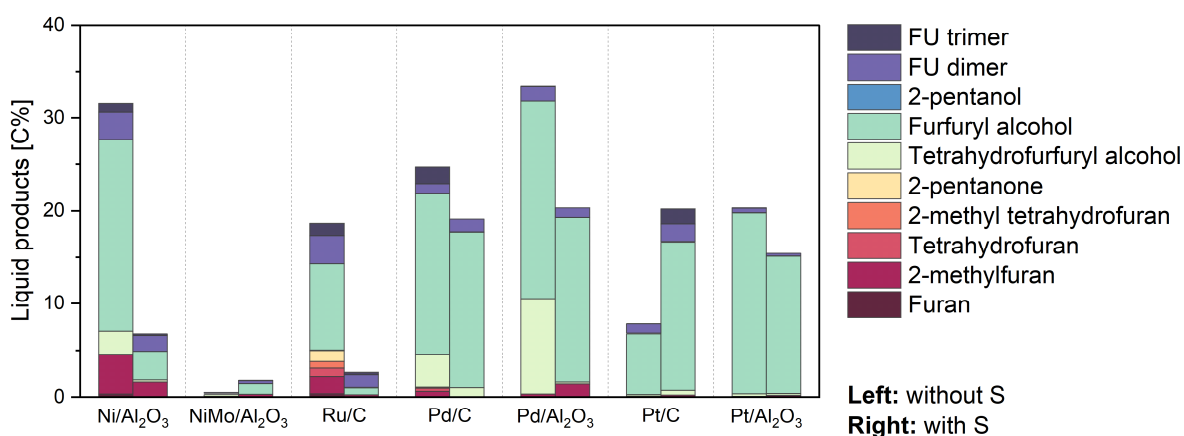


Figure 4. Yield from all experiments without sulfur (**left**), and with sulfur (**right**) added to the feed. Some products were grouped into the following groups for a better overview: FU dimer (7 different furfural-derived dimers) and FU trimer (2 different furfural-derived trimers). All experiments were conducted with 2 g of catalyst and 50 g of furfural with an initial pressure of 90 bar H₂ (at room temperature), at 180 °C for 1 h.

In accordance with the low conversion and hydrogen consumption for the experiments with the sulfided NiMo/Al₂O₃, both without and with sulfur added, the yields were also very low. For the experiment without sulfur added, only small amounts of 2-methyl

furan (0.071 C%), tetrahydrofurfuryl alcohol (0.19 C%), and a dimer (2-(2-furanylmethyl)-5-methyl furan, 0.080 C%) were detected. For the experiment with sulfur, the overall yield was slightly larger (1.8 vs. 0.51 C%), and a slight change in products was observed as well. The main product shifted from tetrahydrofurfuryl alcohol to furfuryl alcohol (1.1 C%), and the amounts of both 2-methyl furan and the dimer increased (0.30 C% in both cases). Furthermore, a trimer was also detected for this experiment (2,2'-(2-furylmethylene)bis(5-methyl furan), 0.030 C%). So, while the addition of sulfur did increase the conversion for the sulfided NiMo/Al₂O₃, the products were less hydrogenated compared to those without sulfur.

When looking at the yield for the Ru/C, the difference between the yield from the two experiments is significant (19 vs. 2.6 C%), though not surprising given the difference in conversion, as seen in Figure 1 (80.5 vs. 29.5%). The primary product in the sulfur-free experiment was furfuryl alcohol (9.28 C%), with the secondary products being the different dimers (3.06 C%). For the experiment with sulfur, the primary product shifted to the dimers, indicating that more polymerization and less hydrogenation took place. This is also in accordance with the much lower hydrogen consumption (see Figure 1).

Both of the Pd catalysts had a high conversion in the experiments without sulfur, and this is reflected in the yields. For both catalysts, the primary product was furfuryl alcohol (Pd/C: 17 C%, Pd/Al₂O₃: 21 C%), followed by tetrahydrofurfuryl alcohol (Pd/C: 3.5 C%, Pd/Al₂O₃: 10 C%). While small amounts of furan (0.014 C%), 2-methylfuran (0.61 C%), tetrahydrofuran (0.34 C%), and 2-methyl tetrahydrofuran (0.11 C%) were detected among the products from the Pd/C experiment, only 2-methyl furan (0.34 C%) was detected among the lighter products for Pd/Al₂O₃. While dimers and trimers were produced in both experiments, the use of Pd/C resulted in a higher total of detected dimers and trimers compared to Pd/Al₂O₃ (2.8 vs. 1.7 C%), with the biggest contributor in the case of Pd/C being the trimer 2,2'-(2-furyl methylene)bis(5-methyl furan) (1.3 C%, see Table S5). While the conversion decreased significantly with the addition of sulfur to the feed for both Pd catalysts, the total GC detected liquid yield was not affected to the same degree. The liquid product distribution, on the other hand, changed for both Pd/C and Pd/Al₂O₃. In the case of Pd/C, the only product left, where the carbonyl group was completely removed, was a very small amount of 2-methyl tetrahydrofuran (0.001 C%). The tetrahydrofurfuryl alcohol yield also decreased significantly (from 3.5 to 1.0 C%), whereas the furfuryl alcohol yield only decreased slightly (from 17 to 17 C%). Interestingly, no trimers were detected for either of the Pd catalysts, although this could be due to the trimers polymerizing into even heavier molecules. For the Pd/Al₂O₃ catalyst, furfuryl alcohol was still the main product (21 vs. 18 C%), whereas tetrahydrofurfuryl alcohol almost completely disappeared (10 vs. 0.20 C%). The total amount of dimers decreased (1.7 vs. 1.0 C%), but more interestingly, the dimers changed from being broadly distributed across all detected dimers to primarily being two specific dimers: difurfuryl ether (0.24 C%) and 2-n-butyl furan (0.74 C%). The 2-methyl furan yield increased with the addition of sulfur (0.34 vs. 1.4 C%).

For the Pt catalysts, the main product was furfuryl alcohol, both without and with sulfur. Furthermore, some polymerization products (dimers and trimers) were also formed. In accordance with the conversion, the total yield for Pt/C increased with the addition of sulfur (from 7.8 to 20 C%) without altering the product distribution significantly. While the yield decreased with the addition of sulfur for the Pt/Al₂O₃ catalyst (from 20 to 15 C%), the product distribution remained relatively unchanged for this catalyst as well.

To summarize, the results show a clear trade-off between activity, sulfur tolerance, and selectivity to products. The catalysts with the highest activity—Ni/Al₂O₃, Pd/C, Pd/Al₂O₃, and Ru/C—were also the most sensitive to sulfur, thus making them less suitable for feeds that contain even modest amounts of sulfur. However, Pt/C emerged as a promising

candidate with a combination of reasonable activity and, surprisingly, an enhanced activity in sulfur-containing environments. The cause for this interesting behavior was not possible to determine from this study and may warrant further investigation.

3.3. Catalyst Characterization

The surface area of the fresh catalysts was determined by N₂ physisorption. The resulting surface areas (shown in Table S1) show the catalysts to be divided into three categories: ~100 m²/g (Pd/Al₂O₃ and Pt/Al₂O₃), ~200 m²/g (Ni/Al₂O₃ and sulfided NiMo/Al₂O₃), and ~1000 m²/g and above (Pd/C, Pt/C, and Pd/C). No general correlation between surface area and activity could be derived.

The spent catalysts were collected, washed in acetone, dried, and weighed after each experiment. In all cases, except for the sulfur-free experiments with Pd/Al₂O₃ and Pt/C, the catalysts were observed to gain mass, as can be seen in Table 2. It should be noted that the decrease in mass in the case of Pd/Al₂O₃ and Pt/C could be explained by a difficulty in retrieving the catalyst powder during filtration (see Figure S2). It can be assumed that any observed increase in catalyst mass is due to coke formation on the catalyst, whereas a decrease in catalyst mass is most likely due to loss of catalyst during filtration.

Table 2. Change in mass, carbon content and sulfur content of the spent catalysts from all experiments without sulfur (wo S) and with sulfur (w S). In the case of the carbon content, “-” means not possible to measure, while “-” means not detected in the case of sulfur content. All experiments were conducted with 2 g of catalyst and 50 g of furfural with an initial pressure of 90 bar H₂ (at room temperature), at 180 °C for 1 h.

	Change in Catalyst Mass		Carbon Content		Sulfur Content	
	wo S	w S	wo S	w S	wo S	w S
Ni/Al ₂ O ₃	39.02%	35.05%	16.3%	10.4%	-	3.20%
Sulf. NiMo/Al ₂ O ₃	53.00%	65.61%	24.7%	28.0%	Not measured	
Ru/C	77.70%	76.25%	-	-	864 ppm	0.61%
Pd/C	33.62%	42.79%	-	-	148 ppm	0.56%
Pd/Al ₂ O ₃	−8.11%	3.88%	3.9%	3.8%	-	1.01%
Pt/C	−7.58%	33.62%	-	-	205 ppm	0.21%
Pt/Al ₂ O ₃	19.20%	4.27%	7.3%	3.0%	-	0.23%

To investigate whether coking was responsible for the observed catalyst mass increase, elemental analysis was performed on the fresh and spent Al₂O₃-supported catalysts to determine the change in carbon content (see carbon content in Table 2). This was not possible for the C-supported catalysts (Ru/C, Pd/C, and Pt/C) since any increase in carbon content would be difficult to determine. The increase in catalyst mass was observed to be the highest for Ru/C (both with and without sulfur), and although it was not possible to determine whether this added mass was carbon due to coke formation on the catalyst, it was deemed the most probable cause. However, for all the Al₂O₃-supported catalysts, the elemental analysis revealed significant carbon deposition on most catalysts. Both Ni/Al₂O₃ and the sulfided NiMo/Al₂O₃ catalyst show significant carbon deposition, both with and without sulfur added to the feed. Of the two, the sulfided NiMo/Al₂O₃ showed a particularly high increase in mass (53.0 and 65.6% from the experiments without and with sulfur, respectively). The degree of carbon deposition in both cases correlates with the degree to which the catalyst mass increased. On the other hand, the similar carbon content of the spent Pd/Al₂O₃ from both experiments supports that a decreased catalyst mass cannot be concluded as indicative of no carbon deposition, but is rather due to loss of catalyst during filtration. The experiment with Pt/Al₂O₃ in the presence of sulfur interestingly showed that the spent catalyst from this experiment had a lower carbon deposition compared to the spent Pt/Al₂O₃ from the sulfur-free experiment. In general,

aside from when a loss of catalyst mass was seen, the carbon content of the spent catalyst correlates well with the degree to which the catalyst mass increased, signifying that any observed catalyst mass increase was most likely due to carbon deposition.

The fresh catalyst and the spent catalysts from the sulfur experiments were characterized using XRF to observe if the sulfur content had increased (see Table 2). Sulfur was detected in the spent Ru/C, Pd/C, and Pt/C catalysts from the sulfur-free experiments, but as sulfur was also present in only the fresh C-supported catalysts (see Table S1), this was deemed to be an impurity in the carbon support of the catalysts. For the experiments with sulfur added to the feed, all catalysts, except the sulfided NiMo/Al₂O₃, were observed to have an increase in sulfur content compared to the fresh catalysts. The theoretical maximum of sulfur content (if all the added sulfur was adsorbed to the catalyst, and the catalyst mass was unchanged) was calculated to be 3 wt%. The highest increase was observed for the Ni/Al₂O₃, which was to be expected with the high Ni load, followed by the Pd/Al₂O₃ catalyst. Furthermore, this aligns with the previously reported sulfur poisoning of Ni [14,32]. This fits well with the observed decrease in conversion for both catalysts in the experiments with sulfur. It can be seen from Table 2 that Ni/Al₂O₃ took up around 3 wt% corresponding to all the available sulfur in the feed, indicating the high propensity for sulfur poisoning of Ni-based catalysts. No significant change in sulfur content of the Al₂O₃-supported catalysts was observed in the sulfur-free experiments. While small changes in sulfur content were observed for the carbon-supported catalysts in the experiments without sulfur, these were so small that they could be attributed to the uncertainty of the characterization method.

Finally, all fresh and spent catalyst samples were subjected to XRD (see Figures S4 and S10 for diffractograms and further description). No structural changes were observed for any of the catalysts, though graphite impurities were present in many spent samples, likely due to the autoclave graphite gaskets. Furthermore, the experiments with sulfur added to the feed did not appear to result in any sulfides being formed of Ni, Ru, Pd, or Pt.

4. Conclusions

The stabilization of the pyrolysis oil model compound furfural was studied in a batch reactor using a range of Al₂O₃- or carbon-supported catalysts: Ni/Al₂O₃, sulfided NiMo/Al₂O₃, Ru/C, Pd/C, Pd/Al₂O₃, Pt/C, and Pt/Al₂O₃. All experiments were conducted at elevated H₂ pressure and 180 °C for 1 h. The performance of all catalysts was tested without and with an organic sulfur source (1170 wt-ppm S) added to the feed.

Without the addition of sulfur, the Ni/Al₂O₃, Ru/C, as well as the two Pd-based catalysts, resulted in the highest conversions. In general, the loss of carbon to the gas phase was minimal (<0.5 C%), except for the sulfur-free experiment with Ru/C, where almost 2 C% was lost to the gas phase (primarily as CH₄). The majority of the liquid yield consisted of furfuryl alcohol for all tested catalysts, though both more hydrogenated products (particularly tetrahydrofurfuryl alcohol) as well as polymerization products were observed as well.

The addition of sulfur to the feed negatively impacted the four most active catalysts from the sulfur-free experiments (Ni/Al₂O₃, Ru/C, Pd/C, and Pd/Al₂O₃). While the conversion for all four was above 75% without sulfur, the presence of sulfur decreased the conversions to 20–40%. This correlated well with the XRF measurements, which showed that sulfur was present on the spent catalysts. The Ni/Al₂O₃ catalyst, in particular, was strongly poisoned with over 3 wt% sulfur corresponding to all the added S in the feed. The sulfided NiMo/Al₂O₃ catalyst experienced an increase in activity with the addition of sulfur to the feed, although the low conversion even in sulfur-rich conditions revealed that the sulfided NiMo/Al₂O₃ catalyst is not very active at the low temperature applied in pyrolysis oil stabilization conditions.

The results in this study revealed that Pt/C may be an interesting candidate for stabilization. While it was not the most active amongst the tested catalysts, its positive performance with sulfur in the feed seems promising. How the presence of sulfur positively affects the performance of this catalyst warrants further investigation.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/reactions7030045/s1>, Figure S1: photograph of batch autoclave setup; Table S1: overview of experiments and catalyst specifics; Table S2: hydrogen consumption for all experiments; Table S3: conversion for all experiments; Table S4: gas products from all experiments; Table S5: chemical structures of all furfural products; Table S6: liquid products from sulfur-free experiments; Table S7: liquid products from sulfur experiments; Figure S2: mass balances for all experiments; Figure S3: GC-detected mass balances for all experiments; Figure S4: powder X-ray diffractograms of all fresh and spent Ni/Al₂O₃ catalysts; Figure S5: powder X-ray diffractograms of all fresh and spent sulfided NiMo/Al₂O₃ catalyst; Figure S6: powder X-ray diffractograms of all fresh and spent sulfided Ru/C catalyst; Figure S7: powder X-ray diffractograms of all fresh and spent sulfided Pd/C catalyst; Figure S8: powder X-ray diffractograms of all fresh and spent sulfided Pd/Al₂O₃ catalyst; Figure S9: powder X-ray diffractograms of all fresh and spent sulfided Pt/C catalyst; Figure S10: powder X-ray diffractograms of all fresh and spent sulfided Pt/Al₂O₃ catalyst; Section S1: mass transfer calculations; Table S8: apparent reaction rates; Table S9: sauter diameter of extruded catalysts; Table S10: results from mass transfer calculations.

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Abbreviations

The following abbreviations are used in this manuscript:

DDO	Direct deoxygenation
FID	Flame ionization detector
FU	Furfural
GC	Gas chromatography
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDS	Hydrosulfurization
HYD	Hydrogenation

MS	Mass spectrometry
PO	Pyrolysis oil
TCD	Thermal conductivity detector
THFA	Tetrahydrofurfuryl alcohol
w S	With sulfur
wo S	Without sulfur
XRD	X-ray diffraction
XRF	X-ray fluorescence

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