Mathematical Modeling and Experimental Analysis of Cashew Nut Shell Char Gasification Using Free Energy Minimization

M. Venkata Ramanan*1, E. Lakshmanan*, R. Sethumadhavan*, and S. Renganarayanan*

Abstract – Cashew nut shell, a waste product obtained during de-shelling of cashew kernels, possess an occluded oil content of 25% by weight. The oil, a source of natural phenol, oozes upon gasification thereby makes the gasifier throat, downstream equipments and associated utilities clogged with oil leading to ineffective gasification and premature failure of utilities due to its corrosive characteristics. To overcome this drawback, the cashew shells were de-oiled, by charring them in closed chambers and were subsequently gasified in an auto-thermal fixed bed downdraft gasifier.

A non-stoichiometric equilibrium model based on free energy minimization was developed to predict the performance of gasifier. The model considered 4 elements and 6 species in both gas and solid phases. The influences of equivalence ratio (ER), reaction temperature (RT) and moisture content (MC) on gasification of cashew nut shell char (CNSC) were simulated. It was observed that the gas composition varies primarily with ER and MC compared to that of RT. The model has been validated with the experimental results for CNSC gasification, with an overall deviation of (-) 3.5%.

The sensitivity analyses revealed that mole fraction of (i) H2, CO, and CH4 decreases while (N2 + H2O) and CO2 increases with ER (ii) H2 and CO increases while CH4, (N2 + H2O), and CO2 decreases with reaction temperature (iii) H2, CH4, CO2, and (N2 + H2O) increases while CO decreases with moisture content. However at lower equivalence ratios (less than 0.15) the model predicts unrealistic composition, probably due to onset of pyrolysis.

Keywords – Cashew shell char, gasification, Gibbs free energy minimization, non-stoichiometric modeling, producer gas.

1. INTRODUCTION

The term biomass is generally applied to renewable organic matter generated by plants through photosynthesis. Biomass is the only renewable source of carbon. Biomass in the form of cashew nut shell (Anacardium occidentale Linn.) represents a renewable and abundant source of energy in India [1]. India is the largest producer, processor, and exporter of cashews in the world. The cashew processed in India dominates more than half of the world cashew market [2]. While cashew tree is native to Central and South America, it is now widely distributed throughout the tropics, particularly in many parts of Africa and Asia [3], thanks to its soil erosion characteristics and better adaptability for any given nature’s vagaries.

Amongst the different biomass energy conversion techniques, gasification – the process of generating burnable low-Btu gas by substoichiometric oxidation – offers abundant promise, for its fuel versatility, better turn down ratio, modularity and amenability to meet both the thermal and electrical energy requirements in an economical fashion at any given size.

The cashew fruit is unusual in comparison with other tree nuts, since the nut is outside the fruit (Figure 1). The cashew apple is an edible false fruit, attached to the externally born nut by a stem. In its raw state, the shell of the nut is leathery, not brittle. It contains the thick vesicant oil, cashew nut shell liquid (CNSL), within a sponge-like interior.

The CNSL is reported to be 15–20% by weight of the unshelled nut in Africa, 25–30% by weight in India and 25% overall [4]. The cashew nut shells (CNS), generated as a waste by-product during processing for kernels, is being sold at a throw away price. Due to its cheaper and abundant availability, cashew shells are utilized in an inefficient manner [5]. These shells are burnt in such a way that they are generally regarded as a disposal option rather than energy source.

Attempts had been made towards conversion of these shells in to a burnable low-Btu gas. However the inherent CNSL content of these shells made the gasification technology a non feasible one for the long run. In order to overcome the drawback posed by CNSL, the shells were charred in a chamber, thereby de-oiling the shells for onward gasification. The characteristics of raw (Figure 2) and charred cashew nut shell (Figure 3) are presented in Tables 1 and 2. The bulk density of cashew nut shell char (CNSC) was measured to be 190 kg/m3, indicating its amenability for gasification.

The main objective of this study was (i) to investigate the feasibility of gasification of cashew nut shells in a down draught gasifier on the long run and (ii) to develop a non-stoichiometric equilibrium model based on Gibbs free energy minimization for predicting the performance of gasifiers under varying equivalence ratio (ER), moisture content (MC) and reaction temperature (RT) on gasification of cashew nut shells.

* Institute for Energy Studies, College of Engineering, Anna University, Chennai 600025, India.

1 Corresponding author; Tel.: +91-44-22203269, Fax: +91-44-22353637. E-mail: venkat@annauniv.edu, madhavanvenkat@gmail.com.
Table 1. Proximate analysis of raw and charred cashew shells

<table>
<thead>
<tr>
<th></th>
<th>CNS (wt% on as received basis)</th>
<th>Charred CNS (wt% on as received basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>10.43</td>
<td>7</td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>69.31</td>
<td>28</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>19.26</td>
<td>59</td>
</tr>
<tr>
<td>Ash</td>
<td>1.00</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2. Ultimate analysis of raw and charred cashew shells

<table>
<thead>
<tr>
<th></th>
<th>CNS (wt% on as received basis)</th>
<th>Charred CNS (wt% on as received basis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>48.7</td>
<td>63</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.96</td>
<td>3.6</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.36</td>
<td>6.4</td>
</tr>
<tr>
<td>Oxygen</td>
<td>43.98</td>
<td>27</td>
</tr>
</tbody>
</table>

2. MODELLING OF GASIFICATION SYSTEMS

Performance prediction of a gasification system is normally carried out under two techniques viz., mathematical (kinetic) modeling and chemical equilibrium modeling. Mathematical modeling is based on the kinetic equations for the reaction network solved together with mass and heat balances associated with several hydrodynamic considerations [6]–[13]. Kinetics model predicts the progress and product composition at different positions along a reactor and requires detailed reaction kinetics. Scanty kinetic data available in open resources are used for the model, while the majority of unavailable kinetics were either generated or assumed [11]. Two unique options are adopted for chemical equilibrium modeling, one is based on minimization of the free energy [14]–[19] (also referred as non-stoichiometric modeling), while the other one is based on equilibrium constants (also referred as stoichiometric modeling) [20]–[24].

3. EXPERIMENTAL SET-UP

Figures 4, 5, and 6 depict the schematic and photograph of the experimental setup. An induced air, closed top, 20 kW, auto thermal, down-draught gasifier was chosen for the study. Provision for air entry to the gasification system had been made through 2 inclined tuyeres unclosed at the throat. A grate made of stainless steel was used for holding the feedstock. The region between throat and grate functions as a reduction zone. The hot gas generated is passed along the annuli of the reduction zone, for maintenance of higher reaction temperature and minimization of heat loss. A cyclone separator was placed at the gasifier outlet – to remove particulates – ahead of the ID blower. An aerated burner had been used for flaring the producer gas generated. The whole gasifier assembly was mounted on a toughened helical spring for enabling it to vibrate to ensure smooth fuel flow. A poking rod was fixed at the bottom and linked to the grate. Pushing and pulling the poking rod creates an impact on the grate, thereby disintegrating and discharging any clogged residual particles to the ash box. Provisions were made in the gasifier - at appropriate locations - for measuring the temperature, pressure and gas composition. A stand with ladder arrangement had been bestowed for feeding the raw material in the fuel feed port.

4. PROCESS INSTRUMENTATION AND CONTROL

The base fuel characteristics were established with a proximate analyzer (muffle furnace + micro weigh balance with associated auxiliaries). The parameters studied include moisture content (ASTM D 3173-73), volatile matter (ASTM D 3175-73) and ash content (ASTM D 3174-73). Fixed carbon (FC) was assumed to be the rest. Calorific value of CNSC was established using standardized (benzoic acid based) bomb calorimeter and the result was observed to match well with the correlations framed for estimation of calorific value for bio fuels [25]. Junkers gas calorimeter was used for determining the calorific value of producer gas. Producer gas composition was analyzed using Siemens make online gas analyzers viz., oxymat 61 (estimates O₂ using Paramagnetic principle), ultramat 23 (estimates CO, CO₂
and CH₄ using non dispersive infrared multilayer technology) and calomat 61 (estimates H₂ using thermal conductivity principle). Details regarding the producer gas composition were logged in to the PC using siprom-GA software, for every second. Gas sampling system consisted of wash bottle, condensation pot, coalesce filter, suction pump, fine filter, flame arrestor and a diaphragm pump. Chromel-Alumel (K type) thermocouples were used for measuring the temperature at different zones (T1 to T6). Thermocouples were fixed permanently and measured continuously in all zones except at throat (T4). For temperature measurement at throat, a flexible K type thermocouple was inserted along the air port at regular intervals. Temperatures from different zones were logged simultaneously using Agilent make (34907 A) data acquisition system. The surface temperature of gasifier was measured with a Kane make infrared thermometer (UEI-INF 200). Airflow make thermo anemometer (TA 35) was used for measuring the air flow to the gasifier. Calibrated ‘S’ type pitot tube and Comark make digital manometer was employed for establishing the producer gas flow. The air entry in to the system, thus ER, is controlled by a globe valve placed at the discharge end of the blower. Water filled U tube manometers were deployed for measuring the pressure buildup across the gasifier bed.

Fig. 4. Schematic of gasifier

Fig. 5. Photograph of experimental set-up

Fig. 6. Gasification of CNSC
5. EXPERIMENTAL PROCEDURE

Pre-weighed batches of CNSC, each weighing approximately 25 kg, were placed near the system for hassle free operation during fuel loading. Gasification of CNSC was initiated by keeping the gas valve in open condition, followed by operation of ID blower and holding a flame near air tuyere. Flame was sucked into the system due to the draught created by the blower. Within 3 minutes, flue gas was observed at the flare port. With time (normally 5-10 minutes), the onset of gasification commences and producer gas emanates in the flare port. Experimental analysis was started once the system attained stabilization. Generally it took 60 – 90 min for attaining stabilization, which is ensured by inferring constant temperature in raw gas and reduction zone. The fuel consumption rate was measured by recharging the gasifier on an hourly basis and filling the gasifier volume to a predetermined level at the top of the gasifier hopper. The ash door was operated at regular intervals to remove ash accumulated on the grate.

The major performance influential parameters for a gasification system are equivalence ratio, bed temperature and moisture content of feed stock. Equivalence ratio was varied by adjusting the air supplied to the gasifier bed and the experimental outcome is compared with the modeled results. The performance of the system was also predicted for varying fuel moisture content and bed temperature.

6. NON-STOICHIOMETRIC EQUILIBRIUM MODELING

Kinetic models though provide essential information on mechanisms and rates, equilibrium models are valuable, because they predict thermodynamic limits, which acts as a guide for process design, performance evaluation and improvement. Compared to both equilibrium and kinetic modeling, non-stoichiometric approach is quite simple and requires only the ultimate analysis of fuel. The basics of non-stoichiometric modeling and the methodology adopted for prediction is detailed below.

A system and its surroundings form an adiabatic system, and for such systems
\[ dS_{sys} \geq \frac{\delta Q}{T} \]

From Equation 1 it is inferred that a chemical reaction in an adiabatic chamber proceeds in the direction of increasing entropy. When the entropy reaches a maximum, the reaction attains equilibrium. Therefore, entropy is a useful property in the analysis of reacting adiabatic systems. When a reacting system involves heat transfer, the increase of entropy principle relation becomes impractical to use, however, since it requires knowledge of heat transfer between the system and its surroundings. A more practical approach would be to develop a relation for the equilibrium criterion in terms of the properties of the reacting system only.

In a reacting simple compressible system of fixed mass, with only quasi-equilibrium work modes at specified temperature T and pressure P, combining first and second law relation gives:
\[ \delta Q - Pdv = dU \]

Alternately we can deduce that
\[ dS \geq \frac{\delta Q}{T} \]

\[ dU + PdV - TdS \leq 0 \]

The differential of the Gibbs function \( G = H - TS \) at constant temperature and pressure is:
\[ (dG)_{T,P} = dH - TdS - SdT \]

\[ = dU - PdV - TdS \]

From Equations 1, 4, and 6
\[ (dG)_{T,P} \leq 0 \]

Therefore, a chemical reaction at a specified temperature and pressure will proceed in the direction of decreasing Gibbs function. The chemical equilibrium will be established when the Gibbs function attains a minima value as shown in Figure 7. Therefore, the criterion for chemical equilibrium can be expressed as \( (dG)_{T,P} \leq 0 \)

![Fig. 7. Criteria for chemical equilibrium](image)

The assumptions made in the non-stoichiometric modeling approach are:
- Ideal gas laws are valid
- All reactions are at thermodynamic equilibrium
- Fuel is made up of only C, H, O, N and S
- Producer gas comprises only CO\(_2\), CO, H\(_2\), CH\(_4\), N\(_2\) and H\(_2\)O.
- Gases are in equilibrium during the flow through the char bed
- The pressure in the char bed is atmospheric and constant.
- Reactions proceed adiabatically.
- Nitrogen present in both fuel and air is inert.
- Ash is inert and is not involved in any of the reactions either as a chemical species or as a catalyst.
- No radial temperature gradients or concentrations exist.
- No accumulation of gas in the char bed.
• No resistance to conduction of heat and diffusion of mass inside the char particles.
• No tar in the gasification zone.
• Carbon conversion efficiency = 100 %
• Heat loss in the system is neglected
• Standard state fugacity = 1

The chemical formula of CNS char, based on single atom of carbon, is observed to be \( \text{CH}_{0.668}\text{O}_{0.32}\text{N}_{0.09} \). Overall gasification reaction using CNSC could be equated as:

\[
\text{CH}_{0.668}\text{O}_{0.32}\text{N}_{0.09} + a(\text{O}_2 + 3.76 \text{ N}_2) + x \text{H}_2\text{O} = b \text{H}_2 + c \text{CO} + d \text{CO}_2 + e \text{H}_2\text{O} + f \text{CH}_4 + g \text{N}_2
\]  

(8)

The procedure adopted for non-stoichiometric equilibrium modeling for gasification of cashew nut shell char is presented below.

**Step 1:** Compute the number of gram-atoms of each atom present in the system.

**Step 2:** Determine the number of gram-atoms of each element present per gram-mole of each substance.

**Step 3:** Determine the Gibbs free energy of formation \( \Delta G^0_i \) for each compound at operating temperature.

**Step 4:** Adopt the Gibbs free energy minimization [26] equation.

\[
\Delta G^0_f + RT \ln \left( \frac{f_i}{P_i} \right) + \sum_k \left( \lambda_k a_{i,k} \right) = 0
\]  

(9)

**Step 5:** Material-balance and mole-fraction equation is:

\[
\sum_i \gamma_i a_{i,k} = \frac{A_k}{n_T}
\]  

(10)

**Step 6:** Solve the non-linear equations from Equations 9 and 10 simultaneously.

**Table 3.** Gibbs functions of formation at 298.15 K [27]

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Phase</th>
<th>( \Delta G^0_{298} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>g</td>
<td>-228572</td>
</tr>
<tr>
<td>Water</td>
<td>l</td>
<td>-237129</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>g</td>
<td>-394359</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>g</td>
<td>-137169</td>
</tr>
<tr>
<td>Methane</td>
<td>g</td>
<td>-50460</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>g</td>
<td>0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>g</td>
<td>0</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>g</td>
<td>0</td>
</tr>
</tbody>
</table>

The model accounts four elements (C, H, O and N) in CNSC and predicts the composition of 6 species in the producer gas (CO, CO\(_2\), CH\(_4\), H\(_2\), H\(_2\)O and N\(_2\)). The model upon execution yields the final molar composition of all species \( (\gamma_{\text{CO}}, \gamma_{\text{CO}_2}, \gamma_{\text{N}_2}, \gamma_{\text{CH}_4}, \gamma_{\text{H}_2}, \gamma_{\text{H}_2\text{O}}) \). The Lagrange multiplier has no physical significance and can be eliminated from the solution scheme. The approach of non-stoichiometric equilibrium model is illustrated in Figure 8. Truncation beyond 5 decimal points had been adopted for terminating the program.

![Flow chart of gasifier model](image-url)
7. RESULTS AND DISCUSSIONS

Influence of Equivalence Ratio on Molar Concentration

Equivalence ratio (ER) is the ratio of actual A/F ratio to that of stoichiometric A/F ratio. Discarding the fuel component, it could also be defined as ratio of actual air supplied to that of stoichiometric air requirement. For an ideal combustion, the value of ER = 1, while in practical cases it is always > 1, the factor predominantly governed by the type of fuel being combusted. For gasifiers, the value of ER would range from 0.15 to 0.4. In the process of auto thermal gasification, part of fuel is burnt to release energy to sustain the endothermic gasification reactions. The lower limit of ER in an auto thermal gasifier is fixed by considering a variety of factors like the minimum quantity of air required to burn a part of the fuel to release energy for supporting endothermic reactions, required carbon conversion efficiency, the fixed loss of heat that need to be accounted for maintaining the reactor temperature etc. Similarly, the upper limit of ER is fixed by factors like tar quantity, gas quality, reactor temperature, ash fusion point.

The influence of ER on gasification of CNSC holding 7% moisture (as determined by proximate analysis) and operating at a throat temperature of 1373 K, as predicted by the models, is depicted in Figures 9 to 13. The maximum HHV of the gas, upon experimentation, was observed to be at an ER of 0.30. The throat temperature attained by the gasifier (1373 K) at this ER of 0.30 was applied for predicting the gas composition. It is a common reality that with increase in ER, the temperature of any oxidation reaction is bound to increase. However, in the formulated models, the temperature had been assumed to be constant at different ERs. As the outcome of the model had been analyzed for its deviation only at an ER of 0.30, this assumption is presumed to be a convincing one.

The influence of ER on gasification of CNSC – on a consolidated fashion - at fixed moisture of 7% and at a reaction temperature of 1373 K is depicted in Figure 24.
Influence of ER on Hydrogen and CO

The yield of hydrogen from the model is observed to follow a decreasing trend with increase in ER. Similar trend is reported by other researchers like [28]. This trend is applicable to only allothermal systems, where the temperature of the gasifier is controlled externally [29]. For auto thermal systems, the increase of ER would have two paradoxical phases, one following the other in a sequential manner. When the ER is increased from low values, the temperature of system increases, leading to marked increase in generation of both gas and its H\(_2\) values, the temperature of system increases, leading to sequential manner. When the ER is increased from low values, the temperature of system increases, leading to marked increase in generation of both gas and its H\(_2\) concentration - phase 1. However beyond a governing limit, the oxidation reaction predominates due to excess availability of oxygen and the yield of H\(_2\) drops for conversion of H\(_2\) to H\(_2\)O - phase 2. The typical ER reported by [30] is 0.19 to 0.23 for phase 1 and 0.23 to 0.27 for phase 2. The model predicts unreasonably high H\(_2\) at lower ER. Ruggiero et al. [31] described the irrelevance of equilibrium models, which assume perfect gas behavior, for very low ERs as these models cannot describe pyrolysis processes, due to the presence of liquid hydrocarbons as pyrolysis products. Desrosiers [32] predicted thermodynamic ER for gasification of dry wood as 0.28. Considering the range of H\(_2\) yield, as predicted by model with experimental values in the ER of 0.25 to 0.35, the model values are quite reasonable with the experimented values. At ER of 1, the H\(_2\) is null, indicating the complete combustion and conversion of all H\(_2\) to water vapor. The prevailing conditions and criteria quoted for H\(_2\) is equally applicable for CO, albeit at different magnitude.

Influence of ER on CO\(_2\) and CH\(_4\)

The molar % of CO\(_2\) is observed to increase with increase in ER, similar to the trend established by [19]. In reality, the trend of CO\(_2\) could be correlated as the trend opposite to that for CO. Decrease in the concentration of CO\(_2\) indicates better efficiency of gasification [33]. The modeled results for charred CNS indicated meager values of CO\(_2\) at lower ER, which is quiet unrealistic. Ruggiero’s [31] statement could be applied for this condition also. However, it was found that the model predicts the CO\(_2\) concentration reasonably well at higher ERs and that pertaining to gasification.

Mansaray et al. [34] inferred that increasing the ER lead to decrease in the concentrations of methane and other light hydrocarbons which have relatively large heating values. The model results validate the statement of decreasing CH\(_4\) concentration for increasing ER. Conversely, the prediction on CH\(_4\) made by the model is lower than the actual ones by a large margin. Pellegrini and de Oliveira, Jr. [15] experienced similar differences in CH\(_4\) predicted by model and experiment and referred the cause as a result of the sudden cease of gasification reactions at the bottom of the reactor. This cease is a consequence of the temperatures at the bottom, which are too low to start-up the reactions. In an equilibrium model, it is assumed that all reactions achieve a steady-state condition, thus no kinetic effects (such as sudden cease) are considered. To overcome the differences in the mole fractions, a fixed CH\(_4\) molar correction need to be adopted, as reported by [35].

Influence of ER on N\(_2\) and H\(_2\)O

Gas analysis was not carried out on dry basis, for want of facilities. Hence the remains of the measured components viz., CO, CO\(_2\), H\(_2\), O\(_2\) and CH\(_4\) is assumed to be mix of N\(_2\) and H\(_2\)O. The devised model predicted the yield of N\(_2\) and H\(_2\)O individually and the molar concentrations of these constituents were combined as a mix to compare with the experimental values. Generally nitrogen formation could be attributed to the N\(_2\) from fuel and N\(_2\) from air. With the nitrogen in fuel remaining constant, the increase of ER increases the N\(_2\) supplied to the system and hence the higher yield of N\(_2\) at higher ERs. While majority of researchers had observed similar pattern, Zainal et al. [33] had reported decreasing trend of N\(_2\) with increase in ER. H\(_2\)O in the product gas also increases with increase in ER for the ascendancy of oxidation reaction of H\(_2\) at higher ERs. The H\(_2\)O and N\(_2\) mix predicted by the model correlates well with the experimental values.

Influence of Temperature on Molar Concentration

Jayah et al. [36] observed that lower temperature reduces the reaction rate and thereby the conversion efficiency. Alatfini et al. [19] stated that equilibrium models are especially good at the high temperatures where the reaction temperatures are above 1500 K. The temperatures generally assumed for equilibrium modeling by different researchers were not coherent and are predominantly modeled between 800 – 1000 K. Moreover the zone of the gasifier experiencing this temperature was also not reported. Prins et al. [37] remarked that for fluidized bed gasifiers, the average bed temperature can be used as the process temperature, whereas for downdraft gasifiers, the outlet temperature at the throat exit should be used. The temperature measured at throat zone [T4] of the gasifier, using charred CNS, was about 1100°C. Dogru et al. [38] reported a throat temperature of 1015°C using hazelnut shells. However keeping in mind the veracity of other literatures, the model was framed for a wide of temperature from 800 K to 1500 K and compared with the experimental results that happened at 1373K (Figures 14 to 18). It is to be noted that the deviation of gas composition among the temperature range selected was not very significant in the depicted figures owing to subtle demarcation between them. A zoomed analysis of Figures 14 to 18, revealed increase in H\(_2\) and CO content while decrease in CH\(_4\), (N\(_2\) + H\(_2\)O), and CO\(_2\) with increase in reaction temperature. Both exothermic and endothermic reactions occur in the gasification system. Based on Le Chatelier’s principle, it is comprehended that higher reaction temperatures favor the reactants in exothermic reactions while it favor the products in endothermic reactions. Methane formed in the gasifier, at high temperatures, undergo endothermic reactions with the already formed water vapor and get converted to CO, CO\(_2\) and H\(_2\). Hence the yield of CH\(_4\) recedes at higher temperatures.

The endothermic reactions use the water vapor generated in the preliminary gasification process, as a result of which the yield of N\(_2\) + H\(_2\)O mix is lowered at higher temperatures. Since N\(_2\) forms majority of the mix, the dip caused by reduction of moisture is almost insignificant. Precisely, it could be inferred that the cause
for drop in methane at higher temperatures and increase in CO, and H₂ is due to the utilization of methane in endothermic reactions (rather a reforming process indeed). The trend obtained matches well with the style established by other researchers for other fuels [15], [21], [23], [28], [39]–[42].

Influence of Moisture on Molar Concentration

Moisture content is one among the most significant properties of any biomass that are known to influence the gasification process. Hos et al. [42] detailed the influence of moisture content of the feed material affecting the composition of the product gas. Bridgewater et al. [43] cited that moisture constraints for any gasifier fuel is dependent on type of gasifier used. Higher values are possible in updraft systems but the upper limit acceptable for a downdraft reactor is generally considered to be around 40% dry basis. Reed et al. [44] specified that moisture content of feedstock should be below 33% (dry basis) for generating a burnable, good quality gas, while moisture contents higher than 67% (dry basis) make the product gas too lean for ignition. McKendry [29] inferred that fuel with moisture content above about 30% makes ignition difficult and reduces the CV of the product gas due to the need to evaporate the additional moisture before combustion or gasification can occur. With this background, the present model was analyzed for the impact of moisture content on gas composition and the results were compared with the experimental values. Moisture content in a biomass could be either intrinsic (inherent) or extrinsic (influenced by weather or handling). The moisture in the producer gas is an amalgamation of the moisture sourced from sub stoichiometric air (specific humidity), water vapor formed due to oxidation of hydrogen in fuel and the intrinsic and extrinsic moisture associated with fuel. Among these contributing factors, the first 2 factors absorbs only...
sensible form of heat for superheating the moisture, while the last component absorbs sensible, latent and super heat for converting the moisture to a super heated vapor form. The higher the fuel moisture content, the higher is heat absorbed by the moisture, paving way for reduced reaction temperature and associated incomplete cracking of the hydrocarbons released from the pyrolysis zone.

Increased levels of moisture and the presence of CO at lower ERs produce more H₂ and CO₂ by the water gas shift reaction. The increased H₂ content of the gas produces more CH₄ by direct hydrogenation. Pellegrini and de Oliveira, Jr. [15] inferred that though more H₂ is formed with increased moisture, however in order to maintain the process, more energy must be supplied, so exothermic reactions are favored, which promotes CO₂ formation. The gain in H₂ and CH₄ of the product gas does not however compensate for the loss of energy due to the reduced CO content of the gas and therefore gives a product gas with a lower CV [29]. Similar results on influence of moisture content have also been reported for other fuels [45]–[47]. The model revealed similar trends for CNSC and the experimental values were observed to follow the suite predicted by the model, in Figures 19 to 23.

Consolidation

Comparison of the non-stoichiometric equilibrium modeling based on Gibbs free energy minimization results against experimental values obtained upon gasification of CNSC is presented in Figure 24. The deviation observed is very minimal on the ER applicable to gasification viz., 0.15 to 0.4 for all constituents except methane. The cause could be attributed to the deviation of the gasification process from chemical equilibrium due to kinetic limitations.
8. CONCLUSIONS

- Cashew shell nuts could be successfully gasified, without any major oil related problems, after charring them.
- The concept of non-stoichiometric equilibrium modeling based on minimization of Gibbs free energy applied well for gasification of CNSC.
- Influence of ER, RT, and MC on the gasification process had been analyzed and presented.
- ER was observed to have a great impact on the composition of producer gas. The model predicts well the trend of producer gas constituents at varying equivalence ratios.
- The deviations among the experimental output and model prediction were observed to be maximum at lowest ER (due to pyrolysis) and minimal at equivalence ratios pertaining to gasification.
- At an ER of 0.3, the overall deviation of the model as against experimental values, excluding methane, was analyzed to be -3.5%, a slight under-prediction indeed owing to kinetic limitations.
- The experimental outcome of CH$_4$ was observed to be much higher than the modeled results, requiring fixed methane molar constants to curtail the deviation.
- The contribution of reaction temperature was significant for yield of hydrogen.
- Higher temperatures favor the formation of CO and minimize the yield of CO$_2$ and CH$_4$. For temperatures higher than 1100 K, CH$_4$ generation is practically nil.
- Model does predict the influence of MC in a relevant manner viz., H$_2$, CH$_4$, CO$_2$ and (N$_2$ + H$_2$O) increases while CO decreases with moisture content.

ACKNOWLEDGEMENT

The financial support provided by Ministry of New and Renewable Energy Sources, Government of India, New Delhi (F. No. 203 / 1 / 10 / 2000 B M) is thankfully acknowledged. The support rendered by Mr. M. Sundaresan, Fitchner Consulting Engineers, Chennai; Mr. S. Kasiraman, GE-Bangalore; Mr. G. Vidyasagar; and Mr. M. Muthukumar are appreciated.

NOMENCLATURE

\[ a_{i,k} \] No. of kg-atom/kg mole  
\[ A_k \] No. of kg-atom  
\[ b, c, d, e, f, g \] Coefficients of constituents of the producer gas  
\[ f_i^\circ \] standard state fugacity  
\[ n_T \] Total number of moles  
\[ P \] Pressure (bar)  
\[ R \] Universal gas constant (kJ/kmolK)  
\[ S \] Entropy (kJ/kgK)  
\[ T \] Temperature (K)  
\[ x \] Amount of water per kmol of CNSC  
\[ y_i \] Mole fraction  
\[ \Delta G^\circ_f \] Gibbs energy formation (kJ/mol)  
\[ \lambda_k \] Lagrange multiplier  
\[ \phi_i \] fugacity coefficient

Subscript

\[ f \] Formation  
\[ i \] Substance  
\[ k \] Element  
\[ T \] Total

Abbreviations

CNSC Cashew nut shell char  
CNSL Cashew nut shell liquid  
ER Equivalence ratio  
HHV Higher heating value kJ/kg  
LHV Lower heating value kJ/kg  
MC Moisture content  
RT Reaction temperature

REFERENCES


