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A Novel Technique for Hydrogen Production from Hog-Manure in Supercritical Partial Oxidation (SCWPO)

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Abstract

In this study, the catalytic hydrogen production from hog manure using supercritical water partial oxidation was investigated in a batch reactor at a temperature of 500 °C, and pressure of 28 MPa using several metallic catalysts. Hog manure was characterized by a total and soluble chemical oxygen demand (TCOD, SCOD) of 57000 and 28000 mg/L, total and volatile suspended solids (TSS, VSS) of 25000, 19000, and ammonia of 2400 mg/L, respectively. The order of H₂ production was the following: Pd/AC > Ru/Al₂O₃ > Ru/AC > AC > NaOH. The order of COD reduction efficiency was as follows: NaOH > Ru/AC > AC > Ru/Al₂O₃ > Pd/AC. The behaviour of the volatile fatty acids (VFA's), ethanol, methanol, ammonia, H₂S, and Sulfate was investigated experimentally and discussed. A 35 % reduction in the H₂ and CH₄ yields was observed in the sequential gasification partial oxidation (oxidant at an 80 % of theoretical requirement) experiments compared to the gasification experiments (catalyst only). Moreover, this reduction in gas yields was coincided with a 45 % reduction in the liquid effluent chemical oxygen demand (COD), 60 % reduction of the ammonia concentration in the liquid effluent, and 20 % reduction in the H₂S concentration in the effluent gas.

1 Introduction

Conversion of waste biomass to energy is of great interest due to simultaneous resource recovery and pollution abatement. Hog manure contains major plant nutrients and organic matter that can be utilized as a potential to produce hydrogen-rich gaseous fuel. Thus, hydrogen production from hog manure may be a solution for cleaner fuel as well as disposal problems. However, hog manure usually contains water and a dry feedstock is required for conventional gasification, and because the drying process is an energy-intensive operation, supercritical water is a promising technology for gasifying waste biomass with high moisture content. Supercritical water (SCW) is an emerging technology that has been developed to treat hazardous waste streams as well as producing green gases such as hydrogen [9, 18, and 28]. Supercritical water can dissolve most organic substances and gases and has low viscosity and strong transport ability. Above water supercritical conditions (T>374 °C,

$P > 22.1$ MPa), the density, dielectric constant, and ionic product of water decrease, and the SCW acts as a non-polar solvent with high diffusivity and excellent transport properties [9, 11, 15, and 19]. This facilitates the dissolution of many non-polar organic compounds and gases in water. The SCW high diffusivity coupled with high solubility of both gases and organic materials provide high mass transfer fluxes which accelerate reactions [22]. Thus, SCWO is considered useful to eliminate a wide range of problematic wastes from a broad variety of industries [19].

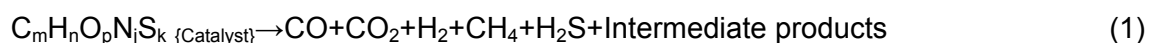
The fact that manure has a very high water content (>95 % on a wet basis), makes it more suitable for the SCW process than other conventional treatment processes. Furthermore, hog manure due to its high water, solids, and ash content is not amenable to treatment in conventional fossil-type furnaces such as incinerators and gasifiers [35] due to high energy consumption and plugging. Moreover, sulfur in the waste is converted to sulfur dioxide and trioxides [35] which increases corrosiveness. Biological treatment of hog manure, although technically feasible, requires extremely long hydraulic retention time (HRTs) of the order of days, high energy input, has a potential for odor generation, and a poor response to dynamic loading conditions as well as exhibits sensitivity to toxins [36]. Each of these treatment methods has shortcomings and therefore may not be the best option for treating organic and toxic wastes [30]. Thus, employing SCW to produce green energy from waste streams such as hog manure has many advantages. Indeed, using SCW as a reaction medium avoids the expensive step of drying. In fact, estimated feedstocks of 30 % or higher moisture content are preferable and more economical in SCW [32]. Moreover, the ability of SCWG to achieve higher conversion (over 99 %) of the solid particles and high hydrogen production coincident with suppression of char and tar formation [23] renders them very attractive.

Several studies have been reported in literature on biomass or biomass model compounds gasification for H_2 production using SCW [2, 3, 5, 7, 9, 10, and 28]. These studies employed both heterogeneous and homogeneous catalysts (such as NaOH, KOH, activated carbon, metallic catalysts). Osada et al. [1, 2, and 3] reported that supported ruthenium, rhodium, platinum, palladium, and nickel catalysts are active in decomposition of aromatic compounds. The aforementioned authors pointed out that lignin is first converted to alkylphenols and formaldehyde through hydrolysis in supercritical water; the alkylphenols and formaldehyde decompose to gases over the above mentioned catalysts. Osada et al [1] who conducted gasification experiments of biomass, coal and waste plastics in an autoclave at 450 °C, 44 MPa, and 120 minutes reported that Ruthenium (Ru) metal particles aggregated during the first run because the surface area of the Al_2O_3 support drastically decreased due to its crystal structure change from $\gamma-Al_2O_3$ to $\alpha-Al_2O_3$.

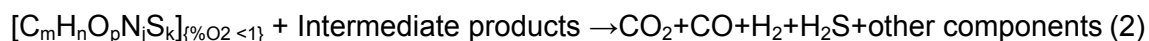
In a recent study, Zhang et al. [8], conducted partial oxidative gasification of municipal sludge (5 wt%) with NaOH catalyst, using a batch type reactor at a temperature ranging of 350-500 °C, pressure range 23-28 MPa and residence time from 5 to 40 min. The aforementioned authors reported that municipal sludge can be gasified in supercritical water with no char and tar at a relatively lower temperature of 500 °C than the 700 °C required for biomass. Their experimental results on hydrogen production from municipal sludge showed that addition of base catalyst (NaOH) coupled with partial oxidation enhanced the hydrogen mole fraction yield from 20 % to 40 %. The addition of NaOH lowered the decomposition temperature of sludge and promoted the water-gas shift reaction.

Osada et al. [4] who studied the effect of both base (NaOH) and metal zirconium oxide (ZrO₂) catalysts on the partial oxidative gasification of *n*-hexadecane and lignin in SCW reported a doubling of the hydrogen yield from lignin by adding zirconia catalyst at an oxygen-to-carbon ratio of 1.0, and four times higher hydrogen yield upon addition of sodium hydroxide (NaOH). Yamaguchi et al [10] reported that ruthenium, rhodium, platinum, palladium, and nickel noble metal catalysts which supported on activated carbon showed higher hydrogen and carbon monoxide selectivity. According to Cortright et al. [21], H₂ selectivity is evaluated to know how many hydrogen atoms in an organic compound can be taken out as H₂ in the gas phase. The role of gasification is to promote the water-gas shift reaction whereas the thermal decomposition of intermediates is enhanced by the partial oxidation. This suggests that the hydrogenation of biomass by employing sequential gasification partial oxidation could enhance the H₂ production rate. Thus, the relevant processes could be approximated by the following general reactions:

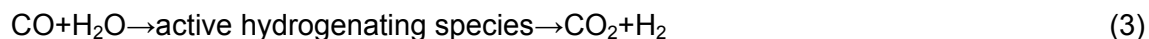
Gasification:



Partial oxidation:



Water-gas shift reaction:



Methanation reactions:



Search of data bases such as SciFinder Scholar, Engineering Village, and Google using the key words of supercritical water gasification; catalysts; hydrogen; hydrogen generation; biomass; gasification; hog manure; wastewater; supported carbon catalyst; hydrogen production revealed that to the best of the authors knowledge no work has been reported on hydrogen production from hog manure in supercritical water despite the selected few aforementioned studies of municipal waste. The challenges of hog manure stem directly from the high solids content and the odorous compounds i.e. ammonia and sulfur. Furthermore, it is evident from the above literature that even studies on thermal hydrogen production from wastes have focused on the energy recovery aspect without due consideration of residual liquid quality and odorous compounds emissions. Thus, while the overall objective of this

study is to demonstrate the feasibility of hydrogen production from hog manure using SCW, the specific goals include:

- Parallel side-by-side assessment of the impact of sequential gasification and partial oxidation relative to the conventional gasification and partial oxidation solely on the fate of ammonia, and organics that has not been reported in literature.
- Evaluate the activity of different commercial heterogeneous and homogenous catalysts including supported activated carbon metallic on the gaseous products as well as the liquid effluent quality.

2 Materials and Methods

2.1 Materials

Hog manure was obtained from a facility in South Western Ontario used as the feed characterized by a total and soluble chemical oxygen demand, Volatile suspended solids, ammonia. 5 % ruthenium supported on alumina and 5 % ruthenium supported on carbon catalysts were purchased from Alfa Aesar (Ward Hill, MA, USA). Alkali NaOH reagent grade and 5 % palladium supported on carbon catalysts were obtained from Sigma-Aldrich Canada Ltd (Oakville, Ontario, Canada). Activated carbon was purchased from Caledon Laboratories Ltd (Georgetown, Ontario, Canada).

2.2 Experimental setup

Experiments were performed in the main reactor body procured from Autoclave Engineers, (Erie, Penna, U.S.A). Figure 1 portrays a schematic diagram of the experimental system setup. The reactor was constructed of Hastelloy C-276 with a capacity of 600 ml, with a maximum pressure rating of 41.4 MPa and maximum temperature rating of 343 °C. From the pressure-temperature rating of the Hastelloy alloy published on the manufacturer's web site, the reactor operating conditions were modified to sustain higher temperature of maximum 500 °C at a lower pressure level of 36 MPa. This facilitated operation of the reactor above the critical conditions of water (374 °C, 22.13 MPa). The reactor was heated with a 1.5 kW electrical furnace that surrounded its main body supplied by Autoclave Engineers, (Erie, Penna, U.S.A). The reactor was a batch reactor, but allowed for sampling of gas and liquid samples throughout the experiments.

series 0-2 L/min, Laval Quebec, Canada). The mass flow meter was equipped with a totalizer that utilizes a K-factor to relate the mass flow rate of nitrogen as an actual calibrated reference gas. The details of gas flow calculations are reported elsewhere [5]. The effluent gases were then collected in 3L Tedlar sampling bag. As soon as the gas bag filled, the flow of product gases was vented. Simultaneously, the liquid product was collected from the bottom of the gas liquid separator.

After each experiment, the reactor was left to cool down. The reactor was then opened and filled with (4:1) acetone-water mixture. The mixture was used to recover both the catalyst and the unconverted carbon. Two phases were observed in the recovered mixture, the catalyst at the bottom and the treated liquid containing the residual contaminant. The catalyst was then recovered by filtration using 0.45 μm sterile membrane filter (Catalog. No 7141104, Whatman Limited, Maidstone, England). Following the recovery of the solid catalyst, the acetone-water mixture containing the residual contaminant was allowed to evaporate at 105 °C for 12 hours in a furnace (Sheldon Manufacturing Inc, Model 1350GM, Cornelius, OR, USA).

After evaporation, the solid of acetone-water mixture was collected, weighed, and then analyzed using thermogravimetric analysis technique. The apparatus used for thermogravimetric analysis was acquired from THE M&P LAB Co (Model TA SDT Q600, NY, USA). Samples of approximately 20 milligrams were placed in 90 μL alumina pans and placed in the apparatus. The samples were run using dual Sample Mode in a Nitrogen atmosphere (100mL/min) at a rate of 20 °C/min from room temperature to 800 °C. The resulting data was analyzed in the form of weight percent versus temperature. Since carbon burns at temperatures below the 800 °C used in the test, the weight of carbon in the sample i.e. the carbon left in the reactor excluding the catalyst and support (which was removed by filtration), was calculated as the initial weight less than the final residual after thermogravimetric analysis. Subsequently in order to assess the COD balance, the residual carbon was converted to COD using a factor of 2.7 gCOD/gcarbon.

2.4 Analytical procedures

Gaseous products were analyzed by gas chromatograph (Shimadzu, GC-2014) equipped with a thermal conductivity detector and 120/80 D Hayesep stainless steel nickel packed column (Grace Davidson, Columbia, MD, USA) with dimensions of 6.2 m length x 3.18 mm internal diameter. Helium was used as the carrier gas. The gas chromatograph was calibrated using a standard gas mixture of known composition obtained from Matheson Tri Gas Co (Coulombs, OH, USA). The analysis was performed manually using 1ml gas tight syringe (SGE, Model number 008100, Reno, NV USA) collected from the Tedlar gas sampling bag. For each analysis, at least three injections were performed and the results were averaged to minimize the analytical error.

The organic content of the process liquid effluent was examined using the following parameters i.e. total and soluble chemical oxygen demand (TCOD & SCOD), volatile fatty acids (VFAs), ethanol, methanol, ammonia, sulfate (PO_4^{2-}), alkalinity, nitrate, total phosphorous, and pH. Total and soluble chemical oxygen demand (TCOD, SCOD) were measured using HACH methods and test kits (HACH Odyssey DR/2500). Individual VFAs were analyzed by a gas chromatograph (Varian 8500) with a flame ionization detector (FID)

equipped with a fused silica column having dimensions of 30 m length x 0.32 mm internal diameter. Helium was used as a carrier gas at a flow rate of 5 ml/min. The temperatures of the column and detector were 110, 250 °C, respectively. For ethanol and methanol measurement, the same gas chromatograph (Varian 8500) with a refractive index detector (RID) was used. The pH was measured using portable pH meter (Oakton, Model WD-35615-22, IL, USA). All analyses were performed according to standard methods for the examination of water and wastewater (APHA and AWWA, 1992).

2.5 Data Interpretation

For the purpose of COD balance calculations, the reactor feed, and liquid effluent COD were measured. The gaseous product COD was also calculated. The product gas yield, gas composition, COD reduction efficiency, and COD balance are defined as follows:

$$\text{Gas composition (\%)} = (\text{mol gas product}) / (\text{sum of mol gas product}) \times 100 \quad (6)$$

$$\text{Product gas yield} = \text{gas volume produced (ml)} / \text{COD removed (g)} \quad (7)$$

$$\text{COD reduction efficiency (\%)} = \{[\text{COD}_{\text{initial}} - \text{COD}_{\text{final}}] / [\text{COD}_{\text{initial}}]\} \times 100 \quad (8)$$

$$\text{COD balance} = [\text{COD}_{\text{gas product}} + \text{COD}_{\text{liquid product}} + \text{COD}_{\text{reactor residual}}] / [\text{COD}_{\text{in}}] \quad (9)$$

The reactor residual carbon i.e. unconverted carbon was determined as described in section 2.3 to assess the COD reactor residual.

3 Results and Discussion

3.1 Effect of residence time and partial oxidation on gas yield from hog manure in SCW

We first investigated the effect of residence time on the gas yield at a temperature of 500 °C, pressure of 31 MPa, oxygen dose (OD) equals to 80 % of the theoretical COD required to oxidize all the initial COD, and residence times of 30, 60, and 90 min. The oxygen dose was optimized in a previous study and was adopted as a base line for catalysts evaluation [5]. Figure 2 shows H₂, CO, and CO₂ yields in the gas stream. As shown in Figure 2, the CO yield was always insignificant, the order of, CH₄, and CO₂ yield was as follows: 60>30>90 minutes.

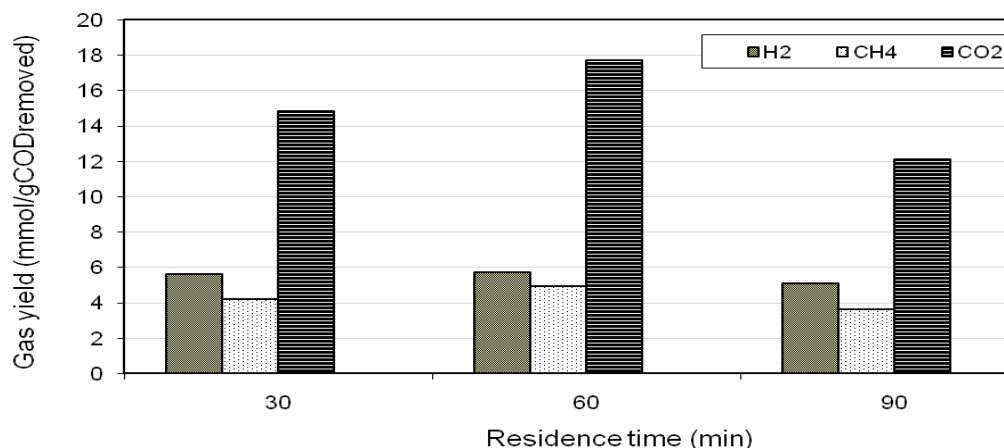


Figure 2: Gas yield distribution in partial oxidation experiment at different residence time.

The H₂ yield at a reaction time of 60 minutes of 5.7 mmol/gCOD removed was higher than the 30 minutes reaction time by an insignificant amount (0.1 mmol/gCOD removed). Thus, since all differences were not substantially significant, we selected the reaction time of 30 minutes as a base line for the subsequent experiments. However, the yield of methane increased from 4.2 mmol/gCOD removed at 30 minutes to 4.9 mmol/gCOD removed at 60 reaction time which implies acceleration of the methanation reactions as per equations 4 and 5. On the other hand, the absence of CO in the effluent gas in the three experiments means that water-gas shift reaction occurred and may be one of the reasons for the enhancement of H₂ production [9, 10]. However, the exact extent of the water-gas shift reaction was not evidently identified since CO₂ could be produced from other reactions or from the thermal decomposition of some intermediates. Another possible way of H₂ formation is the thermal decomposition of the intermediate compounds [8, 28, and 33]. In other words, the presence of oxygen as an oxidant probably contributed to the H₂ formation by oxidizing some of the organic intermediate compounds as reported in our previous study [5].

Table 1 summarizes the liquid effluent quality for the reaction times. It is apparent that residual ammonia at 90 minutes decreased by 20 % to 4180 mg/L relative to 30 and 60 minutes. A COD reduction of 83 %, 85 % and 81 % was achieved at residence times of 30 min, 60 min and 90 min, respectively, and the reduction in COD was found to be independent of the residence time. The lowest residual COD of 8775 mg/L was observed at the 60 minutes reaction time which was 18 % lower than the maximum COD at 90 minutes. This implies that after 60 minutes of reaction, some components were involved in intermediate reactions and formed other liquid components that eventually increased the TCOD and SCOD. The VFAs, ethanol and methanol combined constituted 33 %, 33 % and 24 % of the SCOD at residence times of 30, 60 and 90 minutes, respectively. In all experiments, and as reported in Table 2, the TSS and VSS concentrations were less than 300 mg/L which corresponds to destruction of > 98% of the initial values.

Table 1: Liquid effluent characterization in partial oxidation experiments.

Reaction time	30 min	60 min	90 min
OD	0.8	0.8	0.8
TSS	540	220	440
VSS	400	160	360
TCOD	9740	8775	10740
SCOD	6942	6480	8160
NH ₄	4950	5030	4180
PO ₄ -	454	270	302
VFA	2323	2129	1964
Alkalinity	N/A	31030	28890
Nitrate	15	9	8
pH	9.23	9.3	9.21
COD reduction (%)	83	85	81
COD balance	85.3	85.6	87.4

3.2 Effect of catalysts on gas yield from hog manure in SCW

The effect of different catalysts on SCW gasification of hog manure was investigated by using 2.5 grams of catalyst in each experiment, and eliminating the oxygen addition. Figure 3 shows the product gas distribution for each catalyst. The major components of the product gas yield in all experiments were CO₂, H₂, and CH₄. However, trace amounts of CO was detected only in the case when NaOH was used as a catalyst. The negligible CO yield (almost 0 mmol/gCODremoved) during the Pd/AC, Ru/Al₂O₃, Ru/AC, and AC catalytic experiments was found to be in good agreement with the results obtained for AC catalyst by Antal and Xu [9, 29, and 29]. Furthermore, Elliott and Sealock [33] selected the rate of CO disappearance as a measure of the water-gas shift reaction rate in preference to the rate of CO₂ or H₂ increase. It was noticed that the H₂/CO₂ yield ratio equaled to 1.2 in the case when NaOH was used as a catalyst. Zhang et al [8] reported that alkali salts increase the reaction rate of the water-gas shift reaction, and ultimately the reaction of CO with water to produce H₂ and CO₂ as per equation 3.

The higher than unity H₂/CO₂ yield ratio implies that the CO₂ was not completely recovered since CO₂ tends to dissolve in alkaline solutions (NaOH in this case).

As apparent from Figure 3, the Pd/AC catalyst produced the highest H₂ yield followed by Ru/Al₂O₃. Yamaguchi et al. [10] reported that the selectivity and yield of H₂ was the highest with Pd/C catalyst whereas the Ru/C catalyst was the most active for lignin gasification. However, and as shown in Table 2, COD reduction efficiency with the Pd/AC catalyst was lower than with Ru/Al₂O₃ and Ru/AC catalysts since the Ruthenium metal surface is known to promote the methanation hydrogen-consuming reactions [10] as per equations (4 & 5).

Furthermore, the COD removal efficiency in the absence of oxygen was retarded in all the experiments to less than 70 %, except for the experiments where NaOH was used as a

catalyst where a COD removal efficiency of 81 % was achieved comparable to what was observed with partial oxidation. The Pd/AC catalyst affected the highest removal of ammonia as well as the lower H₂S concentration in the gas, which coupled with highest H₂ yield rationalizes the retention of Pd/AC for subsequent sequential gasification partial oxidation testing.

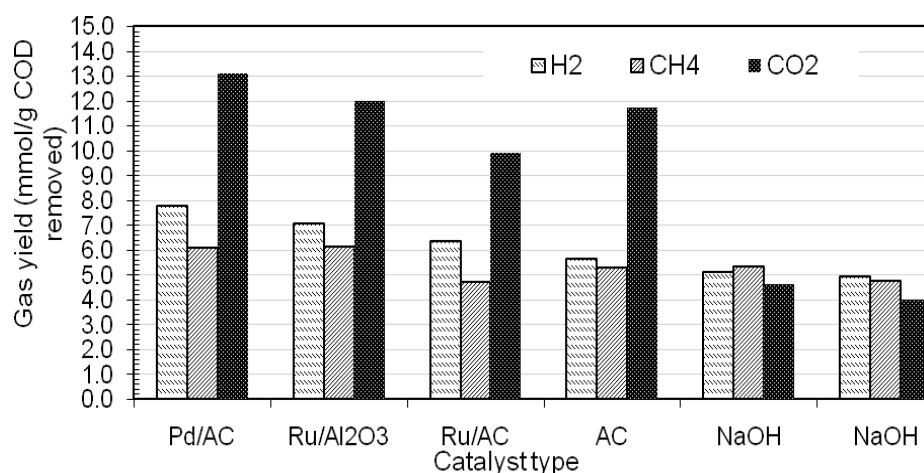


Figure 3: Gas yield distribution with different metal supported catalysts.

Table 2: Liquid effluent characterization in gasification experiments.

Catalyst	Pd/AC	Ru/Al ₂ O ₃	Ru/AC	AC	NaOH	NaOH
Concentration (mg/L)						
TCOD	22000	20100	18660	19460	11140	10760
SCOD	21500	15200	16920	11720	9050	8940
TSS	900	840	1600	420	900	840
VSS	800	720	580	360	800	720
PO ₄ -	519	387	513	309	427	453
Nitrate	26	7	6	0	0	0
Alkalinity	23450	28160	35000	10130	27450	N/A
pH	9.37	9.27	9.46	9.57	9.88	9.83
COD reduction (%)	61	65	71	66	81	81
COD Balance	89	80.7	90.2	99.2	98.6	96

3.3 Effect of partial oxidation and catalyst on gas yield from hog manure in SCW

We studied the effect of two different oxygen dose (OD) of 60 % and 80 % of the theoretical COD required to destroy all the initial COD on the product gas yield in presence of Pd/AC catalyst. Figure 4 reports the product gas yield in mmol/gCOD removed. At an (OD) of 60 %, 3 mmol CH₄/gCOD removed and 3.5 mmol H₂/gCOD removed was produced comparing to 3 mmol CH₄/gCOD removed and 5 mmol/gCOD removed at an (OD) of 80 % was employed.

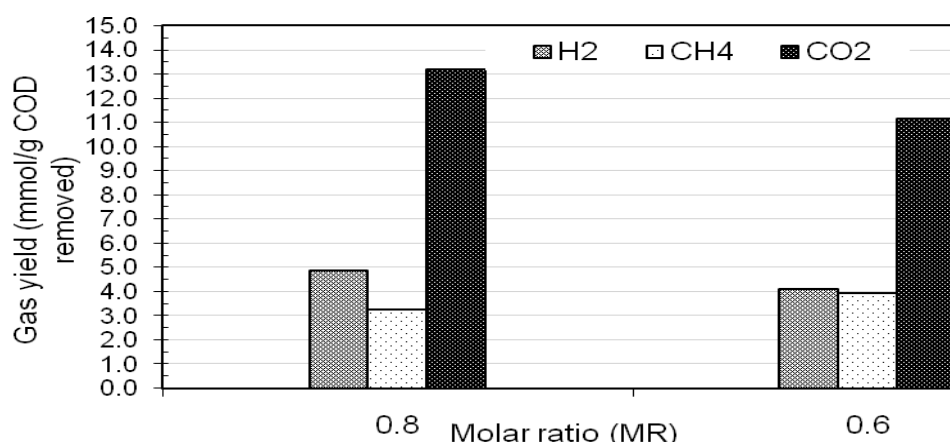


Figure 4: Gas yield distribution at gasification followed by partial oxidation experiments.

These results indicated that at an (OD) of 60 %, the methanation reaction proceeded and consumed part of the produced H₂ to form CH₄ which was also confirmed by the lower CO₂ yield of 11mmol/gCOD removed compared to the 14mmol/gCOD removed at an (OD) of 80 %, [7, 33]. The lower CO₂ yield at an (OD) of 60 %, could be also attributed to the lack of oxygen which affects the formation of CO₂ through direct oxidation of CO to CO₂. Furthermore, and according to Cortright et al [21], the H₂/CO₂ yield ratio of 1.0 at an (OD) of 60 % suggests that CO was consumed through water-gas shift reaction to form H₂ prior the introduction of hydrogen peroxide (H₂O₂) to the reactor as an oxygen source. This is also supported by Zhang et al [8], who reported that the improvement of H₂ yield in the presence of catalyst in the reactor is explained by the production of CO by partial oxidation followed by water-gas shift reaction.

On the other hand, Table 3, showing the main liquid products in the sequential gasification partial oxidation experiments, indicates that COD removal efficiencies at an (OD) of 60 % and 80 % were comparable at 79 % and 81% respectively whereas the COD balance closures were 94 % and 89 % respectively, with COD balance closure of 94 % and 89 %. In all experiments, the liquid effluent collected from the gas-liquid separator was characterized by a dark brown color with burnt smell.

Table 3: Liquid effluent characterization in sequential gasification and partial oxidation experiments.

OD	0.8	0.6
Catalyst	Pd/AC	Pd/AC
TCOD	11920	10800
SCOD	7400	8800
TSS	820	860
VSS	700	600
PO4-	489	504
VFA	1700	1891
Niterate	8	14
Alkalinity	10127	26050
pH	9.24	9.31
COD reduction (%)	79	81
COD Balance	94	89

4 Summary

Catalytic and non-catalytic hydrogen production from hog manure using supercritical water partial oxidation, gasification, and sequential gasification partial oxidation was investigated in a batch reactor at a temperature of 500 °C, and pressure of 28 MPa using several metallic catalysts. The feasibility of hydrogen and methane production was demonstrated using sequential gasification partial oxidation. The order of H₂ production in catalytic gasification was the following: Pd/AC > Ru/Al₂O₃ > Ru/AC > AC > NaOH. The order of COD reduction efficiency was as follows: NaOH > Ru/AC > AC > Ru/Al₂O₃ > Pd/AC. The following can be concluded:

- Sequential gasification and partial oxidation is better than each one individually from an environmental point of view as it produced the lowest ammonia concentration of 1534 mg/L, the lowest effluent COD concentration in liquid phase, and the lowest H₂S concentration of 130 ppm in the gas phase.
- Of all employed catalysts, Pd/AC was the best as it provided the highest H₂ yield as well as the lowest H₂S concentration in the gas phase.

In conclusion, future investigation into higher temperatures and catalyst deactivation is required.

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