INTRODUCTION

The exploiting use of fossil fuels leads to greenhouse gas emissions, global warming, air pollution and other environmental issues. The increasing demand for fossil fuels, especially petroleum-based fuel products in the developing countries is raising many environmental concerns posing both short-term and long-term impacts. In such a scenario, renewable energy from wind, tidal, geothermal, solar, and biomass has many promising applications to sustain the future energy sector. While wind, tidal, geothermal, and solar energy can generate electricity to power our modern homes, industries, and green infrastructures, they barely can fuel our existing vehicles. Biofuels produced from agricultural and...
Biofuels are considered carbon-neutral as the plants recycle the CO₂ released from their combustion during photosynthesis. Biofuels are produced from renewable bioresources such as lignocellulosic biomass (e.g., agricultural crop residues, forestry biomass, and energy crops), algae, and other organic wastes such as municipal solid wastes, cattle manure, sewage sludge, and industrial effluents. These organic wastes can be transformed to biofuels (e.g., bio-oil, syngas, biogas, hydrogen, bioethanol, and biobutanol) through appropriate thermochemical technologies (e.g., liquefaction, pyrolysis, and gasification), and biochemical technologies (fermentation and anaerobic digestion). Typically, lignocellulosic biomass contains cellulose (35-55 wt%), hemicellulose (20-40 wt%), and lignin (10-25 wt%). Enormous amounts of agricultural crop residues are accessible throughout the world in the form of straw, stalks, fibers, shells, husks, pits, de-oiled cakes, pulps, etc. Among all, straws comprise of nearly 15-40% of the total agricultural crop residues, which have tremendous possibilities to be converted to biofuels.

Hydrogen is a clean fuel with a high-energy content of 120 MJ/kg compared to any other conventional fuel. It is a clean fuel because it results in water upon combustion. Although traditionally generated through the reformation of natural gas, H₂ can be produced through gasification, biophotolysis, photo-fermentation, dark fermentation, and electrolysis. Hydrogen can be generated from lignocellulosic biomass through hydrothermal gasification. Organic materials including lignocellulose materials (cellulose, hemicellulose, and lignin) degrade into simple molecules during gasification in subcritical water (SbCW) and supercritical water (SCW) to produce syngas. Syngas, the main gas product of hydrothermal gasification process, is a mixture of H₂, CO, CO₂, CH₄, C₂H₆, and C₂+ gases. Through gas-to-liquid technologies such as Fischer–Tropsch catalysis and syngas fermentation, syngas can be converted to green diesel, light and heavy synthetic petroleum, ethanol, and other hydrocarbons.

Freshly harvested agricultural biomass usually contains high water content. Prior to their thermochemical conversion (pyrolysis, gasification, or liquefaction), it is essential to remove moisture through drying or preheating, which adds cost and energy to the overall process. However, subcritical and supercritical water gasification eliminates the requirement of additional preheating steps because of the use of water as the aqueous reaction medium. Because water is the only medium in hydrothermal gasification, its fluid phases affect the overall process. The critical temperature (T_c) and critical pressure (P_c) of water are 374°C and 22.1 MPa, respectively. Subcritical water gasification is characterized with temperatures and pressures lower than the critical points of water (T < 374°C and P < 22.1 MPa). In contrast, supercritical water gasification employs temperatures and pressures higher than the water's critical points (T > 374°C and P > 22.1 MPa). Supercritical water is known to exhibit superior mass and heat transfer properties with a combination of gas and liquid-like properties.

Hydrothermal gasification has been investigated for H₂-rich syngas production from several varieties of lignocellulosic biomass including agricultural and forestry residues as well as energy crops. Nanda et al. performed SbCW and SCW gasification of pinewood and wheat straw impregnated with catalytic nickel nanoparticles at 300-500°C and 23-25 MPa pressure for 15-45 minutes. Compared to noncatalytic gasification, higher yields of H₂ (2.8-5.78 mmol/g) and total gases (9.5-16.2 mmol/g) were obtained from SCW gasification of Ni-impregnated biomasses under optimal conditions (temperature: 500°C; biomass-to-water ratio: 1:10; residence time: 45 minutes; and pressure: 25 MPa). SCW gasification of timothy grass (an energy crop) at 650°C with 1:8 biomass-to-water ratio for 45 minutes led to higher yields of H₂ (5.15 mol/kg) and total gases (17.2 mol/kg). However, addition of 3% KOH as catalyst to the gasification process maximized H₂ and total gas yields up to 8.91 and 30.6 mol/kg, respectively. Safari et al. reported maximum H₂ yields of 4.1, 4.63, and 7.25 mmol/g from noncatalytic SCW gasification of almond shell, walnut shell and wheat straw, respectively, at 440°C and 10-20 minutes of reaction time. In another study, SCW gasification of 2.5 wt% of wheat straw black liquor at 750°C for 50 minutes resulted in maximum H₂ yields of 62.4 mol/kg and carbon gasification efficiency of 98.2%.

The use of homogeneous catalysts (e.g., alkalis, carbonates, and hydroxides) and heterogeneous catalysts (e.g., metals) in hydrothermal gasification has also found to enhance the gas yields. The catalysts have the potential to crack the biomass and its fragmented derivatives (e.g., intermediates, tars, and char) by several mechanisms, especially by: (a) the cleavage of C–C bonds; (b) dehydration of oxygenated compounds via C–O bond cleavage; and (c) suppression of re-polymerization of formed intermediates to tar and char. In addition, metal catalysts can also degrade the organic acids and complex phenolic compounds, which are key intermediates during the fragmentation of lignocellulosic biomass.

Transitions metal catalysts have proved to be active for the degradation of biomass at supercritical conditions. However, the harsh operating conditions (high temperatures and high pressures) during SCW gasification often result in the sintering of metallic catalysts, deactivation and nondurable repeat cycles. In addition, to make the metallic catalysts more selective toward H₂ production rather than CH₄ or any other gases, it is important to modify the catalyst surface with a stable support for activity toward dehydrogenation...
reactions. This directs toward the implication of the metallic supports for the active metals to make them more stable and durable without losing activity, selectivity, and stability.

Reports suggest that the use of Ni and Ru-based catalysts in SCW gasification of biomass has shown superior performances in gas yields.11,26-28 The performances of Ni-supported catalysts were tested for gasification of different feedstocks with results inferring that Ni/α-Al2O3 and Ni/hydrotalcite enhanced H2 selectivity and yields.29 In another study by Kang et al,30 the screening of Ni-based catalysts onto different supports with various promoters was tested for the SCW gasification of lignin. They found that the activity of Ni-based catalysts with Al2O3 support and cerium as a promoter improved H2 yields and selectivity. Afif et al31 employed Raney nickel catalyst to gasify activated sludge at 380°C and 3 wt% feed concentration for 15 minutes. A gas product constituting 46% H2, 25% CH4, and 29% CO2 was reported.

On the other hand, Azadi et al25 performed comparative evaluation of gas yields from SCW reforming of several model compounds of activated sludge (ie, glucose, glycine, glycerol, lactic acid, and humic acid) at 380°C using Raney nickel, Ni/α-Al2O3, Ru/γ-Al2O3, and Ru/C catalysts. Ru/γ-Al2O3 (0.3-18.3 mmol/g) demonstrated higher H2 yields compared to Ru/C (0.6-12.9 mmol/g) and noncatalytic gasification (0.1-5.8 mmol/g) of all model compounds. Similarly, Raney nickel (6.6-30.6 mmol/g) showed improved catalytic activity for H2 production than Ni/α-Al2O3 (2.6-23.3 mmol/g) during the decomposition of all model compounds of activated sludge.

In a study on the SCW gasification of lignin at 400°C, Osada et al32 reported that the stability of different Ru-supported catalysts varied as Ru/TiO2 > Ru/γ-Al2O3 > Ru/C. While Ru/TiO2 maintained its high gasification activity for three subsequent cycles, Ru/C lost its activity after the first run due to the decrease in its surface area. Although Ru/γ-Al2O3 showed good catalytic performance at the initial stage, its activity gradually reduced during repetitive cycles. This was due its structural transition from gamma-state to alkaliphase and dissolution of active Ru species in SCW. Nevertheless, alumina (Al2O3) has shown high performance toward their stability and activity than other catalyst supports.24 Moreover, depending on chosen biomass species and the operating conditions, the metallic catalysts may show variable selectivity to a particular gas.

One of the main objectives of the current study was to investigate the catalytic performances of commercial ruthenium (Ru/Al2O3) and nickel (Ni/Si-Al2O3) catalysts in SbCW and SCW gasification of wheat straw, which is a model agricultural crop residue representing lignocellulosic biomass. There is lack of literature on the comparative SbCW and SCW gasification of wheat straw using metallic catalysts. To fill this knowledge gap, the current study aimed at examining the aqueous decomposition behavior of wheat straw at variable process parameters such as temperature, feed concentration, reaction time, and catalysts.

2  MATERIALS AND METHODS

2.1  Biomass and catalysts

Wheat straw (Triticum aestivum) used in this study was obtained as straw bales from a local farm in Saskatoon, Saskatchewan, Canada. After collection, wheat straw was roughly chopped, mechanically dusted to remove any soil particles and air dried for a week. Prior to gasification, the chopped wheat straw was ground to an average particle size of <1 mm using an IKA MF10 Basic Microfine S1 grinder (ThermoFisher Scientific Inc., Mississauga, ON, Canada). The pulverized wheat straw was stored in airtight containers at room temperature prior to its gasification.

Two metal catalysts such as Ru/Al2O3 and Ni/Si-Al2O3 used in gasification experiments were procured from Sigma-Aldrich Canada Co., Oakville, ON, Canada. The two commercial metal catalysts such as Ru/Al2O3 (PubChem SID: 24867548) and Ni/Si-Al2O3 (PubChem SID: 24852528) had the reported surface areas of 90 and 175 m2/g, respectively.

2.2  Hydrothermal gasification

Hydrothermal gasification of wheat straw was performed under a pressure range of 21-23 MPa to examine the effects of temperature (300-550°C), feed concentration (20-35 wt%) and reaction time (40-70 minutes). For all experiments, deionized water served as the medium of hydrothermal gasification. In a typical experiment, a calculated amount of wheat straw (eg, 2 g at 20 wt%) was loaded into the tubular reactor along with 8 mL of deionized water. After determining the optimal temperature, feed concentration and reaction time, the effects of Ru/Al2O3 and Ni/Si-Al2O3 at a constant loading of 5 wt% were studied for catalyzing the hydrothermal gasification.

Hydrothermal gasification was conducted in a tubular batch reactor made of stainless steel SS316 (length: 10 in., outer diameter: 0.5 in. and inner diameter: 0.37 in.). The schematics, geometry and design of the gasification reactor have been mentioned in Figure 1. The reactor assembly was custom-made using the tubing and fittings of SS316 grade procured from Swagelok (Swagelok Central Ontario, Mississauga, ON, Canada). The tubular reactor was electronically heated using an ATS split furnace, controlled by ATS temperature controller and monitored by Omega Type-K thermocouple (Spectris Canada, Inc., Laval, QC, Canada).
The inert gas nitrogen was used to create an initial reactor pressure of 10-15 MPa that expanded to the desired subcritical and supercritical pressure of 21-23 MPa depending on set gasification temperature following the equation of state. Furthermore, as the reactor was heated to the desired temperature, the initial reactor pressure increased from 10-15 MPa up to 21-23 MPa following the ideal gas law. Depending on the heating rate of the furnace and the final test temperature, the reactor took nearly 30-40 minutes to reach water’s critical state. After the desired test conditions were attained (ie, pressure: 21-23 MPa and temperature: 300-550°C), the reaction was started by monitoring the reaction time (40-70 minutes). The pressure gauges monitored the pressure inside the reactor assembly and pressure relief valves aided in releasing any extra pressure beyond 27 MPa (safety limit for the reactor assembly).

After the completion of the gasification experiments, the hot gaseous products passed through the 2-μm filter to entrap any char fines. The gas products then passed through the gas-liquid separator where they were cooled by the cold-water spray. The condensed liquid effluent was collected gravimetrically from the bottom of the separator, whereas the noncondensable gas products passed through the desiccant column (LabClear, Oakland, CA, USA) to trap the moisture after being collected in gas sampling bags. After the collection of gases, the solid products (biochar) were allowed to cool inside the reactor. The cooled biochar was collected, weighed, and stored in dry and airtight glass jars placed inside a desiccator.

### 2.3 Gas phase analysis

An Agilent 7820A gas chromatography (Agilent Technologies, Santa Clara, CA, USA) was used to analyze the gaseous products. The gas chromatography was equipped with a thermal conductivity detector (TCD) consisting of three columns, namely Ultimetal Hayesep Q T 80/100 mesh column (H₂, CO, and CH₄), Ultimetal Hayesep T 80/100 mesh column (CO₂), and Ultimetal molsieve13 80/100 mesh column (N₂ and O₂). All the columns were maintained at 60°C using argon as the carrier gas.

The individual gas yield (in mmol/g) and total gas yield (in mmol/g) were calculated as the moles of individual gases and total gases, respectively, per gram of biomass. Carbon gasification efficiency or CGE (in %) and lower heating value or LHV (in kJ/Nm³) of the gas phase were calculated using the following equations.

\[
\text{CGE} (\%) = \left( \frac{\text{Total number of carbon moles in } \text{CO}, \text{ CO}_2, \text{ CH}_4 \text{ and } \text{C}_2\text{H}_6}{\text{Number of carbon moles in the feedstock}} \right) \times 100.
\]

\[
\text{LHV (kJ/Nm}^3\text{)} = [(30 \times \text{CO}) + (25.7 \times \text{H}_2) + (85.4 \times \text{CH}_4) + (151.3 \times \text{C}_2\text{H}_6)] \times 4.2
\]

### 2.4 Biomass and biochar characterization

Proximate analysis of wheat straw and its biochars was performed to determine the moisture, ash, volatile matter and fixed carbon using the standard ASTM protocols. To determine the moisture content, about 1 g of sample was taken in a crucible and heated to 105°C for 2 hours in a muffle furnace. The difference in the weight of the crucible with
the sample after drying was attributed to moisture. Ash and volatile matter content were determined as the difference in the weight of the crucible with 1 g of sample after heating to 575 ± 10°C for 4 hours and 950 ± 10°C for 7 minutes, respectively. The fixed carbon in the biomass and biochar was calculated from the difference of moisture, volatile matter, and ash.

Ultimate analysis of wheat straw and its biochars was performed using an Elementar vario EL III CHNOS analyzer (Elementar Analysensysteme, Hanau, Germany) to determine carbon, hydrogen, nitrogen, sulfur, and oxygen contents. Oxygen was determined as the difference of carbon, hydrogen, nitrogen, sulfur, and ash. The higher heating value (HHV) of wheat straw and its biochars was measured using a 6400 Automatic Isoperibol Calorimeter (Parr Instrument Company, Moline, IL, USA).

3 | RESULTS AND DISCUSSION

3.1 | Product distribution

Wheat straw was gasified at temperatures of 300-550°C with feed concentrations of 20-35 wt% for reaction times of 40-70 minutes under a pressure range of 21-23 MPa to understand their individual and combined effects. The yield of products from the hydrothermal gasification of wheat straw is given in Table 1. The yields of gases increased with the rise in temperature (from 300 to 550°C), decreased with the upsurge in feed concentration (from 20 to 35 wt%) and increased with the elevation in reaction time (from 40 to 70 minutes). On the contrary, the solid product yield (ie, biochar) was at the expense of gas yields. The yield of liquid products was relatively higher in the downstream always due to the medium of gasification being water.

The estimated mass balance for solid, liquid and gas products was up to a maximum of 83 wt% while the unaccounted portion was attributed to the constraints in product collection. Most researchers have also reported a total assessed mass balance up to 60, 66 and 85% from SCW gasification of cellulose,38 glucose,39 and lignocellulosic biomass,17 respectively. As reported from the studies, several reasons owing to the discrepancy in mass balance from hydrothermal gasification systems are related to the entrainment of fine char particles in the liquid phase and the presence of condensable fractions in the gas phase during the time of product collection.

3.2 | Effect of gasification temperature

Temperature is the prime operating parameter that decides the quantity of product gas yields. To detail the impact of temperature on product gas yields from wheat straw, SbCW (300 and 370°C at 21 MPa) and SCW (450 and 550°C at 23 MPa) conditions were comparatively studied at a fixed feed concentration of 20 wt% and reaction time of 60 minutes. The increase in the temperature from 300 to 550°C resulted in around 10-fold rise in \( H_2 \) yield, that is, from 0.26 to 2.98 mmol/g (Figure 2). The yields of \( \text{CO}_2 \) (5.30 mmol/g), \( \text{CH}_4 \) (1.42 mmol/g), and \( \text{C}_2\text{H}_6 \) (0.69 mmol/g) also increased at 550°C compared to lower temperatures. At SCW temperatures (450 and 550°C), steam reforming and water-gas shift reaction become predominant contributing to the yields of \( H_2 \) and \( \text{CO}_2 \).40 Since the reforming of biomass is usually endothermic in nature and requires high amount of energy, the temperature has a positive influence on their conversion.41,42 Biomass undergoes complex degradation pathways with many concurrent thermal cracking and reforming reactions to produce product gas mixture. Thermal cracking reactions majorly produce hydrocarbons, whereas the reforming reactions mostly result in the formation of \( H_2 \). The pyrolytic and cracking reactions become significant to supplement the yield of hydrocarbons (ie, \( \text{CH}_4 \) and \( \text{C}_2\text{H}_6 \)) at high SCW temperatures.

Figure 2 also reveals an increasing trend of CO yield up to 450°C following which it decreases at 550°C. A slight
decline in CO yield at high SCW temperature (550°C) indicates its consumption in water-gas shift reaction as the combination of water and CO is termed as “water-gas”. Water-gas shift reaction is exothermic; hence, the active participation of CO as a reactant produces H$_2$ and CO$_2$.\textsuperscript{43} It has been underlined that the conversion of CO decreases and that of H$_2$ increases at high temperatures since the reaction is exothermic.\textsuperscript{42,44} In accordance to our findings, Resende and Savage\textsuperscript{45} highlighted contrasting differences in CO yields at high temperatures. During SCW gasification of 9 wt% lignin for 45 minutes, Resende and Savage\textsuperscript{45} reported an increase in the yields of H$_2$, CO$_2$, and CH$_4$ with increase in temperature from 365°C to 725°C. In contrast, the yield of CO varied as 365°C (0.9 mmol/g) < 500°C (2.0 mmol/g) > 600°C (1.5 mmol/g) > 725°C (0.45 mmol/g). This varying trend in CO yield was due to inconsistent gasification behavior of certain intermediate biomass degradation products at high temperatures. As evident from Figure 2, a very similar trend in CO yield was noticed in the current study 300°C (0.08 mmol/g) < 370°C (0.15 mmol/g) < 450°C (0.29 mmol/g) > 550°C (0.25 mmol/g).

Although water-gas shift reaction is exothermic, it becomes active at excess water concentrations and high water densities.\textsuperscript{42,45} Therefore, the yields of H$_2$ and CO$_2$ consistently increases with rising temperature and water density, whereas the yield of CO decreases because of its consumption in water-gas shift reaction promoted at higher water densities, which is in turn determined by elevated temperatures. Moreover, in our parametric study on the influence of gasification temperature, the feed concentration of wheat straw used was 20 wt% with the remainder being water (ie, 80 wt%). This high concentration of water in the reaction medium favored water-gas shift reaction at high temperatures of 550°C despite its exothermic nature.

The overall rise in the individual gas yields also led to an increment in the total gas yields from 1.7 to 10.6 mmol/g (Table 2). The CGE also heightened from 4% (at 300°C) to 22.7% (at 550°C). High-temperature cracking and reforming reactions are a few key factors in determining the gas yields along with the conversion efficiencies of the organic materials.\textsuperscript{46,47} The LHV of the gas products also improved from 167 to 1301 kJ/Nm$^3$ with the elevation in temperature from 300 to 550°C. The superior calorific value of the product gases from gasification of waste biomass in the presence of high-pressure steam or oxygen over the air gasification opts for its degradation via thermochemical routes.\textsuperscript{48}

The improved gas yields at higher temperatures indicate the efficiency of SCW over SbCW reaction conditions. At SbCW temperatures, where hydronium and hydroxide ions prevail, the conversion of the biomass happens through ionic mechanisms.\textsuperscript{24,40} In contrast, at SCW conditions, the highly active free radicals are generated from water that attacks the long-chain molecules and branched-ring molecules into simple hydrocarbons and oxygenated molecules.\textsuperscript{11} The thermodynamics of degradation of organic compounds at lower temperatures (SbCW) convey that CH$_4$ dominates in the gas mixture while H$_2$ is favored at high temperatures (SCW).\textsuperscript{40,49}

The proximate and ultimate characterization of wheat straw and its biochars derived at SbCW (300 and 370°C) and SCW (450 and 550°C) temperatures are presented in Table 3. Wheat straw contained 44.1 wt% carbon, 6 wt% hydrogen, 0.4 wt% nitrogen, 0.01 wt% sulfur and 45.1 wt% oxygen. The rise in gasification temperature resulted in the decrease in the biochar yields (Table 1), as well as gradual lowering of the
biochars’ moisture and volatile matter contents. In contrast, the rise in temperature from 300 to 550°C also led to the increase in the ash and fixed carbon contents. Because of gasification at higher SCW temperatures, the organic components in wheat straw underwent thermal cracking, decomposition, and dehydration leading to the removal of volatile matter and development of fixed carbon moieties. In our study, SCW at 550°C acted as a suitable reaction medium with enhanced hydrothermal degradation biomass leading to high gas yields and low biochar yield with large carbon content.

Moreover, biochar produced at 550°C (76.4 wt%) demonstrated the highest carbon content when compared to biochars generated at 300°C (55.8 wt%), 370°C (61.1 wt%) and 450°C (68.2 wt%) (Table 3). This indicates that biochar produced at high temperatures (and SCW conditions) is more carbonaceous and stable due to the removal of volatile matter. As determined experimentally, the HHV elevated in the following order: wheat straw (15.6 MJ/kg) < 300°C (22.6 MJ/kg) < 370°C (23.4 MJ/kg) < 450°C (25.8 MJ/kg) < 550°C (29.5 MJ/kg) owing to the amplification of the carbon content in the biochars (Table 3).

### 3.3 Effects of feed concentration

The effect of variable feed concentrations of 20-35 wt% on wheat straw gasification at 550°C, 23 MPa for 60 minutes is shown in Figure 4. Prior to understanding the impacts of feed concentration, the role of water needs to be interpreted during the gasification. The increase in organic feed concentration leads to a decrement in the water content lowering its activity during the degradation process. During SCW gasification, water plays important roles both as a reactant and as a medium in many vital reactions such as hydrolysis, steam reforming, and water-gas shift reaction, all leading to the main product of interest, that is, H₂. Hence, a decrease in water content in experiments with high feed concentration indicates the suppression of the above-mentioned reactions, which could inhibit H₂ yields.

At a constant temperature (550°C), pressure (23 MPa), and reaction time (60 minutes), the H₂ yields decreased from 2.98 mmol/g (at 20 wt% feed concentration) to 1.12 mmol/g (at 35 wt% feed concentration) (Figure 4). The

| TABLE 3 | Proximate and ultimate analyses of wheat straw and biochars derived from subcritical and supercritical water gasification with 20 wt% feed concentration for 60 minutes at 21-23 MPa |
|----------|-------------------------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Parameter | Wheat straw | Biochar-300°C | Biochar-370°C | Biochar-450°C | Biochar-550°C |
| Proximate analysis (wt%) | | | | | |
| Moisture | 7.4 | 6.4 | 3.9 | 3.1 | 2.6 |
| Ash | 4.4 | 4.7 | 5.1 | 5.9 | 6.2 |
| Volatile matter | 56.7 | 52.4 | 48.7 | 42.1 | 35.5 |
| Fixed carbon | 31.5 | 36.5 | 42.3 | 48.9 | 55.7 |
| Ultimate analysis (wt%) | | | | | |
| C | 44.1 | 55.8 | 61.1 | 68.2 | 76.4 |
| H | 6 | 5.8 | 4.8 | 3.9 | 3.3 |
| N | 0.4 | 0.8 | 1.5 | 1.8 | 1.9 |
| S | 0.01 | 0.15 | 0.07 | 0.05 | 0.05 |
| O | 45.1 | 32.7 | 27.5 | 20.2 | 12.1 |
| Atomic ratios | | | | | |
| H/C | 1.63 | 1.25 | 0.94 | 0.69 | 0.52 |
| O/C | 0.77 | 0.44 | 0.34 | 0.22 | 0.12 |
| N/C | 0.008 | 0.013 | 0.021 | 0.022 | 0.022 |
| HHV (MJ/kg) | 15.6 | 22.6 | 23.4 | 25.8 | 29.5 |

The data presented in the table is an average of triplicate measurements.
yields of CO₂ also reduced from 5.3 to 2.38 mmol/g with the rise in feed concentration, thus indicating the suppression of reforming and water-gas shift reactions. The reforming reactions are retarded largely at high feed concentrations, thus lowering the yields of H₂ and CO₂. However, the lower gas products of reforming reactions are compensated by the gas yields from secondary cracking reactions including methanation of CO₂ that become significant at high feed concentrations. Therefore, the yields of CO, CH₄, and C₂H₆ increased up to 0.84, 2.3, and 1.08 mmol/g, respectively, at 35 wt% feed concentration.

With the conquest of major gas products, that is, H₂ and CO₂, a little decline in the total gas yields was observed with the rising feed concentration (Table 2). The total gas yields from SCW gasification wheat straw decreased from 10.6 mmol/g (at 20 wt% feed concentration) to 7.7 mmol/g (at 35 wt% feed concentration). Consequently, a reduction in the CGE was found with 35 wt% feed concentration (20.9%) compared to 20 wt% feed concentration (22.7%). Similarly, the increase in the concentration of combustible gas products (ie, CO, CH₄, and C₂H₆) at higher feed concentration resulted in greater LHV of the gas phase. For example, the LHV of the gas products improved from 1301 to 1739 kJ/Nm³ as the feed concentration increased from 20 to 35 wt%, respectively. The greater LHV of the product gas mixture at higher feed concentrations was also due to heightened concentrations of hydrocarbons from the predominant secondary cracking reactions and methanation. Since higher gas yields of 10.6 mmol/g were obtained at a low feed concentration of 20 wt%, it was selected as the optimal condition along with 550°C as the prime temperature for further parametric studies. It should be noted that higher temperatures and lower feed concentration when combined improve free-radical mechanism and reforming reaction in supercritical water gasification, thereby increasing H₂ yields.

3.4  |  Effects of reaction time

The impacts of reaction time were studied for wheat straw gasification at an optimal SCW temperature (550°C) and pressure (23 MPa) with optimal feed concentration (20 wt%). From Figure 5, it is evident that H₂ yield increased exponentially from 40 minutes (1.68 mmol/g) to 60 minutes (2.98 mmol/g) and thereby decreased at 70 minutes (2.06 mmol/g). A gradual increase in CO₂ yield from 2.53 mmol/g (at 40 minutes) to 7.48 mmol/g (at 70 minutes) indicates the oxidation of intermediate products of wheat straw gasification. Like CO₂ yields, there was steady improvement in CH₄ yields from 0.42 to 2.52 mmol/g with the increase in reaction time from 40 to 70 minutes. The yield of C₂H₆, although mediocre than the major gases, showed a stable amplification from 0.59 to 0.82 mmol/g as the reaction time increased to 70 minutes. Interestingly, CO yield followed a reverse trend to H₂, CO₂, and CH₄ but its maximum yield was achieved within a least reaction time of 40 minutes, after which it declined at longer time intervals. The main gas products at longer reaction times were CO₂ and CH₄, which resulted in an increase in the total gas yields from 5.8 to 12.9 mmol/g (Table 2). Owing to the high concentration of CH₄, the LHV of the gas phase increased from 782 kJ/Nm³ (in 40 minutes) to 1655 kJ/Nm³ (in 70 minutes). The CGE increased from an initial 12.8% (in 40 minutes) to 31.9% (in 70 minutes) of SCW gasification of 20 wt% wheat straw at 550°C under 23 MPa pressure.

Thermal cracking of biomass is favored at longer reaction times and high temperatures. However, an optimal reaction time is essential for superior H₂ yields. The yield
of H2 was maximum at 60 minutes (2.98 mmol/g) and then decreased at 70 minutes (2.06 mmol/g) because of many secondary reactions such as hydrogenation, methanation (or Sabatier reaction) and Boudouard reaction. Water is a major product of methanation and hydrogenation reactions that consume H2 and CO. Moreover, along with water another major product of hydrogenation and Boudouard reaction is carbon (or char).

Boudouard reaction and water-gas shift reaction primarily consumes CO to produce char and CO2; hence a decrement in CO yield and increment in CO2 yield were noticed after 70 minutes of reaction time (Figure 5). Longer residence time also favor water-gas shift reaction that produces CO2 and H2. Although CO2 accumulated in the system due to its additional supply from Boudouard reaction, the H2 was consumed during hydrogenation and methanation to produce CH4.

3.5 | Effects of metal catalysts

The effects of two metal catalysts, that is, Ru/Al2O3 and Ni/Si-Al2O3 at 5 wt% loading were studied to maximize H2 yields at optimal SCW gasification conditions of 550°C and 23 MPa pressure with 20 wt% feed concentration for 60 minutes of reaction time (Figure 6). Ni/Si-Al2O3 was superior to Ru/Al2O3 in increasing the yields of H2, CO2, CH4, and C2H6. The H2 yield reached its maximum with 5 wt% Ni/Si-Al2O3 (5.1 mmol/g) when compared to Ru/Al2O3 (4.18 mmol/g) and noncatalytic gasification (2.98 mmol/g). CO formation was not detected in the gas phase with the application of catalysts confirming the activation of water-gas shift and methanation of CO resulting in the overall contribution of H2 (4.18-5.1 mmol/g) and CH4 (2.99-3.84 mmol/g). Nickel- and ruthenium-based catalysts are capable of depolymerizing lignocellulosic biomasses with the potential to improve methanation and water-gas shift reactions even at near-critical conditions. Nickel has high selectivity for CH4 even at their low loading concentrations. Ruthenium also exhibits some catalytic activity toward the formation of CH4 via methanation of CO and CO2, although it performance is relatively lower than Ni.

With catalyst application, the total gas yields and carbon gasification efficiency were highest in the case of 5 wt% Ni/Si-Al2O3 (18.2 mmol/g and 38.2%) followed by 5 wt% Ru/Al2O3 (15 mmol/g and 31.7%) and noncatalytic gasification (10.6 mmol/g and 22.7%) (Table 2). The LHV of the gas products also increased in the order: noncatalytic gasification (1301 kJ/Nm3) < 5 wt% Ru/Al2O3 (2038 kJ/Nm3) < 5 wt% Ni/Si-Al2O3 (2544 kJ/Nm3). The higher total gas yields were attained with Ni/SiO2-Al2O3 compared to Ru/Al2O3, which might be attributed to the higher surface area resulting in the adsorption and catalytic action of Ni on aqueous intermediates. The CGE was also higher in the case of Ni/Si-Al2O3 (38.2%) compared to that of Ru/Al2O3 (31.7%). At low SbCW temperatures, the formation of tar from biomass is quite evident, which could hinder the gas yields. This directs to look out for possible alternates to reduce tar and improve the gas yields. With the capability to cleave O–H, C–H, and C–C bonds, nickel can effectively decompose recalcitrant tars as well as long-chain and oxygenated compounds into gases. The catalytic activity of nickel compared to other noble metals is significant higher toward H2 and CH4 production through hydrogenation and methanation, making it a suitable catalyst for SCW gasification of biomass. Although undesirable for the H2 market, Ni and Ru supported on Al2O3 can strongly contribute to the exothermic Sabatier reaction, where CO2 reacts with H2 to produce CH4.
Overall reaction mechanisms

Based on the overall experimental observations, the following reactions are proposed for the gas yields. A mechanistic representation of the overall reaction pathways involved in SbCW and SCW gasification of wheat straw is shown in Figure 7. Initially, the lignocellulosic biomass (wheat straw) undergoes depolymerization and hydrolysis to form soluble carbohydrates and organic acids at SbCW temperatures. These intermediates approach the active sites of the catalysts, where they are further degraded by either dehydrogenation or secondary hydrolysis into simpler C1 to C2 compounds (e.g., aldehydes, ketones, alcohols, aromatics, and phenolics) and a small amount of gases products.64 The formed aqueous products are easily catalyzed into permanent fuel gases at higher SCW temperatures. Depending on the gasification temperature, reaction time, water content, the gas products may undergo water-gas shift reaction, hydrogenation, methanation or Sabatier reaction and Boudouard reaction as represented in the following equations.12,14,40

Water-gas shift reaction: \( \text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \) (3)

Hydrogenation of CO: \( \text{CO} + \text{H}_2 \rightarrow \text{C} + \text{H}_2\text{O} \) (4)

Hydrogenation of \( \text{CO}_2 \): \( \text{CO}_2 + 2\text{H}_2 \rightarrow \text{C} + 2\text{H}_2\text{O} \) (5)

Methanation of \( \text{CO}_2 \): \( \text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \) (6)

Methanation of CO: \( \text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \) (7)

Methanation of coke or carbon: \( \text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 \) (8)

Boudouard reaction: \( 2\text{CO} \rightarrow \text{C} + \text{CO}_2 \) (9)

The role of water in hydrothermal gasification is not only as a gasifying medium but also as a reactant, which results in the higher carbon gasification efficiencies.24,42 Considering water as a medium with its reaction conditions beyond its critical point enables to degrade waste biomass and organics with higher conversion efficiencies yielding a high quantity of \( \text{H}_2 \) rich fuel gas mixture. Moreover, the exothermic reactions during SCW gasification can supplement additional heat energy to lower the activation energy, aid in the participation of most reactant molecules for near-complete gasification and maximize the syngas yields.65,66 Nevertheless, the presence of catalysts can lead to the degradation of intermediate components contributing to gas yields, improved gasification efficiency and superior heating value of the syngas.27

CONCLUSIONS

This study investigated the hydrothermal gasification of wheat straw, which is abundantly found agricultural crop residue at a global scale. The study investigated the influence of temperature, feed concentration, reaction time, and catalysts on \( \text{H}_2 \) and total gas yields along with carbon gasification efficiency and lower heating value of the gas products. SCW conditions were found to be more favorable for wheat straw gasification than SbCW conditions. The optimal temperature, feed concentration and reaction time were found to be 550°C, 20 wt% and 60 minutes, respectively, at 23 MPa pressure. The noncatalytic SCW gasification at the above-mentioned optimal reaction conditions resulted in high yields of \( \text{H}_2 \) (2.98 mmol/g), total gases (10.7 mmol/g) with an LHV of 1301 kJ/Nm³. Furthermore, 5 wt% Ni/Si-\( \text{Al}_2\text{O}_3 \) maximized the \( \text{H}_2 \) yield to 5.1 mmol/g compared to Ru/\( \text{Al}_2\text{O}_3 \) (4.18 mmol/g). Due to high \( \text{H}_2 \) and \( \text{CH}_4 \) yields, the LHV of the gas phase from catalytic SCW gasification of wheat straw also increased up to 2544 kJ/Nm³ with Ni/Si-\( \text{Al}_2\text{O}_3 \). The overall results indicate that wheat straw could be a promising agricultural crop residue through hydrothermal gasification with Ni and Ru-based catalysts to produce \( \text{H}_2 \)-rich syngas.
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CONFLICT OF INTEREST

None declared.

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REFERENCES

1. Rana R, Nanda S, Maclellan A, Hu Y, Kozinski JA, Dalai AK. Comparative evaluation for catalytic gasification of petroleum coke and asphaltene in subcritical and supercritical water. J Energy Chem. 2018; https://doi.org/10.1016/j.jechem.2018.05.012
2. Nanda S, Golemi-Kotra D, McDermott JC, Dalai AK, Gökalp I, Kozinski JA. Fermentative production of butanol: perspectives on synthetic biology. New Biotechnol. 2017;37:210-221.
3. Boffito DC, Pirola C, Galli F, Di Michele A, Bianchi CL. Free fatty acids esterification of waste cooking oil and its mixtures with rapeseed oil and diesel. Fuel. 2013;108:612-619.
4. Nanda S, Azargohar R, Dalai AK, Kozinski JA. An assessment on the sustainability of lignocellulosic biomass for biorefining. Renew Sustain Energy Rev. 2015;50:925-941.
5. Naik SN, Goud YY, Rout PK, Dalai AK. Production of first and second generation biofuels: a comprehensive review. Renew Sustain Energy Rev. 2010;14:578-597.
6. Nanda S, Mohammad J, Reddy SN, Kozinski JA, Dalai AK. Pathways of lignocellulosic biomass conversion to renewable fuels. Biomass Convers Bioref. 2014;4:157-191.
7. Nanda S, Mohanty P, Pant KK, Naik S, Kozinski JA, Dalai AK. Characterization of North American lignocellulosic biomass and biochars in terms of their candidacy for alternate renewable fuels. Bioenerg Res. 2013;6:663-677.
8. Bowyer JL, Stockmann VE. Agricultural residues: an exciting bio-based raw material for the global panels industry. Forest Prod J. 2001;51:10-21.
9. Nanda S, Rana R, Zheng Y, Kozinski JA, Dalai AK. Insights on pathways for hydrogen generation from ethanol. Sustain Energy Fuel. 2017;1:1232-1245.
10. Holladay JD, Hu J, King DL, Wang Y. An overview of production technologies. Catal Today. 2009;139:244-260.
11. Reddy SN, Nanda S, Dalai AK, Kozinski JA. Subcritical water gasification of biomass for hydrogen production. Int J Hydrogen Energy. 2014;39:6912-6926.
12. Correa CR, Kruse A. Subcritical water gasification of biomass for hydrogen production — review. J Supercrit Fluids. 2018;133:573-590.
13. Nanda S, Kozinski JA, Dalai AK. Lignocellulosic biomass: a review of conversion technologies and fuel products. Curr Biochem Eng. 2016;3:24-36.
14. Nanda S, Reddy SN, Hunter HN, Butler IS, Kozinski JA. Supercritical water gasification of lactose as a model compound for valorization of dairy industry effluents. Ind Eng Chem Res. 2015;54:9296-9306.
15. Nanda S, Reddy SN, Hunter HN, Dalai AK, Kozinski JA. Supercritical water gasification of fructose as a model compound for waste fruits and vegetables. J Supercrit Fluids. 2015;104:112-121.
16. Gong M, Nanda S, Romero MJ, Zhu W, Kozinski JA. Subcritical and supercritical water gasification of humic acid as a model compound of humic substances in sewage sludge. J Supercrit Fluids. 2017;119:130-138.
17. Nanda S, Reddy SN, Dalai AK, Kozinski JA. Subcritical and supercritical water gasification of lignocellulosic biomass impregnated with nickel nanocatalyst for hydrogen production. Int J Hydrogen Energy. 2016;41:4907-4921.
18. Nanda S, Dalai AK, Kozinski JA. Supercritical water gasification of timothy grass as an energy crop in the presence of alkali carbonate and hydroxide catalysts. Biomass Bioenergy. 2016;95:378-387.
19. Safari F, Salimi M, Tavasoli A, Ataei A. Non-catalytic conversion of wheat straw, walnut shell and almond shell into hydrogen rich gas in supercritical water media. Chin J Chem Eng. 2016;24:1097-1103.
20. Cao C, Xu L, He Y, Guo L, Jin H, Huo Z. High-efficiency gasification of wheat straw black liquor in supercritical water at high temperatures for hydrogen production. Energy Fuels. 2017;31:3970-3978.
21. Lu YJ, Guo LJ, Ji CM, Zhang XM, Hao XY, Yan QH. Hydrogen production by biomass gasification in supercritical water: a parametric study. Int J Hydrogen Energy. 2006;31:822-831.
22. Resende FL, Savage PE. Effect of metals on supercritical water gasification of cellulose and lignin. Ind Eng Chem Res. 2010;49:2694-2700.
23. Elliott DC. Catalytic hydrothermal gasification of biomass. Biofuels Bioprod Bioref. 2008;2:254-265.
24. Guo Y, Wang SZ, Xu DH, Gong YM, Ma HH, Tang XY. Review of catalytic supercritical water gasification for hydrogen production from biomass. Renew Sustain Energy Rev. 2010;14:334-343.
25. Azadi P, Afif E, Foroughi H, Dai T, Azadi F, Farnood R. Catalytic reforming of activated sludge model compounds in supercritical water using nickel and ruthenium catalysts. Appl Catal B Environ. 2013;134:265-273.
26. Azadi P, Afif E, Azadi F, Farnood R. Screening of nickel catalysts for selective hydrogen production using supercritical water gasification of glucose. Green Chem. 2012;14:1766-1777.
27. 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.
28. Yamaguchi A, Hiyoshi N, Sato O, Bando KK, Shirai M. Gaseous fuel production from nonrecyclable paper wastes by using supported metal catalysts in high-temperature liquid water. Chemsuschem. 2010;3:737-741.
29. Azadi P, Khan S, Strobel F, Azadi F, Farnood R. Hydrogen production from cellulose, lignin, bark and model carbohydrates in supercritical water using nickel and ruthenium catalysts. Appl Catal B Environ. 2012;117:330-338.
30. Kang K, Azargohar R, Dalai AK, Wang H. Systematic screening and modification of Ni based catalysts for hydrogen generation from supercritical water gasification of lignin. Chem Eng J. 2016;283:1019-1032.
31. Afif E, Azadi P, Farnood R. Catalytic hydrothermal gasification of activated sludge. Appl Catal B Environ. 2011;105:136-143.
32. Osada M, Sato O, Arai K, Shirai M. Stability of supported ruthenium catalysts for lignin gasification in supercritical water. Energy Fuels. 2006;20:2337-2343.
33. Xu D, Wang S, Hu X, Chen C, Zhang Q, Gong Y. Catalytic gasification of glycine and glycerol in supercritical water. *Int J Hydrogen Energy*. 2009;34:5357-5364.

34. Lv PM, Xiong ZH, Chang J, Wu CZ, Chen Y, Zhu JX. An experimental study on biomass air–steam gasification in a fluidized bed. *Bioresour Technol*. 2004;95:95-101.

35. ASTM D3175-11. *Standard Method for Volatile Matter in the Analysis Sample of Coal and Coke*. West Conshohocken, PA: ASTM International; 2011.

36. ASTM E1755-01. *Standard Test Method for Ash in Biomass*. West Conshohocken, PA: ASTM International; 2007.

37. ASTM E871-82.

38. Ding N, Azargohar R, Dalai AK, Kozinski JA. Catalytic gasification of cellulose and pinewood to H2 in supercritical water. *Fuel*. 2014;118:416-425.

39. Ding N, Azargohar R, Dalai AK, Kozinski JA. Catalytic gasification of glucose to H2 in supercritical water. *Appl Catal A: Gen*. 2014;127:33-40.

40. Kruse A. Supercritical water gasification. *Biofuels Bioprod Bioref*. 2008;2:415-437.

41. Duan PG, Li SC, Jiao JL, Wang F, Xu YP. Supercritical water gasification of microalgae over a two-component catalyst mixture. *Sci Total Environ*. 2018;630:243-253.

42. Susanti RF, Dianingrum LW, Yum T, Kim Y, Lee BG, Kim J. High-yield hydrogen production from glucose by supercritical water gasification without added catalyst. *Int J Hydrogen Energy*. 2012;37:11677-11690.

43. Nanda S, Isen J, Dalai AK, Kozinski JA. Gasification of fruit wastes and agro-food residues in supercritical water. *Energy Convers Manag*. 2016;110:296-306.

44. Utaka T, Okanishi T, Takeguchi T, Kikuchi R, Eguchi K. Water gas shift reaction of reformed fuel over supported Ru catalysts. *Appl Catal A: Gen*. 2003;245:343-351.

45. Resende FLP, Savage PE. Expanded and updated results for supercritical water gasification of cellulose and lignin in metal-free reactors. *Energy Fuels*. 2009;23:6213-6221.

46. Schaffel-Mancini N, Mancini M, Szlęk A, Weber M. Novel conceptual design of a supercritical pulverized coal boiler utilizing high temperature air combustion (HTAC) technology. *Energy*. 2010;35:2752-2760.

47. Strügjas N, Zakaraukas K, Stravinskas G, Grigaiteiene V. Comparison of steam reforming and partial oxidation of biomass pyrolysis tar over activated carbon derived from waste tire. *Catal Today*. 2012;196:67-74.

48. Zhang Y, Li B, Li H, Zhang B. Exergy analysis of biomass utilisation via steam gasification and partial oxidation. *Thermochim Acta*. 2012;538:21-28.

49. Reddy SN, Nanda S, Kozinski JA. Supercritical water gasification of glycerol and methanol mixtures as model waste residues from biodiesel refinery. *Chem Eng Res Des*. 2016;113:17-27.

50. Azargohar R, Nanda S, Kozinski JA, Dalai AK, Sutarto R. Effects of temperature on the physicochemical characteristics of fast pyrolysis biochars derived from Canadian waste biomass. *Fuel*. 2014;125:90-100.

51. Mohanty P, Nanda S, Pant KK, Naik S, Kozinski JA, Dalai AK. Evaluation of the physiochemical development of biochars obtained from pyrolysis of wheat straw, timothy grass and pinewood: effects of heating rate. *J Anal Appl Pyrolysis*. 2013;104:485-493.

52. Nanda S, Dalai AK, Berruti F, Kozinski JA. Biochar as an exceptional bioresource for energy, agronomy, carbon sequestration, activated carbon and specialty materials. *Waste Biomass Valor*. 2016;7:201-235.

53. Nanda S, Azargohar R, Kozinski JA, Dalai AK. Characteristic studies on the pyrolysis products from hydrolyzed Canadian lignocellulosic feedstocks. *Bioenergy Res*. 2014;7:174-191.

54. Chen G, Andries J, Luo Z, Spleithoff H. Biomass pyrolysis/gasification for product gas production: the overall investigation of parametric effects. *Energy Convers Manag*. 2003;44:1875-1884.

55. Abdullah B, Ghani NAA, Vo DVN. Recent advances in dry reforming of methane over Ni-based catalysts. *J Clean Prod*. 2017;162:170-185.

56. Kılıçak E, Akgün M. Biofuel production from olive mill wastewater through its Ni/Al2O3 and Ru/Al2O3 catalyzed supercritical water gasification. *Renew Energy*. 2017;124:155-164.

57. Hossain MZ, Chowdhury MB, Alsharari Q, Jhwaw AK, Charpentier PA. Effect of mesoporosity of bimetallic Ni-Ru-Al2O3 catalysts for hydrogen production during supercritical water gasification of glucose. *Fuel Process Technol*. 2017;159:55-66.

58. Yamaguchi A, Hiyoshi N, Sato O, Bando KK, Osada M, Shirai M. Hydrogen production from woody biomass over supported metal catalysts in supercritical water. *Catal Today*. 2009;146:192-195.

59. Jiménez V, Sánchez P, Panagiotopoulou P, Valverde JL, Romero A. Methanation of CO, CO2 and selective methanation of CO, in mixtures of CO and CO2, over ruthenium carbon nanofibers catalysts. *Appl Catal A Gen*. 2010;390:35-44.

60. Osada M, Yamaguchi A, Hiyoshi N, Sato O, Shirai M. Gasification of sugarcane bagasse over supported ruthenium catalysts in supercritical water. *Energy Fuel*. 2012;26:3179-3186.

61. Guan G, Chen G, Kasai Y, et al. Catalytic steam reforming of biomass tar over iron–nickel-based catalyst supported on calcined scallop shell. *Appl Catal B Environ*. 2012;115:159-168.

62. Gong M, Nanda S, HunterHN, Zhu W, Dalai AK, Kozinski JA. Lewis acid catalyzed gasification of humic acid in supercritical water. *Catal Today*. 2017;291:13-23.

63. Nguyen HT, Yoda E, Komiyama M. Catalytic supercritical water gasification of proteinaceous biomass: catalyst performances in gasification of ethanol fermentation stillage with batch and flow reactors. *Chem Eng Sci*. 2014;109:197-203.

64. Fang Z, Sato T, Smith RL Jr, Inomata H, Arai K, Kozinski JA. Reaction chemistry and phase behavior of lignin in high-temperature and supercritical water. *Bioresour Technol*. 2008;99:3424-3430.

65. Croiset E, Rice SF, Hanush RG. Hydrogen peroxide decomposition in supercritical water. *AIChE J*. 1997;43:2343-2352.

66. Xu D, Lin G, Ma Z, Guo Y, Farooq MU, Wang S. Partial oxidative gasification of sewage sludge in supercritical water with multi-component catalyst. *Chem Eng Res Des*. 2017;124:145-151.

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