Article

Potential Application of Canola Hull Fuel Pellets for the Production of Synthesis Gas and Hydrogen

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Abstract: The production of biopellets from agricultural residues is an effective method to overcome the expected shortage in the supply of fuel pellets in the future. This work focused on the new potential applications of fuel pellets to produce liquid and gas fuels through thermochemical and hydrothermal biomass-to-gas technologies. The outcomes also provide a basis to compare the effects of steam and hydrothermal gasification techniques on the properties of product and byproduct, as well as their potentials. For steam gasification, the syngas yield increased from 10.7 to 27.8 mmol/g (on a dry and ash-free basis) by a rise in the gasification temperature at a constant steam-to-biomass ratio. In the case of hydrothermal gasification, there was no carbon monoxide, and hydrogen was the main gas product, and with an increase in the temperature, the hydrogen yield rose from 0.4 mmol/g to 3.17 mmol/g with temperatures from 350 to 650 °C. CO had the largest share in the gas product from steam gasification, which was between 23.3 and 31.3 mol%. The range of the molar ratio of H₂/CO for the steam gasification (1.13–1.40) showed the necessity of the further purification of gas products to utilize them as feed for liquid fuel production using the Fischer–Tropsch process. Examination of the mineral content of biochar that remained after the gasification techniques showed large essential elements in them compared with heavy metals, which shows potential for soil amendment. The results highlight the possibility of converting an agricultural residue into a value-added product with potential applications in the energy sector and agriculture.

Keywords: canola hull; biopellets; steam gasification; supercritical water gasification; biochar; hydrogen

1. Introduction

Agricultural residues can be considered as one of the sources of sustainable solid bioenergy. Crop residues are considered renewable, sustainable, and abundant resources of energy with much lower carbon emissions compared to fossil fuels. These agricultural residues can be converted to fuel pellets to improve the storage and transportation efficiency of these residues. Fuel pellets produced from waste biomass have heating applications in the industry, and they can also be used for power generation. At the beginning of this decade, bioenergy globally accounts for ~60% of renewable energy and covers ~13% of energy consumption in the world [1].

The canola hull used in this research work was collected during the harvesting and screening of canola seeds. This residue is a combination of hulls, pods, tiny grains, and pieces of leaves. Of the 22.4 × 10⁶ tons of canola grown in Canada in 2021, approximately 10% was canola hull [2]. This residue can be densified using bio-additives in the form of fuel pellets [3]. Produced pellets can be used as fuel for industrial applications (such as cofiring with coal in power plants) or can be converted to synthesis gas (syngas), which can be used further for power generation or biofuel production.

Thermochemical processes such as gasification are known as efficient techniques to convert biomass feedstock to valuable biofuels. Gas phase products can be considered
as the source of hydrogen (as a clean fuel) and synthesis gas (as described earlier). Tars collected during the process are large molecular weight organic compounds [4] that can be distilled and converted to biocrude oil for the production of fuels. In contrast to the combustion process that releases the energy using breaking chemical bonds of feedstocks, gasification modifies the chemical bonds to generate gaseous fuels with a higher H/C ratio compared with that of the original feedstock [5]. Gasification is a complex process and includes different exothermic (e.g., oxidation) and endothermic (e.g., drying, pyrolysis, and reduction) stages [6]. Steam gasification is an effective technique to produce a high yield of syngas in an oxygen-deficient environment. This process converts fuel pellets to gas products (including H₂, CO, CO₂, CH₄, and light hydrocarbons); biochar; and tar [7]. The use of densified biomass (fuel pellets) instead of original biomass for this thermochemical process is a solution for some disadvantages of biomass precursors for gasification, such as the large bulk volume of biomass, its storage, and transportation, as well as its seasonal availability. Steam gasification is a well-known and established technique for the production of syngas [8,9]. Hydrothermal gasification is another technique used for the conversion of biomass to gaseous products. This technique can substantially decrease the formation rate of tar and coke [10]. In hydrothermal gasification, water is used as an oxidizing agent and reaction medium. The high diffusivity coefficient of water, its low dielectric index, and its small value of viscosity in supercritical condition make water an appropriate solvent and medium for the gasification of biomass [11]. Hydrothermal gasification is shown as an efficient technique to generate a gas product with a high concentration of hydrogen [12,13]. A steam gasification technique has been used by researchers for biomass-based material. Pinto et al. [14] investigated steam gasification of torrefied stump pellets in the temperature range of 700–800 °C and a steam-to-feed ratio of 1. They could obtain hydrogen and carbon monoxide yields in the ranges of 21.6–40.2 and 37–28 vol%, respectively. Bartocci et al. [15] used steam gasification for wood char pellets at 550 °C and 0.25 g/min/g pellet. They could collect gas products with 58.3 vol% and a CO yield of 20.5 vol%. Abedi et al. [16] investigated the steam gasification of oat hull pellets at a temperature range of 650–850 °C and an equivalence ratio of 0.2–0.4. They obtained gas products with hydrogen and CO concentrations in the range of 20–50 mol% and 35–45 mol%, respectively. Chojnacki et al. [17] performed steam gasification of wood pellets at a temperature range of 750–850 °C and a steam-to-biomass ratio of 0.5–1.0. Their product gas had 33–44 mol% of H₂ and 19–25 mol% of CO.

In the last decade, there have been some notable research works on supercritical water gasification (SCWG) of biomass with a focus on the production of H₂-rich syngas. Macri et al. [18] performed SCWG of biomass and agro-food waste such as almond shells, digestate, algae, and sludge and indicated that wet biomass led to enhancing the concentration of H₂ in the syngas at low temperatures. When dry biomass was gasified, the CH₄ yield was enhanced. Bakari et al. [19] demonstrated the SCWG of rice husk using catalysts prepared from alkaline earth metals (iron oxide on dolomite or limestone) in a batch autoclave reactor using response surface methodology. The catalyst loading of 15% with 5% Fe/limestone increased the gasification efficiency by 16%, resulting in 42.2 vol% of the gas product, a tar yield of 93%. The overall results indicated that alkaline earth metals such as limestone, dolomites, and olivine can be low-cost and effective catalytic materials to enhance the gas yields and gasification efficiency in SCWG processes. Although there are promising studies on SCWG of biomass, the literature on SCWG of biomass pellets is lacking.

This research focuses on one possible application of fuel pellets as a value-added material produced from residues of an agricultural feedstock. Biomass fuel pellets can be used to generate synthesis gas or a hydrogen-rich gaseous fuel. Steam gasification and hydrothermal gasification were investigated in this research to show the capability of biomass-based pellets for the above-mentioned purposes. The effects of two main operating parameters of steam gasification, including the process temperature (650–850 °C) and steam-to-biomass (fuel pellet) ratio (SBR, 0.31–0.62 kg/kg), on the fuel characteristics of
the gas phase product, as well as on the mineral composition and textural characteristic of biochar as a byproduct of the process, were investigated. For the hydrothermal gasification, the effects of the process temperature (350–650 °C), biomass-to-water ratio (10–25 wt%), and residence or reaction time (15–60 min) were studied. The main objective of the current study was to evaluate the fuel properties of the gas product generated using fuel pellets. The composition of the gas production and its quantity are basic data to determine the fuel properties of the gas phase, such as a lower heating value, yield, and carbon efficiency. In addition, the biochar that remained after the gasification process was investigated with respect to its porosity and composition. This research work has made a direct comparison between two common gasification techniques in terms of gas product characteristics and solid residue (biochar) properties. The outcomes of this work and similar studies for other biomass-based pellets can open up a new avenue in the integration of fuel pellets and all related products and byproducts in a general biorefinery plan. In addition, this study showed the possibility of expansion of the applications of fuel pellets from a solid fuel with limited application for combustion to a possible feedstock for the production of liquid fuels and hydrogen. The outcomes of this research have also shown that a residue without a specific application can be used as a feedstock for the production of a wide range of clean fuels. Both the agricultural sector and industries can benefit from this conversion of agricultural residue to value-added products.

2. Experimental

2.1. Steam Gasification

A canola hull pellet was prepared using canola hull feedstock supplied by Milligan Bio (SK, Canada). The densification procedure is mentioned elsewhere [3]. A combination of two series fixed-bed Inconel reactors, with an internal diameter of 1.05 cm, was used for the steam gasification of the canola hull. The set-up is described elsewhere [20]. The second reactor was loaded with silica sand to facilitate tar decomposition by increasing the tar compounds’ residence time at the set temperature of gasification. Approximately 2 g of canola hull pellets (equivalent to four fuel pellets) were used for each gasification run. These 4 pellets for each gasification run were randomly selected from 4 different batches of canola hull densification to represent the general composition and characteristics of fuel pellets. Argon was used as the carrier gas at the volumetric flow rate of 44 mL/min. Experiments were performed under atmospheric pressure, and the effects of the process temperature and SBR were investigated at 650–850 °C and 0.31–0.62 kg/kg, respectively. These ranges of temperatures and SBR were chosen based on the effective ranges of the biomass gasification temperature and SBR (or equivalence ratio) [21]. Other operating parameters such as gasification pressure and carrier gas flow rate were not studied in this research work, and they were kept constant for all experiments. Experiments of steam gasification were performed for three levels of temperature (650 °C, 750 °C, and 850 °C) at each levels of steam-to-biomass ratio (0.31, 0.47, and 0.62). Gas produced using the process was accumulated in a water displacement system installed after the reactors. Six samples of this gas were injected into a micro-GC (CP-4900) and the average concentration values for these samples were used as the gas composition. The standard deviation of the concentration values measured using micro-GC (CP-4900) was as follows for different gas components:

\[ \text{H}_2: <0.9, \text{CO}: <0.8, \text{CO}_2: <0.7, \text{CH}_4: <0.6, \text{and C}_2^+: <0.03. \]

The synthesis gas yield (SGY) was calculated using Equation (1):

\[
\text{SGY} = \frac{\text{Mole numbers of H}_2 + \text{CO in gas product}}{\text{Ash free mass of pellets}}
\]  

The liquid product was condensed under an ice-bath system and collected from the reactors and their assemblies after each run. Solid product (biochar) was collected after cooling under N2 flow from the reactor after each gasification experiment.
2.2. Supercritical Water Gasification

The supercritical water (SCW) gasification of canola hull pellets was done in stainless-steel batch mode in a tubular reactor. The design and description of the SCWG reactor are described elsewhere [22]. The major elements of the SCWG assembly are the tubular reactor, furnace, temperature controller, thermocouple, pressure gauge, pressure relief valve, check valve, filters, and gas–liquid separator. The tubular batch reactor used for SCWG experiments was built using stainless steel (SS316) 40.5 cm in length, with a 1.27-cm outer diameter and 0.94-cm inner diameter.

SCWG of canola hull pellets was achieved at 23–25 MPa to study the effects of the gasification temperature (350, 450, 550, and 650 °C); feed concentration (10, 15, 20, and 25 wt%); and residence time (15, 30, 45, and 60 min). For each parameter, four levels were chosen, and the experiments were performed at 12 different operating conditions. The ranges of temperatures, reaction time, and feed concentration were based on the critical temperature (375 °C) and critical pressure (22.1 MPa) of water. The process conditions selected in this work are also in accordance with the findings from the literature [23,24]. The SCWG experiments were performed under a pressurized nitrogen atmosphere (10–12 MPa). The SCWG reactor was maintained at the desired temperature for a particular residence time; after which, the reaction was stopped by opening the reactor and spraying ice-cold water. The non-condensable gas products passed through the gas–liquid separator and were collected in gas sampling bags. The gas samples were analyzed in an Agilent 7820A gas chromatography system. The standard error margin for the gas yield analysis was less than 2%.

2.3. Characterization Techniques

The lower heating value (LHV) of the gases was measured using the following equation [25]:

\[
LHV \ (kJ/Nm^3) = (30 \times CO + 25.7 \times H_2 + 85.4 \times CH_4 + 151.3 \times C_nH_m) \times 4.2
\]  

CO, H_2, CH_4, and C_nH_m indicate the molar concentration (%) of these gases. C_nH_m indicates the levels of all hydrocarbons (except CH_4) found in the gas phase.

For the quantification of the minerals in the pellet samples, a Sciex Elan 5000 inductively coupled plasma-mass spectrometer (ICP-MS) (PerkinElmer, Waltham, MA, USA) was used. First, the ashing of the samples was performed, and then, they were dissolved in aqua Razia (HCL/HNO_3 = 3:1) solution. Before injection of the samples into the equipment, the solution was filtered by a 0.2-μm filter.

A thermogravimetric analysis was performed in a Pyris Diamond TG/DTA instrument (Perkin-Elmer, Waltham, MA, USA) to evaluate the fuel properties of the canola hull pellet. The analysis was carried out under an air atmosphere (with a volumetric flow rate of 60 mL/min) and a heating rate of 10 °C/min.

Porous characteristics of biochar, including the BET surface area and total pore volume of biochar, were measured using an automated gas adsorption analyzer (ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA). After degassing the biochar samples at 200 °C to a vacuum of 550 μm Hg, nitrogen adsorption–desorption isotherms at −196 °C were measured. About 0.2 g of the sample was used for each analysis.

3. Results and Discussion

3.1. Steam Gasification

The composition of gas products collected from the steam gasification process is shown in Figure 1. Except for the CO_2 and N_2 feed, the rest of the gases have positive heating values. In all runs, the concentration of nitrogen was less than 4.3 mol% and oxygen was ≤1.5 mol%. The concentrations of hydrogen sulfide (H_2S) and sulfur dioxide (SO_2) were measured for gas products of some runs, which were less than 1700 ppm and 1300 ppm, respectively.
In general, a larger concentration of CH$_4$ was obtained at the lower gasification temperature. The largest change in the biochar yield with the gasification temperature accelerates the formation of these gas products using the cracking of volatile matter and tars, as well as improving the reaction rate of endothermic reactions. Tilay et al. [20] had the same observation regarding the CH$_4$ concentration as an exothermic reaction and methane-consuming reactions (Equations (4) and (5)) (which is related to the CH$_4$ concentration at constant ER, the hydrogen concentration increased with an increase in the gasification temperature. In addition, at a constant gasification temperature, there was an increase in the H$_2$ concentration for larger values of SBR. The only exception was at 850 °C, at which the largest hydrogen concentration was at 750 °C instead of 850 °C. The difference between these two values was smaller than 1.2 mol%. The range of changes in the hydrogen concentration with respect to the SBR value was more significant at lower temperatures (650 °C) and decreased with an increase in the gasification temperature. The increase of hydrogen concentration with an increase in the SBR value can be related to the availability of oxygen as an oxidation agent at higher SBR values. This trend was also observed by other researchers [26–28]. The higher concentration of hydrogen at larger gasification temperatures, for the cases with constant SBR, can be due to the endothermic nature of the water–gas reaction (Equation (3)). In addition, the endothermic nature of the reforming reactions (Equations (4) and (5)) (which is related to the CH$_4$ formed in the process) can help for the production of hydrogen at higher gasification temperatures.

Water–gas reaction:

\[
C(s) + H_2O(g) \rightarrow CO(g) + H_2(g) \quad [\Delta H = +131 \text{ kJ/mol}] \quad (3)
\]

Dry reforming of methane:

\[
CH_4(g) + CO_2(g) \rightarrow 2CO(g) + 2H_2(g) \quad [\Delta H = +124 \text{ kJ/mol}] \quad (4)
\]

Steam reforming of methane:

\[
CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g) \quad [\Delta H = +205 \text{ kJ/mol}] \quad (5)
\]

After H$_2$, CO had the largest share in the gas composition, which was between 23.3 and 31.3 mol%. The CO concentration showed the same trend of changes as hydrogen gas. The lowest CO concentration was at 650 °C with a SBR of 0.33, and the largest value was at 850 °C with a SBR of 0.47. The same parameters described for the effects of the gasification temperature and SBR on the hydrogen yield can be effective on the CO yield. In the case of
CO, higher process temperatures improved the CO concentration due to the endothermic nature of the Boudouard reaction (Equation (6)) at a constant SBR.

Boudouard reaction:

\[
\text{C}_\text{(s)} + \text{CO}_2 \text{(g)} \rightarrow 2\text{CO} \text{(g)} \quad [\Delta H = +173 \text{ kJ/mol}] (6)
\]

The CO\(_2\) concentration, at a constant SBR, was reduced at higher gasification temperatures. It is related to the endothermic nature of Boudouard and methane dry reforming (Equation (4)) reactions, as well as the exothermic nature of the water–gas shift reaction (Equation (7)).

Water–gas shift reaction:

\[
\text{CO} \text{(g)} + \text{H}_2\text{O} \text{(g)} \rightarrow \text{CO}_2 \text{(g)} + \text{H}_2 \text{(g)} \quad [\Delta H = -42 \text{ kJ/mol}] (7)
\]

The methane concentration, at constant SBR values of 0.31 and 0.47, decreased at higher gasification temperatures. However, at a SBR of 0.62, it showed no special trend. In general, a larger concentration of CH\(_4\) was obtained at the lower gasification temperature and smaller values of SBR. It can be due to the methanation reaction (Equation (8)) as an exothermic reaction and methane-consuming reactions (Equations (4) and (5)) as endothermic reactions. Tilay et al. [20] had the same observation regarding the CH\(_4\) concentration.

Methanation:

\[
\text{C}_\text{(s)} + 2\text{H}_2 \text{(g)} \rightarrow \text{CH}_4 \text{(g)} \quad [\Delta H = -75 \text{ kJ/mol}] (8)
\]

Heavier hydrocarbons (C\(_2^+\)) showed a concentration range of 2.2–9.9 wt%. Its concentration at a constant SBR decreased with an increase in the gasification temperature three to four times between 650 °C and 850 °C. The decrease of this concentration, at a constant gasification temperature, was smaller than that for the case of a constant SBR.

The syngas yield (SGY) and total gas yield (TGY) are shown in Figure 2. At a constant SBR, the TGY increased with the temperature rise. The vapors and liquids formed in the primary stage of gasification are converted to permanent gases at the secondary stage of gasification when the temperature is greater than 700 °C [29]. This increase in the gasification temperature accelerates the formation of these gas products, using the cracking of volatile matter and tars, as well as improving the reaction rate of endothermic reactions [7,30], which results in larger values of TGY. A similar observation was made by other researchers [20,31].

At a constant SBR, the SGY increased with an increase in the gasification temperature. The maximum increase observed at a SBR of 0.47 was approximately 1.3 times, with a temperature rise from 650 °C to 850 °C. These ratios for SBR values of 0.31 and 0.62 were 0.68 and 0.73, respectively. This observation is in agreement with the increase in the concentrations of H\(_2\) and CO with the gasification temperature shown in Figure 1. Biochar that remained after the gasification process was enriched in carbon, which contained condensed organic compounds and inorganic compounds [32]. The biochar yield was at the maximum value (55.6 wt%) for the mildest operating conditions (SBR of 0.31/T of 650 °C) and the minimum value (32.8 wt%) for the most severe operating conditions (SBR of 0.62/T of 850 °C). At the constant SBR, the biochar yield decreased with an increase in the gasification temperature. The largest change in the biochar yield with the gasification temperature was observed for SBR of 0.47. Biochar produced at higher temperatures is porous, with greater aromatic carbon [33]. It can be related to the elimination of some functional groups, at higher temperatures, in char structures, such as olefinic, carbonyl, hydroxyl, and aliphatic C–H bonds [29].
With a rise in the gasification temperature (Figure 1), the CH$_2$ production of methanol and Fischer–Tropsch synthesis, further cleaning processes (primary and secondary) will be required for the conditioning of syngas for these purposes [34,35].

The LHV of the gas phase produced by steam gasification decreased at a constant SBR with an increase in the gasification temperature (Figure 3). The largest value of LHV (179 kJ/kg) was obtained at operating conditions of SBR of 0.31 at 650 °C. Considering higher heating values of C$_2$+ compounds compared with those of other compounds, the observed trend is reasonable, because the total concentration of C$_2$+ compounds decreased with a rise in the gasification temperature. In general, all these reactions increase the carbon content in the gas phase. In addition, at higher gasification temperatures, tar undergoes cracking reactions [29] and can be converted to lighter liquid or gaseous molecules, which transfer more carbon to the gas phase. In the current study, at SBR values of 0.47 and 0.62, the liquid product yield decreased with a rise in the process temperature. In the case of a SBR of 0.31, there was no significant change in the liquid product with the gasification temperature. The combination of all these phenomena affects the carbon efficiency.

The LHV of the gas phase produced by steam gasification decreased at a constant SBR with an increase in the gasification temperature (Figure 3). The largest value of LHV (179 kJ/kg) was obtained at operating conditions of SBR of 0.31 at 650 °C. Considering higher heating values of C$_2$+ compounds compared with those of other compounds, the observed trend is reasonable, because the total concentration of C$_2$+ compounds decreased with a rise in the gasification temperature (Figure 1).

Figure 4 shows H$_2$/CO and CH$_4$/H$_2$ molar ratios in the gas products. Both ratios, at constant SBR, increased with an increase in the gasification temperature. The ratios of these components indicate the possible application of gas products. H$_2$/CO was in the range of 1.13–1.40 mol/mol. Considering the optimized range of this molar ratio (>2) for the production of methanol and Fischer–Tropsch synthesis, further cleaning processes (primary and secondary) will be required for the conditioning of syngas for these purposes [34,35]. The CH$_4$/H$_2$ molar ratio was in the range of 0.26–0.64. The largest value of this ratio was obtained due to more CH$_4$ generation at mild operating conditions (i.e., 650 °C and SBR of 0.31). Methane is a suitable fuel for combined heat and power systems to generate electricity and heat.
Figure 3. Lower heating value and carbon efficiency for the steam gasification of fuel pellets at different gasification temperatures and steam-to-biomass ratios.

Figure 4 shows H₂/CO and CH₄/H₂ molar ratios in the gas products. Both ratios, at constant SBR, increased with an increase in the gasification temperature. The ratios of these components indicate the possible application of gas products. H₂/CO was in the range of 1.13–1.40 mol/mol. Considering the optimized range of this molar ratio (>2) for the production of methanol and Fischer–Tropsch synthesis, further cleaning processes (primary and secondary) will be required for the conditioning of syngas for these purposes [34,35]. The CH₄/H₂ molar ratio was in the range of 0.26–0.64. The largest value of this ratio was obtained due to more CH₄ generation at mild operating conditions (i.e., 650 °C and SBR of 0.31). Methane is a suitable fuel for combined heat and power systems to generate electricity and heat.

Figure 4. H₂/CO and CH₄/H₂ molar ratio values for the steam gasification of fuel pellets at different gasification temperatures and steam-to-biomass ratios.

3.2. Supercritical Water Gasification

Canola hull pellets at a constant feed concentration of 10 wt% were gasified in SCW at 350–650 °C for 30 min to understand the effects of gasification temperature. It can be seen from Table 1 that the total gas yields increased with temperatures from 4.16 mmol/g at 350 °C to 8.68 mmol/g at 650 °C. As the temperature rose from 350 to 650 °C, the H₂ yields rose from 0.4 mmol/g to 3.17 mmol/g. Similarly, as shown in Figure 5, the concentrations of CO₂, CH₄, and C₂H₆ also increased at higher temperatures. The LHV of the gas products was gradually greater for gases generated at higher SCW temperatures (Table 1). For example, the LHV of the gas product generated from canola hull pellets at 650 °C (970 kJ/Nm³) was greater than that of the gas products produced at 350 °C (339 kJ/Nm³).
A higher temperature is known to enhance H\textsubscript{2} yields by improving the carbon gasification efficiency [36]. Water demonstrates poor intramolecular and intermolecular hydrogen bonding at elevated temperatures and pressures, which disintegrates the biomass components during gasification or oxidation [37]. Moreover, high SCW temperatures promote a water–gas shift reaction, which proceeds with the use of CO as the reactant to produce H\textsubscript{2} and CO\textsubscript{2} [38]. Hence, the concentration of CO is reduced at high temperatures, and those for H\textsubscript{2} and CO\textsubscript{2} are amplified. The yield of CO decreased by 2.5-fold at 650 °C (0.22 mmol/g) in contrast to that at 350 °C (0.54 mmol/g) (Figure 5a). On the other hand, the yields of H\textsubscript{2} and CO\textsubscript{2} increased by eight-fold and two-fold, respectively.

After the optimal temperature of SCWG of the canola hull pellets was determined to be 650 °C, the impacts of the feed concentration were further studied. Figure 5b shows the drift of gas yields from SCWG of canola hull pellets at variable feed concentrations (10–25 wt%) and a fixed temperature of 650 °C and a residence time of 30 min. As the feed concentration was augmented from 10 wt% to 25 wt%, the total gas yields decreased from 6.35 mmol/g to 5.59 mmol/g, respectively (Table 1). The yield of H\textsubscript{2} was comparatively higher at 10 wt% (3.17 mmol/g) than at 25 wt% (1.56 mmol/g). Similarly, the concentration of CO\textsubscript{2} was greater at 10 wt% feed concentration (1.59 mmol/g) than at 25 wt% feed concentration (0.98 mmol/g). In contrast, the yields of CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6} were found to be larger at high feed concentrations. The yield of CH\textsubscript{4} almost doubled from 0.98 mmol/g at 10 wt% feed concentration to 1.95 mmol/g at 25 wt% feed concentration. This indicates that the methanation reaction is preferable at higher feed concentrations and higher temperatures [39]. Due to the higher concentrations of CO, CH\textsubscript{4}, and C\textsubscript{2}H\textsubscript{6}, the LHV was greater for the gas products generated at 25 wt% feed concentration (226.5 kJ/m\textsuperscript{3}) than that at 10 wt% feed concentration (152.6 kJ/m\textsuperscript{3}) (Table 1).

**Table 1.** Influence of process conditions on the gas yields and quality obtained from SCWG of canola hull pellets.

<table>
<thead>
<tr>
<th></th>
<th>H\textsubscript{2}/CO (mol/mol)</th>
<th>CH\textsubscript{4}/H\textsubscript{2} (mol/mol)</th>
<th>TGY (mol/kg of Feed)</th>
<th>SGY (mol/kg of Feed)</th>
<th>LHV (kJ/m\textsuperscript{3})</th>
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</thead>
<tbody>
<tr>
<td><strong>Effect of temperature (T) on 10 wt% biomass for 30 min</strong></td>
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<tr>
<td>T = 350 °C</td>
<td>0.74 ± 0.02</td>
<td>1.05 ± 0.02</td>
<td>2.23 ± 0.06</td>
<td>0.94 ± 0.02</td>
<td>151.6 ± 4.51</td>
</tr>
<tr>
<td>T = 450 °C</td>
<td>1.57 ± 0.06</td>
<td>0.82 ± 0.02</td>
<td>2.96 ± 0.08</td>
<td>1.18 ± 0.03</td>
<td>173.1 ± 5.18</td>
</tr>
<tr>
<td>T = 550 °C</td>
<td>5.54 ± 0.15</td>
<td>0.40 ± 0.01</td>
<td>4.80 ± 0.14</td>
<td>2.42 ± 0.07</td>
<td>159.4 ± 6.75</td>
</tr>
<tr>
<td>T = 650 °C</td>
<td>14.41 ± 0.34</td>
<td>0.31 ± 0.01</td>
<td>6.35 ± 0.19</td>
<td>3.39 ± 0.15</td>
<td>152.6 ± 3.5</td>
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<tr>
<td><strong>Effect of feed concentration (FC) at 650 °C for 30 min</strong></td>
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<tr>
<td>FC = 10 wt%</td>
<td>14.41 ± 0.34</td>
<td>0.31 ± 0.01</td>
<td>6.35 ± 0.19</td>
<td>3.39 ± 0.15</td>
<td>152.6 ± 4.51</td>
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<tr>
<td>FC = 15 wt%</td>
<td>7.69 ± 0.26</td>
<td>0.47 ± 0.02</td>
<td>6.17 ± 0.24</td>
<td>3.04 ± 0.02</td>
<td>170.7 ± 5.45</td>
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<tr>
<td>FC = 20 wt%</td>
<td>4.33 ± 0.12</td>
<td>0.88 ± 0.04</td>
<td>6.11 ± 0.54</td>
<td>2.56 ± 0.07</td>
<td>204.4 ± 6.15</td>
</tr>
<tr>
<td>FC = 25 wt%</td>
<td>2.64 ± 0.1</td>
<td>1.25 ± 0.04</td>
<td>5.59 ± 0.12</td>
<td>2.15 ± 0.02</td>
<td>226.5 ± 4.58</td>
</tr>
<tr>
<td><strong>Effect of residence time (t) on 10 wt% biomass at 650 °C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T = 15 min</td>
<td>4.17 ± 0.08</td>
<td>0.33 ± 0.04</td>
<td>4.00 ± 0.02</td>
<td>2.17 ± 0.05</td>
<td>156.0 ± 4.35</td>
</tr>
<tr>
<td>T = 30 min</td>
<td>14.41 ± 0.34</td>
<td>0.31 ± 0.01</td>
<td>6.35 ± 0.09</td>
<td>3.39 ± 0.15</td>
<td>152.6 ± 4.51</td>
</tr>
<tr>
<td>T = 45 min</td>
<td>20.37 ± 0.49</td>
<td>0.32 ± 0.05</td>
<td>8.06 ± 0.05</td>
<td>4.06 ± 0.09</td>
<td>150.6 ± 5.36</td>
</tr>
<tr>
<td>T = 60 min</td>
<td>40.10 ± 0.64</td>
<td>0.41 ± 0.01</td>
<td>9.87 ± 0.08</td>
<td>4.11 ± 0.05</td>
<td>146.7 ± 2.39</td>
</tr>
</tbody>
</table>

TGY: total gas yield, SGY: synthesis gas yield, LHV: lower heating value.
Figure 5. (a) Effect of temperature on the gas yields from SCWG of a canola hull at 10 wt% feed concentration and 30 min of residence time. (b) Effect of feed concentration on the gas yields from SCWG of a canola hull at 650 °C and 30 min of residence time. (c) Effect of residence time on the gas yields from SCWG of canola hull at 650 °C and 10 wt% feed concentration. The data presented in an average of replicate measurements with a standard error of less than 3.5%.

The impact of the residence time was further studied after determining that the optimal temperature and feed concentration for the SCWG of canola hull pellets were 650 °C and 10 wt%, respectively (Figure 5c). The total gas yields were higher in 60 min of residence time (9.87 mmol/g) compared to that of 15 min (4 mmol/g) (Table 1). The thermal denaturation reactions are enhanced at higher temperatures and longer residence times, which increased the total gas yields. The LHV of gases was lower at 60 min (146.7 kJ/m³) compared to that at 15 min (156 kJ/m³), 30 min (152.6 kJ/m³), and 45 min (150.6 kJ/m³).

The H₂ yields were amplified from 1.75 mmol/g at 15 min to 4.01 mmol/g at 60 min, indicating about a 56% increase (Figure 5c). With an exception for CO, the yields of CO₂, CH₄, and C₂H₆ gradually increased at longer residence times. Similar to the H₂ yield, the yield of CO₂ was also elevated by 72% at 60 min (3.46 mmol/g) compared to that of 15 min (0.98 mmol/g). The CO yield was lower in the case of 60 min (0.1 mmol/g) than that of 15 min (0.42 mmol/g). The lowering CO yield and rising H₂ and CO₂ yields are indicative...
of the water–gas shift reaction that is prevalent at longer residence times [22,38,40,41]. Besides the water–gas shift reaction, CO is also used up in methanation and hydrogenation reactions. While H\textsubscript{2} and CO\textsubscript{2} are the main products of the water–gas shift reaction, CH\textsubscript{4} is the chief product of methanation and hydrogenation [36]. Hence, the concentration of CH\textsubscript{4} was higher at 60 min (1.66 mmol/g) than that at 15 min (0.57 mmol/g). In addition, due to polymerization reactions at lengthier residence times of 60 min, the yields of gases such as C\textsubscript{2}H\textsubscript{4} were also amplified.

Table 1 shows a larger molar ratio of H\textsubscript{2}/CO for the hydrothermal process (0.74–40.1) compared with that for steam gasification (1.13–1.4). It confirms that the hydrothermal process is an effective process for hydrogen production. The range of CH\textsubscript{4}/H\textsubscript{2} for the hydrothermal process (0.31–1.25) was much wider than that for steam gasification (0.26–0.65). That LHV for both processes was not so different, but in some cases (such as feed concentrations larger than 20 wt%), it was higher than the values for steam gasification.

In summary, for steam gasification at a constant ER, the hydrogen and CO concentration increased with an increase in the gasification temperature. In addition, at a constant gasification temperature, there was an increase in the H\textsubscript{2} concentration for larger values of SBR. There was no special trend for methane concentration with respect to the temperature and SBR. Lower temperatures resulted in higher concentrations of heavier hydrocarbons. The TGY and SGY were increased with an increase in the temperature, but this parameter has the opposite effect on LHV. In the case of hydrothermal gasification, higher temperatures increased the hydrogen yield and TGY. A higher feed concentration decreased the TGY but increased the hydrogen yield. A higher residence time increased the TGY but decreased the LHV.

3.3. Physicochemical Characterization of Biomass and Biochar

To investigate the combustion characteristics of a canola hull pellet, a thermogravimetric (TGA) analysis was performed (Figure 6). This analysis was performed under the airflow. The mass of the sample (wt%), differential thermogravimetric (%/°C), and temperature (°C) are plotted in Figure 6 versus time. In addition to the initial process of moisture elimination (up to 120 °C), there are two more distinct zones of mass loss. One zone was in the temperature range of 280–320 °C, and the second zone of mass loss was between 410 °C and 500 °C. The first zone could be due to the combustion of volatiles. The second zone is related to the combination of combustions of volatiles and fixed carbon.

![Figure 6](image-url)  
Figure 6. Thermogravimetric analysis of a canola hull pellet.
The burnout temperature ($T_b$) and ignition temperature ($T_i$) were estimated as 250 °C and 660 °C, respectively [42]. These two temperatures for canola hull pellets are lower than those for coal. It indicates the more convenient combustion of the pellets at a lower range of temperature. Considering the lower ash content of the pellets compared with the two common types of coal (lignite and sub-bituminous) [43], there are obvious advantages to using this type of fuel pellet in combustion or gasification processes along the coal in industrial units to generate heat and energy.

An analysis of the biochar properties, including the minerals present in its ash portion and its porous characteristics, is required to identify the potential industrial and agricultural applications of canola meal-based biochar from gasification. The mineral compounds in the ash portion of the biochar can be effective in the industrial or agricultural applications of biochar obtained from gasification. Some of the mineral elements present in biochar help in plant growth and have beneficial effects [44]. To quantify these elements in biochar samples, the ICP-MS technique was used. The types of elements and their concentrations in biochar samples are shown in Table 2. The detected elements were divided into the following two groups, based on their nutritious effect on plant growth such as essential metals (e.g., Na, K, Mg, Ca, Fe, and P) and heavy/toxic metals (e.g., Al, Cu, Cr, Zn, Ni, Mo, and Mn). The essential metals contribute substantially to plant growth. For example, phosphorous as the main element in fertilizer formulations, along with nitrogen and potassium, are involved in the photosynthesis process. Iron is effective in enzyme functions and chlorophyll formation. Alkaline metals are a main part of fertilizers and contribute to enzyme functionalities. However, heavy metals with an atomic density of more than 6000 kg/m$^3$ show deleterious effects on the crops and microorganisms present in the soil [45,46]. As shown in Table 2, biochar samples obtained from steam gasification showed a higher value of essential elements under more severe gasification operating conditions. However, biochar obtained by SCWG at 650 °C with 10 wt% of a pellet in 60 min showed a lower value of essential elements compared with that for steam-gasified biochar, which is related to the demineralization of precursors during the hydrothermal process by hydrolysis and the acid solvation mechanisms [47–49].

Table 2. ICP-MS results for biochar samples produced from steam and SCW gasification of canola hull fuel pellets.

<table>
<thead>
<tr>
<th>Elements</th>
<th>Biochar (T = 650 °C/SBR = 0.31)</th>
<th>Biochar (T = 750 °C/SBR = 0.47)</th>
<th>Biochar (T = 850 °C/SBR = 0.62)</th>
<th>Biochar (SCW-650 °C, 10 wt%, 60 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Essential elements (mg/g of biochar)</td>
<td>Essential elements (mg/g of biochar)</td>
<td>Essential elements (mg/g of biochar)</td>
<td>Essential elements (mg/g of biochar)</td>
</tr>
<tr>
<td>Na</td>
<td>3</td>
<td>12</td>
<td>13</td>
<td>3</td>
</tr>
<tr>
<td>K</td>
<td>9</td>
<td>12</td>
<td>17</td>
<td>9</td>
</tr>
<tr>
<td>Mg</td>
<td>7</td>
<td>12</td>
<td>17</td>
<td>7</td>
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<tr>
<td>Ca</td>
<td>13</td>
<td>11</td>
<td>17</td>
<td>13</td>
</tr>
<tr>
<td>P</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>Total (essential elements)</td>
<td>47</td>
<td>61</td>
<td>96</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>Heavy/toxic elements (mg/g of biochar)</td>
<td>Heavy/toxic elements (mg/g of biochar)</td>
<td>Heavy/toxic elements (mg/g of biochar)</td>
<td>Heavy/toxic elements (mg/g of biochar)</td>
</tr>
<tr>
<td>Al</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
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<tr>
<td>Cr</td>
<td>&lt;1</td>
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<td>Cu</td>
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<td>Ni</td>
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<td>&lt;1</td>
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<tr>
<td>Zn</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Total (heavy elements)</td>
<td>2.2</td>
<td>2.1</td>
<td>2.6</td>
<td>1.2</td>
</tr>
</tbody>
</table>

1 T: gasification temperature and SBR: steam-to-biomass ratio.
Biochar samples produced through steam gasification showed relatively large porous characteristics. Biochar prepared at 650 °C (with a SBR of 0.31), 750 °C (with a SBR of 0.47), and 850 °C (with a SBR of 0.62) had BET surface areas of 194, 333, and 401 m²/g, respectively, and a total pore volume of 0.084, 0.211, and 0.271 m³/g, respectively. It shows that severe operating conditions resulted in a highly developed porous structure due to the pronounced structural changes in the precursor biomass by gasification reactions. These porous characteristic values for these biochar samples produced from the gasification of canola hull pellets indicate the potential of these biochar samples for many industrial applications such as adsorbents, catalysts, catalyst supports, or additives for biocomposites [50,51]. However, the hydrothermally developed biochar samples were different, and they did not have a developed porosity. For example, BET surface area values for biochar samples obtained from SCWG of canola hull fuel pellets at a 10 wt% feed concentration and 30 min at the entire range of temperatures were less than 6 m²/g.

4. Conclusions

Biomass fuel pellets can be produced from agricultural residues. In this research work, it was observed that this type of fuel pellet can be used for the production of hydrogen, as a clean fuel, or synthesis gas as a feedstock to produce liquid fuel. This investigation provides a direct comparison between outcomes from two gasification techniques applied to the same feedstock. The large H₂/CO molar ratio of gas products from hydrothermal gasification of the pellet showed the suitability of hydrothermal gasification for hydrogen production. For hydrothermal gasification, a temperature increase towards the water critical temperature increased the hydrogen yield, and a lower feed concentration was more effective in hydrogen production. A residence time increase of up to 45 min was effective on hydrogen production, but after that, there was not a significant change. However, the synthesis gas produced by steam gasification was higher than that for SCWG, and this technique was more suitable to produce syngas feed for liquid fuel production industries. For steam gasification, a temperature increase was particularly effective in the increase of hydrogen production, and decreasing in the share of hydrocarbons heavier than methane in the gas phase. As a general trend, at any specific temperature, an increase in SBR increased the syngas quantity for steam gasification. In addition, the combustion characteristics of this pellet showed a lower burnout and ignition temperatures compared with those for coal, which leads to the possibility of using this pellet alongside coal for existing combustion and gasification processes.

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