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Alkali-promoted Hydrothermal Gasification of Biomass for High Yield/ High Purity Hydrogen Gas (and Methane) Production

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1 Introduction

A significant amount of research has been carried out over the last two decades in the area of hydrothermal biomass gasification. A search of publications from this field in *ScienceDirect* with the topic - '*hydrothermal gasification of biomass'* - produced 439 related journal articles. Of this number, almost 400 articles were published within the last 10 years. Infact, 24 % of the total publications occurred in 2009 alone, with 65 furthers articles already published, less than 3 months into 2010. This simple analysis demonstrates the high volume of activities involved in this developing technology. Much of the research in hydrothermal gasification of biomass involves the use of catalysts and additives that can positively influence the predominant reactions with the aim of lowering the production cost of high calorific value gases produced from the process. Hydrogen and methane production from this process have been well demonstrated in research. Attempts have been made regarding a deeper understanding of the mechanisms of the gasification process [1, 2]. While the need of catalysts may not be very significant for gasification in supercritical water, certainly, they are required under subcritical and near-critical water conditions [3]. Several catalysts and additives have found use in the promotion of hydrothermal biomass gasification for hydrogen production. Different nickel catalysts, activated carbon, metal oxides and alkali-metal compounds have been reported to significantly influence the production of gases from biomass under hydrothermal conditions. It appears, however, that the alkali-type additives or catalysts have become very attractive for high hydrogen yields as they have been shown to catalyze the water-gas shift reaction – a predominant reaction in hydrogen production. In the literature, the alkali additives commonly used include NaOH, KOH, LiOH, Na_2CO_3, K_2CO_3 and $Ca(OH)_2$. Beyond that, some researchers [1, 2, 3] have shown that alkali catalysts play significant roles in the hydrothermal biomass degradation mechanism. It has been found that the composition of products from the gasification process depended on the formation of gasifiable intermediate compounds such as formic acid (as alkali-metal formate e.g. sodium formate) and acetic acid (as alkali-metal acetate e.g. sodium acetate). Many researchers have corroborated these findings regarding the effects of alkali additives, which include increased gasification efficiency and suppression of oil/tar and char formation [4]. In related studies, Jin et al [5, 6], isolated and quantified similar compounds obtained during the hydrothermal decomposition of different biomass and biomass model compounds at temperatures ranging from 250 – 300 °C, in the presence of hydrogen peroxide and alkali. Kruse et al [7] suggested a mechanism involving the formation of intermediate alkali metal formates prior to hydrogen production. Hence, the role of alkalis in hydrothermal biomass conversions has been found to be highly significant.

In this paper, a parametric study of the decomposition of sodium formate and sodium acetate was investigated in relation to reaction temperature. All experiments were carried out in the absence of oxygen or oxygen source. The behaviour of these compounds which are regarded as the intermediate compounds of hydrothermal biomass gasification would provide more understanding of the reaction mechanisms. Furthermore, the influence of reaction temperature on the composition of gasification products of some biomass samples was investigated. The biomass samples included glucose, cellulose, starch, rice husk, rice straw and potato. The gasification experiments have been carried out in the presence of sodium hydroxide as promoter or additive.

2 Materials and Experimental Procedure

Glucose, microcrystalline cellulose and starch were obtained from Alfa Aesar, UK. Rice husk, rice straw, and potato were sourced as real-world biomass samples. The biomass samples have been characterized and reported elsewhere [2]. Analytical grade sodium hydroxide in the form of pellets, sodium formate and anhydrous sodium acetate were purchased from Sigma-Aldrich, UK.

The hydrothermal reactions of the samples were investigated in a Hastelloy-C batch reactor obtained from the Parr Instrument Co., Inc. USA. The reactor has 75 ml of volume capacity and the maximum operating temperature and pressure are 600 °C and 45 MPa, respectively. The schematic and operational procedure of the reactor has been detailed in an earlier paper [2]. 1 g of each sample was weighed into the reactor and mixed with a known volume of liquid. The biomass samples were reacted in a known volume of 2M aqueous sodium hydroxide.

The reactor loading was carried out under nitrogen atmospheres to exclude air. The reactor was then sealed and placed in a ceramic heater to raise the reaction temperature at a rate of 12 °C/min. Since the reactor was a closed system, increasing the temperature led to increase in pressure, which was read off the gauge fitted. The reaction time started once the desired temperature was reached. The reaction time was designated as zero minute, when the reaction was stopped immediately the set temperature was reached. At the end of each experiment, the heating was stopped and the reactor was removed from the heater and rapidly cooled to room temperature by an air cooling system. After cooling, the final ambient temperature and pressure were noted, respectively. The gas outlet valve was then opened to collect the gas samples. After the gas sampling, the reactor was opened to sample the liquid sample and solid residues (if any).

3 Products Analyses

Analysis of the effluent gas mixtures was carried out with two gas chromatographs with packed columns for the separation of components of permanent gases and hydrocarbon (C1-C4) gases, respectively. The analytical procedures have been detailed in several earlier papers [2, 8]. The liquid effluent obtained from the reactor at the end of the experiment was analyzed to determine the presence of organic carbon (TOC), inorganic carbon (TIC) and dissolved solids. These analyses were done for samples from the decomposition of sodium acetate and sodium formate. The instrument used was a Hach-Lange IL550 TOC-TN analyzer fitted with two NDIR held at 800 °C. The instrument was operated in the differential TOC determination mode, in which case the same sample was analyzed consecutively for TOC and TIC contents. The analyzer was set up to make four determinations (n = 4) on each sample and the average results used. Typical standard deviation of replicate determinations ranged from 0.2-2 %.

4 Results and Discussion

4.1 Hydrothermal decomposition of ‘intermediate’ compounds

In order to better understand the function of sodium hydroxide in the biomass gasification process, the ‘intermediates’ species suspected to be formed during the reaction were reacted under conditions similar to those used for the biomass samples. Sodium formate and sodium acetate were each individually studied as precursors to hydrogen and methane formation, respectively.

4.1.1 Sodium formate

Sodium formate was reacted within the temperature range of 250 °C to 450 °C, corresponding to running pressures of 4 MPa to 34 MPa. The reactions were used to monitor the effect of reaction temperature on sodium formate decomposition. Results showed that even at 250 °C, gas analysis results showed that hydrogen and CO, albeit, in very low concentrations were the only gases present. However, CO disappeared completely from the gas product beyond this temperature, such that at 300 °C, no CO was detected. Throughout the temperature range studied, in terms of the volume percent of gas, the proportion of hydrogen was consistently greater than carbon dioxide as shown in Fig. 1.

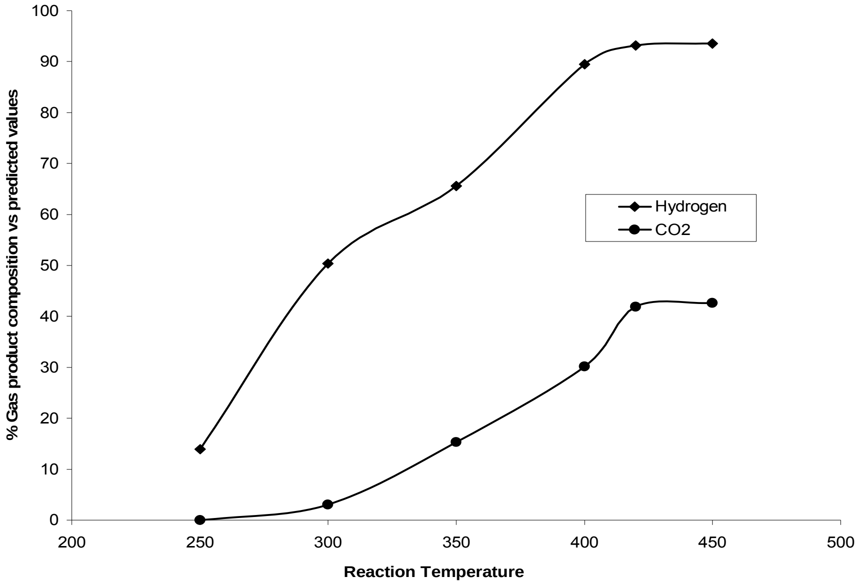

Figure 1: Hydrogen and carbon dioxide produced as percentage of predicted values.

Subsequently, the reaction equation for the hydrothermal decomposition of sodium formate was proposed as follows;

$$2HCOONa + H_2O \rightarrow 2H_2 + Na_2CO_3 + CO_2 \qquad (1)$$

The presence of carbon dioxide in the gas stream underlies the requirement for a little excess of sodium hydroxide more than the biomass sample. For example in the production of sodium formate 1:1 mole ratio is required of formic acid and sodium hydroxide. Hence, its decomposition will also be in the same ratio pattern, providing no excess sodium ions to capture all the CO_2 during reactor cooling. Fig. 1 is therefore based on the comparison of the amounts of hydrogen and carbon dioxide produced during the reaction and those predicted by the equation. While hydrogen gas production agreed with the prediction at temperature around 400 °C and above, CO_2 values only achieved a maximum of 42 % of predicted value even at 450 °C. This could be as a result of the apparent solubility of CO_2 in a solution of sodium carbonate. It was observed that the liquid effluent released gas bubbles just by simple agitation. The lower values of both hydrogen and CO_2 temperature below 400 °C, was an indication of incomplete decomposition of sodium formate. This much is corroborated by the TOC and TIC values of the corresponding liquid effluents obtained. Increasing reaction temperature led to a gradual decrease in TOC values at first and then the rate of TOC removal increased sharply between 300 °C and 350 °C. At 420 °C and above the TOC values of the liquid effluents were less than 0.001 mg/L. The rate of increase of TIC formation was a mirror image of the trend in TOC removal, such that over 99 % of the organic carbon in the sodium formate was obtained as inorganic carbon at temperatures above 420 °C. Hence complete decomposition of sodium formate to mainly hydrogen gas occurred after reaching 420 °C and above.

4.1.2 Sodium acetate

Sodium acetate was reacted within the temperature range of 350 °C to 500 °C, corresponding to running pressures of 12 MPa to 43 MPa. The conditions at 500 °C were at the limits of the reactor capability. Results showed that methane formation only became measurably significant from 400 °C, indicating that sodium acetate required higher temperature to decompose than sodium formate. No significant amount of hydrogen was produced up to 400 °C. A small amount of carbon dioxide was detected all through the temperature range when methane was produced. Hence the predominant reaction equation was suggested to be as follows;

$$2CH_3COONa + H_2O \rightarrow 2CH_4 + Na_2CO_3 + CO_2 \qquad (2)$$

The formation of methane according to equation (2), did not become significant until about 450 °C. The thermal decomposition of sodium acetate is known to occur around 450 °C, this research shows that in hydrothermal media, the decomposition actually started around the critical point of water (374 °C, 22.1 MPa). However, as shown in Fig. 2, the decomposition produced about 50 % of the predicted amount of methane at 480 °C, 38 MPa and was further enhanced to just over 70 % at 500 °C, 43 MPa. The continuous increase in methane gas is an indication of the decomposition behaviour of sodium formate in hydrothermal conditions.

However, as the temperature of reaction increased beyond 400 °C, there was a slight increase in hydrogen gas product while methane increased dramatically. The formation of hydrogen could have resulted from the supercritical water reforming of the formed methane to produce hydrogen and CO_2 according to the equation;

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \qquad (3)$$

The rate of formation of hydrogen and carbon dioxide was much slower than the predominant reaction leading to methane formation. As shown in Fig. 2, just about 1/10th of methane reforming efficiency was achieved against what equation (3) predicted. The maximum TOC removal from sodium acetate removal was nearly 73 %, for the reaction at 500 °C, 43 MPa, corresponding to the highest methane yield.

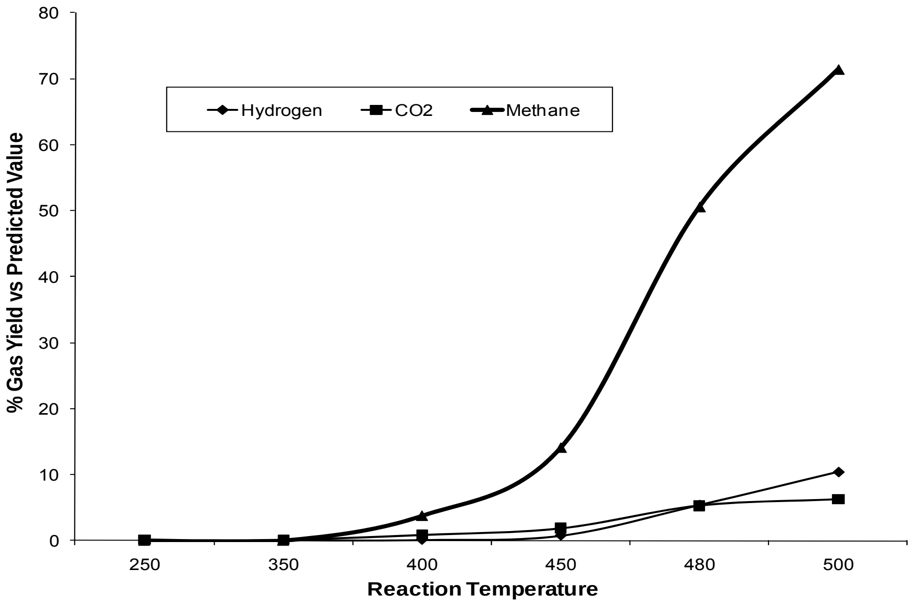

Figure 2: **Evolution of gaseous products from CH_3COONa in relation to reaction temperature.**

4.2 Gasification results from biomass samples

Earlier studies [2] attempted to outline a reaction scheme for the alkali promoted gasification of glucose as a model compound of biomass. The work showed that the major reaction occurring for glucose in the presence of alkali could be represented by the following;

$$C_6H_{12}O_6 + 6NaOH + 6H_2O \rightarrow 6NaHCO_3 + 12H_2 \qquad (4)$$

This equation predicts that no carbon dioxide or carbon monoxide should be detected in the gas products from the reaction. However, sodium bicarbonate is not stable at high temperatures, whereas sodium carbonate is stable. Hence, while the formation and stability of sodium carbonate is favoured under the reaction conditions, its formation signifies that carbon dioxide would still remain in the gas phase. Experiments did not show this, indicating that the formation of sodium bicarbonate may have occurred during or after reactor cooling as shown below;

$$Na_2CO_3 + CO_2 + H_2O \rightarrow 2NaHCO_3 \tag{5}$$

Hydrogen gas was the major gas product, with some methane of up to 15 % of the total gas formed. The ability sodium hydroxide to catalyze this gasification process is underscored by its ability to capture the CO_2 from the water-gas shift reaction, thereby driving the reaction in the forward reaction. The detailed discussion of this research can be found in Onwudili and Williams [2]. Fig. 3 shows that irrespective of the biomass type, hydrogen remained the predominant gas at 450 °C.

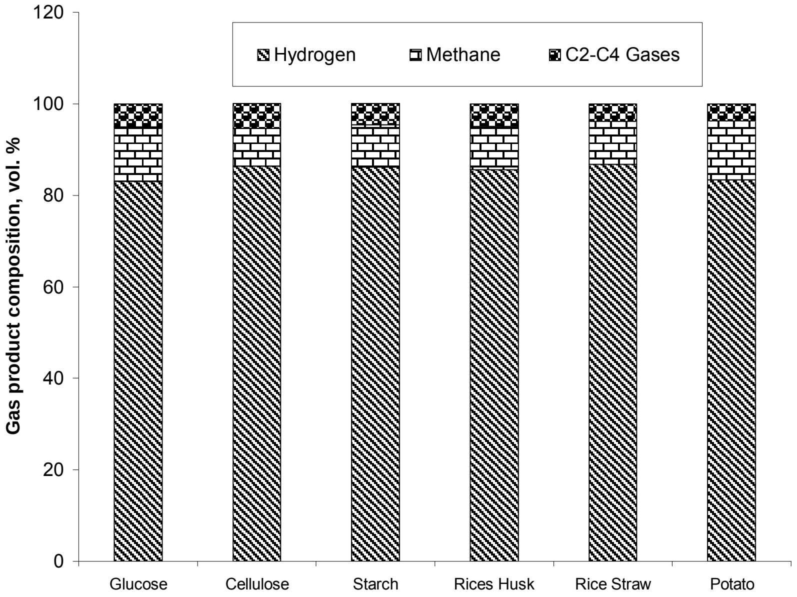

Figure 3: Gas product compositions in volume percent.

Moreover, it shows that similar amounts of the gases have been produced by the different biomass samples, indicating that the effect of sodium hydroxide was essentially similar for all the different types of biomass. This means that similar amounts of different carbonaceous materials of the type found in these biomass samples could react in a similar manner, generating similar intermediate compounds, which then undergo identical reactions, to produce similar gaseous compounds of fairly similar concentrations. It is therefore interesting to see that the function of sodium hydroxide in this hydrothermal gasification process was nearly specific. A careful examination of Fig.3 shows that glucose and potato produced a little bit less hydrogen and a little bit more methane than the other biomass samples. This may indicate that these two sugar-type biomass samples are more likely to produce more sodium acetate than the others.

5 Conclusion

The process of hydrogen and methane formation during alkali-promoted hydrothermal biomass gasification has been investigated using sodium formate and sodium acetate as ‘intermediate’ decomposition products. Results confirmed that sodium formate may be responsible for almost all the hydrogen produced, while sodium acetate produced mainly methane. However, it is also possible to produce hydrogen gas from sodium acetate at much higher temperatures (450 -500 °C), possibly from supercritical water reforming of the initial methane produced. The hydrothermal gasification of several biomass samples showed that similar types and concentrations of hydrogen and methane could be produced from different biomass materials in the presence of sodium hydroxide. Experimental results show that hydrogen and methane can be obtained at significantly high purity from the process.

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