Biohydrogen Production by Catalytic Supercritical Water Gasification: A Comparative Study

Mohammad Shahed Hasan Khan Tushar, Paul C. DiMaria, Sultan Majed Al-Salem, Animesh Dutta, and Chunbao Charles Xu

ABSTRACT: In this article, supercritical water gasification of biocrude at different conditions was performed and compared to each other. Three scenarios were considered while treating biocrude originating from cattle manure (CM) and corn husk (CH), namely, uncatalyzed feedstock, catalyzed with 10% Ni−0.08% Ru/Al2O3 and finally catalyzed with 10% Ni−0.08% Ru/Al2O3−ZrO2. It was found that 10% Ni−0.08% Ru/Al2O3−ZrO2 has performed significantly better than the other two scenarios over the 5 hour run time with a 193% and 187% higher hydrogen yield compared to the uncatalyzed and 10% Ni−0.08% Ru/Al2O3 catalyzed scenarios, respectively. Compared to CM gasification in the presence of a 10% Ni−0.08% Ru/Al2O3−ZrO2 catalyst, the catalyst got deactivated because of the high phenol and furan content in the corn husk biocrude, therefore hydrogen yield performance fell significantly. It was observed that the carbon gasification efficiency of the biocrude was independent of temperature.

1. INTRODUCTION

The need for environmentally benign alternatives to current fossil fuels has been developed in the past few decades. Hydrogen (H2) is becoming more attractive because of its nature as a clean combustible fuel. However, current H2 production largely comes from fossil sources (96%), rendering it as a nonenvironmentally friendly substance. Furthermore, H2 is distributed around the globe in the form of various compounds. As such, “suitable technology” is required to extract it from a primary source because of the nature of those hydrogen-rich compounds. Biomass would be a better source of renewable energy as it is theoretically carbon-neutral. The validity of fuels generated from biomass should consider the renewable energy as it is theoretically carbon-neutral. Hydrogen-rich compounds. Biomass would be a better source of hydrogen from a primary source because of the nature of those hydrogen-rich compounds. Biocatalysis would be a better source of renewable energy as it is theoretically carbon-neutral.

It is a well-established fact that beyond the critical point [supercritical water (SCW), Tc = 373.95 °C, and Pc = 22.06 MPa], water becomes very reactive. Water is in single phase, which allows it to overcome any mass-transfer limitation during the gasification process and has thus faster reaction rates. SCW gasification (SCWG) of biomass is more advantageous over conventional gasification. It can be used in wet biomass treatment effectively with moisture contents greater than 70%, which in turn reduces the cost and time required in drying for the conventional process. Although this cost is not completely mitigated in a SCW gasifier, some of the energy used to heat the water in the reaction is recoverable in a heat exchanger system. Carbon dioxide (CO2), produced as a byproduct of SCWG, can be sequestered or may be used in industries and chemical processes. Figure 1 shows the scheme of low-grade biomass conversion through the SCWG process (adapted from Matsumura et al. and Loppinet-Serani et al.).

The water in a SCWG reaction acts as a solvent, reactant, and catalytic precursor in the process. Under supercritical conditions, water becomes a homogeneous medium, and the dielectric constant becomes low enough to enable the solubility of organic compounds. It uses a combination of water–gas shift, hydrolysis, and pyrolysis reactions, which enables an exceptionally high level of H2 production when compared with conventional gasification. In addition to these, catalysts are
The current work is a follow-up study to the feasibility investigated by many researchers. A novel dual-metal support or dual metal on single support catalysts were also during the gasification process, which enhances H₂ production. Ruthenium (Ru)-based catalysts have also been found to be highly effective in the gasification of biomass. Furthermore, the Ni catalyst with Ru as a promoter shows better H₂ yields in comparison to Ni or Ru catalyst alone. Single metal on dual support or dual metal on single support catalysts were also investigated by many researchers. A novel dual-metal support catalyst is also applied in SCWG, showing a comparatively better H₂ yield for liquefied cattle manure (CM). The current work is a follow-up study to the feasibility of the best catalyst applied to different hydrothermally liquefied (HTL) biomass [liquefied corn husk (CH)]. Hydrothermal treatment of biomass is an advanced thermochemical conversion process to obtain biocrude using water as a reaction medium. Unlike conventional thermochemical conversion processes, hydrothermal treatment is flexible and energy-efficient because it does not require predrying of the biomass feedstock. The obtained biocrude is an oxygenated and energy-dense, yet renewable liquid from which transportation fuels and various useful chemicals may be produced through further processing; one of these processes is SCWG.

It is reported by Yan et al. that SCW acts as catalyst because of high H⁺ and OH⁻ ions. As the product gas can be discharged at high pressure, the compression cost for storing hydrogen is thus eliminated. SCWG is a technology in the early stages of technical development. A better understanding of the fundamental phenomena is essential for an adequate SCWG reactor and process design. In order to maximize the conversion and optimize the gas yield and composition, research on the key parameters influencing the overall process efficiency is of great importance. Compared to the biochemical conversion process of biomass, the SCWG process shows higher H₂ yields. Thus, H₂ production using SCWG provides a more sustainable and environmentally friendly alternative in the future. In this study, the SCWG of real-life biomass in the presence of catalysts is performed. The purpose of this research is to gasify HTL CH and compare the results with HTL CM using SCW in the presence of catalysts. The catalysts tested are 10% Ni−0.08% Ru supported on either Al₂O₃ or Al₂O₃−ZrO₂ (10% Ni−0.08% Ru/Al₂O₃ and 10% Ni−0.08% Ru/Al₂O₃−ZrO₂) for CH biocrude and only 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalyst is used during gasification of CM biocrude. The use of 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ is due to the fact that it has previously proved effective for the production of H₂ in SCWG processes. Additionally, the Al₂O₃-supported catalyst is tested because it is an industry-approved and standardized catalyst support providing a realistic benchmark for comparison. Also, ZrO₂ is known to help in gasifying carbon through reforming during the gasification process.

CH is an ideal material to be used for fuel generation, considering its origin as a byproduct of food production. The HTL CH is chosen to be tested because it has high moisture content and had not been previously tested in a SCW gasifier. An Eley−Rideal (ER)-based mechanistic model with elementary steps is proposed to understand the SCWG kinetics of the dried CH biocrude. The obtained data are also fitted using a basic power law (PL) model to find different kinetic parameters and are later compared with dried CM biocrude. The findings and observations of the experiments and their derivations are outlined in this article.

2. MATHEMATICAL MODELING OF REACTION KINETICS

Kinetic modeling was performed with elementary steps in the presence of catalysts. Therefore, an Eley-Rideal (ER)-based mechanistic model was derived. The models were then justified against the experimental data to obtain the slowest (governing) step. This slowest step is also called the rate-determining step (RDS) as the overall reaction scheme depends on it. Based on the elemental analysis, the CH biocrude may be expressed as C₆H₁₂O₆ to deal with the stoichiometry and reaction kinetics. The overall CH biocrude gasification in SCW can be written as follows

![Figure 1. Plausible scheme of biomass SCWG process. (Adapted from Matsumura, Y.; Minowa, T.; Potic, B.; Kersten, S. R.; Prins, W.; van Swaaij, W. P.; van de Beld, B.; Elliott, D. C.; Neuenschwander, G. G.; Kruse, A.; Antal Jr, M. J. Biomass gasification in near-and super-critical water: status and prospects. Biomass Bioenergy. 2005, 29(4), 269–292; Copyright 2005 Elsevier Ltd. and Loppinet-Serani, A.; Aymonier, C.; Cansell, F. Current and foreseeable applications of supercritical water for energy and the environment. ChemSusChem. 2008, 1(6), 486–503; Copyright 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).](image-url)
Table 1. Rate Models Formulated Using ER Mechanisms

| model no. | equation |
|-----------|----------|
| ER11      | \[ r_A = \frac{k_0 \exp(-E/RT)}{1 + K_A C^0 + K_C C + K_{A\alpha \alpha} C_{\alpha}^{1/2} + K_{C\alpha \alpha} C_{\alpha}^{1/2}} \] |
| ER12      | \[ r_A = \frac{k_0 \exp(-E/RT)}{1 + K_A C^0 + K_C C + K_{A\alpha \alpha} C_{\alpha} + K_{C\alpha \alpha} C_{\alpha}} \] |
| ER13      | \[ r_A = \frac{k_0 \exp(-E/RT)}{1 + K_A C^0 + K_C C + K_{A\alpha \alpha} C_{\alpha}^{1/2} + K_{C\alpha \alpha} C_{\alpha}^{1/2}} \] |
| ER14      | \[ r_A = \frac{k_0 \exp(-E/RT)}{1 + K_A C^0 + K_C C + K_{A\alpha \alpha} C_{\alpha} + K_{C\alpha \alpha} C_{\alpha}} \] |
| ER15      | \[ r_A = \frac{k_0 \exp(-E/RT)}{1 + K_A C^0 + K_C C + K_{A\alpha \alpha} C_{\alpha}^{1/2} + K_{C\alpha \alpha} C_{\alpha}^{1/2}} \] |
| ER16      | \[ r_A = \frac{k_0 \exp(-E/RT)}{1 + K_A C^0 + K_C C + K_{A\alpha \alpha} C_{\alpha} + K_{C\alpha \alpha} C_{\alpha}} \] |
| ER17      | \[ r_A = \frac{k_0 \exp(-E/RT)}{1 + K_A C^0 + K_C C + K_{A\alpha \alpha} C_{\alpha}^{1/2} + K_{C\alpha \alpha} C_{\alpha}^{1/2}} \] |

\(^\text{a}\): C_{10}H_{18}O_{12}; B: H_2O; C: CO_2; D: H_2; K_i are the adsorption constants for the species (i = 1, 2, 3, ...); and K_p is the equilibrium constant.

\[ C_{10}H_{18}O_{12} + 8H_2O \rightarrow 10CO_2 + 17H_2 \]
\[ \Delta H = 127.11 \text{ kJ/mol} \]  

However, in order to justify the outcome, it is imperative to test the result against a very basic rate model. As such, an empirical PL rate model assuming the overall reaction is irreversible, and the feed concentration is constant, \( r_A \) (concentration/time), which is shown below with respect to the first-order Arrhenius equation expression for \( k_A \):

\[ r_A = k_A C^p = k_0 e^{-E/RT} C_A^p \]

where \( k_0 \) is the pre-exponential factor (frequency factor), \( n \) is the reaction order, \( E \) is the activation energy, J/mol, and \( C_A \) is the concentration of CH dry oil in kmol/m^3. A regression software (NLRGREG) was used to determine the unknown parameters \( k_0, E \), and \( n \) using the obtained data. However, the reaction rate constant \( (k_A) \) was directly related to the order of reaction and hence has a variable unit. As mentioned earlier, an ER-based mechanistic model was developed to determine the RDS. An ER model assumes that only dissolved oxygenated hydrocarbons are adsorbed and interact with the active sites of catalysts. The steps are depicted as follows

\[ C_{10}H_{18}O_{12} + [S] \xrightarrow{k_{1-1}} C_{10}H_{18}O_{12}[S] \text{ (adsorption)} \]
where SR depicts the surface reaction, [S] is the active sites on catalysts, $k_i$ is the rate of forward reaction, and $k_i$ is the rate of backward reaction. Catalysts either accelerate or retard the reaction rate toward completion by staying unaffected during the chemical reaction. Nonetheless, the active sites shown in the elementary steps are a clear indication of the presence of the catalyst. Equations 4 and 12 were not used to develop any model. In total, seven ER models were proposed and investigated. Table 1 shows all the models and related assumptions on these reactions.

### 3. Results and Discussion

#### 3.1. Effects of Temperature on SCWG of Biocrude.

Figure 2 shows the effect of temperature on product yield and carbon gasification efficiency (CGE, % = the mass of carbon in the product gas phase/the mass of carbon entered as feed in the reactor) between the CH biocrude and CM biocrude in the presence of the catalyst. As can be seen from Figure 2, the hydrogen and carbon dioxide yield decreased and the methane yield increased with the increase in time on stream. As discussed and mentioned earlier, the catalyst got deactivated in terms of hydrogen production because of the presence of phenolic and furan compounds. Interestingly, CGE remained almost constant over the experimental procedure. This might be described as although the CO2 yield decreases, the increase in CH4 yield balances the deficit and thus retains the CGE almost constant.
Besides, this study assumes that lack of catalyst active sites led to higher methane yield, which also explained the increase in CH₄ yield and a decrease in CO₂ and H₂ yield. However, in both the gasification cases, the system reached near equilibrium in terms of carbon conversion even at low temperature.

3.2. Noncatalytic and Catalytic SCWG. In order to perform the SCWG reaction, the HT liquid was required to have a carbon concentration of 10−20 g/L. This range was selected for the following reasons. The minimum carbon concentration in which the system can effectively operate is 10 g/L and the maximum concentration at which a high-performance liquid chromatography (HPLC) pump can withstand without clogging is 20 g/L.¹⁴ The carbon content was determined by SHIMADZU.

A TOC analyzer (TOC-VPN, Shimadzu Corporation, Kyoto, Japan) is used in this experiment to determine the total organic carbon content in the biocrudes. The organic carbon content is found to be 24.96 g/L for CH biocrude and 21.97 g/L for CM biocrude, which are above the desired range. As a result, the HT liquid is diluted to achieve a desired carbon concentration of below 20 g/L. An in-house research by Tushar et al.¹⁴ finds the highest H₂ yield at 700 °C in the absence of catalysts and in the presence of 10% Ni−0.08% Ru/Al₂O₃−ZrO₂. Hence, this study has performed the experiments at 700 °C in the absence of a catalyst and in the presence of 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ and 10% Ni−0.08% Ru/Al₂O₃. The reason behind the use of two catalysts is to check the effect on product yield for different biomass and obtain a feedstock-flexible catalyst.

The pressure was kept constant at 25 MPa as the pressure does not have any significant effect on H₂ yield.²⁵−²⁷ Figure 3a shows the H₂ yield at various catalytic conditions of CH biocrude SCWG. The average H₂ yields of the 10% Ni−0.08% Ru/Al₂O₃−ZrO₂, 10% Ni−0.08% Ru/Al₂O₃, and uncatalyzed SCWG runs were 1.26, 0.44, and 0.43 mol/mol carbon, respectively, over 5 hours of continuous run time.

As can be seen from Figure 3b, the initial H₂ yield from catalytic SCWG of CH biocrude is higher compared to CM biocrude up to 3.5 h. After 5 hours, the performance of the 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalyst with CH biocrude was significantly dropped compared to that of CM biocrude. The H₂ yield from CM biocrude also decreased compared to that from CH biocrude; however, the trend is not significant. These results suggest that the 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalyst underwent rapid deactivation in the case of CH biocrude as a result of a contaminant because it showed more promising results in the first 2 hours of run time. Gas chromatography−mass-selective detection (GC−MSD) testing was performed on both biocrude liquids to determine the chemical compounds, which may have caused the deactivation of the catalyst, which is shown in Table 2.

The components shown in Table 2 were chosen because it has been found that phenols and furfurals in the raw materials used for SCWG are likely to form tarry substances, which lead to catalyst deactivation.²⁹ Both the biocrude contain phenolic and furan compounds. However, the CH biocrude contains higher phenolic and furan compounds. The high phenol and furan content in CH biocrude is a likely cause of the catalyst deactivation.²⁹,³⁰

Table 2. Phenolic and Furan Compounds

| Compound                        | CM biocrude | CH biocrude |
|--------------------------------|-------------|-------------|
| Phenol                          | nd*         | 6.53        |
| phenol, 2-methoxy               | 9.72        | 11.10       |
| phenol, 4-ethyl-2-methoxy       | 5.41        | 6.13        |
| 2,4-dimethoxyphenol             | 7.73        | nd          |
| ethanone, 1-(4-hydroxy-3,5-dimethoxyphenol) | 7.28 | 5.12 |
| phenol, 4-ethyl                 | nd          | 6.77        |
| phenol, 2,6-dimethoxy           | nd          | 10.51       |
| Vanillin                       | nd          | 3.16        |
| Apocynin                       | nd          | 1.90        |
| homovanillic alcohol           | nd          | 1.54        |
| Total phenolic compounds       | 30.14       | 52.74       |
| 2(3H)-benzofuranone, 3a,4,5,7a-tetrahydro   | 2.37 | nd |
| ethanone, 1-(2-furanyl)         | nd          | 4.51        |
| Total Furan Compounds          | 2.37        | 4.51        |

*nd: not detected.

Table 2 shows the H₂ yield at various catalytic conditions of CH biocrude SCWG. The average H₂ yields of the 10% Ni−0.08% Ru/Al₂O₃−ZrO₂, 10% Ni−0.08% Ru/Al₂O₃, and uncatalyzed SCWG runs were 1.26, 0.44, and 0.43 mol/mol carbon, respectively, over 5 hours of continuous run time.

As can be seen from Figure 3b, the initial H₂ yield from catalytic SCWG of CH biocrude is higher compared to CM biocrude up to 3.5 h. After 5 hours, the performance of the 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalyst with CH biocrude was significantly dropped compared to that of CM biocrude. The H₂ yield from CM biocrude also decreased compared to that from CH biocrude; however, the trend is not significant. These results suggest that the 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalyst underwent rapid deactivation in the case of CH biocrude as a result of a contaminant because it showed more promising results in the first 2 hours of run time. Gas chromatography−mass-selective detection (GC−MSD) testing was performed on both biocrude liquids to determine the chemical compounds, which may have caused the deactivation of the catalyst, which is shown in Table 2.

The components shown in Table 2 were chosen because it has been found that phenols and furfurals in the raw materials used for SCWG are likely to form tarry substances, which lead to catalyst deactivation.²⁹ Both the biocrude contain phenolic and furan compounds. However, the CH biocrude contains higher phenolic and furan compounds. The high phenol and furan content in CH biocrude is a likely cause of the catalyst deactivation.²⁹,³⁰

Table 2. Phenolic and Furan Compounds

| Compound                        | CM biocrude | CH biocrude |
|--------------------------------|-------------|-------------|
| Phenol                          | nd*         | 6.53        |
| phenol, 2-methoxy               | 9.72        | 11.10       |
| phenol, 4-ethyl-2-methoxy       | 5.41        | 6.13        |
| 2,4-dimethoxyphenol             | 7.73        | nd          |
| ethanone, 1-(4-hydroxy-3,5-dimethoxyphenol) | 7.28 | 5.12 |
| phenol, 4-ethyl                 | nd          | 6.77        |
| phenol, 2,6-dimethoxy           | nd          | 10.51       |
| Vanillin                       | nd          | 3.16        |
| Apocynin                       | nd          | 1.90        |
| homovanillic alcohol           | nd          | 1.54        |
| Total phenolic compounds       | 30.14       | 52.74       |
| 2(3H)-benzofuranone, 3a,4,5,7a-tetrahydro   | 2.37 | nd |
| ethanone, 1-(2-furanyl)         | nd          | 4.51        |
| Total Furan Compounds          | 2.37        | 4.51        |

*nd: not detected.

Figure 3. Hydrogen yield: (a) three tested scenarios of CH biocrude and (b) CH and CM biocrude with the catalyst 10% Ni−0.08% Ru/Al₂O₃−ZrO₂. Experimental conditions for both cases: T = 700 °C, P = 25 MPa, WHSV = 2 h⁻¹, and time on stream = 5 h.

at temperatures above 250 °C.³¹ As a result, the furan content may still have contributed to the deactivation of the catalysts.

The scanning electron microscopy (SEM) images with energy-dispersive X-ray (EDX) spectra of fresh (not reduced) and spent catalysts 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ are shown
in Figure 4. A magnification of 250 μm was used for fresh catalysts, and 100 μm was used for spent catalysts. Because of the technical limitation of the SEM resolution, the catalyst metal diffusion in the supports cannot be explained. However, it is possible to show the presence of different elements on the sample through EDX, which is shown in the figure. The main difference in the EDX spectra is the presence of carbon. The fresh catalyst sample (Figure 4a) does not have any carbon present in it, whereas both the spent catalysts have carbon in the sample. This is an indication of carbon deposition, in the form of char and/or coke, on the catalyst surface, causing gradual deactivation over time. Besides, the carbon count on the catalyst used in CH biocrude (Figure 4c) gasification is higher compared to that used in CM biocrude (Figure 4b) gasification, which explains the significant decrease in H₂ yield. This finding is also further confirmed by thermogravimetric analysis (TGA). The whitish flaky materials seen on the used catalyst images are an indication of the formation of char and/or coke. The transmission electron microscopy (TEM) images of fresh and spent 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalysts for CM and CH dry oils are shown in Figure 5. It was observed that the surfaces of the fresh catalyst particles are slightly rough, which is an indication of poor crystallinity. Because of the presence of these rough surfaces, random graphene layers were formed, which ultimately led to the formation of T-(turbostatic) carbon. These T-carbons could not be separated from the amorphous carbon using TEM because of their nature. The arrow indicates the area of formed T-carbons on the spent catalyst. Further investigation was performed using TGA.

Figure 4. SEM images and EDX spectra for the (a) fresh (not reduced) and used 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalyst for both (b) CM and (c) CH biocrude, T = 700 °C, P = 25 MPa, and WHSV = 2 h⁻¹.

Figure 5. TEM images of spectra for the (a) fresh (not reduced) and used 10% Ni−0.08% Ru/Al₂O₃−ZrO₂ catalyst for both (b) CM and (c) CH biocrude, T = 700 °C, P = 25 MPa, and WHSV = 2 h⁻¹.
Figure 6 shows the X-ray photoelectron spectroscopy (XPS) spectra of fresh and spent 10% Ni–0.08% Ru/Al$_2$O$_3$–ZrO$_2$ catalysts. It can be observed that both the fresh and spent catalysts have Ni, O, Zr, and Ru, whereas the spent catalysts have C peaks. The binding energies (BEs) and the chemical shifts of Ni and Ni oxides are used to determine the oxidation state. The BEs of these elements are shown in Table 3 for fresh and spent catalysts. It can be observed that the BE of the Ni 2p spectra just increased over 1 eV in the case of spent catalyst that proves the presence of atomic sputtering. In Figure 6a of the fresh catalyst, stepped peaks are observed at BEs of 280.85 and 284.85 eV. The peak at 280.85 is attributed to ruthenium 3d, and the peak at 284.84 is assigned as carbon 1s. It is also observed in the case of fresh catalyst that the Ru 3p peak is detected at a BE of 460.05 eV. The carbon peak intensity for spent catalyst for CH biocrude is higher than that of spent catalyst of CM biocrude, which proves the findings of SEM–energy-dispersive spectroscopy (EDS) spectra.

The TGA profile of used catalysts is shown in Figure 7. Biomass-derived char contains two different types of carbons: amorphous and graphitic. Because of the presence of two different structures, the TGA profile shows a two-stage combustion. Mass loss at lower temperature (below 350 °C) can be attributed to the moisture content and amorphous carbon, and high-temperature combustion can be attributed to graphitic carbon. As per Figure 7, the accumulated carbon amount on the spent catalyst is about 15% for the catalyst used in CM biocrude gasification and about 30% for the catalyst used in CH biocrude gasification after 6 hours. These results indicate that the catalyst used in CH biocrude gasification got highly poisoned with higher amount of char and/or coke and thus got deactivated in terms of hydrogen yield. These TGA findings resemble the findings obtained in the EDX spectra during SEM of the spent catalysts considering char and/or coke formation.

3.3. Comparison with Previous Study. Table 4 shows the comparison of the current study with the in-house and other researchers’ studies for the first 2.5 h run. Byrd et al. and Zhang et al. used liquefied biomass, and Behnia et al. used an aqueous fraction of pyrolysis oil from hardwood sawdust to perform SCWG using a packed bed continuous flow reactor with almost similar parameters. The experimental conditions and parent feedstocks used to prepare the liquid feed are also listed in the table. As can be seen from the table, the highest hydrogen yield was obtained using 10% Ni–0.08% Ru/Al$_2$O$_3$–ZrO$_2$ for CH biocrude; however, CGE was comparatively low. The catalyst activity order in terms of H$_2$ yield can be shown as 10% Ni–0.08% Ru/Al$_2$O$_3$–ZrO$_2$ (CH) > 20% Ni–2% Ru/Al$_2$O$_3$ > Ni/ZrO$_2$ > Ni 10%–Ru 0.1%/AC > Ru/TiO$_2$, whereas for the CGE by the catalysts can be shown as Co/ZrO$_2$ > 10% Ni–0.1% Ru/Al$_2$O$_3$ > Ni/ZrO$_2$ > 10% Ni–0.08% Ru/Al$_2$O$_3$–ZrO$_2$ (CM). Faster deactivation was observed in the case of Al$_2$O$_3$-supported Ni catalysts, while AC-supported Ni catalysts were comparatively more stable and highly active during the SCWG of biocrude obtained from real biomass. Nevertheless, Behnia et al. showed that 20% Ni–2% Ru/Al$_2$O$_3$ was highly stable and no significant deactivation was observed at high-temperature experiments (700 °C, 6 h). Thus, it can be said that addition of Ru in the catalyst makes Ni more stable and active. Although ZrO$_2$-supported catalysts showed higher biocrude conversion, the reactor became plugged because of the formation of...
excessive char even after a few hours of run. Byrd et al.40 also mentioned that hydrogen yield was lower, although char formation was the lowest with TiO2-supported catalysts. Louw et al.43 found that, compared to the noncatalytic gasification process of paper waste sludge, addition of 65% Ni/Al2O3−SiO2 increased the hydrogen yield and CGE, which are close to the equilibrium value. Xu et al.44 mentioned that noncatalytic SCWG yielded higher hydrogen, whereas the Ru/C catalyst showed higher CGE. According to their study, the activity of various catalysts in terms of hydrogen production is none > Pd/C > Pt-Pd/C > Ru/C. Another research by Su et al.45 showed that addition of a certain amount of La (15% Ni/Al2O3) promoted the activity of 15% Ni/Al2O3 catalyst and improved both the hydrogen yield and CGE. However, in the present study, the highest hydrogen yield and CGE were obtained using the 10% Ni-0.08% Ru/Al2O3−ZrO2 catalyst even in the presence of ZrO2. Thus, it can be said that significant increase in H2 yield can be attained by adding a very small amount of Ru and using ZrO2 as a support. Ru is very costly, and hence, this research showed that addition of a smaller amount in the catalyst will be very cost-effective. Nevertheless, the H2 yield decreased slowly over time as the catalyst lost its activity because of the presence of phenolic compounds and furans in the hydrothermal liquid.

3.4. Estimation of the Rate Model Parameters and Validation. The nonlinear regression using NLREG, a regression software, was performed to predict various model parameters. Converged and basic PL model parameters are shown in Table 5. Models were validated using average absolute deviation (AAD, %), which is a comparison of experimental and predicted reaction rates using the obtained model parameters.

As it can be clearly seen from the table, three models were converged. In order to determine the RDS, additional analyses were performed based on the AAD and activation energies of the converged models. The converged models should have AAD ≤ 15%, and the activation energy should be close to that of the PL model. By considering these conditions carefully, it was found that the first ER model can be accepted to predict the SCWG of the CH biocrude.

Table 4. Comparison of Hydrogen Yield and CGE to Other Researches

| study and experimental conditions                                      | catalytic condition                      | hydrogen yield (mol/mol carbon) | CGE |
|-----------------------------------------------------------------------|------------------------------------------|--------------------------------|-----|
| present study CM biocrude (700 °C, 25 MPa)                            | no catalyst                              | 0.50                          | 0.89|
| present study CH biocrude (700 °C, 25 MPa)                            | 10% Ni-0.08% Ru/Al2O3−ZrO2 no catalyst   | 1.10                          | 0.95|
| Byrd et al.40 switchgrass biocrude (600 °C, 25 MPa)                   | Ru/TiO2                                   | 0.81                          | 0.78|
| Zhang et al.41 sludge and waste newspaper biocrude (700 °C, 24 MPa)   | Ru/ZrO2                                   | 0.67                          |     |
| Louw et al.43 paper waste sludge (450 °C, 26.5 MPa)                    | Ni/TiO2                                   | 0.68                          | 0.74|
|                        | Ni/ZrO2                                   | 0.95                          | 0.96|
|                        | Co/TiO2                                   | 0.56                          | 0.83|
|                        | Co/ZrO2                                   | 0.71                          | 1.02|
|                        | no catalyst                               | 0.52                          | 0.90|
| Behnia et al.42 hardwood sawdust (700 °C, 27.5 MPa)                   | 10% Ni-0.1% Ru/Al2O3 no catalyst          | 0.49                          | 0.97|
|                        | 10% Ni-0.1% Ru/AC no catalyst              | 0.85                          | 0.92|
|                        | 20% Ni-2% Ru/Al2O3 no catalyst             | 1.18                          | 0.89|
|                        | 65% Ni/Al2O3−SiO2 no catalyst              | 1.19                          | 0.90|
|                        | Pt-Pd/C                                   | 0.86                          | 0.65|
|                        | Ru/C                                      | 0.63                          | 0.74|
|                        | Pd/C                                      | 0.86                          | 0.64|
|                        | no Catalyst                               | 0.76                          | 0.20|
|                        | 15% Ni/Al2O3 no catalyst                  | 1.05                          | 0.25|
|                        | 15% Ni/9La-Al2O3 no catalyst               | 1.26                          | 0.27|

Table 5. Estimate of the Values of the Parameters of the Models

| parameters | PL | ER1 | ER2 | ER6 |
|------------|----|-----|-----|-----|
| $k_0$      | 1.97 $\times 10^7$ | 2.29 $\times 10^{15}$ | 1.13 $\times 10^9$ | 1.25 $\times 10^9$ |
| $E$        | 4596.25 | 4638.12 | 100 | 762.18 |
| $n$        | 1.17 |     |     |     |
| $k_A$      | 2.23 $\times 10^{12}$ | 1 $\times 10^{12}$ | 0.01 |     |
| $k_B$      | 1 $\times 10^9$ | 1000 | 0.01 |     |
| $k_C$      | 1 | 1 | 1 |     |
| $k_D$      | 1 | 1 | 5.29 $\times 10^9$ |     |
| $k_E$      | 1 | 1 | 1 |     |
| $k_F$      | 1 | 1 | 1 |     |
| $k_G$      | 1 | 1 | 1 |     |
| $k_H$      | 1 | 4.10 | 1 |     |
| AAD, %     | 2.91 | 3.55 | 27.86 | 48.35 |
and by considering the thermodynamic equilibrium constant and values from data as follows

\[
r_A = \frac{2.29 \times 10^{13} e^{-4638.12/8.3147 T} C_A}{(1 + 2.23 \times 10^{12} C_A + 1 \times 10^6 C_J)^2}
\]  

(20)

Basically, eq (20) is a reduced form of eq (13). It is now concluded that the ER1 model can be termed the RDS. In other words, it needs two active sites to dissociate the oxygenated hydrocarbon. Thus, this step is slower compared to other elementary steps, making it the RDS and can be said that the dissociation of oxygenated hydrocarbon needs longer time before proceeding to the next step. The kinetic modeling of SCWG is assumed as a first-order reaction by many researchers.46−50 The current finding corroborates with the published articles as the reaction order is 1.17. Activation energies and pre-exponential factors are different for different types of feedstocks. However, the pre-exponential factor is close to some of the findings such as Goodwin and Rorrer47 and Olanrewaju.51 Olanrewaju also found that the value of pre-exponential factor increases for the first-order kinetic conversion reaction of biomass in SCW compared to subcritical water. This indicates that SCW becomes very reactive and have faster rate compared to conventional gasification of biomass.

4. CONCLUSIONS

In this study, SCWG of CH biocrude is performed with and without a catalyst to observe the effect on hydrogen yield. It is found that 10% Ni=0.08% Ru/Al2O3−ZrO2 shows better hydrogen yield experimentally compared to uncatalyzed SCWG and in the presence of a 10% Ni=0.08% Ru/Al2O3 catalyst. The highest hydrogen yield obtained is 1.65 mol/mol carbon in the feed for the CH biocrude with 90% CGE. In terms of carbon conversion, the SCWG process reaches near equilibrium even at lower temperature. However, the catalyst becomes deactivated after 2.5 h because of the presence of higher phenolic and furan compounds in CH biocrude. It is also observed that the catalyst used for CH biocrude has more carbon adsorption compared to CM biocrude, which led to faster catalyst deactivation. An Eley−Rideal-based mechanistic model, dissociation of oxygenated hydrocarbon, was found to be the RDS having AAD = 3.55%. The samples should be taken more frequently rather than in every 1 hour for checking the catalyst activity in future. Also, the spent catalysts should go through the Brunauer−Emmett−Teller (BET) surface area and Raman spectra to check the surface area for catalyst activity. In addition to these, other liquefied biomass may be examined using the same catalyst to check the feasibility of the catalyst. A detailed kinetic study may also be performed for better understanding of the reaction mechanism of the SCWG process.

5. MATERIALS AND METHODS

5.1. Feedstock and Catalyst Preparation. The biocrude from CM is prepared using vapor-assisted liquefaction in the dual-phase mode,14 and the biocrude from CH is prepared using a liquid-assisted liquefaction (single-phase) method, which are described elsewhere.22 A Parr Instrument setup (211 Fifty-Third Street, Moline, IL 61265-1770, USA) is used to perform the CH liquefaction, which is shown with its specification elsewhere.22 Table 6 shows the ultimate and proximate analyses of CM and CH along with the proximate analyses of both biocrude (dry oil). The proximate analyses are performed by following the ASTM standards using a muffle furnace (Thermo Scientific, F48055−60, Waltham, MA). The ultimate analyses are performed using an elemental analyzer from a Thermo Fisher Flash EA 1112, Waltham, MA. The biomass-to-water ratio is maintained at 1:6 as per Kambo and Dutta.23 Three scenarios were considered in this work to perform SCWG: uncatalyzed, 10% Ni=0.08% Ru/Al2O3, catalyzed, and 10% Ni−0.08% Ru/Al2O3−ZrO2 catalyzed. The CM biocrude is tested in both noncatalytic and 10% Ni=0.08% Ru/Al2O3−ZrO2 catalyst. The catalysts are prepared using the incipient wetness impregnation method outlined in Sietsma et al24 by using the following compounds: alumina and zirconia powder from Fischer Scientific; 1.8 mm diameter γ-alumina spheres from Sasol; nickel(II) nitrate hexahydrate (Ni(NO3)2·6H2O); and ruthenium(III) nitrosyl nitrate solution in dilute nitric acid (HN3O6·Ru) from Sigma-Aldrich. Compounded catalysts are oven-dried, calcined at 600 °C for 5 hours, and then stored in an airtight bag. The catalysts are crushed and sieved using ASTM standard size sieves (nos. 20 and 50 from Fisher Scientific) prior to each experiment to maintain an average particle size of 575 μm.

Table 6. Properties of Biomass and Biomass Biocrude

| sample | proximate analyses (wt %) | ultimate analyses (wt %) |
|--------|--------------------------|-------------------------|
|        | volatile matter (d.b.) | moisture content (as received) | Ash content (d.b.) | fixed carbon (d.b.) | nitrogen (N) | carbon (C) | hydrogen (H) | sulfur (S) | oxygen (O) |
| CM     | 80.02                    | 65.40                    | 1.49                | 18.49                | 1.39        | 45.02      | 6.10        | 0.16      | 47.33      |
| CH     | 83.84                    | 80.76                    | 4.35                | 11.82                | 1.56        | 43.91      | 6.29        | 11.33 × 10^-4 | 43.89      |
| CM biocrude |                  |                          |                     |                      | 2.04        | 39.48      | 5.14        | 0.14      | 53.20      |
| CH biocrude |                  |                          |                     |                      | 1.18        | 35.40      | 5.38        | 0.23      | 57.81      |
For each of the gasification experiment, a sample is taken every hour of testing for five continuous hours. Each of the five samples taken are tested twice using GC. This effectively enables a testing sample size of 10 for each scenario. The schematic for the SCWG unit with specifications and operating conditions is illustrated elsewhere.  

5.2. SCWG Process. Prior to the SCWG process, catalyst activation is performed by reducing the catalyst using H2. A weighted amount of catalyst (1.5 g) is loaded during each experimental run. Catalyst reduction is started when the reactor temperature reached 700 °C with a H2 flow of 5 mL/min for approximately 90 minutes. Following the reduction, the system is pressurized to 6.9 MPa using H2. The system is then pressurized to a desired pressure of 25 MPa using a HPLC pump at a feed flow rate of 5 mL/min. The back-pressure regulator is then adjusted to maintain a pressure of 25 MPa. Once the pressure reached a desired level, the feed flow is reduced to the desired flow rate of 2 mL/min, which is equivalent to the weight-hourly space velocity (WHSV) of 2 h⁻¹. The first gas sample is taken from the system after 1 hour of stabilization. Then, the gas samples are taken once per hour for 5 hours. For biocrude experiments, the biocrude are diluted to obtain a certain carbon concentration. This also enables the greatest degree of dilution of the biocrude, thereby reducing the amount of time spent producing liquid for testing.

5.3. HTL Biocrude Characterization. GC–MSD testing was performed on the HT liquid to determine the chemical compounds, which may have caused deactivation of the catalyst. The testing was performed offline in an Agilent 6890N GC–5975 MSD (Agilent Technologies Inc., Palo Alto, CA).

5.4. Catalyst Characterization. A Quantachrome 4200e Surface Area and Pore Analyzer was used to perform the BET analysis. The samples were degassed in vacuum first for 3 hours at room temperature. The weights before and after degassing of the catalyst were recorded to verify any mass loss. After the degassing, the catalyst samples were then set in the analyzer for BET analysis. Helium (He) gas was used to calibrate the tubes before each run. Physiosorption was then performed using N2 at liquid nitrogen temperature. The pressures were kept within the range of 0.03 < P/P0 < 0.4 when the isotherm was recorded. As per the analysis, the BET surface area, the total pore volume, and the average pore radius of 10% Ni–0.08% Ru/Al2O3 and 10% Ni–0.08% Ru/Al2O3−ZrO2 are 160.471 m²/gm, 0.383 cc/gm, 43.756 Å and 5.178 m²/gm, 0.021 cc/gm, and 22.961 Å, respectively. The surface morphology and constituents of the fresh and used catalysts were investigated using an FEI Inspect S50 that consists of a tungsten electron beam energy of 10 cm, 3.5, and 30 kV, respectively, for all SEM images. Over the specified spot size, an Oxford X-max 20 supported by Aztec Software was used to collect the EDS spectra. An accelerating voltage of 30 kV was used to ensure that the Ru Kα line was excited at 19.24 keV.

A Tecnai G2 F20 (FEI, Hillsboro, OR) transmission electron microscope equipped with a 4K Gatan GT digital camera (Gatan, Pleasanton, CA) was used to perform the TEM analyses of fresh and spent catalysts. The catalyst samples were mounted on a 300 mesh carbon grid prior to the analyses. In order to control the image quality, Digital Microgram software was used. XPS of the fresh and spent catalysts was performed using a PE5600 XPS system (Physical Electronics, Chanhassen, MN) equipped with a monochromatic A1 Kα X-ray source (operates at 350W), a multichannel detector, and a hemispherical analyzer. An indium foil was used to mount the catalyst samples. A low-energy electron flood gun (~1 eV) was used to neutralize charge. By using different energy and step sizes, two different spectra were collected. The analyzer pass energy and step size for survey spectra were 187.85 and 0.8 eV per step, respectively, and those for high-resolution spectra were 23.50 and 0.1 eV per step, respectively. The obtained data were analyzed using CasaXPS software. The spent catalysts from CM biocrude and CH biocrude were investigated for the char produced with an SDT Q600 model thermogravimetric analyzer from TA Instruments. The samples were then placed in an alumina crucible and heated to a final temperature of 900 °C with a heating rate of 20 °C/min and an air flow of 40 mL/min.

5.5. Gas Characterization. The gas samples were purged and diluted with N₂ gas prior to the analyses. After dilution, the gas bag was attached to the gas chromatograph (SRI 8610C Gas Chromatograph) and analyzed using both flame ionization detection and thermal conductivity detection.

ASSOCIATED CONTENT
Supporting information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b01782.
Schematic diagram of the SCWG process with description, HTL biocrude characterization, and statistical analyses of data (PDF).

AUTHOR INFORMATION
Corresponding Author
Animesh Dutta — Mechanical Engineering Program, School of Engineering, University of Guelph, Guelph, Ontario N1G 2W1, Canada; orcid.org/0000-0002-9995-807X; Phone: 519-824-4120 ext. 52441; Email: adutta@uoguelph.ca; Fax: 519-836-0227

Authors
Mohammad Shahed Hasan Khan Tushar — Mechanical Engineering Program, School of Engineering, University of Guelph, Guelph, Ontario N1G 2W1, Canada; Rajshahi University of Engineering & Technology, Rajshahi 6204, Bangladesh; orcid.org/0000-0003-2346-6025
Paul C. DiMaria — Mechanical Engineering Program, School of Engineering, University of Guelph, Guelph, Ontario N1G 2W1, Canada

Sultan Majed Al-Salem — Environment & Life Sciences Research Centre, Kuwait Institute for Scientific Research (KISR), Safat 13109, Kuwait; orcid.org/0000-0003-0652-4502
Chunbao Charles Xu — Department of Chemical and Biochemical Engineering, Western University, London, Ontario N6A 5B9, Canada; orcid.org/0000-0001-6543-3817

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.9b01782

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
The authors gratefully acknowledge the funding from NSERC [Discovery Grant Program (400495)]. The authors also acknowledge the BET analyses by Dr. Jay Leitch, Nanoscience Laboratory Technician; TEM analysis by Robert (Bob) Harris,

15399
https://dx.doi.org/10.1021/acsomega.9b01782
ACS Omega 2020, 5, 15390–15401
manager, Microscopy Imaging Facility and the GC–MS analyses by Dr. Dyanne Brewer, Manager, Mass Spectrometry Facility, Associate Graduate Faculty, Advanced Analysis Centre; the XRD analyses by Dr. Lawrence Margulies, Post-Doctoral Fellow, Department of Physics, University of Guelph, ON. The authors show their heartfelt gratitude for XPS analyses by Dr. Mark C. Biesinger, Manager, Research and Business Development, Surface Science Western, Western University.

**REFERENCES**

(1) Acharya, B.; Dutta, A.; Basu, P. Chemical-looping gasification of biomass for hydrogen-enriched gas production with in-process carbon dioxide capture. *Energy Fuels* 2009, 23, 5077–5083.

(2) Tilmann, D.; Hill, J.; Lehman, C. Carbon-Negative Biofuels from Low-Input High-Diversity Grassland Biomass. *Science* 2006, 314, 1598–1600.

(3) McLeod, K. Supercritical water gasification. *Biofuels, Bioprod. Biorefin.* 2008, 2, 415–437.

(4) Matsunuma, Y.; Minowa, T.; Potic, B.; Kersten, S.; Prins, W.; Vanswaaie, W.; Vandevelde, B.; Elliott, D.; Neuenschwander, G.; Kruse, A. Biomass gasification in near- and super-critical water: Status and prospects. *Biomass Bioenergy* 2005, 29, 269–292.

(5) Loppinet-Serani, A.; Aymonier, C.; Cansell, F. Current and foreseeable applications of supercritical water for energy and the environment. *ChemSusChem* 2008, 1, 486–503.

(6) Reddy, S. N.; Nanda, S.; Dalai, A. K.; Kozinski, J. A. Supercritical water gasification of biomass for hydrogen production. *Int. J. Hydrogen Energy* 2014, 39, 6912–6926.

(7) Calzavar, Y.; Joussot-Dubien, C.; Boissonnet, G.; Sarrade, S. Evaluation of biomass gasification in supercritical water for process hydrogen production. *Energy Convers. Manage.* 2005, 46, 615–631.

(8) Azadi, P.; Farnood, R. Review of heterogeneous catalysts for sub- and supercritical water gasification of biomass and wastes. *Int. J. Hydrogen Energy* 2011, 36, 9529–9541.

(9) Elliott, D. C. Catalytic hydrothermal gasification of biomass. *Biofuels, Bioprod. Biorefin.* 2008, 2, 254–265.

(10) Osada, M.; Yamaguchi, A.; Hiyoshi, N.; Sato, O.; Shirai, M. Gasification of sugarcane bagasse over supported ruthenium catalysts in supercritical water. *Energy Fuels* 2012, 26, 3179–3186.

(11) Barati, M.; Babatabar, M.; Tavasoli, A.; Dalai, A. K.; Das, U. Hydrogen production via supercritical water gasification of bagasse using unpromoted and zinc promoted Ru/γ-Al2O3 nanocatalysts. *Fuel Process. Technol.* 2014, 123, 140–148.

(12) Tushar, M. S. H. K.; Dutta, A.; Xu, C. Catalytic supercritical gasification of biocoke from hydrothermal liquefaction of cattle manure. *Appl. Catal., B* 2016, 189, 119–132.

(13) Pedersen, T. H. Hydrothermal liquefaction of biomass and model compounds. Doctoral Thesis, Aalborg Universitetsforlag, Aalborg, Denmark, 2016.

(14) Johnson, M. C. Hydrothermal processing of high-lipid biomass to fuels. Doctoral Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, 2012.

(15) Yan, Q.; Guo, L.; Lu, Y. Thermodynamic analysis of hydrogen production from biomass gasification in supercritical water. *Energy Convers. Manage.* 2006, 47, 1515–1528.

(16) Ortiz, F. J. G.; Campanario, F. J.; Aquilera, P. G.; Ollero, P. Hydrogen production from supercritical water reforming of glycerol over Ni/Al2O3–SiO2 catalysts. *Energy* 2015, 84, 634–642.

(17) Al-Mouzali, D.; Barghi, S.; Fang, Z.; Xu, C. C. Techno-economic Analysis of Renewable Hydrogen Production via SCWG of Biomass Using Glucose as a Model Compound. In *Near-critical and Supercritical Water and Their Applications for Bioenergy*; Fang, Z., Xu, C. C., Eds.; Springer: Netherlands, 2014; pp. 445–471.

(18) Kuznetsova, T. G.; Sadykov, V. A.; Veniaminov, S. A.; Alikina, G. M.; Moroz, E. M.; Rogov, V. A.; Martyanyov, O. N.; Yudanov, V. F.; Abornev, I. S.; Neophytides, S. Methane transformation into syngas over Ce–Zr–O systems: role of the surface/bulk promoters and oxygen mobility. *Catal. Today* 2004, 91, 161–164.

(19) Dong, F.; Suda, A.; Tanabe, T.; Nagai, Y.; Sobukawa, H.; Shinjoh, H.; Sugura, M.; Descorme, C.; Duprez, D. Characterization of the dynamic oxygen migration over Pt/CeO2–ZrO2 catalysts by 18O/16O isotopic exchange reaction. *Catal. Today* 2004, 90, 223–229.

(20) Minaret, J.; Dutta, A. Comparison of liquid and vapor hydrothermal carbonization of corn husk for the use as a solid fuel. *Bioresour. Technol.* 2016, 200, 804–811.

(21) Kambo, H. S.; Dutta, A. Strength, storage, and combustion characteristics of densified lignocellulosic biomass produced via torrefaction and hydrothermal carbonization. *Appl. Energy* 2014, 135, 182–191.

(22) Sietsma, J. R. A.; van Dillen, A. J.; de Jongh, P. E.; de Jong, P. Application of ordered mesoporous materials as model supports to study catalyst preparation by impregnation and drying. In *Studies in Surface Science and Catalysis*, Gaigneaux, E. M., Devillers, M., De Vos, D. E., Hermans, S., Jacobs, P. A., Martens, J. A., Ruiz, P., Eds.; Elsevier B. V.: Amsterdam, 2006; Vol. 162; pp 95–102.

(23) Wang, K.; Azagohar, R.; Dalai, A. K.; Wang, H. Hydrogen production from lignin, cellulose and waste biomass via supercritical water gasification: Catalyst activity and process optimization study. *Energy Conserv. Manage.* 2016, 117, 528–537.

(24) Okolie, J. A.; Rana, R.; Nanda, S.; Dalai, A. K.; Kozinski, J. A. Supercritical water gasification of biomass: a state-of-the-art review of process parameters, reaction mechanism and catalysts. *Sustainable energy fuels* 2019, 3, 578–598.

(25) Hu, Y.; Dong, H.; Xing, X.; Wang, H.; Zeng, Y.; Xu, C. C. Supercritical water gasification of biomass model compounds: A review. *Renewable Sustainable Energy Rev.* 2020, 118, 109529.

(26) Kruse, A.; Henningsen, T.; Sinag, A.; Pleiffer, J. Biomass gasification in supercritical water: influence of the dry matter content and the formation of phenols. *Ind. Eng. Chem. Res.* 2003, 42, 3711–3717.

(27) Cordero-Lanzac, T.; Palos, R.; Hita, I.; Arandes, J. M.; Rodríguez-Mirasol, J.; Cordero, T.; Bilbao, J.; Castaño, P. Revealing the pathways of catalyst deactivation by coke during the hydrodeoxygenation of raw bio-oil. *Appl. Catal., B* 2018, 239, 513–524.

(28) Chen, G.; Zhang, R.; Ma, W.; Liu, B.; Li, X.; Yan, B.; Cheng, Z.; Wang, T. Catalytic cracking of model compounds of bio-oil over HZSM-5 and the catalyst deactivation. *Sci. Total Environ.* 2018, 631–632, 1611–1622.

(29) Hoydonckx, H. E.; Van Rhijn, W. M.; Van Rhijn, W.; De Vos, D. E.; Jacobs, P. A. Furfural and derivatives. *Ullmann’s Encyclopedia of Industrial Chemistry*, Wiley, 2007.

(30) Lin, W.-H.; Lee, T.-T.; Li, Y.-Y. Chlorine effect on formation of turbostratic carbon nanofibers by a mixture of 1,2-dichloroethane and dimethylformamide. *ACS Omega* 2018, 3, 9601–9611.

(31) Sato, O.; Shirai, M.; Osada, M.; Tanaka, T.; Sato, T. Hydrothermal liquefaction of biomass and model compounds. Doctoral Thesis, Aalborg Universitetsforlag, Aalborg, Denmark, 2016.

(32) Johnson, M. C. Hydrothermal processing of high-lipid biomass to fuels. Doctoral Thesis, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, 2012.

(33) Yudanov, V. F.; Jiang, L.; Muhammad, U.; Li, C.; Zhang, S. Catalytic Methanation of CO and CO2 in Coke Oven Gas over Ni-Co/ZrO2-CeO2. *Ind. Eng. Chem. Res.* 2013, 52, 2247–2256.

(34) Yuan, J.; Yang, X.-x.; Ding, J.; Wei, X.-l.; Yang, J.-p.; Wang, W.-l.; Yang, M.-l. Carbon dioxide reforming of methane over bimetallic catalysts of Pt-Ru/γ-Al2O3 for thermochemical energy storage. *J. Cent. South Univ.* 2013, 20, 1307–1313.

(35) Wang, Z.-B.; Zuo, P.-j.; Yin, G.-P. Effect of W on activity of Pt-Ru/C catalyst for methanol electrooxidation in acidic medium. *J. Alloys Compd.* 2009, 479, 395–400.
(38) Tushar, M. S. H. K.; Mahinpey, N.; Khan, A.; Ibrahim, H.; Kumar, P.; Idem, R. Production, characterization and reactivity studies of chars produced by the isothermal pyrolysis of flax straw. Biomass Bioenergy 2012, 37, 97–105.

(39) Wang, S.; Lu, G. Q. Effects of promoters on catalytic activity and carbon deposition of Ni/γ-Al2O3 catalysts in CO2 reforming of CH4. J. Chem. Technol. Biotechnol. 2000, 75, 589–595.

(40) Byrd, A. J.; Kumar, S.; Kong, L.; Ramsum, H.; Gupta, R. B. Hydrogen production from catalytic gasification of switchgrass biocrude in supercritical water. Int. J. Hydrogen Energy 2011, 36, 3426–3433.

(41) Zhang, L.; Champagne, P.; Xu, C. Supercritical water gasification of an aqueous by-product from biomass hydrothermal liquefaction with novel Ru modified Ni catalysts. Bioresour. Technol. 2011, 102, 8279–8287.

(42) Behnia, I.; Yuan, Z.; Charpentier, P.; Xu, C. C. Supercritical water gasification of aqueous fraction of pyrolysis oil in the presence of a Ni-Ru catalyst. AIChE J. 2016, 62, 2786–2793.

(43) Louw, J.; Schwarz, C. E.; Burger, A. J. Catalytic supercritical water gasification of primary paper sludge using a homogeneous and heterogeneous catalyst: experimental vs thermodynamic equilibrium results. Bioresour. Technol. 2016, 201, 111–120.

(44) Xu, D.; Liu, L.; Wei, N.; Guo, Y.; Wang, S.; Wu, Z.; Duan, P. Catalytic supercritical water gasification of aqueous phase directly derived from microalgal hydrothermal liquefaction. Int. J. Hydrogen Energy 2019, 44, 26181–26192.

(45) Guo, Y.; Wang, S.; Huelsman, C. M.; Savage, P. E. Products, pathways, and kinetics for reactions of indole under supercritical water gasification conditions. J. Supercrit. Fluids 2013, 73, 161–170.

(46) Goodwin, A. K.; Rorrer, G. L. Reaction rates for supercritical water gasification of xylose in a micro-tubular reactor. Chem. Eng. J. 2010, 163, 10–21.

(47) Kipcak, E.; Akgün, M. Biofuel production from olive mill wastewater through its Ni/Al2O3 and Ru/Al2O3 catalyzed supercritical water gasification. Renewable Energy 2018, 124, 155–164.

(48) Guan, Q.; Wei, C.; Savage, P. E. Kinetic model for supercritical water gasification of algae. Phys. Chem. Chem. Phys. 2012, 14, 3140–3147.

(49) Amrullah, A.; Matsumura, Y. Supercritical water gasification of sewage sludge in continuous reactor. Bioresour. Technol. 2018, 249, 276–283.

(50) Olanrewaju, K. B. Reaction kinetics of cellulose hydrolysis in subcritical and supercritical water. Doctoral Thesis, The University of Iowa, Iowa, USA, 2012.