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Experimental Investigation on Upgrading of Lignin Derived Bio-oils: Kinetic Analysis of Anisole Conversion on Sulfided CoMo/Al₂O₃ Catalyst

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Abstract

Kinetics of the hydroprocessing of anisole, a compound representative of lignin-derived bio-oils, catalyzed by a commercial sulfided CoMo/Al₂O₃ were determined at 8–20 bar pressure and 573–673 K with a once-through flow reactor. The catalyst was sulfided in an atmosphere of H₂ + H₂S prior to the measurement of its performance. Selectivity-conversion data were used as a basis for determining an approximate, partially quantified reaction network showing that hydrodeoxygenation, hydrogenolysis, and alkylation reactions take place simultaneously. The data indicate that these reactions can be stopped at the point where HDO is virtually completed and hydrogenation reactions (and thus H₂ consumption) are minimized. Phenol was the major product of the reactions, with direct deoxygenation of anisole to give benzene being kinetically almost insignificant under our conditions. We infer that the scission of the C_{methyl}–O bond is

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more facile than the scission of the C_{aromatic}–O bond, so that the hydrodeoxygenation of anisole likely proceeds substantially through the reactive intermediate phenol to give transalkylation products such as 2-methylphenol. The data determine rates of formation of the major primary products. The data show that if oxygen removal is the main processing goal, higher temperatures and lower pressures are favored.

Keywords: Bio-oil; Lignin; Kinetics; Catalytic upgrading; Hydrodeoxygenation.

1. Introduction

The environmental concerns related to the burning of fossil fuels motivate interest in the development of renewable raw materials as feedstocks for the production of fuels and even chemicals. The depolymerization of biomass and the upgrading the resulting fragments into compounds with properties that approximate those of petroleum represent substantial challenges.¹⁻⁵ The compositions of liquids formed from biomass depend on the raw materials and the methods of conversion.^{4,6-11} Generally, these liquids include high concentrations of oxygen-containing compounds, and improvements in the stability of these liquids and their compatibility with petroleum products requires a reduction in their oxygen contents. Thus, catalytic hydroprocessing to convert the compounds primarily into hydrocarbons and water (hydrodeoxygenation, HDO) is a candidate process for upgrading of biomass-derived liquids, and such processes are usually catalytic, performed at high temperatures and in the presence of high partial pressures of H₂.

Among the various polymers present in lignocellulosic biomass, lignin, with its polyaromatic structure, is the one that is chemically most similar to petroleum. Nonetheless, lignin contains

much more oxygen than crude oil.¹²⁻¹⁴ and lignin-derived bio-oils are good candidates for hydroprocessing for oxygen removal.

Only little information characterizing the kinetics of HDO of lignin-derived bio-oil compounds has been reported. HDO processes are similar to the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) used widely in petroleum refining,^{15,16} and the catalysts of choice for the latter processes are metal sulfides, exemplified by molybdenum sulfide promoted with cobalt and supported on porous γ -Al₂O₃. These catalysts have also been investigated for HDO, and we chose to investigate anisole HDO in the presence of this catalyst, referred to simply as CoMo/Al₂O₃. Because such catalysts revert from the sulfided to oxide forms in the absence of sulfur-containing compounds and H₂, we carried out our investigation with the reactant in the presence of added H₂S. Earlier work has shown that HDO proceeds by two reaction paths on different kinds of active sites on the sulfided catalyst, one involving direct hydrogenolysis (breaking of the bond between the oxygen atom and the aromatic carbon in a compound such as anisole) and the other involving a hydrogenation–hydrogenolysis route whereby the aromatic ring is hydrogenated prior to the rupture of the carbon– oxygen bond.^{15,17-23}

The presence of cobalt improves the activity of molybdenum sulfide catalysts for hydroprocessing reactions.²⁴⁻²⁸ Bui *et al.*^{24,25} considered the promoting effect of cobalt on molybdenum sulfide catalysts for lignin-derived bio-oil conversion. They observed that the addition of cobalt increased the rates of the direct demethoxylation and direct deoxygenation pathways.²⁵

Lee *et al.*²⁹ concluded that deoxygenation, demethoxylation, and demethylation reactions following saturation of the aromatic ring in guaiacol were essential to account for the product distributions observed with sulfided CoMo/Al₂O₃ and sulfided NiMo/Al₂O₃ catalysts. Furimsky *et al.*^{27,30} investigated HDO of phenolic compounds catalyzed

by sulfided CoMo/Al₂O₃, finding that presulfiding of the catalyst improved the conversion of phenols to benzene and cyclohexane. In related work, Vuori *et al.*²⁸ reported that sulfiding of catalysts had a pronounced effect on the conversion of guaiacol.

H₂S play a role in addition to that of maintaining the catalyst in a sulfided state. H₂S is also an inhibitor of HDO reactions, as illustrated for a mixture of lignin-derived bio-oil compounds by Laurent and Delmon,^{19,20,31} who investigated the performance of CoMo/Al₂O₃ catalysts under various conditions and found that oxygen removal reactions are inhibited by both sulfur- and nitrogen-containing compounds. Ferrari *et al.*³² inferred that increasing the H₂S partial pressure led to inhibition of both the hydrogenolysis and hydrogenation pathways, and Senol *et al.*³³ observed that the formation of both benzene and cyclohexene in the conversion of phenol was inhibited by H₂S. Gutierrez *et al.*³⁴ observed that in guaiacol HDO with a sulfided CoMo/Al₂O₃ catalyst, the products were contaminated with sulfur and the catalyst underwent deactivation associated with carbonaceous deposits.

Because of the complexity and variability of structures of compounds in bio-oils and the variations in molecular weight and concentration of these compounds, only little quantitative information characterizing the kinetics of bio-oils hydroprocessing is available.⁶ Massoth *et al.*³⁵ investigated the kinetics of HDO of methyl-substituted phenols catalyzed by a sulfided CoMo/Al₂O₃ and represented their data with Langmuir–Hinshelwood expressions, but the results are too few data to justify any generalizations. Bui *et al.*^{24,25} investigated HDO of guaiacol in the presence of similar CoMo catalysts in a fixed-bed reactor and represented their data with simple first-order kinetics. In related work, Saidi *et al.*,^{8,12,14} Runnebaum *et al.*,^{9,17,36,37} and Nimmanwudipong *et al.*³⁸ used first-order kinetic to approximate their data and provide a basis

for comparison of the reactivities of various lignin-derived compounds in HDO, but their catalyst was an unsulfided supported noble metal, Pt/Al₂O₃.

Runnebaum's investigation is one of the few to include quantitative kinetics characterizing catalytic HDO. They elucidated an approximate reaction network characterizing anisole conversion catalyzed by Pt/Al₂O₃ and determined pseudo-first-order rate constants for the formation of individual products. The catalytic hydrotreating of anisole with sulfided hydrotreating catalysts was also investigated by Bredenberg *et al.*³⁹ and by Hurff and Klein,⁴⁰ but reaction networks were either not reported or simplified to include only a few main products.

The literature of catalytic HDO of lignin-derived bio-oils has been reviewed in detail,⁶ but there is still a lack of fundamental understanding of the reactions, networks, kinetics, and mechanisms. Specifically, there is a lack of data characterizing kinetics and reaction networks for HDO with sulfided hydroprocessing catalysts.

Our goals in the work summarized below were to investigate the HDO of a compound representative of lignin-derived bio-oils, namely, anisole, and to assess quantitatively the promoting effect of cobalt by determining an approximate reaction network with values of approximate rate constants and activation energies.

2. Experimental

Catalytic reaction experiments were performed with a once-through fixed-bed tubular micro flow reactor. The flow system is shown schematically in [Figure 1](#), and details are represented in [Table 1](#). The catalyst used in all experiments was American Cyanamid HDS 16A. The catalyst properties before sulfiding are as follow: surface area, 176 m²/g; pore volume, 0.50 cm³/g; Co content, 4.4 wt%; and Mo content, 7.5 wt%. Particles of the catalyst were placed on

the porous plate in the once-through reactor operated in down-flow mode, mixed with about 2 g of inert, nonporous α -Al₂O₃ particles. Sulfiding was achieved by passing 10% H₂S in H₂, through the bed at a rate of 20 L/h while the catalyst was heated at a rate of about 10°C/min to 500°C. After two hours at 500°C, the H₂S/H₂ stream was replaced by N₂, and the reactor was cooled to the operating temperature. A sample of catalyst powder (less than 100 mesh particles) was charged to the reactor. Fresh catalyst (0.25–2.00 g) was used for each experiment, and each experiment was typically run for 6 h of continuous operation.

Figure 1

Table 1

The liquid reactant (anisole 99.8%, Merck) was introduced into the reactor at room temperature by means of an HPLC pump. N₂ was used as the carrier gas and H₂, when present as a reactant, was mixed into the carrier gas stream. Liquid and gas streams were introduced into a hot-box system that included an electric forced-convection heater that held the components at a temperature of 453 K to avoid possible condensation of reactants or products. Preheated liquid was vaporized, and the vapor stream was mixed with the gas feed stream and flowed to the reactor. At the reactor outlet, the product stream flowed out of the hot box to a condenser, which operated at 275–280 K. Liquid product samples were taken periodically at intervals of 30 min downstream of the condenser for analysis.

Product analysis was performed with a Bruker 450 gas chromatograph (GC) equipped with a flame ionization detector. Samples were diluted with acetone to make them single-phase. The GC parameters were as follows: sample volume, 0.5 μ L; injector temperature, 573 K; temperature program starting temperature, 323 K; temperature ramp, 20 K/min, followed by a soak of 35 min. The GC was equipped with an OPTIMA 5 Macherey-Nagel capillary column

(30 m × 0.25 mm, with a 0.25-μm film thickness). The detector temperature was set at 548 K, and the gas flow rates were as follows: H₂, 30 mL/min; air, 300 mL/min. The carrier gas flow rate was constant within the column, with a makeup flow to give a combined flow rate of 30 mL/min; the makeup gas was argon. Moreover, for identification of trace compounds, a few liquid samples were analyzed qualitatively with a Shimadzu QP 50/50 gas chromatograph-mass spectrometer (GC-MS) equipped with a SGE BPX5 capillary column (0.32 mm × 30 m × 0.25 μm), with helium (50 mL/min) used as the carrier gas. Chromatographic peaks were identified with individual compounds on the basis of mass spectra by matching to a Willy library. The identifications of the most abundant products were verified by comparison with the analysis of authentic standards purchased from Sigma Aldrich; these standards were benzene, phenol, 2-methylphenol, 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2,3,5,6-tetramethylphenol, and 2-*tert*-butyl-4-methylphenol.

Conversion (X) and selectivity to various products i (S_i) are defined as follows:

$$X = \frac{(\text{moles of anisole})_{in} - (\text{moles of anisole})_{out}}{(\text{moles of anisole})_{in}} * 100\% \quad (1)$$

$$S_i = \frac{\text{molar flow rate of product } i}{\text{molar flow rate of main products formed}} \quad (2)$$

The catalytic conversion of anisole was carried out at temperatures in the range of 573–673 K and pressures in the range of 8–20 bar; the liquid anisole flow rates were in the range of 0.03–0.5 mL/min, and the N₂ and H₂ flow rates were each 20 L/h. The value of the weight hourly space velocity ($WHSV$) was in the range of 3–120 (g of anisole)/(g of catalyst × h), varied by changing the catalyst mass and liquid flow rate.

3. Results

The conversion of anisole catalyzed by commercial sulfided CoMo/Al₂O₃ was investigated under HDO conditions. The catalyst was presulfided, but the sulfiding agent H₂S was not added to the feed mixture because it was expected that it would have inhibited the reactions involving anisole and H₂. GC analysis of the liquid reaction products demonstrated the formation of complex reaction mixtures in which the main products were benzene, phenol, 2-methylphenol, 2,4-dimethylphenol, 2,4,6-trimethylphenol, 2,3,5,6-tetramethylphenol, and 2-*tert*-butyl-4-methylphenol. GC-MS analyses of the product also gave evidence the minor products methane, methanol, and water. The conversion data demonstrate a lack of dependence on the mass of catalyst (in the range 0.25–2.00 g) at fixed values of the *WHSV* in the range of 3–120 (g of anisole)/(g of catalyst × h), consistent with the inference that extraparticle mass transfer limitations were negligible. Calculations representing the intraparticle mass transfer resistance indicate that it was also negligible: the calculated values of the modified Thiele modulus (Weisz modulus) were less than 0.4, indicating that the anisole conversion rate was not limited by internal diffusion and therefore that the catalytic reaction experiments determined intrinsic chemical kinetics. The mass balance closures were generally between 95 and 100% ([Table 2](#)).

Table 2

3.1 Approximate Reaction Network

The complexity of the product distribution makes it challenging to determine an exact reaction network to summarize the anisole conversion data. Thus, one of our goals was to establish a good approximation of the network—on the basis of selectivity-conversion data determining which products are primary and which are non-primary. The evolution of the selectivities of the

main products as a function of anisole conversion in the presence of H₂ at 8 bar, 573–673 K, and 0.008–0.667 (g of catalyst × h)/ (g of anisole) is shown in **Figures 2, S-1, and S-2** (the latter two in the Supporting Information). The lines shown in these figures were used for extrapolation to estimate the selectivities at zero conversion. The selectivity-conversion plots provide the following information about the reaction network: The main products phenol, benzene, and 2-methylphenol appeared with positive intercepts on the plots (consistent with the values determined by linear regression), indicating primary products. In contrast, the other main products, 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2,3,5,6-tetramethylphenol, and 2-*tert*-butyl-4-methylphenol, appeared with approximately zero intercepts, indicating non-primary products. The maximum selectivity is that for formation of phenol. As indicated in **Figure 2**, the selectivities for the formation of phenol derivatives remained approximately unchanged with increasing conversion, but that of benzene decreased.

Figure 2

The formation of these products in the hydroprocessing of anisole suggests that both HDO (indicated, for example, by the formation of benzene) and hydrogenolysis by O-demethylation (indicated, for example, by the formation of phenol and methane) are kinetically significant reaction pathways and that they are accompanied by transalkylation (indicated, for example, by the formation of 2-methylphenol). Thus, a partial statement of the network for conversion of anisole by the sulfided CoMo/Al₂O₃ catalyst under our conditions, accounting for just the primary products and the other major products, is that represented in **Figure 3**.

Figure 3

As indicated in **Figure 3**, we infer two routes for the conversion of anisole to benzene: one, the direct deoxygenation pathway (DDO) whereby benzene is formed via loss of the methoxy

functionality and, another, demethylation of the methoxy group followed by HDO. The observation of methane, methanol, and water as products is consistent with the occurrence of these reactions. The absence of cyclohexanes with oxygen-containing functional groups among the main products shows that the demethylation and HDO reactions that take place on the CoMo catalyst dominate kinetically over the formation of hydrogenation products—thus the data indicate that the reactions can be stopped at the point where HDO is virtually completed and H₂ consumption is minimized. We infer that sequential methyl group transfer from compounds including anisole to methylphenols produces 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2,4,5,6-tetramethylphenol and 2-*tert*-butyl-4-methylphenol. According to the selectivity-conversion data, the selectivity for one route may decline in favor of another as conversion increases. Nonetheless, the conversion of the anisole at various operating conditions on the sulfided CoMo/Al₂O₃ catalyst leads to the formation of phenolic products via a combination of demethylation/alkylation steps that are known to take place on acidic surfaces such as that of the alumina support.^{6,17,36,41} The high selectivities to phenol suggest that the demethylation pathway is the major pathway in the anisole conversion, as might be expected because of the higher strength of the MeO–C_{aromatic} bond relative to the O–C_{methyl} bond. O-demethylation is inferred to be accompanied by methylation of the aromatic ring, a class of reaction that is often associated with support acidity. Formation of 2-methylphenol as one of the main products, in contrast to 4-methylphenol, indicates that the *o*-position is strongly favored over the *p*-position in the alkylation.

3.2 Kinetics

In investigations of catalytic reaction kinetics it is common to report initial reaction rates as measures of catalytic activity, and we report such data below. In investigations of catalytic hydroprocessing it is common to report kinetics in terms of rate constants that are pseudo-first-order in the organic reactant,^{35-37,42-45} and we report such data also, with results showing that the approximation is good at the intermediate conversions we have investigated. Because catalyst deactivation was observed to be negligible during 6 h of continuous operation in our experiments, we have used average conversions over the entire 6-h period of time on stream to determine the reported rate constants.

Conversions of anisole were determined from changes in the anisole concentration, and conversions to individual products were determined from analyses of those products. Data showing the conversion of anisole as a function of the inverse *WHSV* and the conversions to individual major products in a typical run are presented in Figures 4, 5, S-3, and S-4. The data fall near straight lines that pass through the origin, so that the slopes of the lines determine the rates of the reactions. As shown in Figure 4, the conversion of anisole at a given *WHSV*, and the rate of formation of each of the products, increases with increasing temperature in the observed range, from 573 to 673 K, and at a give temperature, the conversion increases with increasing inverse *WHSV* at a given temperature, as expected. The rates of anisole conversion at 573, 623, and 673 K were found to be 5.26×10^{-3} , 8.54×10^{-3} , and 1.28×10^{-2} (g of anisole/g of catalyst $\times$ h), respectively. The initial rates of appearance of the various products of anisole conversion (Table 3) show that the primary product formed at the highest initial rate is phenol, and it is formed more than 10 times faster than benzene.

Table 3

Figure 4

Figure 5

To estimate rate constants for the primary reactions, we made plots of $(1 - X_i)$ (where X_i is the conversion of anisole to species i) on logarithmic scales vs. inverse space velocity (Figures 6, S-4 and S-5). The pseudo-first-order rate constants for the three primary products shown in the reaction network of Figure 5 were determined according to eqs. (3-7). As indicated in these figures, the slopes of the linear plots indicate pseudo first-order reactions. These are composite rather than fundamental rate constants because the primary products were consumed in non-primary reactions. But because phenol was formed much faster than the other products, the rate constant for phenol formation is close to accurate.

$$r_i = \frac{dc_i}{d(c_{Anisole,0}/WHSV)} = k_i c_{Anisole} \quad (3)$$

$$c_i = c_{Anisole,0} X_i \quad (4)$$

$$c_{Anisole} = c_{Anisole,0} (1 - X_i) \quad (5)$$

$$r_i = \frac{dX_i}{d(c_{Anisole,0}/WHSV)} = k_i (1 - X_i) \quad (6)$$

$$\ln(1 - X_i) = -k_i (c_{Anisole,0}/WHSV) \quad (7)$$

Figure 6

As shown in Table 4, the maximum rate constants among those determined in this work at each temperature are those for the formation of phenol. The pseudo first-order rate constants for phenol formation were determined to be 3.03, 3.56, and 6.56 L/(g of catalyst × h), respectively, at 573, 623, and 673 K and a pressure of

Table 4

These values of the apparent rate constants were used to determine values of the apparent activation energies, calculated on the basis of the Arrhenius equation (Eq. 8). The corresponding plots are shown in **Figure 7** and the estimated values of apparent activation energies are summarized in **Table 4**. The values of these apparent activation energies are the following: for the formation of benzene, approximately 18 kJ/mol; for phenol, approximately 24 kJ/mol; and for 2-methylphenol, approximately 14 kJ/mol. We emphasize that these kinetics parameters are composite values and do not represent a quantitative resolution of the reaction network of Figure 3.

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (8)$$

Figure 7

3.2 Effects of Operating Conditions

The effects of operating conditions on the anisole conversion was investigated at a constant *WHSV* (3 (g of anisole)/(g of catalyst × h)). As shown in **Figure 8**, the anisole conversion at 8 bar increased from 17 to 57% as the temperature increased from 573 to 673 K. The selectivities for formation of phenol and 2-methylphenol decreased with increasing temperature, whereas the selectivities to benzene and other phenol derivatives increased (**Figure 9**).

Figure 8

Figure 9

At 623 K, the conversion increased from 57 to 69% as the pressure increased from 8 to 20 bar (**Figure 10**). The effect of pressure on selectivity for the formation of the major products at conversions in the range of to is shown in **Figure 11**. Under our

conditions, increasing the pressure increased the selectivity for formation of phenol, but it decreased the selectivity for formation of benzene and other products formed from phenol. We infer that although increasing the pressure improved conversion and selectivity to hydrogenolysis product (phenol), it led to decreased selectivity to HDO products, as the selectivity to benzene was reduced from 0.12 to 0.08 as the pressure increased from 8 to 20 bar. We infer that if oxygen removal is the principal processing goal, higher temperatures and lower pressures are more favorable, within the range of our operating conditions.

Figure 10

Figure 11

4. Discussion

The results presented here are more complete than reported data^{20,46-49} for anisole conversion catalyzed by sulfided CoMo/Al₂O₃ under hydroprocessing conditions, including kinetics data that provide a preliminary quantitative basis for determining the initial product distributions at several temperatures and pressures and a basis for identifying the reaction classes to help identify major reaction pathways.

The selectivity-conversion data represented in **Figures 2, S-1, and S-2** were used to identify primary and non-primary products, with phenol, benzene, and 2-methylphenol being primary products and other phenol derivatives being non-primary products. But we emphasize that if a secondary product is formed faster than primary product, it may appear to be primary by our criterion of a positive intercept on a selectivity-conversion plot indicating a primary product.

The results demonstrate the occurrence of HDO, hydrogenolysis, and alkylation as the main reaction pathways for anisole conversion catalyzed by our sulfided CoMo/Al₂O₃. The data show that under our conditions these reactions dominated over hydrogenation.

Our data are consistent with the premise that CoMo sites are active for HDO reactions, and we thus consider it likely that Co-Mo catalyzes (a) hydrogenolysis, to form phenol, and (b) HDO to form benzene, which are kinetically significant reactions under our conditions. Alkylation reactions are expected to occur in the presence of acidic sites on the catalyst support (γ -Al₂O₃). Consistent with results observed previously,^{21,24,39,46,47,49} no evidence was observed in our work for hydrogenated phenols. Ring hydrogenation may require the aromatic molecule ring to adsorb almost flat on the catalyst surface, and the substituents on the ring may have led to non-planar coordination and hampering of hydrogenation pathways.

We suggest that the kinetics parameters presented here may be of value for preliminary design predictions for the conversion of anisole and perhaps related lignin-derived bio-oils components. The data summarized in Table 2 show that among the various reactions on sulfided CoMo/Al₂O₃, hydrogenolysis (in our case, to form phenol) is characterized by the highest rate and that selectivities for oxygen removal are favored by operation at higher temperatures and lower pressures. Increasing the temperature enhances the selectivity for HDO and alkylation products, but reduces the selectivity for hydrogenolysis. But we emphasize that because of the complexity of bio-oils feedstocks and the limitations of available data characterizing reaction networks and kinetics, much work is required for a firm foundation to allow even rough design predictions.

Conclusions

The catalytic upgrading of anisole catalyzed by sulfided CoMo/Al₂O₃ was investigated in the temperature range of 573 to 673 K and the pressure range of 8 to 20 bar. The primary observed products were phenol, benzene, and 2-methylphenol, with major non-primary products being 2,6-dimethylphenol, 2,4,6-trimethylphenol, 2,3,5,6-tetramethylphenol, and 2-*tert*-butyl-4-methylphenol. An approximate reaction network accounts for hydrogenolysis of methoxy groups in anisole to form phenol, followed by deoxygenation to give benzene or transalkylation to give other phenol derivatives; benzene was the only fully deoxygenated organic product. We infer that the Co-Mo sites are active for hydrogenolysis, HDO, and hydrogenation and that the acidic alumina support is responsible for the transalkylation reactions. The rates of anisole conversion at 573, 623, and 673 K and bar were found to be 5.3×10^{-3} , 8.5×10^{-3} , and 1.3×10^{-2} (g anisole/g of catalyst $\times$ h), respectively. The data suggest that oxygen removal of lignin-derived bio-oils is favored by operation at higher temperatures and lower pressures.

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Table 1: Flow reactor system specification and operating conditions.

Table 2: Overall mass balance closure data.

Table 3: Initial rates of formation of the main products.

Table 4: Pseudo-first-order rate constants and apparent activation energies for reactions in the network representing anisole conversion in the presence of H₂ and sulfided CoMo/Al₂O₃ catalyst. See notes in the text for limitations of these values.

Table 1

Specification of equipment components	Property
Reactor length, mm	305
Reactor external diameter, mm	14.5
Reactor internal diameter, mm	9
Reactor material	316–L stainless steel
Reactor volume, mL	20
Reactor operating temperature range, K	573–673 (± 1.5)
Reactor operating pressure, bar	8-20 (± 0.1)
Carrier gas (N ₂) flow rate, L/h	20
H ₂ flow rate, L/h	20
Liquid feed (4-methylanisole) flow rate range, mL/min	0.03–0.5 ($\pm 1\%$)
Catalyst (sulfided CoMo/Al ₂ O ₃ - American Cyanamid HDS 16A) mass, g	0.25–2.00

Table 2

Experiment number	Mass balance closure (%)	Time on stream (min)	Liquid flow rate (mL/min)	Mass of liquid fed (g)	Mass of liquid collected from condenser (g)	Mass of reactant leaving condenser as vapor (g)	Approximate mass of liquid remaining in condenser (g)
1	96.2	150	0.1	14.93	13.07	0.29	1
2	98.7	150	0.1	14.93	13.52	0.21	1
3	95.7	150	0.1	14.93	12.98	0.3	1
4	98.5	150	0.1	14.93	13.49	0.21	1
5	98.1	150	0.1	14.93	13.36	0.28	1
6	95.8	150	0.1	14.93	12.98	0.31	1
7	96.6	150	0.1	14.93	13.18	0.24	1
8	99.7	180	0.05	8.96	7.78	0.15	1
9	95.4	180	0.05	8.96	7.39	0.15	1
10	95.9	180	0.05	8.96	7.4	0.19	1
11	97.4	180	0.05	8.96	7.58	0.14	1
12	97.3	180	0.05	8.96	7.56	0.15	1
13	96.9	180	0.05	8.96	7.51	0.17	1
14	95.5	180	0.05	8.96	7.36	0.19	1
15	96.8	180	0.05	8.96	7.44	0.23	1
16	96.0	360	0.03	10.75	9.14	0.18	1
17	97.6	360	0.03	10.75	9.28	0.21	1
18	97.4	360	0.03	10.75	9.25	0.22	1
19	96.5	360	0.03	10.75	9.19	0.18	1
20	98.1	360	0.03	10.75	9.35	0.19	1

Table 3

Product	Rate (mol/(g of catalyst $\times$ h))		
	at $T = 573$ K	at $T = 623$ K	At $T = 673$ K
Phenol	2.31×10^{-3}	4.20×10^{-3}	7.25×10^{-3}
Benzene	2.19×10^{-4}	3.52×10^{-4}	5.36×10^{-4}
2-Methylphenol	1.76×10^{-3}	2.76×10^{-3}	3.64×10^{-3}
2,6-Dimethylphenol	2.15×10^{-4}	1.09×10^{-3}	2.10×10^{-3}
2,4,6-Trimethylphenol	1.89×10^{-4}	3.00×10^{-4}	5.69×10^{-4}
2,3,5,6-Tetramethylphenol	8.14×10^{-5}	2.42×10^{-4}	5.12×10^{-4}
2- <i>tert</i> -Butyl-4-methylphenol	3.24×10^{-5}	7.31×10^{-5}	1.81×10^{-4}

Table 4

Product	T , K	k_i , L/(g of catalyst $\times$ h)	Ea , kJ/mol
Phenol	573	3.03	24.3
	623	3.56	
	673	6.56	
Benzene	573	0.23	18.4
	623	0.29	
	673	0.41	
2-Methylphenol	573	1.92	14.4
	623	2.25	
	673	3.02	
2,6-Dimethylphenol	573	0.22	56.0
	623	0.90	
	673	1.23	
2,4,6-Trimethylphenol	573	0.19	24.3
	623	0.23	
	673	0.41	
2,3,5,6-Tetramethylphenol	573	0.08	51.6
	623	0.19	
	673	0.40	
2- <i>tert</i> -Butyl-4-methylphenol	573	0.03	49.2
	623	0.06	
	673	0.14	

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Figure 1: Schematic representation of fixed-bed tubular micro-flow reactor system.

Figure 2: Selectivity for the formation of the following products in the conversion of anisole catalyzed by sulfided CoMo/Al₂O₃ in the presence of H₂ at temperature = 573 K and pressure = 8 bar. Data for each of the main products were fitted with a straight line and extrapolated to zero conversion; intercepts of the lines that are significantly different from zero selectivity at zero conversion indicate primary products.

Figure 3: Approximate reaction network for the conversion of anisole catalyzed by sulfided CoMo/Al₂O₃ at 573–673 K and 8–20 bar.

Figure 4: Conversion of anisole at various temperatures and 8 bar. [IN FIGURE, CHANGE *T* TO *T* (ITALIC). CHANGE OVERALL ANISOLE CONVERSION TO ANISOLE CONVERSION. CHANGE WHSV TO *WHSV* (ITALIC).]

Figure 5: Conversion to main products at 573 K and 8 bar; the term X_i represents the conversion of anisole to product *i*. [IN FIGURES, CHANGE X_i to X_i (*i* IS NOT ITALIC). CHANGE g of catalyst × h to g of catalyst × h]

Figure 6: Conversion of anisole in the presence of H₂ at 573 K and 8 bar to give the main products, where X_i is conversion of anisole to product *i*. [IN THE FIGURES, CHANGE X_i to X_i ; *X* is italic. CHANGE g of catalyst × h to g of catalyst × h]

Figure 7: Arrhenius plots for formation of main products in the reaction of anisole catalyzed by CoMo/γAl₂O₃, where k is rate constant and T is the reaction temperature. [IN THE FIGURE, CHANGE *T* to *T* (THIS IS ITALIC) AND CHANGE (*L/g catalyst.h*) to (*L/g of catalyst × h*) (NOT ITALIC)]

Figure 8: Conversion of anisole at 8 bar and $WHSV = 3.6$ (g of anisole)/(g of catalyst $\times$ h) and various temperatures.

Figure 9: Temperature dependence of selectivity for the formation of the main products of the reaction of anisole with H_2 at 8 bar and $WHSV = 3.6$ (g of anisole)/(g of catalyst $\times$ h). [CHANGE *Temperature*, (K) to Temperature (K) (NOT ITALIC). CHANGE trimethylphenol to Trimethylphenol and tetramethylphenol to Tetramethylphenol and 2-tert-Butyl-4-Methylphenol to 2-*tert*-Butyl-4-methylphenol. NOTE ITALICS.]

Figure 10: Conversion of anisole at 623 K and $WHSV = 3.6$ (g of anisole)/(g of catalyst $\times$ h) and various pressures. [CHANGE *Pressure*, (bar) to Pressure (bar) (NOT ITALIC). REMOVE WORD OVERALL]

Figure 11: Pressure dependence of selectivity for the formation of the main products of the reaction of anisole with H_2 at 623 K and $WHSV = 3.6$ (g anisole)/(g of catalyst $\times$ h). [CHANGE *Pressure*, (bar) to Pressure (bar) (NOT ITALIC).]

Figure 1

Figure 2-a

Figure 2-b

Figure 2-c

Figure 2-d

Figure 3

Figure 4

Figure 5-a

Figure 5-b

Figure 5-c

Figure 6

Figure 7-a

Figure 7-b

Figure 8

Figure 9-a

Figure 9-b

Figure 10

Figure 11-a

Figure 11-b