Design of a High-Pressure Flow-Reactor System for Catalytic Hydrodeoxygenation: Guaiacol Conversion Catalyzed by Platinum Supported on MgO

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Ⓢ *Supporting Information*

ABSTRACT: A high-pressure once-through plug-flow-reactor system is reported for characterization of hydroprocessing reactions of biomass-derived compounds. All of the reactants are liquids. Data are presented for conversion of guaiacol catalyzed by Pt/MgO and, in much less detail, CoMo/Al$_2$O$_3$. The data demonstrate the advantages of high pressure in such reactions, determining a pseudo-first-order rate constant for guaiacol conversion at 523 K and 69 bar of approximately 55 L of organic reactant solution (g of catalyst)$^{-1}$ h^{-1}. This value is 2 orders of magnitude greater than that observed at 573 K and 1.4 bar.

1. INTRODUCTION

The goal of replacing fossil fuels and petrochemicals with biomass-derived fuels and chemicals has motivated extensive recent research. Routes for biomass conversion that involve catalysis are in prospect the routes expected to come closest to meeting the goals of application of sustainable fuels. A potentially viable route to biofuels from cellulosic biomass involves pyrolysis of the biomass followed by catalytic upgrading of the resultant bio-oils, which themselves offer poor prospects as fuels because of their thermal and chemical instability, low heating values, corrosiveness, and immiscibility with petroleum-derived fuels. Many of the undesirable properties of bio-oils as fuels are associated with their high oxygen contents. Thus, one of the needs for bio-oil upgrading is to discover catalysts that remove oxygen selectively; candidate reaction classes include dehydration and hydrodeoxygenation[1] (HDO).

HDO has been investigated by numerous authors recently, with the most widely investigated catalysts being supported metals, such as platinum,[1−6] ruthenium,[7−10] and palladium,[11−13] or sulfided catalysts,[14−23] such as supported cobalt- or nickel-promoted molybdenum; the latter are widely used in petroleum refining to remove sulfur and nitrogen by hydrodesulfurization (HDS) and hydrodenitrogenation (HDN). When the feedstocks are heavy, these petroleum hydroprocessing operations are carried out at high pressures (some in the range of approximately 100 bar) with catalysts that are maintained in the sulfided form by the sulfur-containing reactants and a product of their HDS, namely, H$_2$S.

It is still not evident what the optimum catalysts or processing conditions may be for HDO of bio-oils. The literature of catalytic hydroprocessing of whole bio-oils does not lend itself to fundamental interpretation, and consequently, numerous researchers have investigated the hydroprocessing reactions of individual compounds representative of bio-oils; most of these investigations have been carried out at pressures near ambient.

Our goals were to design and test a reactor system for investigation of high-pressure catalytic hydroprocessing of compounds representative of bio-oils. We present the design here and illustrate its operation with data characterizing the hydroprocessing of guaiacol, a well-investigated compound representative of lignin-derived bio-oils. Data are presented for the conversion of guaiacol catalyzed by platinum supported on MgO (Pt/MgO).[24] For comparison, data are also presented for a cobalt-promoted molybdenum catalyst; the latter was used in the oxidic form rather than the sulfidic form because bio-oils contain only little sulfur. Experiments were carried out primarily to characterize the catalytic conversion of guaiacol in the presence of H$_2$ and a solvent, *n*-hexadecane. Specific goals were to demonstrate the measurement of kinetics of the guaiacol conversion, provide evidence of the reaction network, and compare high- and low-pressure data.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Catalysts. The reactants were guaiacol (Sigma-Aldrich, 99.5 wt %) and H$_2$ (formed by electrolysis of water in a Domnick Hunter gas generator, 99.999%, or from Praxair, 99.995%). Batches, typically 250 mL, of the organic reactant dissolved in *n*-hexadecane (Sigma-Aldrich, 99 wt %) were prepared in an autoclave, with the solution pressurized with H$_2$ and allowed to equilibrate for a few hours to produce the liquid feed. This liquid was pumped to a once-through flow reactor; all of the reactants were maintained in the liquid phase in the reactor, because the pressure was maintained higher than that used to prepare the feed solutions. The products were analyzed with an online gas chromatograph.
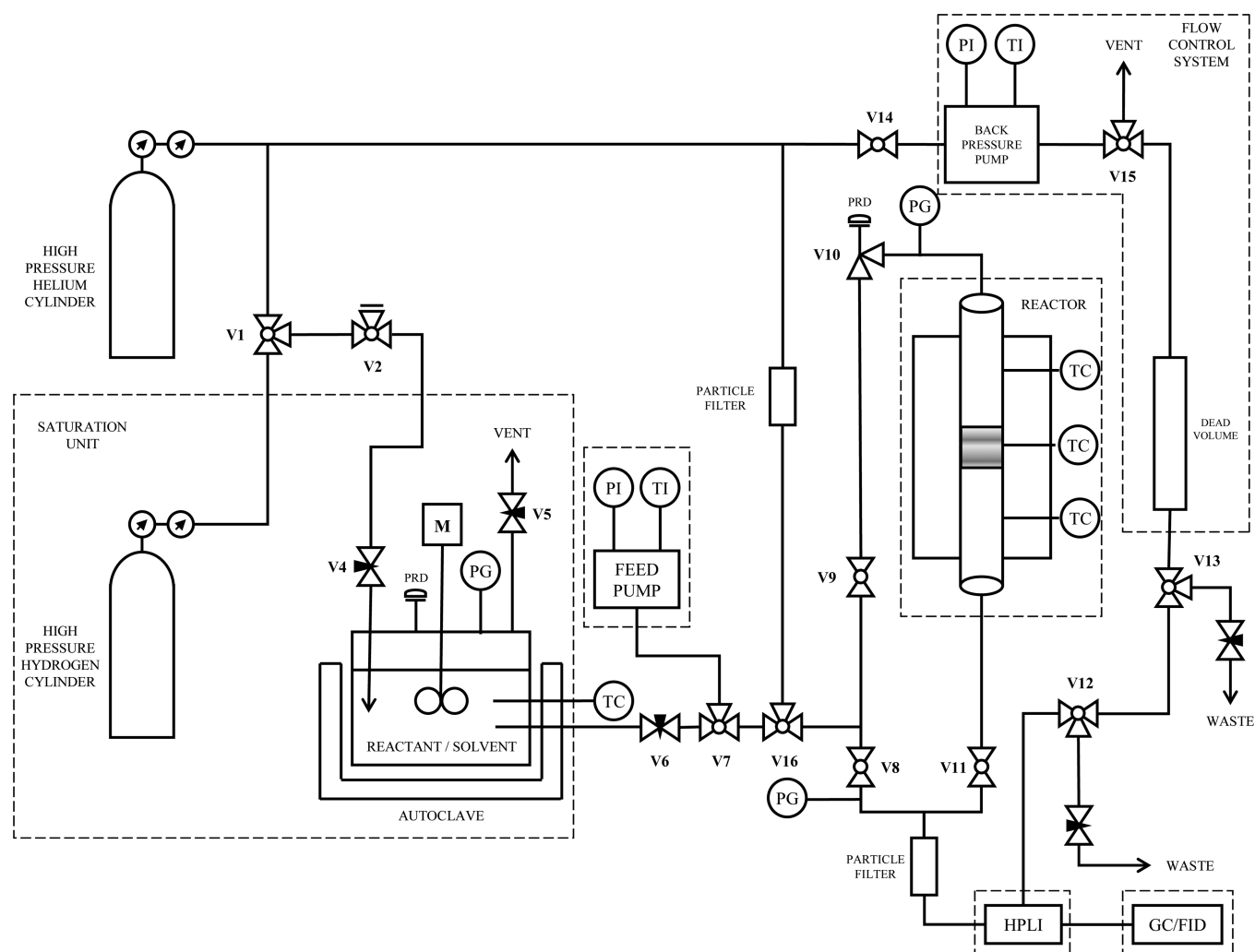
Figure 1. Schematic diagram of the high-pressure flow-reactor system.

The catalysts, described previously, were Pt/MgO,[24] Pt/γ-Al$_2$O$_3$,[3] and American Cyanamid HDS-16A, CoMo/γ-Al$_2$O$_3$ (surface area of 176 m^2/g and pore volume of 0.50 mL/g, as reported by the supplier). The catalyst mass in the reactor was varied between 0.01 and 0.1 g.

n-Hexadecane was chosen as a solvent for the reactants because it is relatively unreactive and high enough in molecular weight not to interfere with the product analysis. However, in our experiments *n*-hexadecane was converted substantially into lighter hydrocarbons at temperatures higher than 523 K, and therefore this temperature was chosen as the upper limit of the investigation.

The conversions were limited by the solubility of H$_2$ in *n*-hexadecane. Estimates of this solubility based on the Chao−Seader vapor−liquid equilibrium equation are shown in Figure S1 of the Supporting Information; the saturated solution at 69 bar and 300 K contained approximately 4 mol % H$_2$. This solubility limitation meant that we needed to keep the organic reactant concentration in the feed relatively low to have a stoichiometric excess of H$_2$ in the reactor. For example, for a molar ratio of H$_2$/guaiacol of 10:1, we prepared a feed solution of 0.4 mol % guaiacol in *n*-hexadecane. At the low guaiacol concentrations used, the gas chromatographic responses were so low that only the major and minor products could be quantified; trace products were not determined. Conversion data were collected under various operating conditions, as summarized in Table S1 of the Supporting Information.

2.2. Design of the Flow-Reactor System. The design of the flow-reactor system is an improved version (with modern hardware) of that reported by Eliezer et al.[25] A goal was to allow for flow of liquid feed over particles of a solid catalyst in an essentially isothermal plug-

flow reactor. Because the system was required to operate at pressures as high as 196 bar, the design required (a) a device upstream of the reactor for high-pressure saturation of reactant solution with H$_2$, (b) a pump to supply saturated feed to the reactor at a constant flow rate against a back pressure higher than the saturation pressure, and (c) the capability to draw samples from the product stream without disturbing the flow. The system, for safety, was also designed to minimize the volume of reactants and products and allow for unencumbered placement of valves, pressure gauges, vents, and other components. A schematic diagram of the reactor system is shown in Figure 1. The components represented within dashed lines in this figure are described in detail in the following paragraphs.

2.2.1. Reactor. The reactor was a stainless-steel tube with an outside diameter of 0.64 cm and a wall thickness of 0.16 cm. The length of the catalyst bed was typically 3.8 cm, and the volume was approximately 0.30 mL. Sintered stainless-steel disks (Swagelok frit, Designator SG, 40 μm nominal pore size) were mounted at the ends of the reactor to contain the inert packing and catalyst particles.

The reactor was designed for essentially plug-flow, isothermal operation. The catalyst was used in the form of particles with a nominal diameter of 250 μm or less, and upstream of the catalyst section there was a 14 cm long flow distribution section packed with particles of inert α-Al$_2$O$_3$ (A620 alundum, Fisher, 60-mesh particle size). There was also a 14 cm long section packed with α-Al$_2$O$_3$ particles downstream of the catalyst bed. The catalyst was mixed with particles of α-Al$_2$O$_3$, typically in a ratio of 1:4 by mass (for example, 0.1 g of catalyst was mixed with 0.4 g of α-Al$_2$O$_3$). The dimensions of

Table 1. Effect of the Temperature on the Conversion of Guaiacol in *n*-Hexadecane at 69 bar at WHSV = 46.4 g of Organic Reactant Solution (g of catalyst)$^{-1}$ h^{-1} [a]

product	conversion (%)	C_{H_2} (mol/L)	C_{GUA} (mol/L)	product selectivity at reaction temperature (K)		
				423	473	523
methane	5.16	0.19	0.011	0.073		
benzene				0		
cyclopentane				0		
cyclopentanol				0		
cyclopentanone				0		
cyclohexanol				0.10		
cyclohexanone				0		
phenol				0.041		
methoxycyclohexanol				0.78		
1,2-dimethoxybenzene				0		
methane	13.2	0.18	0.010		0.23	
benzene					0	
cyclopentane					0.022	
cyclopentanol					0	
cyclopentanone					0	
cyclohexanol					0.32	
cyclohexanone					0	
phenol					0.014	
methoxycyclohexanol					0.29	
1,2-dimethoxybenzene					0.12	
methane	62.9	0.17	0.010			0.10
benzene						0
cyclopentane						0.25
cyclopentanol						0
cyclopentanone						0
cyclohexanol						0.39
cyclohexanone						0.24
phenol						0.006
methoxycyclohexanol						0.006
1,2-dimethoxybenzene						0.01

[a]Data are shown for various reactant concentrations.

the packed reactor section conform to design criteria for essentially plug flow (see the Supporting Information for details).

The reactor was mounted in a three-zone electrically heated furnace (series 3210, Applied Test Systems), designed for precise temperature control. Three thermocouples (KQMSS-020G-6, Omega) were used to measure temperatures outside the reactor. A well in each of the three zones of the furnace allowed for placement of the thermocouples. The top (upstream) zone of the reactor was used as a feed preheat section; the middle zone was the reaction zone; and the bottom zone was normally not heated. The temperatures of the top two zones were controlled separately, by a Labview-based program powered by a real-time controller (NI-cRIO, National Instruments). Temperatures were maintained within 1 K.

2.2.2. Saturation Unit. High-pressure H$_2$ was sparged into a 300 cm^3 stirred autoclave (EZE-Seal, Autoclave Engineers) typically containing 200 mL of the reactant/solvent mixture. The time required for saturation was typically less than 2 h. The stirring speed was adjusted by variable speed-torque SCR DC motor control (KBPC-240D, Penta-Drive). The operating pressure was in the range of 0−200 bar, monitored with a pressure gauge.

2.2.3. Feed Pump. The reactant/solvent liquid mixture saturated with H$_2$ was fed to the reactor with a high-pressure syringe pump (260D, Teledyne Isco). The pump maintained the desired flow rate in the range of 0.001−100 mL/min against any pressure up to 500 bar. This pump has a low dead volume (<2.1 mL), and it drew saturated feed from the autoclave continuously. When feed was drawn from the saturator autoclave, care was taken to avoid sudden pressure changes to prevent changes in the H$_2$ concentration in the liquid.

2.2.4. Flow Control System. The back-pressure regulators and metering valves could not provide sufficient pressure control at the very low flow rates used in the experiments. Consequently, a second high-pressure syringe pump (similar to the feed pump) was included at the downstream end of the system to sustain adequate back pressures. The pump was linked to a 200 mL liquid reservoir (dead volume) pressurized with helium (99.995%, Praxair) by the pump. With this large surge volume for collecting liquid product from the reactor, there were minimal pressure fluctuations during each experiment. The dead volume was drained after each experiment.

2.2.5. High-Pressure Liquid Injector. The high-pressure injection device for the gas chromatograph (G3505, Agilent Technologies) could be used to transfer liquid samples to the gas chromatograph at pressures up to 346 bar. An internal sample valve (08N-0621V, Valco Instruments) was used to collect samples. The valve has four ports with a sample volume of 0.06 μL. The operation of the sample valve was automatically controlled by Agilent Chemstation software (G1701EA, version A.01.10.1, Agilent Technologies). The sample valve could be in position A or B, as shown in Figure S2 of the Supporting Information. When it was in position A, the product stream from the reactor passed through the sample loop before flowing to the dead volume. When the sample valve was switched to position B, the product stream from the reactor bypassed the sample loop and the sample was injected into gas chromatograph by applying pressure from an auxiliary helium flow from the gas chromatograph; the helium flow rate could be set in the range of 50−200 mL/min.

2.2.6. Safety Considerations. The system was designed to operate at pressures as high as 196 bar, limited by a pressure rupture disc rating

Table 2. Effect of the Pressure on the Conversion of Guaiacol in *n*-Hexadecane at 523 K at WHSV = 46.4 g of Reactant Solution g^{-1} of Catalyst h^{-1}

				product selectivity at reaction pressure (bar)		
product	conversion (%)	C_{H_2} (mol/L)	C_{GUA} (mol/L)	41	55	69
methane	34.2	0.095	0.010	0.13		
benzene				0.003		
cyclopentane				0.16		
cyclopentanol				0		
cyclopentanone				0.06		
cyclohexanol				0.28		
cyclohexanone				0.31		
phenol				0.03		
methoxycyclohexanol				0.002		
1,2-dimethoxybenzene				0.02		
methane	42.4	0.13	0.010		0.11	
benzene					0	
cyclopentane					0.23	
cyclopentanol					0	
cyclopentanone					0	
cyclohexanol					0.30	
cyclohexanone					0.32	
phenol					0.03	
methoxycyclohexanol					0	
1,2-dimethoxybenzene					0.01	
methane	62.9	0.17	0.010			0.10
benzene						0
cyclopentane						0.25
cyclopentanol						0
cyclopentanone						0
cyclohexanol						0.39
cyclohexanone						0.24
phenol						0.006
methoxycyclohexanol						0.006
1,2-dimethoxybenzene						0.01

(Swagelok, SS-RDK-16-2850). The $^1/_{16}$ in. outer diameter × 0.03 in. inner diameter stainless-steel tubing, primarily used as transfer lines in the system, can withstand pressures up to 1000 bar at temperatures from 295 to 923 K. The reactor (McMaster-Carr, 9926T121), which was the only part of the system operated at high temperatures, was rated for 1000 bar at 295−923 K.

Safety features enabled redundant monitoring of key control points. For example, both the pressure transducers associated with the pumps and analogue pressure gauges were used to monitor pressure up- and downstream of the reactor. The entire system, except the inert gas cylinders, was enclosed in a floor-mounted fume hood. The system was tested with helium gas at pressures exceeding the operating pressure before every experiment. Details of the operation and safety considerations are available in the Supporting Information.

3. RESULTS

3.1. Preliminary Results Obtained with Each Catalyst. In the reactor pre-filled with helium, the temperature of the catalyst was ramped to 523 K and held for 0.5 h before the start of feed flow. Data were obtained with guaiacol as the reactant with H$_2$ (thermodynamics data were used to estimate the solubility of H$_2$ in the reactant solution; see the Supporting Information). Temperature and pressure were also varied.

The results of initial experiments characterizing guaiacol conversion in the presence of H$_2$ catalyzed by Pt/MgO demonstrated the formation of phenol, with the selectivity decreasing with increasing temperatures. Methoxycyclohexanol also formed in high selectivities at 423 K, but the selectivity was

markedly less at higher temperatures. Cyclopentane formed in significant yields only at temperatures exceeding 523 K. Cyclohexanol also formed, with the selectivities being higher when the temperature was higher. Cyclohexanone was detected in the product only when the temperature was 523 K, the highest investigated. Quantitative results are presented below, but because of the limitations of our analytical methods, they do not include data for water and methanol as possible products.

Preliminary catalytic reaction experiments with guaiacol and H$_2$ were also carried out in the same way with the Pt/γ-Al$_2$O$_3$ catalyst. The results show that, under our typical reaction conditions [523 K, 69 bar, and weight hourly space velocity (WHSV) = 46.4 g of organic reactant solution (g of catalyst)$^{-1}$ h^{-1}], the *n*-hexadecane solvent was substantially cracked to give smaller hydrocarbons, in reactions inferred to be catalyzed in large measure by the acidic γ-Al$_2$O$_3$ support. These reactions complicated the interpretation of the guaiacol conversion data so substantially that no further experiments were carried out with this catalyst.

The conversion of guaiacol catalyzed by CoMo/γ-Al$_2$O$_3$ was investigated at 69 bar and 523 K. The catalyst was used in the as-supplied oxidic form; it was pretreated as stated above for Pt/MgO. In contrast to the typical pretreatment applied with a petroleum hydroprocessing catalyst, no sulfur-containing precursor was added to the feed to sulfide the catalyst.
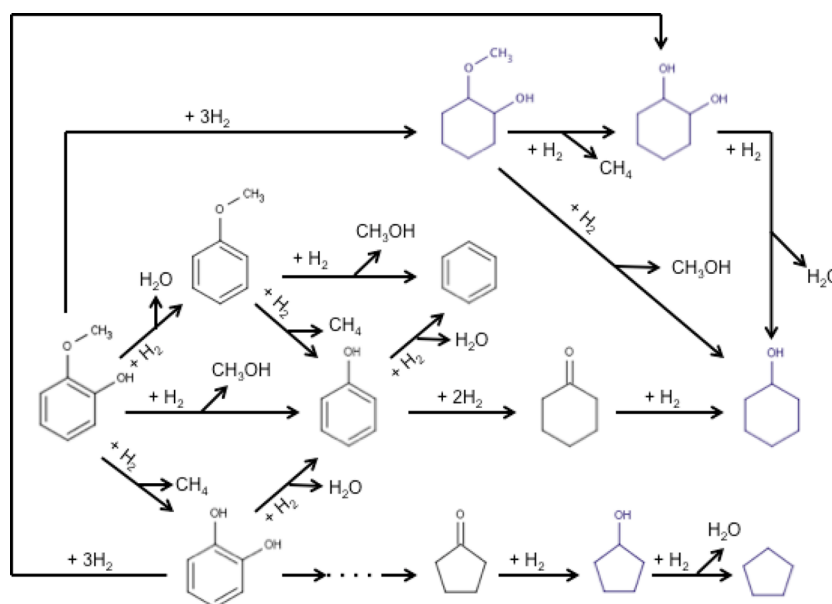
Figure 2. Approximate reaction network characterizing the conversion of guaiacol and H_2 catalyzed by Pt/MgO at 523 K and 69 bar.

Under our conditions, this catalyst was barely active. The conversions were too low to allow for quantification of the products. The qualitative data indicate very low conversions to phenol and methane at 523 K, demonstrating that some guaiacol hydrogenolysis occurred.

3.2. Conversion Data Characterizing Reaction of Guaiacol with H_2 Catalyzed by Pt/MgO: Evidence of Reaction Pathways and Kinetics. The conversion data characterizing the reaction of guaiacol with H_2 catalyzed by Pt/MgO are summarized in Tables 1 and 2. As expected, conversions were higher at higher temperatures. At a given space velocity, the conversion increased more than about 12 times when the temperature was raised from 423 to 523 K. The product distribution also changed markedly as the temperature increased.

The most informative data were obtained at 523 K; data showing selectivity for the formation of each of the major products at this temperature as a function of conversion are shown in Figures S3−S8 of the Supporting Information.

These results provide evidence of the kinetics of the reactions and the reaction pathways. The data obtained at 423 K show that hydrogenation of guaiacol leads to the formation of methoxycyclohexanol as the only major product. Cyclohexanone might also have formed, but if it did, it was presumably hydrogenated to form the observed cyclohexanol. The pathway for the formation of cyclohexanone is not evident from the data; it could have formed by sequential hydrogenation via phenol as an intermediate. The data obtained at 473 K suggest that methoxycyclohexanol was further converted to other products; this inference is based on a trend in the data showing that the selectivities for the formation of this compound were less than those observed at 423 K. The trends in the data also indicate that methane formed in higher selectivity at 473 K than at 423 K; this result might lead one to suggest that methane formed by hydrogenolysis of the methoxy group of methoxycyclohexanol at 473 K. However, we did not observe the formation of cyclohexanediol with methane, a result that weighs against the possibility of this hydrogenolysis. However, we do not rule out the possibility that cyclohexanediol did form and was further converted into other

products, such as cyclohexanol (which could have formed via HDO of cyclohexanediol). Cyclopentane also formed in low selectivities, and the pathway is unclear from the available data. At 523 K, methoxycyclohexanol must have been converted almost completely into other products, because the selectivity for its formation was very low. Correspondingly, cyclohexanol formed in relatively high selectivities along with cyclohexanone. It is likely that cyclohexanol formed in a primary reaction and was dehydrogenated to give cyclohexanone. The pathway to cyclopentanone is not evident from the data.

The influence of pressure (reflected in the concentrations of H_2) on the guaiacol conversion catalyzed by Pt/MgO is shown by the data of Table 2, representing reaction at 523 K. Conversions increased with pressure at this temperature, as expected, but the product distribution did not depend strongly upon the pressure.

The deactivation of the Pt/MgO catalyst was tested using the same catalyst charge for three consecutive reaction experiments. The guaiacol conversion decreased by a factor of about 2 after two runs, but it was almost unchanged thereafter, as shown by the data of Table S2 of the Supporting Information.

The product selectivities changed as the catalyst operated, suggesting that different catalytic sites may have undergone deactivation at different rates. For example, the sites associated with the formation of cyclopentane had deactivated significantly after the third run, but the sites associated with methane formation (hydrogenolysis) underwent only slow deactivation over the three runs.

4. DISCUSSION

4.1. Guaiacol Conversion Catalyzed by Pt/MgO: Comparison of Reaction Networks at Low and High Pressures. The data provide a basis for the statement of an approximate reaction network for the conversion of guaiacol under our conditions. Because the conversions were not sufficiently low (Tables 1 and 2), we infer that some primary products were not observed. However, a rather complete reaction network has been reported[4] for the guaiacol conversion catalyzed by the same Pt/MgO catalyst in the presence of gas-phase reactants; the network is based on low-

conversion data obtained at 573 K (recall that we did not make high-pressure measurements at this temperature because the cracking of the *n*-hexadacane carrier liquid was so substantial).

On the basis of the results reported here and the recently reported reaction network determined from data measured at atmospheric pressure and low guaiacol conversions, we infer the approximate reaction network shown in Figure 2. This network is consistent with the reported low-pressure network and is based on the assumption that some products formed but were not observed because they were converted substantially to other products under our high-pressure conditions. Identifications of apparent primary and higher order products were made on the basis of selectivity versus conversion plots shown in Figures S3−S8 of the Supporting Information. We emphasize that the designation of a product as primary or non-primary is just empirical; details are given in the captions of Figures S3−S8 of the Supporting Information.

4.2. Kinetics of Guaiacol Conversion Catalyzed by Pt/ MgO. Data representing the conversion of guaiacol at 523 K and 69 bar are shown in Figure 3. They are represented
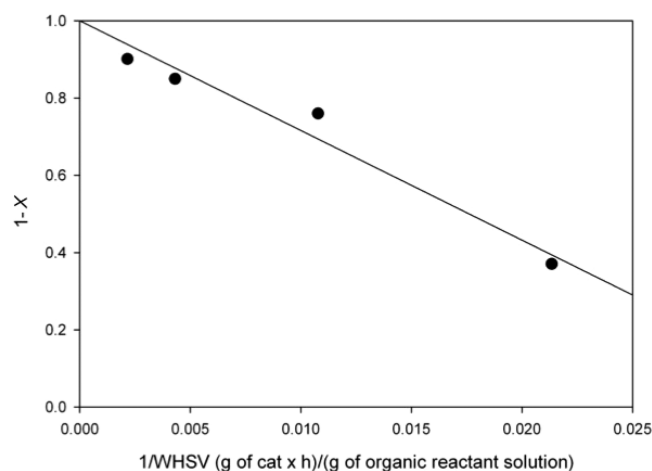

Figure 3. Guaiacol conversion catalyzed by Pt/MgO at 523 K and 69 bar. *X* is guaiacol conversion.

satisfactorily with pseudo-first-order kinetics (i.e., first-order reaction in the concentration of guaiacol; recall that H_2 was present in a stoichiometric excess), with the overall rate constant being 56.1 L of reactant solution (g of catalyst)$^{-1}$ h^{-1} (the concentration of guaiacol was 0.010 mol/L, estimated on the basis of the initial feed concentrations and an estimate based on the density of the solution at the reaction temperature). The data determined at 523 K provide a basis for estimation of the rate constants for the formation of each of the major products of the guaiacol conversion. The data of Figure 4 show that each reaction is satisfactorily represented by the approximation that it is first-order in guaiacol. The pseudo-first-order rate constants were estimated from the slopes of the lines fitting the data in Figure 4; the values are summarized in Table 3.

The sum of these rate constants (55.3 L of organic reactant solution (g of catalyst)$^{-1}$ h^{-1}) is close to the value of the rate constant for overall conversion of guaiacol (56.1 L of organic reactant solution g^{-1} of catalyst h^{-1}), determined from the data showing disappearance of guaiacol; thus, the formation of products other that the major products (methane, cyclo-
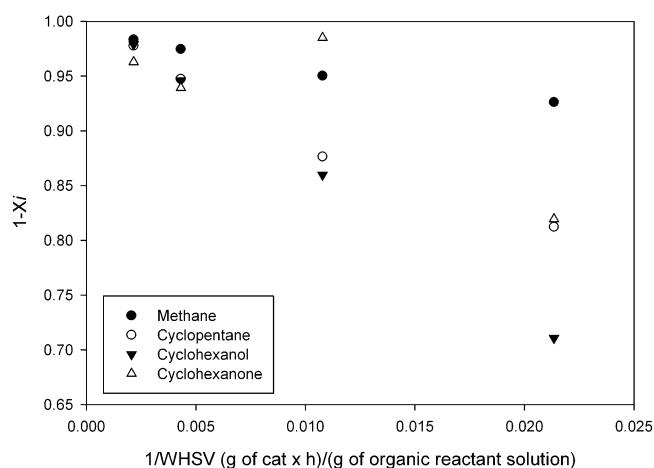

Figure 4. Formation of products in the conversion of guaiacol catalyzed by Pt/MgO at 523 K and 69 bar. X_i is guaiacol conversion to product *i*.

Table 3. Pseudo-First-Order Rate Constants for the Formation of the Major Products in the Conversion of Guaiacol in *n*-Hexadecane at 523 K and 69 bar[a]

product	first-order rate constant (L of organic reactant solution (g of catalyst)$^{-1}$ h^{-1})
methane	6.3
cyclopentane	15
cyclohexanol	22
cyclohexanone	12

[a]The catalyst was Pt/MgO.

hexanone, cyclohexanol, and cyclopentane) was kinetically insignificant under the stated conditions.

Data determined in this work are compared to data characterizing the same reactions with the same catalyst in experiments performed with vapor-phase reactants at a total pressure of 1 bar (Table 4). The comparison shows the advantage of high pressure (high H_2 concentration); the reactions are markedly faster at high pressure. The data point to the potential advantage of high-pressure operation in the practice in bio-oil conversion.

4.3. Strengths and Limitations of the High-Pressure Flow-Reactor System. The advantage of the flow-reactor system reported here is that all of the reactants are maintained in the liquid phase, so that the reactor operates essentially isothermally with plug flow. Thus, the design allows for the determination of fundamental, quantitative kinetics of high-pressure catalytic reactions, such as those occurring in biofuel hydroprocessing. Such information is valuable for comparisons of catalysts under realistic processing conditions, measurements of catalyst deactivation, and determination of reaction networks.

A limitation of the system is that the concentrations of H_2 are low, limited by its solubility in the carrier solvent (*n*-hexadecane). Another limitation is the complication introduced by the reactivity of the carrier liquid; practically, this complication restricted our measurements to temperatures no higher than about 523 K. It would be helpful to combine measurements such as ours with those determined in batch autoclave reactors and trickle-bed flow reactors, but those reactors suffer from their own limitations: catalyst deactivation is not easily decoupled from changes in the rate resulting from

Table 4. Comparison of Data Characterizing the Conversion of Guaiacol Catalyzed by Pt/MgO at Low and High Pressures[a]

reactor system	reaction temperature (K)	C_{H_2} (mol/L)	C_{GUA} (mol/L)	first-order rate constant (mol of GUA (g of catalyst)$^{-1}$ h^{-1})
high pressure (liquid-phase reactants)	523	0.17	0.010	0.55
low pressure (vapor-phase reactants)	573	0.01	7.3×10^{-4}	5.7×10^{-3}

[a]The high-pressure data were obtained at 523 K and 69 bar. The low-pressure data were obtained at 573 K and 1.4 bar, as reported elsewhere.[4] GUA is guaiacol. Note that the temperatures of the low- and high-pressure experiments were not the same (see the text).

depletion of reactants in batch reactors, and flow patterns in trickle beds are complex enough that one may not readily determine fundamental reaction kinetics data.

5. CONCLUSION

The high-pressure reactor system described here allows for measurements of kinetics of hydroprocessing reactions of compounds characteristic of bio-oils under nearly plug-flow, isothermal conditions. A key to the design is the maintenance of all of the reactants (including H$_2$) in the liquid phase in the reactor, so that the reactor operates with essentially plug flow. Data presented here illustrate the operation of the system and determine rate constants for the Pt/MgO-catalyzed removal of guaiacol (approximately 55 L of organic reactant solution (g of catalyst)$^{-1}$ h^{-1} at 523 K) and the formation of the major products: methane, cyclohexanol, cyclohexanone, and cyclopentane. The data also determine an approximate reaction network for hydroprocessing of guaiacol.

◼ ASSOCIATED CONTENT

ⓢ Supporting Information

Calculated mole fractions of H$_2$ dissolved in *n*-hexadecane at 26.9 and 76.9 °C (Figure S1), list of experiments: measurement of guaiacol conversions with a high-pressure reactor system (Table S1), schematic representation of the operation of the high-pressure sample valve (Figure S2), and selectivity for the formation of methane (Figure S3), cyclopentane (Figure S4), cyclohexanol (Figure S5), cyclohexanone (Figure S6), phenol (Figure S7), and methoxycyclohexanol (Figure S8) in the conversion of guaiacol catalyzed by Pt/MgO in the presence of H$_2$ at 523 K and 69 bar. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

◼ ACKNOWLEDGMENTS

◼ REFERENCES

(1) Saidi, M.; Samimi, F.; Karimipourfard, D.; Nimmanwudipong, T.; Gates, B. C.; Rahimpour, M. R. *Energy Environ. Sci.* **2014**, *7*, 103−129.
(2) Wang, Y.; He, T.; Liu, K.; Wu, J.; Fang, Y. *Bioresour. Technol.* **2012**, *108*, 280−284.
(3) Runnebaum, R. C.; Lobo-Lapidus, R. J.; Nimmanwudipong, T.; Block, D. E.; Gates, B. C. *Energy Fuels* **2011**, *25*, 4776−4785.
(4) Nimmanwudipong, T.; Runnebaum, R. C.; Block, D. E.; Gates, B. C. *Energy Fuels* **2011**, *25*, 3417−3427.
(5) Zhu, X.; Lobban, L. L.; Mallinson, R. G.; Resasco, D. E. *J. Catal.* **2011**, *281*, 21−29.
(6) Gonzalez-Borja, M. A.; Resasco, D. E. *Energy Fuels* **2011**, *25*, 4155−4162.
(7) Lin, Y. C.; Li, C. L.; Wan, H. P.; Lee, H. T.; Liu, C. F. *Energy Fuels* **2011**, *25*, 890−896.
(8) Gutierrez, A.; Kaila, R. K.; Honkela, M. L.; Siloor, R.; Krause, A. O. I. *Catal. Today* **2009**, *147*, 239−246.
(9) Yakovlev, V. A.; Khromova, S. A.; Sherstyuk, O. V.; Dundich, V. O.; Ermakov, Yu. D.; Novopashina, V. M.; Lebedev, M. Yu.; Bulavchenko, O.; Parmon, V. N. *Catal. Today* **2009**, *144*, 362−366.
(10) Elliott, D. C.; Hart, T. R. *Energy Fuels* **2009**, *23*, 631−637.
(11) Zhao, C.; Kou, Y.; Lemonidou, A. A.; Li, X. B.; Lercher, J. A. *Angew. Chem., Int. Ed.* **2009**, *48*, 3987−3990.
(12) Zhao, C.; Lercher, J. A. *ChemCatChem* **2012**, *4*, 64−68.
(13) Zhao, C.; He, J.; Lemonidou, A. A.; Li, X.; Lercher, J. A. *J. Catal.* **2011**, *280*, 8−16.
(14) Loricera, C. V.; Pawelec, B.; Infantes-Molina, A.; Alvarez-Galvan, M. C.; Huirache-Acuna, R.; Nava, R.; Fierro, J. L. G. *Catal. Today* **2011**, *172*, 103−110.
(15) Bui, V. N.; Laurenti, D.; Afanasiev, P.; Geantet, C. *Appl. Catal., B* **2011**, *101*, 239−245.
(16) Bui, V. N.; Laurenti, D.; Delichere, P.; Geantet, C. *Appl. Catal., B* **2011**, *101*, 246−255.
(17) Bui, V. N.; Toussaint, G.; Laurenti, D.; Mirodatos, C.; Geantet, C. *Catal. Today* **2009**, *143*, 172−178.
(18) Centeno, A.; Laurent, E.; Delmon, B. *J. Catal.* **1995**, *154*, 288−298.
(19) Gevert, B. S.; Otterstedt, J. E.; Massoth, F. E. *Appl. Catal.* **1987**, *31*, 119−131.
(20) Massoth, F. E.; Politzer, P.; Concha, M. C.; Murray, J. S.; Jakowski, J.; Simons, J. *J. Phys. Chem. B* **2006**, *110*, 14283−14291.
(21) Senol, O. I.; Ryymin, E.-M.; Viljava, T.-R.; Krause, A. O. I. *J. Mol. Catal. A: Chem.* **2007**, *277*, 107−112.
(22) Jongerius, A. L.; Jastrzebski, R.; Bruijnincx, P. C. A.; Weckhuysen, B. M. *J. Catal.* **2012**, *285*, 315−323.
(23) Kallury, R. K. M. R.; Restivo, W. M.; Tidwell, T. T.; Boocock, D. G.; Crimi, A.; Douglas, J. *J. Catal.* **1985**, *96*, 535−543.
(24) Nimmanwudipong, T.; Aydin, C.; Lu, J.; Runnebaum, R. C.; Brodwater, K. C.; Browning, N. D.; Block, D. E.; Gates, B. C. *Catal. Lett.* **2012**, *142*, 1190−1196.
(25) Eliezer, K. F.; Bhinde, M.; Houalla, M.; Broderick, D.; Gates, B. C.; Katzer, J. R.; Olson, J. H. *Ind. Eng. Chem. Fundam.* **1977**, *16*, 380−385.