



Catalytic supercritical gasification of biocrude from hydrothermal liquefaction of cattle manure



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ABSTRACT

In this article, we performed catalytic supercritical water gasification (SCWG) of biomass to enhance hydrogen production. First we used glucose as a model compound to screen the best catalyst and then we used this catalyst to gasify biocrude from hydrothermal liquefaction of cattle manure. We introduced a novel dual metal (Ni, Ru)–dual support (Al₂O₃, ZrO₂) catalyst for the first time in SCWG in order to improve the H₂ yield. A continuous flow tubular reactor was employed to perform the experiments. Novel 10%Ni-0.08%Ru/Al₂O₃-ZrO₂ catalyst showed the highest H₂ yield (1.34 mol/mol of C for glucose and 1.01 mol/mol of C for biocrude) and highest carbon gasification efficiency (88% for glucose and 92% for biocrude). It was found that Ru promoted Ni and ZrO₂ showed some catalytic activities towards hydrogen production. The pressure was 25 MPa for all experiments. Stability test showed that 10%Ni-0.08%Ru/Al₂O₃-ZrO₂ was highly stable for a 20 h run. Among the parameters studied, higher temperature favored H₂ yield, whereas higher concentration led to lower H₂ yield. We found that carbon gasification efficiency of cattle manure biocrude was independent of variation in temperature and concentration. Also the equilibrium condition was attained at lower temperature and concentration in terms of carbon conversion of the feed. An Eley–Rideal (ER) based mechanistic model was devised and tested against the obtained data. It was found the dissociation of adsorbed oxygenated hydrocarbon is the rate determining step with an average absolute deviation 6.65%.

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1. Introduction

The urge for hydrogen economy is increasing due to its cleaner combustion. Hydrogen is abundantly distributed around the world. However, it is not free and a 'suitable' technology is required to extract it from a primary source. Ninety six percent of current hydrogen demand are fulfilled from the conversion of fossil fuel [1].

The depleting nature of fossil fuel sources, strict regulations against pollution, and the unexpected price hikes necessitate the search for renewable sources for a sustainable and environmentally benign energy infrastructure. Being a local product, biomass offers environmentally friendly renewable energy resource. Increasing interest in thermochemical conversion of biomass for extracting energy has been boosted in recent years [2–4]. In contrast to the conventional thermochemical conversion process, supercritical water gasification (SCWG) of biomass does not require drying

biomass, which in turn saves energy and time. The unique property of supercritical water (SCW, $T_c = 373.95\text{ }^\circ\text{C}$ and $P_c = 22.06\text{ MPa}$) allows a mass transfer limitation free reaction condition as water becomes a single phase beyond its critical point.

The heat of evaporation at higher pressure (say $P > 20\text{ MPa}$) becomes very insignificant comparing with ambient conditions, which means ΔH_{vap} becomes zero at P_c . Besides, hot compressed water is a promoter of ionic reactions over radical reactions, which lead to decreased char formation. In addition to this, organic molecules become more reactive in compressed water while the temperature is more than $250\text{ }^\circ\text{C}$ [5,6]. These advantages stipulate a major impulse to use hot compressed water for treating various carbonaceous wastes.

SCWG using catalyst for hydrogen production is among the various processes to produce high quality fuels. Many industrial processes require hydrogen; such as the syntheses of ammonia and methanol, various hydrogenation and hydrotreating processes and most importantly, in fuel cells. Nevertheless, use of biomass as feed to produce hydrogen is gaining more attention due to the detrimental consequences on the environment by using fossil fuels. As lignocellulosic materials are the most bountiful biomass species

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Nomenclature

AAD	Average absolute deviation
C_i	Concentration of various species, kmol/m ³
E	Activation energy, J/mol
k_0	Frequency factor
K_i	Adsorption constants for various species ($i = 1, 2, 3, \dots$)
K_p	Equilibrium constant
n	Reaction order
N_i	Mole flow rate of various species, kmol/s
r_i	Reaction rate for a specie, kmol/kg cat s ($i = A, B, C, \dots$)
R	Universal gas constant, kJ/kmol-K
S	Catalyst active sites
T	Temperature, K
X_i	Conversion of component i

Subscripts

O	Reactor inlet
A	Hydrothermal oxygenated hydrocarbon
B	Water
C	Carbon dioxide
D	Hydrogen

around the world, they become eminently preferable feed material for producing biorenewable hydrogen [7]. Tentative reaction pathways of the SCWG of carbohydrates are shown in Fig. 1, adapted from Azadi et al. [8] and Cortright et al. [7]. The reactant undergoes dehydrogenation steps on the metal surface to give adsorbed intermediates before the cleavage of C–C or C–O bonds.

Due to the nutritional value and worldwide availability, cattle manure has been used as fertilizers since ancient times, as well as a fuel in developing countries. However, as the number of cattle are increasing, their excreta is being considered as waste due to methane (CH₄) emissions, which has 25 times more Global Warming Potential (GWP) compared to carbon dioxide (CO₂) on

a 100-year timescale [9,10]. SCWG of liquefied cattle manure is a potential technology for the passive use of cattle manure. The major products of SCWG are hydrogen (H₂) and CO₂, and the emissions are biorganic, which means they have a negative impact on GHG emissions compared to fossil fuel.

Biomass liquefaction is one of the conversion techniques which is used to produce biocrude for further processing that can be easily transported. This biocrude contains various carbohydrates of oxygenated hydrocarbons of varying molecular structure and molecular weights, including lignin derived products, sugars and their decomposition products. In this article, an alternative approach of using cattle manure was presented. Firstly the manure was liquefied using a batch reactor at 260 °C for 30 min to produce the biocrude. This phase is aqueous, hence made it possible to pump continuously to the SCWG reactor using an HPLC pump. Secondly, this aqueous phase was then introduced into the reactor to produce an H₂ rich gas in the presence of a catalyst.

Both homogeneous (e.g., various alkali metals) and heterogeneous (e.g., transition metal catalysts, on various support) were reported by researchers to promote the water-gas shift reaction and/or C–C bond cleavage to obtain better carbon gasification efficiency and higher H₂ yield. The advantageous characteristics of the heterogeneous catalysts over homogeneous catalysts are recyclability and higher selectivity [11]. Elliott [12] and Guo et al. [11] have reported in their review about some major heterogeneous transition metal catalysts, on various supports (mainly Ni, Ru, Pt, Pd, Rh etc.) that have been broadly investigated for SCWG processes. It has been reported that Ru showed the highest activity in gasifying lignin and its derivatives (alkylphenols) compared to Rh, Pd, and Pt in SCW at 400 °C [13,14]. Additionally, it was reported that Ru can maintain high stability for a longer period of time [15]. Ni is another most commonly utilized catalyst due to its ability to promote the water-gas shift reaction [16–18]. Compared to the noble metal catalysts, Ni is cheaper even though it is less stable and has the possibility of gradually losing the activity during SCWG.

Researchers used single metal single support catalysts, dual metal single support catalysts and single metal dual support catalysts to investigate SCWG of biomass [11,12]. However, dual

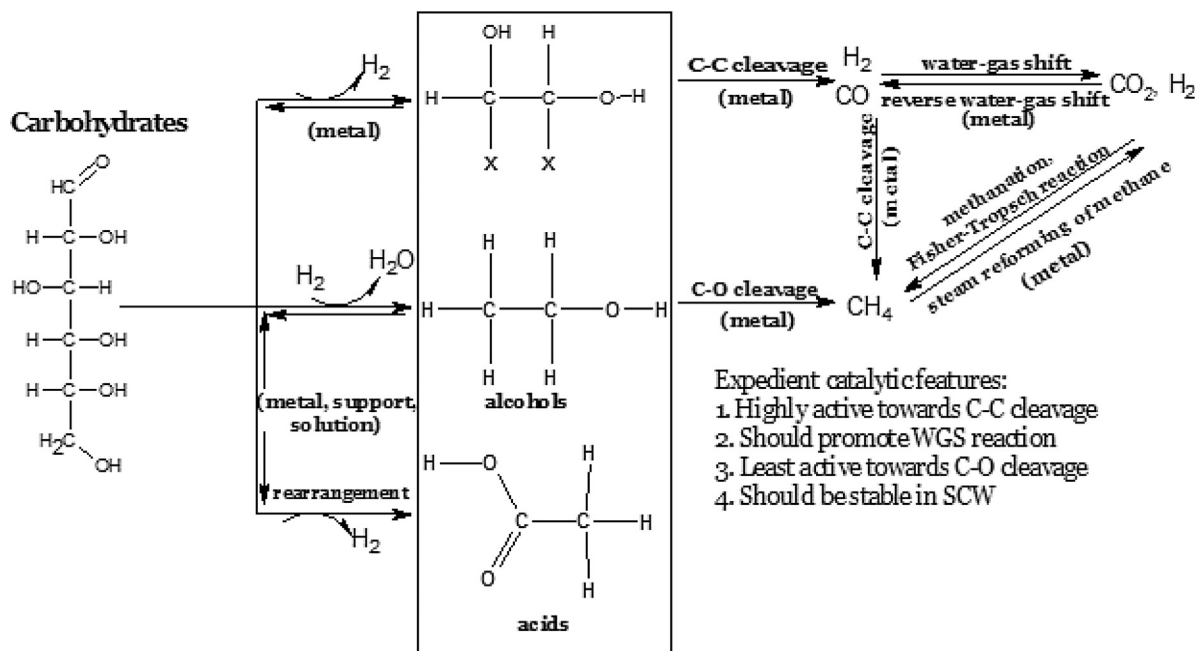


Fig. 1. Hydrogen production pathways through various reactions of oxygenated carbohydrates in the presence of water adapted from Azadi et al. [8] and Cortright et al. [7] (the □ sign represents a surface metal site).

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