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Research article

An assessment of pinecone gasification in subcritical, near-critical and supercritical water

Sonil Nanda[a], Miao Gong[b], Howard N. Hunter[c], Ajay K. Dalai[d], Iskender Gökalp[e], Janusz A. Kozinski[a],*

[a] *Department of Earth and Space Science and Engineering, Lassonde School of Engineering, York University, Toronto, Ontario, Canada*
[b] *School of Civil Engineering, Hefei University of Technology, Hefei, Anhui, China*
[c] *Department of Chemistry, York University, Toronto, Ontario, Canada*
[d] *Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada*
[e] *Institut de Combustion, Aérothermique, Réactivité et Environnement (ICARE), Centre National de la Recherche Scientifique (CNRS), Orléans, France*

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ABSTRACT

Pinecone is a lignocellulosic forest residue with value-added industrial importance in terms of energy and materials production. Although promising, pinecone has received inadequate attention as a biofuel feedstock for thermochemical conversion. Water above its critical temperature ($T_C \geq 374\ ^\circ C$) and critical pressure ($P_C \geq 22.1$ MPa), termed as supercritical water, has high kinetic energy and densities similar to that of gases and liquids, respectively. When employed in gasification, supercritical water has an ability to completely dissolve organics and gases. Therefore, this study identifies the candidacy of pinecone as a precursor for conversion to hydrogen through hydrothermal gasification. Pinecone was gasified in subcritical water (300 and 350 °C; 21 MPa), near-critical water (370 °C; 22 MPa) and supercritical water (450 and 550 °C; 23 MPa) to investigate the impacts of temperature (300–550 °C), feed concentration (10–25 wt%) and residence time (15–60 min). The impacts of alkali catalysts (e.g., Na_2CO_3, NaOH and KOH) at a loading of 30 wt% were examined to maximize hydrogen yields. The hydrochar generated from gasification in subcritical water, near-critical water and supercritical water were physico-chemically characterized through proximate and ultimate analysis (carbon-hydrogen-nitrogen-sulfur-oxygen), thermogravimetric analysis, X-ray diffraction, Fourier transform infra-red spectroscopy, Raman spectroscopy, Scanning electron microscopy and Nuclear magnetic resonance spectroscopy. In the non-catalytic gasification of pinecone, highest hydrogen (1.42 mmol/g) and total gas yields (6.6 mmol/g) with lower heating value (488 kJ/Nm^3) of the gas products were obtained in supercritical water at 550 °C with 10 wt% feed concentration for 60 min. Moreover, at 30 wt% catalyst loading, highest hydrogen yield was obtained from KOH (3.26 mmol/g) followed by NaOH (2.71 mmol/g) and Na_2CO_3 (1.96 mmol/g). Hydrochars generated in supercritical water at 550 °C had a greater content of aromatic carbon and were thermally stable. The findings reveal, for the first time, the potential of pinecone for hydrogen production through subcritical, near-critical and supercritical water gasification, as well as the prospective of its hydrochar for environmental and material applications.

1. Introduction

The aggregating energy demands, exhausting fossil fuel resources, accelerating greenhouse gas emissions and the resulting global warming are some of the leading environmental concerns of the present day. Lignocellulosic materials are attractive feedstocks for the sustainable production of biofuels that can supplement the mounting demands for energy. It is likely that a significant fraction of energy supply by 2050 (i.e., 250–500 EJ/year) could be provided by lignocellulosic biomass [1]. The biochemical constituents of lignocellulosic biomass are cellulose (35–55 wt %), hemicellulose (20–40 wt%), lignin (10–25 wt%) and extractives [2]. Lignocellulosic feedstocks include agricultural crop residues (e.g., bagasse, straw, husk, etc.), forestry biomass (e.g., sawdust, wood shavings and chips, etc.) and energy crops (e.g., perennial grass and short rotation coppice) [3]. Lignocellulosic materials can be converted to biofuels (e.g. bio-oil, bioethanol, biobutanol, biodiesel, syngas and biogas) through many thermochemical (e.g., pyrolysis, liquefaction, gasification, torrefaction and carbonization) and biochemical (e.g., fermentation and biomethanation) technologies [4–8].

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* Corresponding author at: Lassonde School of Engineering, York University, Toronto, ON M3J 1P3, Canada.
E-mail address: janusz.kozinski@lassonde.yorku.ca (J.A. Kozinski).

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Hydrothermal gasification is a promising technology for the conversion of organics to synthesis gas in an environmentally benign environment. Water is used both as a solvent and reaction medium in hydrothermal gasification as its thermo-physical properties can be tuned by altering its critical temperature (T_C) and critical pressure (P_C) [9]. Depending on the critical temperature and critical pressure of water, hydrothermal gasification processes employs subcritical ($T_C < 374$ °C and $P_C < 22.1$ MPa), near-critical ($T_C \sim 374$ °C and $P_C \sim 22.1$ MPa) and supercritical ($T_C > 374$ °C and $P_C > 22.1$ MPa) water. It should be noted that subcritical water exists at temperatures between the boiling point of water and its critical temperature. Water exists in the liquid state in subcritical conditions, whereas it transforms into a fluid state at supercritical conditions. Water in its supercritical state imparts enhanced mass transfer and heat transfer properties with higher solvation potential. It acts as an ideal solvent for biomass conversion because of its liquid-like densities and gas-like transport properties [10].

Other thermochemical technologies such as pyrolysis, liquefaction, torrefaction and carbonization are also available to convert lignocellulosic feedstocks to fuel products. Pyrolysis and liquefaction primarily generate bio-oil as the main liquid fuel product [11], whereas torrefaction and carbonization produce torrefied biomass or char as the main solid fuel [7,8,12]. In contrast, supercritical water gasification is a hydrothermal technology capable of transforming lignocellulosic biomass to produce combustible syngas. The efficiency of syngas yields from supercritical water gasification is determined by the process temperature, applied pressure, feed concentration, reaction time and catalysts loading [13]. H_2-rich syngas obtained from hydrothermal gasification can serve as a direct fuel or converted to hydrocarbon fuels, green diesel and fine chemicals through Fischer-Tropsch synthesis [14]. H_2-rich syngas can also be used efficiently in combustion engines, power generation systems and fuel cells for vehicular transportation and electricity generation.

The annual availability of forest residues in Canada ranges up to 46 million dry tons [15]. Most of the forested areas in the Northern Hemisphere host native pine trees. Pine trees are long-lived, evergreen, and coniferous trees in the genus *Pinus* and family Pinaceae. Pine trees are regarded as coniferous as they bear cones and can be monoecious (bearing male and female cones together) or sub-dioecious (either male or female cones). The male cones are relatively smaller (1–5 cm long) and usually appear in the spring season and fall off after shedding the pollens. In contrast, female cones are comparatively larger (3–60 cm) and take up to 3 years to mature after pollination. Pinecones can occur in one of more clusters of 3–5 around the branch and can symmetrically have numerous scales arranged in a spiral pattern to bear seeds. Pinecones are produced annually, and mature cones remain attached to the branch [16]. Pinecones open and release seed during warm and dry weather, and close rapidly when the temperature drops and the relative humidity increases. Round the year (but mostly in autumn), pine trees shed a tremendous amount of pinecones. Owing to their widespread occurrence, pinecones have long been a traditional part of arts and crafts such as in seasonal wreaths, decorations, potpourri, fire starters, bird feeders, toys, etc. [17].

Biochemically, pinecone contains approximately 33–37% cellulose, 35–38% hemicellulose and 23–25% lignin [18,19]. In a study by Brebu et al. [19], the carbon content and volatile matter in pinecone were found to range up to 44 wt% and 78 wt%, respectively. Pinecones are candidate biomass that can be of use as solid fuel (briquettes and pellets) or converted to biofuels (bio-oil or syngas) through thermochemical technologies. Pinecone is a subject of interest because there are very limited studies concerning its thermal degradation through combustion, pyrolysis and gasification. Font et al. [20] studied the thermal decomposition through pyrolysis and combustion of pine needles and pinecone. They reported a kinetic model for pyrolysis and combustion of pine needles and pinecones to correlate dynamic and isothermal runs. In another study by Brebu et al. [19], pinecone was *co*-pyrolyzed with synthetic polymers (i.e., polyethylene, polypropylene and polystyrene). *Co*-pyrolysis generated many polar oxygenated compounds and hydrocarbon oils with composition depending on the synthetic polyolefin. Furthermore, Haykırı-Açma et al. [21] performed pyrolysis of pinecone followed by gasification of its char in the steam-nitrogen mixture. Haykiri-Acma and Yaman [22] investigated different agricultural wastes biomasses (e.g. cotton refuse, olive refuse, pinecone and sunflower shell) and determined that pinecone gave highest gasification yield, lowest ash and maximum fixed carbon due to its greater lignin content. The kinetic studies also reported that pinecone has high activation energy for gasification.

Duman et al. [5] performed CO_2 gasification of char obtained from pinecone under isothermal conditions and studied the effect of surface area and alkali/alkali earth metals on the char reactivity. Haykırı-Açma [23] has reported the combustion characteristics of pinecone through non-isothermal thermogravimetric studies. Pinecone has also been used as a precursor for activated carbons [24,25], and biosorption of heavy metals and dyes [26–29]. High surface area activated carbon has been produced through KOH activation and carbonization of pinecone at 800 °C for supercapacitor application [30]. In a similar study by Barzegar et al. [31], pinecone-derived activated carbon demonstrated a higher specific surface area of 808 m^2/g in contrast to that of activated expanded graphite (457 m^2/g). Kumar et al. [25] synthesized a series of iron-exchanged heteropoly tungstate (TPA-Fe) supported on activated carbon produced from pinecone for use as catalysts for benzylation reaction. Rambabu et al. [32] have also used pinecone as a precursor for producing nanocellulose fibers using alkaline pretreatment, delignification and mechanical grinding techniques.

A better understanding of the thermal degradation of pinecone would facilitate many aspects of its management and valorization. With this objective, the current study aims to investigate the thermal events leading to the decomposition of pinecone in subcritical, near-critical and supercritical water. The process parameters under investigation include temperature (300–550 °C), pressure (21–23 MPa), feed concentration (10–25 wt%), residence time (15–60 min) and catalysts loading.

2. Materials and methods

2.1. Biomass

Pinecone was used as the feedstock for gasification in this study. Fallen mature pinecones with length ranging from 8 to 12 cm were collected from pine trees (*Pinus strobus*) on Keele Campus of York University in Toronto during the autumn of 2016. Pinecones were brushed to remove any soil particles, air-dried and crushed to a particle size < 1.0 mm using an IKA MF 10 Basic S1 grinder (ThermoFisher Scientific Inc., Mississauga, Ontario, Canada). The pulverized feedstock was stored in clean glass jars at ambient conditions before characterization and gasification.

2.2. Supercritical water gasification reactor

Hydrothermal gasification of pinecone was conducted in a tubular reactor made of stainless steel (SS 316). The tubular batch reactor was 10 in. long and had an inner diameter of 0.37 in. and outer diameter of 0.5 in. Nanda et al. [33] have systematically described the schematics of the gasification reactor and its operating procedures. The gasification assembly consisted of the tubular reactor, split furnace, pressure gauge, pressure relief valve, thermocouple, check valve, 2 μm filter, gas-liquid separating cylinder and moisture trap. All the tubing and fittings were of SS 316 grading, and purchased from Swagelok® (Swagelok Central Ontario, Mississauga, Ontario, Canada).

Nitrogen was used to create an inert atmosphere inside the gasification reactor and also to pressurize it to an initial 5–10 MPa depending on the gasification temperature. The gasification reactor was heated