



# Valorization of horse manure through catalytic supercritical water gasification



Sonil Nanda<sup>a</sup>, Ajay K. Dalai<sup>b</sup>, Iskender Gökalp<sup>c</sup>, Janusz A. Kozinski<sup>a,\*</sup>

<sup>a</sup> Department of Earth and Space Science and Engineering, Lassonde School of Engineering, York University, Ontario, Canada

<sup>b</sup> Department of Chemical and Biological Engineering, University of Saskatchewan, Saskatchewan, Canada

<sup>c</sup> Institut de Combustion Aérothermique Réactivité et Environnement (ICARE), Centre National de la Recherche Scientifique (CNRS), Orléans, France

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## ABSTRACT

The organic wastes such as lignocellulosic biomass, municipal solid waste, sewage sludge and livestock manure have attracted attention as alternative sources of energy. Cattle manure, a waste generated in surplus amounts from the feedlot, has always been a chief environmental concern. This study is focused on identifying the candidacy of horse manure as a next generation feedstock for biofuel production through supercritical water gasification. The horse manure was gasified in supercritical water to examine the effects of temperature (400–600 °C), biomass-to-water ratio (1:5 and 1:10) and reaction time (15–45 min) at a pressure range of 23–25 MPa. The horse manure and resulting biochar were characterized through carbon-hydrogen-nitrogen-sulfur (CHNS), inductively coupled plasma-mass spectrometry (ICP-MS), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy and scanning electron microscopy (SEM). The effects of alkali catalysts such as NaOH, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> at variable concentrations (1–2 wt%) were investigated to maximize the hydrogen yields. Supercritical water gasification of horse manure with 2 wt% Na<sub>2</sub>CO<sub>3</sub> at 600 °C and 1:10 biomass-to-water ratio for 45 min revealed maximum hydrogen yields (5.31 mmol/g), total gas yields (20.8 mmol/g) with greater carbon conversion efficiency (43.1%) and enhanced lower heating value of gas products (2920 kJ/Nm<sup>3</sup>). The manure-derived biochars generated at temperatures higher than 500 °C also demonstrated higher thermal stability (weight loss <34%) and larger carbon content (>70 wt%) suggesting their application in enhancing soil fertility and carbon sequestration. The results propose that supercritical water gasification could be a proficient remediation technology for horse manure to generate hydrogen-rich gas products.

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## 1. Introduction

The consumption of fossil fuels has intensified dramatically in the last few decades. The worldwide energy consumption in 2010 being 524 quadrillion Btu is projected for escalation to 630 quadrillion Btu by 2020 and 820 quadrillion Btu by 2040 (USEIA, 2013). The global consumption of gasoline and other liquid fuels

being 85.7 million barrels per day (BPD) in 2008 is estimated for acceleration to 97.6 million BPD in 2020 and 112.2 million BPD in 2035 (USEIA, 2011). The awareness in alternative energy sources is gaining momentum due to several socio-economic and environmental concerns such as depleting fossil fuel reserves, increasing energy demand, rising fuel prices, vulnerable energy security, increasing greenhouse gas emissions and global warming (Nanda et al., 2015a).

Biofuels seem to be a promising alternative to fossil fuels and an objective towards the mitigation of global warming. Additionally, biofuels are carbon-neutral and can be produced from renewable feedstocks that are not subject to shortages in supply. The CO<sub>2</sub> released from the burning of biofuels is equivalent to the CO<sub>2</sub> fixed by the plants during photosynthesis. Hence, there is no net increase in the atmospheric CO<sub>2</sub> levels (Demirbas, 2011). Biofuels can be produced from plant-based residues classified as first-generation and second-generation feedstocks. The first-generation feedstocks

*Abbreviations:* BPD, barrels per day; BTW, biomass-to-water; CCE, carbon conversion efficiency; CHNS, carbon-hydrogen-nitrogen-sulfur; DTA, differential thermogravimetric analysis; FTIR, Fourier transform infrared; HHV, higher heating value; HM, horse anure; ICP-MS, inductively coupled plasma-mass spectrometry; LHV, lower heating value; SCW, supercritical water; SCWG, supercritical water gasification; SEM, scanning electron microscopy; TGA, thermogravimetric analysis; WGS, water-gas shift.

\* Corresponding author at: Lassonde School of Engineering, York University, Toronto, Ontario M3J 1P3, Canada.

E-mail address: [janusz.kozinski@lassonde.yorku.ca](mailto:janusz.kozinski@lassonde.yorku.ca) (J.A. Kozinski).

primarily include edible plant residues and food crops such as cereals, sugar and starch-based crops (e.g., corn, cassava, etc.) and oil seeds (e.g., rapeseed, jatropha, cameline, etc.). Depending on the sugar, starch or lipid contents, the first-generation feedstocks are primarily used to produce bioethanol and biodiesel (Naik et al., 2010; Borugadda and Goud, 2012). The second generation feedstocks mostly comprise of non-edible plant biomass such as lignocellulosic residues from forestry (e.g., pinewood, spruce wood, beechwood, etc.), agriculture (e.g., wheat straw, corn cob, rice husk, etc.) and energy crops (e.g., switchgrass, timothy grass, willow, poplar, etc.) (Nanda et al., 2014b).

The first-generation biofuels although industrially viable in production suffer from several disadvantages such as food versus fuel debate, limited diversity in feedstock selection, and competition for arable lands (Graham-Rowe, 2011). In contrast, the second-generation feedstocks (i.e., lignocellulosic biomass) are potential candidates for bioethanol, biobutanol, bio-oil and biodiesel as they pose no or negligible threat to the ecosystem and food chain (Osmont et al., 2010). However, lignocellulosic biomass usually requires physicochemical and enzymatic pretreatments to release cellulose (C<sub>5</sub> sugars) and hemicellulose (C<sub>5</sub> and C<sub>6</sub> sugars) for fermentation to bioethanol and biobutanol (Nanda et al., 2014b). Besides, the thermochemical conversion technologies viz. pyrolysis, gasification and liquefaction also require physical biomass pretreatments such as pulverizing and drying to prevent heat/mass transfer limitations, subsequently adding to the net process expenditure (Wright et al., 2010).

Recently, organic wastes in the form of municipal solid waste, sewage sludge, poultry litter, cattle manure and industrial effluents have attracted attention as renewable sources for energy. Manure is the organic waste matter derived from animal feces that can be used as an organic fertilizer in agriculture. The breeding of livestock animals has increased significantly in the past decade especially for food (meat and milk), fibre and labor. About 24,100 lb of manure is generated per day in a typical barn with at least 200 cows (USEPA, 2015). The daily manure production from a typical bovine farm animal weighing 450 kg is about 27 kg representing 5–6% of its body weight (Queensland Government, 2015). The use of animal manure as a bioenergy feedstock has many advantages for invigorating the rural communities by diversifying farm income, moderating the impacts of commodity prices, and securing the local energy demands (Cantrell et al., 2008).

Other than composting and application in agronomy, effective management of livestock litter or manure are indispensable owing to the issues such as odor, pests as well as CH<sub>4</sub> and N<sub>2</sub>O emissions (Junior et al., 2015). Cattle manure can be converted to biofuels through biological and thermochemical pathways. Despite yielding energy products, these conversion processes can reduce manure volume, recover inherent nutrients, prevent odors and reduce pollution problems. The thermochemical conversion of animal manure results in the production of liquid and gaseous biofuels along with solid carbon residues (char) that can be used for soil applications. The biological anaerobic digestion involves the breakdown of organic components in manure to produce biogas (primarily CH<sub>4</sub> and CO<sub>2</sub>) by the action of methanogenic bacteria. Moreover, anaerobic digestion of manure is sensitive to several rate-limiting factors such as temperature, organic loading rate, oxygen, pH and hydraulic retention time (Cantrell et al., 2008). There is also a conundrum associated with the loss of soil organic carbon in the event of using cattle manure for bioenergy production rather than composting in agricultural farms.

Although the knowledge of anaerobic digestion is not new, yet its main biogas product, i.e. CH<sub>4</sub> is 20 times more potent greenhouse gas than CO<sub>2</sub> (Nanda et al., 2016c). In contrast, the thermochemical conversion pathways include pyrolysis, gasification and liquefaction that can potentially convert animal manure to biofuels

such as bio-oil and syngas. Unlike biological conversion that requires extended amount of reaction time (from days to months), thermochemical conversion pathways can conclude in seconds or minutes although impacted by temperature, heating rate, residence time, feed concentration and inherent biomass properties (Bridgwater, 2012; Yakaboylu et al., 2013). Gasification, a thermochemical biomass conversion technology, is attractive for energy and fuel production by offering non-oxidative conversion conditions with negligible pollutant emissions (Ferdous et al., 2001; Tavasoli et al., 2009).

Supercritical water gasification (SCWG), an attractive thermochemical technology proving its effectiveness for lignocellulosic biomass conversion, can be extended towards valorization of cattle manure. The physical properties of water change beyond its critical temperature ( $\geq 374$  °C) and critical pressure ( $\geq 22.1$  MPa), making it behave as a homogeneous fluid. Supercritical water (SCW) has gas-like viscosity and liquid-like density which enhance mass transfer and solvation properties, respectively (Basu and Mettanant, 2009). The viscosity of SCW is much lower than that of water (at ambient conditions), which increases the diffusion coefficients and reaction rates. The high critical pressures of SCW increase the chances of particle collision and chemical reactions within the medium (Bocanegra et al., 2010; Xu et al., 2011).

SCW features low dielectric constant, high mass-transport and thermal conduction as well as complete miscibility of hydrocarbons. SCWG involves several hydrothermal reactions including depolymerization, decomposition, bond cleavage, dehydration, decarboxylation, deamination and recombination of reactive fragments (Toor et al., 2011). However, the operating conditions such as pressure, temperature, feed concentration, residence time and catalyst concentration can influence the gas yields and gasification efficiency (Reddy et al., 2014). Catalytic SCWG can reduce the high-temperature requirements, improve H<sub>2</sub> selectivity and lessen the tar and char formation (Elliott, 2008).

There are only a few notable studies reporting the thermochemical conversion of animal manure to biofuels. Agblevor et al. (2010) performed fast pyrolysis of poultry litter in a fluidized bed reactor with the yields of bio-oil, biochar and gases ranging up to 50.2, 40.8 and 23.6 wt%, respectively. In a study by Gaskin et al. (2008), poultry litter broiler houses were subjected to low temperatures (400–500 °C) pyrolysis to produce biochar and bio-oil. The resulting biochar had high carbon (40%) and nitrogen (27%) contents along with beneficial soil nutrients (e.g., Mg, P, K and Ca). Hence, pyrolysis of manure can not only yield energy-dense bio-oil, but also result in biochar for use in improving soil fertility and sequestering carbon. Ro et al. (2010) reported higher concentrations of P and K in biochar derived from chicken litter and swine manure than the original manure feedstocks. In their pyrolysis experiment at 620 °C, nearly 17.2 and 15.7 mol% of H<sub>2</sub> were generated from chicken litter and swine manure, respectively.

It is noteworthy that H<sub>2</sub>, a major product of SCWG of biomass, has a lower heating value (LHV) of 120.2 MJ/kg that is far superior than biogas (LHV: 19 MJ/kg) and natural gas (LHV: 47.1 MJ/kg). Although most of the thermochemical studies have focused on pyrolysis of animal manure (Kim and Agblevor, 2007; Das et al., 2008; Agblevor et al., 2010; Ro et al., 2010) and biochar characterization for soil applications (Gaskin et al., 2008; Cao and Harris, 2010; Cantrell et al., 2012; Song and Guo, 2012; Azargohar et al., 2014), there is scarce literature available on its gasification (Nam et al., 2016; Maglinao Jr. et al., 2015). With this objective, the current research focuses on the SCWG of horse manure to produce H<sub>2</sub>-rich syngas. Besides, several parameters that affect H<sub>2</sub> yields from horse manure including temperature (400–600 °C), feed concentration (1:5 and 1:10 biomass-to-water ratio) and reaction time (15–45 min) were investigated. Three homogeneous alkali catalysts, namely NaOH, Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> were also assessed

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