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THERMODYNAMIC ANALYSIS OF HYDROGEN PRODUCTION FROM CONVENTIONAL STEAM REFORMING OF GROUNDNUT SHELL

[1]*Zainab Ibrahim S G Adiya and [1,2] Samira Shehu Adamu

[1] Department of Pure and Applied Chemistry, Usman Danfodiyo University Sokoto, P.M.B. 2346, Sokoto State, Nigeria

[2] Central Advanced Science Laboratory, Usmanu Danfodio University Sokoto, P.M.B. 2346, Sokoto State, Nigeria

Corresponding author E-mail addresses: Zainab.adiya@udusok.edu.ng and xeeadiya@yahoo.com

ABSTRACT

Hydrogen production was simulated (with CEA and Aspen Plus software) using conventional steam reforming process and groundnut shell as feedstock. Chemical equilibrium application (CEA) that works based on minimisation of Gibbs Energy was used for the study. It is found that H_2 yield, and purity increased steeply as temperature increased. However, at steam to carbon ratio (S:C) 0 at least 900 K is required to undergo thermal decomposition and to start converting the feedstock significantly to H_2. H_2 yield and purity also increases in succession of steam to carbon ratio i.e., S:C 5 > S:C 4 > S:C 3 > S:C 2 > S:C 1 > S:C 0. It was concluded that H_2 yield, and purity was completely dependent on temperature and S:C ratio. The conditions of S:C 5 and temperature range of 850 to 1000 K are optimal conditions for conventional steam reforming of groundnut shell based on the conditions investigated in this study.

Keywords: Hydrogen, Groundnut shell and Steam reforming

Introduction

Hydrogen is a colourless, odourless and non-toxic gas. Hydrogen is the lightest element and will explode at concentrations ranging from 4-75 percent by volume in the presence of sunlight, a flame or a spark. Hydrogen is present in many different compounds. Three naturally occurring isotopes of hydrogen exist: protium, deuterium, and tritium, each with different properties due to the difference in the number of neutrons in the nucleus.

Hydrogen is of enormous value in the production of synthetic fertilizers through ammonia manufacture and an important reagent in refinery operations [1]. 50 % of all the global hydrogen production is consumed by ammonia production [1-4]. Hydrogen production and use is also increasing in petroleum refinery processes, especially in the production of fuels with small quantity of sulphur and diesel fuels using hydrotreating and hydrocracking processes [2, 3]. Hydrogen can also be used in power generation. Particularly in rural areas away from the urban areas where electrification expense will be very costly [5]. Hydrogen is regarded as the most important utility in a modern oil refinery [6]. Armor, 2019 [7] reported that fifty million tonnes of hydrogen are traded annually worldwide. With the increasing demand on hydrogen and diminishing fossil fuel reserves, hydrogen production using renewable biomass as feedstock is very promising [8].

Conventional steam reforming (C-SR) process is the most established and frequently used technique in hydrogen production on a large scale for over 70 years [9-13]. Overall, about 90% of the global hydrogen production is by C-SR of fossils fuels [14]. Thus, there is need to search for other feedstock to augment and/or replaced fossils fuels. Moreover, increase in human population is playing a vital role in the depletion of fossils fuels. Additionally, finding an alternative to hydrocarbon-based fuel is a very important issue owing to economic and environmental problems they cause such as global warming. These perspectives form the basis of this study, whereby groundnut shell (a herbaceous and agricultural biomass regarded as waste) is used in the production of hydrogen using conventional steam reforming process. Increasing environmental concern, diminishing fossil fuel reserves and agriculture-based economy of Nigeria including the driving forces to promote renewable energy sources originate this research study.

Materials and Methods

Feedstock used for the thermodynamic analysis

Table 1 shows the composition of groundnut shell elemental analysis used for the simulation. The choice of feedstock is because is readily available in Nigeria as a waste and is one of the herbaceous and agricultural biomass with the highest H_2 composition [15]. Furthermore, Nigeria is the largest groundnut producer in West Africa with 51% of production in the region. Overall, Nigeria contributes 10% of entire global production and 39% production in Africa. Interestingly, in

Nigeria, groundnut was one of the major sources of revenue and foreign exchange earnings before the fossil oil boom. What is more interestingly is the fact that groundnut production has been increasing since 1984 owing to area expansion and increase productivity. This makes the case of using groundnut shell as feedstock for hydrogen production in Nigeria stronger [16]. The selected feedstock composition was based on values found in literature [15]. Groundnut shell containing up to 50.9% C and 7.5% H_2 (Table 1), representing a mixture rich in carbon and considerable amount of H_2. Conditions at equilibrium were provided based on moles of each specie input (C, O, H, N and S), the molar steam to carbon ratio (S:C), as well as system temperature and pressure. The six S:C equilibrium conditions of 0, 1, 2, 3, 4 and 5 were calculated in the study, where ‘C’ represents ‘moles of carbon in the feed, and S the moles of water feed, as steam.

Table 1 Composition of groundnut shell used for stimulations [15]

Feed	**Composition (wt.% on dry basis)**
C	50.9
O	40.4
H	7.5
N	1.2
S	0.02
Total	100

Methodology used for the thermodynamic analysis

Chemical Equilibrium Applications (CEA) software by NASA [17] was used to perform the thermodynamic equilibrium calculations of conventional steam reforming of groundnut shell. The NASA computer program utilises a solution procedure based on minimisation of Gibbs energy function of a feed mixture consisting of feedstock and water to calculate the mole fractions of the equilibrium mixture of products. The CEA calculations were conducted at isothermal and isobaric conditions.

The species considered at equilibrium in the feedstock-water system in addition to all the reactants (see Table 1) were: CH_4,

CO, CO_2, NH_3 and H_2S. Other related species such as CH_2, CH_3, C_3O_2, CH_2OH, C_2H_4, C_2H_5, CN, CS_2, HCN, HCO and CH_3COOH were also included in the equilibrium calculations but their molar fractions were less than 5×10^{-6} and considered negligible.

Aspen Plus software's RGibbs model reactor with ideal and Peng-Robinson thermodynamic properties were used to further verify the results of CEA.

A carbon balance was used to enable the calculation of the equilibrium total moles generated for the initial mixture chosen. The following post processing equations 1-7 permitting the calculations of reactants conversions and H_2 yield, and purity was used.

$$N_{eq} = \frac{\sum_{i,in} \alpha_i n_{Ci,in}}{\sum_{j,eq} \alpha_j n_{Cj,eq}} \quad (1)$$

"Where n_C represents number of moles of carbon species represented by the subscript indices i in the initial '*in*' mixture, and j in the equilibrium '*eq*' mixtures. α is the number of carbon atoms in the relevant carbon species". Thus, molar amounts $n_{j,eq}$ was calculated according to equation 2:

$$n_{j,eq} = y_{j,eq} \times N_{eq} \quad (2)$$

where y stands for molar fraction of a particular species in the relevant mixture. Feedstock and steam conversions in percentage were calculated using equation 3 and 4 respectively.

$$X_{feedstock} = \frac{n_{feedstock,in} - n_{feedstock,eq}}{n_{feedstock,in}} \quad (3)$$

$$X_{H20} = \frac{n_{H2O,in} - n_{H2O,eq}}{n_{H2O,in}} \quad (4)$$

where n is the number of moles of the relevant species for example $n_{feedstock,in}$ stand for feedstock inputted while $n_{feedstock,eq}$ stand for feedstock generated at equilibrium.

H_2 yield was calculated in mass basis expressed as weight (mass) percentage of feedstock as depicted in equation 5 and on an absolute molar basis i.e mole basis as shown in equation 6

$$H_2\ yield\ (\text{wt.}\%) = \frac{100 \times 2.02 \left(\frac{g\ of\ H_2}{mol\ of\ H_2}\right) \times n_{H2,eq}}{MW_{gas} \left(\frac{g\ of\ gas}{mol\ of\ gas}\right) \times n_{gas\ in}} \quad (5)$$

$$H_2\ yield\ (\text{mole basis}) = y_{H2,eq} \times \text{Neq} \quad (6)$$

Calculation of H_2 purity was conducted as shown in equation 7.

$$H_2\ purity\ (dry\ basis) = \frac{n_{H2,eq}}{\sum n_{j,eq}} \times 100 \quad (7)$$

Results and discussion

Effect of temperature on hydrogen yield and purity

The effect of temperature on H_2 yield and purity is shown in Figure 1 from 500 to 1250 K at S:C ratios of 0, 1, 2, 3, 4 and 5. The Figure 1 depicts a comparative analysis on the effect of temperature on H_2 yield and purity. In all the investigated S:C ratios, H_2 yield, and purity increases as temperature increases. However, at S:C 0 i.e., in the absence of water, at least 900 K is required to undergo thermal decomposition and to start converting the feedstock significantly to H_2. For S:C of 1, 2, 3, 4 and 5, H_2 yield, and purity increased precipitously as temperature increased. This was caused by conditions shifting from being favourable of methanation (major products CH_4 and CO_2 below 900 K) and other solid carbon forming reactions at a low temperature, to promoting steam reforming (major products H_2 and CO_2) [4]. This observed phenomenon happens up to about 1100 K, where H_2 yield and purity declined and a gentle decreased in both hydrogen yield and purity was seen with further temperature increase, independent of the S:C ratio, and owning by reverse water gas shift reaction.

To further validate the results, the conditions of S:C 5, 4 and 0 were modelled with Aspen Plus V8.8 (reactor option RGibbs, with ideal and Peng Robinson properties method). The result depicts a good agreement with the results obtained from CEA. Similar thermodynamic studies were also conducted using several feedstocks including shale gas [4,10], hydroxyacetone [18], palm empty fruit bunch and pine pyrolysis oils [19], and urea [20]. There results showed same trend to those of this study with regards to H_2 yield and purity.

Effect of steam to carbon ratio on hydrogen yield and purity

Le Chatelier's principle governs the behaviour of H_2 yield and purity whereby an increase in the water reactant concentration in the system shift the equilibrium towards higher water conversion, thus causing higher H_2 yield and purity (Figure 1). The disadvantage of operating at high S:C ratio is that higher reactor volume will be needed, furthermore, there will be high cost for raising steam [4,10]. Additionally, operating at higher S:C ratio is one of the reasons behind catalyst deactivation owing to pore blockage [4,10,21-23].

Effect of temperature on feedstock conversion

Feedstock (groundnut shell) conversion is higher at lower temperatures (roughly between 500 K to 700 K) for all the investigated S:C ratios as shown in Figure 2(a). At about 750 K approximately, a gentle decrease of feedstock conversion was observed which almost stabilises at 950 K. The observe phenomenon is vague and complicated. But might be attributed to the numerous side reactions taking place during the steam reforming process. Same trend has been reported by Adiya *et al.*, 2019 [12] during the pre-breakthrough and break- through periods of sorption enhanced chemical looping steam reforming. However, they concluded that the conversion result is not reliable and gave reason ("inability to quantify the carbonation rate on the solid sorbent at any given time") for the observe phenomenon.

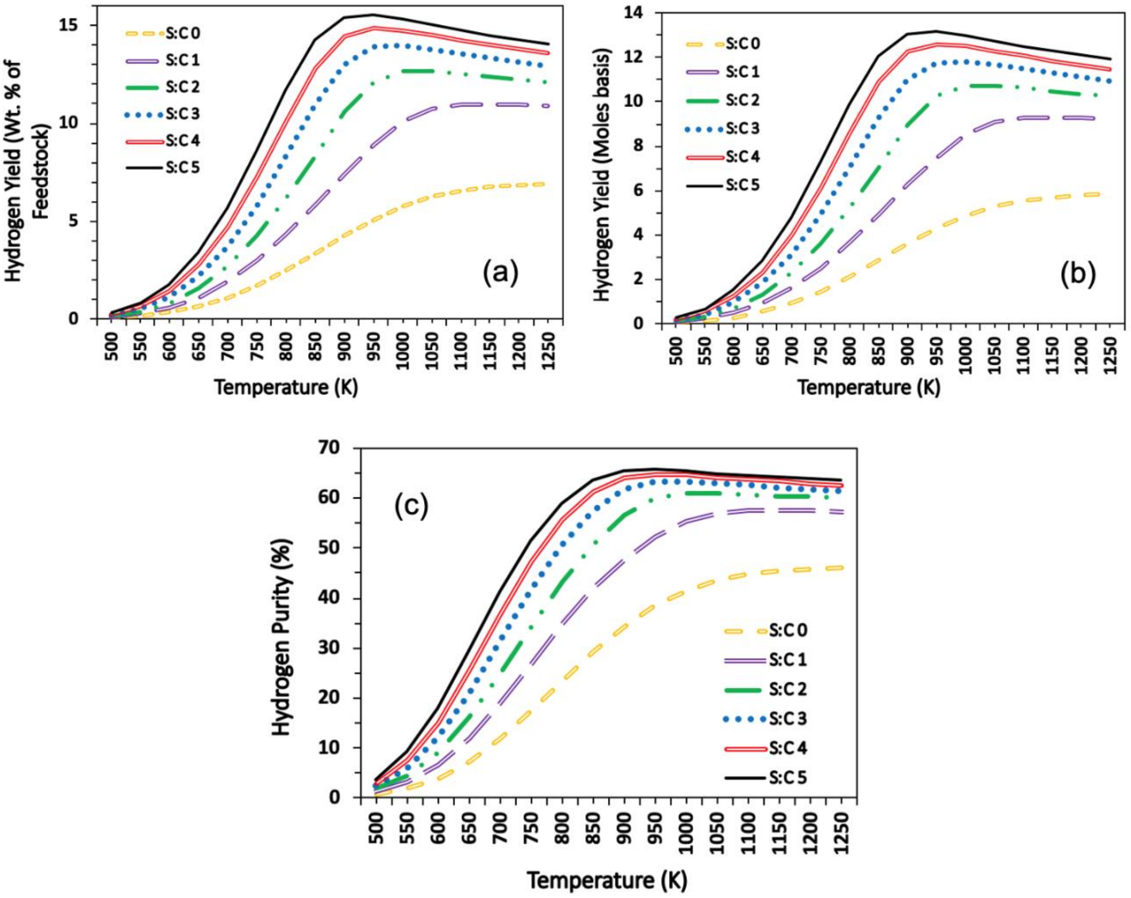

Figure 1 Effect of Temperature and Steam to Carbon Ratio on Hydrogen Yield and Purity (a) Hydrogen Yield VS Temperature in Weight Percentage of Feedstock (b) Hydrogen Yield VS Temperature in Moles Basis (c) Hydrogen Purity VS Temperature in Percentage

As expected, water conversion was higher at S:C ratio of 1 and lower at S:C ration of 5. This was not surprising because the later (S:C 5) represent condition of excess steam, thus, the steam will not be used much and/or completely. In a nutshell, water conversion follows the following order S:C 1 > S:C 2 > S:C 3 > S:C 4 > S:C 5 as depicted in Figure 2(b). In all the investigated S:C ratio, low water conversion was observed at lower temperatures between 500 to 700 K approximately which later increases at higher temperatures from 750 K roughly before stabilising. The later could be explained by shift from the methanation process (favoured in low temperatures) to steam reforming process (favoured at high temperatures).

Similar study on the potential of hydrogen production using agricultural biomass (rice, sugarcane, cotton, wheat, and maize) has been perform by Irfan *et al*., 2022 [24]. They concluded that the highest potential derives from sugarcane trash followed by maize straw.

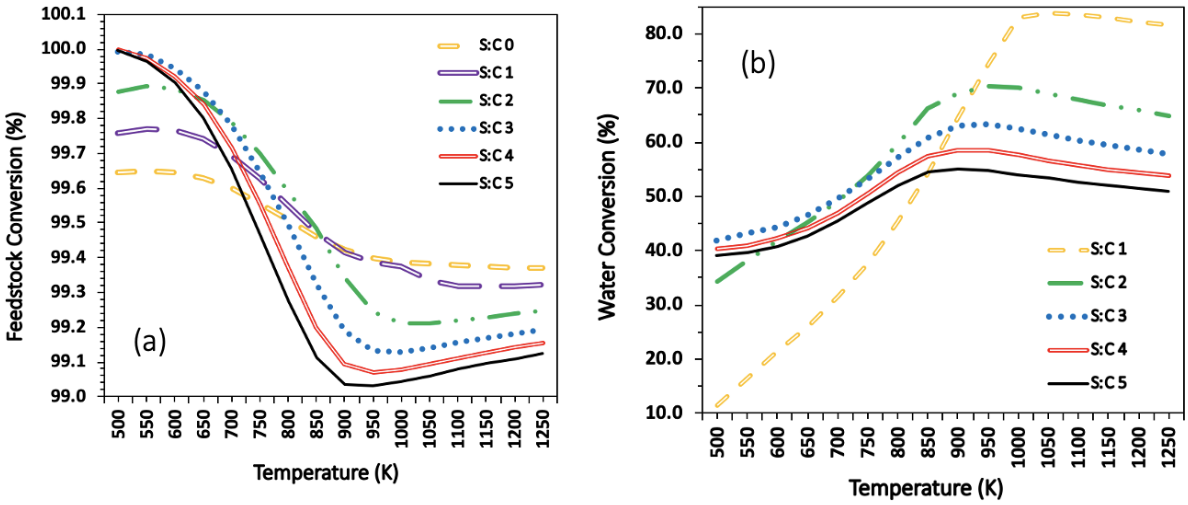

Figure 2 Effect of Temperature and Steam to Carbon Ratio on Feedstock and Water Conversion (a) Feedstock Conversion VS Temperature (b) Water Conversion VS Temperature

Conclusion

Hydrogen yield and purity completely depend on temperature and S:C ratio. The conditions of S:C 5, 1 bar, and temperature range of 850 to 1000 K are optimal conditions for conventional steam reforming of groundnut shell based on the conditions investigated in this study.

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