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An overview on gasification of biomass for production of hydrogen rich gas

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ABSTRACT

Gasification was chosen as one of the more conventional methods for conversion of biomass due to some important reasons such as space consideration, flexibility of fuels used, reducing the volume of solid waste and recovery of energy. Essentially, the process of gasification involves partial combustion of the organic part of the fuels to combustible gas rich in carbon monoxide, hydrogen and some saturated hydrocarbon gases, principally methane. The affecting parameters on the performance of the gasification such as (temperature, catalysts, gasifying agent/biomass ratio) and the type of raw materials were reviewed and discussed.

INTRODUCTION

There are serious problems facing the world today. Perhaps one of the world wide problems is the shortage of energy. For the past 50 years, most of the world energy has come from petroleum and natural gas. But much of the existing supply has already been used up. If we continue to use these fuels at our constantly increasing rate, reserves will run out in perhaps few years. So, we must look for other sources and forms of energy. Biomass energy can be substituted for petroleum in important ways-such as for generating electricity [1].

Fuels derived from biomass may be classified in a number of ways, but basically they fall into three main categories: solid, liquid and gaseous fuels. The conversion process that turns biomass resource into a fuel can be either biological or thermo-chemical. Among these conversion processes, the thermo-chemical process is the most promising route. There are four main thermo-chemical methods of converting biomass: combustion, pyrolysis, gasification and liquefaction [2]

Gasification was chosen as one of the more conventional methods for conversion of biomass due to some important reasons such as space consideration, flexibility of fuels used, reducing the volume of solid waste and recovery of energy. Essentially, the process of gasification involves partial combustion of the organic part of the fuels to combustible gas rich in carbon monoxide, hydrogen and some saturated hydrocarbon gases, principally methane [1-10].

Gasification is a thermo-chemical process taking place at high temperatures typically >700^{o}C to convert carbonaceous materials including biomass, fossil fuels, plastics, and coal into syngas; which is a mixture of H_2,CH_4, CO, and CO_2. Limited amount of oxygen and/or steam is used as the gasifying agent and heat carrier agent.

The produced syngas is itself a fuel that can be burnt directly producing heat at temperatures higher than the combustion products. Moreover, the syngas - if well cleaned - can be employed through different pathways to yield useful outputs including 1) purified syngas used in gas engine, gas turbines, and/or fuel cells to generate electricity, 2) production of methanol, 3) production of dimethyl ether DME by methanol dehydration, 4) production of hydrogen, 5) production of fuels like gasoline and diesel through Fischer-Tropsch reaction, and 6) methane via Sabatier reaction [11]

Based on the current situation, it can be noticed that gasification process is inefficient, which at present render biomass gasification economically unviable. Gasification of biomass for the production of hydrogen rich gas will be emphasized in this project. However, it is well known that the gasification of biomass still has some technical problems. Some of these problems is the quality of the gas produced and tar cracking. There appears to be a clear necessity of reforming or modifying the gas produced. Together with other possible technical solutions, oxygen introduction, use of high temperature and the use of catalysts could be a solution.

In order to reduce energy consumption of biomass derived hydrogen, this study will introduce a fixed bed gasification system to investigate the production of hydrogen rich gas from biomass and other hydrocarbon resources.

The selection of the gasifier is determined by their different features. A fixed bed gasifier is characterized in achieving a higher hydrogen content of the gaseous product; therefore this investigation chooses it as the gasifier.

The effect of the operating parameters such as (temperature, gasifying agent/biomass ratio, pressure) and of the materials, type of biomass) , type of the gasifier reactor on the performance of the gasification system will be discussed.

3. Literatuer Review

3.1 Basic chemistry of gasification

The reaction taking place in the gasifier can be summarized as indicated below:

Partial oxidation:

$$C + \frac{1}{2} O_2 \longleftrightarrow CO \ldots\ldots\ldots\ldots\ldots\ldots dH = -268 MJ/kg\ mol$$

Complete oxidation:

$$C + O_2 \longleftrightarrow CO_2 \ldots\ldots\ldots\ldots\ldots dH = -406 MJ/kg\ mol$$

Water gas phase reaction:

$$C + H_2O \longleftrightarrow CO + H_2 \ldots\ldots\ldots\ldots\ldots dH = 118 MJ/kg\ mol$$

Boudouard Reaction

$$C + CO_2 \longleftrightarrow 2CO \ldots\ldots\ldots\ldots\ldots dH = 170.7 MJ/kg\ mol$$

The heat of reaction for the three processes show that the greatest energy release is derived from the complete oxidation of carbon to carbon dioxide i.e. combustion while the partial oxidation of carbon monoxide accounts for only about 65% of the energy released during complete oxidation. Unlike combustion that produces only a hot gas product, carbon monoxide, hydrogen and steam can undergo further reactions during gasification as follows;

Water gas shift reaction:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \ldots\ldots\ldots\ldots dH = -42\ MJ/Kgmol$$

Methane formation:

$$CO + 3H_2 \longleftrightarrow CH_4 + H_2O \ldots\ldots\ldots\ldots dH = -88\ MJ/kgmol$$

The arrows indicate that the reactions are in equilibrium and can be proceed in either direction, depending on the temperature, pressure and concentration of the reaction species. It follows that the product gas from gasification consist of mixture of carbon monoxide, carbon dioxide, hydrogen and water vapour.

Three product gas qualities can be produced from gasification by varying agent, the method of operation and the process operating conditions. The main gasifying agent is usually air but oxygen/steam gasification and hydrogenation are also used. Catalytic steam gasification is another method of operation that influence both the over all performance and efficiency.

Three types of product gas have different calorific value (CV)

Low CV	4-6	MJ/Nm^3	using air and air/steam
Medium CV	12-18	MJ/N m^3	using oxygen/steam
High CV	40	MJ/N m^3	using hydrogen

Low CV gas is used directly in combustion or as an engine fuel, while medium/high CV gases can be utilized as feed stocks for subsequent conversion into basic chemicals principally methane and methanol.

As the use of oxygen for gasification is expensive, air is normally used for processes up to about 50 MW thermal. The disadvantage is that the nitrogen introduced with the air dilutes the product gas, giving gas with a net CV of 4-6 MJ/Nm^3 compared with natural gas at 36 MJ/Nm^3. Gasification with oxygen gives a gas with a net CV 10-15 MJ/N m^3 and with steam , 13-20 MJ/N m^3. It can be seen that while a range of product gas qualities can be produced, economic factores are a primary consideration [(12)]. The over all energy efficiency of conversion of biomass to energy using gasification is estimated as 75-80%.

3.2 Feedstock pre-treatment and properties

The degree of pretreatment of the biomass feedstock is dependent on the gasification technology used. The main challenges area are:

Drying; the biomass moisture content should be below 10-15 % before gasification.

Particle size, in most gasifiers, gas has to pass through the biomass and the feed has to have sufficient compressive strength to withstand the weight of the feed above. Feed particle size in the range of 20-80 mm are typical.

Biomass characteristics: The characteristics of the biomass feed stock have a significant effect on the performance of the gasifier of these, the most significant characteristics are:

- **Moisture content.** 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 gasification can occur [(23)] . A high moisture content reduces the temperature achieved in the oxidation zone, resulting in the incomplete cracking of hydrocarbons released from pyrolysis zone. Increased levels of moisture content and the presence of CO produces H_2 by the water gas shift reaction and in turn the increased hydrogen content of the gas produces more CH_4 by direct hydrogenation.
- **Ash content.** High mineral matter can make gasification impossible. The oxidation temperature is often above the melting point of the biomass ash, leading to clinkering/slagging problems in the hearth and subsequent feed blockages. Clinker is a problem for ash contents above 5%, especially if the ash is high in alkali oxides and salts which produce eutectic mixtures with low melting points [(12)].
- **Volatile compounds:** The gasifier must be designed to destroy the tars and the heavy hydrocarbons released during the pyrolysis stage of the gasification processes.
- **Particle size:** The particle size of the feedstock material depends on the hearth dimension but is typically 10-20% of the hearth diameter. Large particles can form bridges which prevent the feed moving down, while smaller particles tend to clog the available air voidage, leading to a high pressure drop and the subsequent shutdown of the gasifier.

3.3. Types of gasifiers

Several types of gasifiers such as fixed bed and fluidized bed have been developed; Theses gasifiers have different hydrodynamics especially the way in which the solid fuel and the gasification agent and operating conditions such as temperature and pressure.

The reactor used in the gasification of crop residue can be classified as fixed bed fluidized bed and entrained flow gasifiers:

3.3.1. Fixed bed gasifier

The moving bed reactors are those reactors in which solid move either counter current or concurrent to the flow of the gas as reaction takes place and the solids are converted to gases In moving bed gasifiers, as air is passed through the bed of fuel, fairly discrete reaction zones developed along the reactor. Theses are drying, pyrolysis, gasification and oxidation zones. The location of these zones in the gasifier depend on the relative movement of the fuel and air. Moving bed gasifiers are usually classified as updraft, down draft and cross draft.

Upraft fixed bed gasifiers: In the updraft gasifiers, the feed is introduced at the top of the reactors and the air at the bottom of the unit of the grate. Immediately above the grate the solid char formed higher up the gasifier is combusted and the temperature reaches about 1000 °C. Ash falls through the grate at the bottom and the host gases pass upwards and are reduced. Higher up the gasifier, the biomass is pyrolysed in the top zone, the feed is dried, cooling the gases to around 300-400 °C. In the pyrolysis zone, where the volatile compounds are released, considerable quantities of the tar are formed which condense partly on the biomass higher up and partly leave the gasifier with the product gas. The temperature in the gasification zone is controlled by adding steam to the air used for the gasification. Due to the low temperature of the gas leaving the gasifier, the overall energy efficiency of the process is higher but so also is the tar content of the gas. The filtering effect of the feed helps us to produce a gas with a low particulate content.

For heat applications at capacities below 10 MWt, updraft gasifiers are most popular. Because the gas leaves this gasifiers at relatively low temperatures, the process has a high thermal efficiency

Downdraft fixed bed gasifiers: In the down draft gasifiers, the feed and the air move in the same direction. The product gases leave the gasifier after passing through the hot zone, enabling the partial cracking of the tars formed during gasification and giving a gas with low tar content. Because the gases leave the gasifier unit at temperatures about 900-1000 °C, the overall energy efficiency of a down draft gasifiers is low, due to the high heat content carried over by the hot gas. The tar content of the produced gas is lower than for an updraft gasifier but the particulates content of the gas is high [1,12].

Khater et al [13] have studied the gasification of rice hulls in down draft gasifiers. The feeding rate of rice hulls 1.3-5.1 kg/h and the air flow rates of 2-4.4 m3/h were used. They found that at a stoichio-metric air to fuel ratio of 55 %, the maximum yield of combustible constituents in the produced gas (13.6%CO, 5.1%H_2, 2.4% CH_4) .

Kumabe et al [14] have studied the co-gasification of coal and biomass with air and steam for production of synthesis gas. The experiment was performed using a downdraft fixed bed gasifiers at 900 °C. The effect of feed stocks with varying content of the biomass and coal on the gasification was studied by varying the biomass ratio from 0 to 1. They found that the conversion to gas increased with the biomass ratio while the conversion to char and tar decreased. The gas efficiency of 65-85% was obtained under the condition of co-gasification.

Cross-flow fixed bed gasifier: In a cross flow gasifier, the feed moves downwards while the air is introduced from the side, the gas being withdrawn from the opposite side of the unit at the same level. A hot combustion/gasification zone form around the entrance of the air, while the pyrolysis and drying zone being formed higher up the vessel. Ash is removed at the bottom and the temperature of the gas leaving the unit is about 800-900 °C; as a consequence this gives a low overall energy efficiency for the process and a gas with higher tar content.

3.3.2. Fluidized bed gasification

In the gasification of crop residues, the material is heated to a high temperature causing a series of physical and chemical changes resulting in evolution of volatile products and carbonaceous solid residues. The amount of the volatile products and their composition depend on: the heating rate, the temperature, and the type of fuel materials. It is generally accepted that the char gasification stage is the rate limiting factor in the gasification of crop residues because the devolaitization stage is very fast. The composition of the final product gas is also dependent on the degree of equilibrium attained by various gas phase reactions particularly the water gas shift reaction [1, 15]. In the absence of a catalyst, gasification of char with reactive gases such as oxygen occurs at high temperatures.

When char is gasified in the presence of the steam, the gas produced is composed mainly of CO, CO_2, H_2 and CH_4. In reactor operating at low temperatures, low heating rates and very high pressure secondary reactions are very important because of long residence time. On the other hand, at low pressure, high temperature and high heating rates, most of the volatile products escape from the fuel particle during the pyrolysis, hence, reducing the chance of solid char gas interaction. In fluidized bed gasifiers the latter prevails but because of the mixing nature of the bed, secondary reactions in the gas solid and gas phase takes place.

Crop residues gasification process is considered to be occur in four stages: drying of the feed stock pyrolysis to produce the volatile matters and char, gasification of the char with reactive gases such as O_2, H_2, H_2O and secondary reactions of primary gases and tars. These processes can not, however, be entirely separated from each other [26].
The advantages of the fluidized bed reactors are good gas solid contact, better temperature control, excellent heat transfer characteristics and high volumetric capacity. The temperature can be controlled by varying the feed rate or the rate at which the gasifying agent is introduced. In addition, because of the low operating temperature that can be

achieved slag and clinker formation can be avoided. Fluidized bed reactors have wider adaptability to handle different types of fuel. High ash or moisture content of the feed stocks pose no problems to the fluidized gasifiers such as those commonly encountered with moving bed gasifiers. The tar content of the gas obtained from fluidized bed is less than that in the gas obtained in the updraft. These desirable features of the fluidized bed gasifers makes it more suitable for large scale operation than downdraft type [16, 17] .

The disadvantages of the fluidized reactors are large pressure drop, particle entrainment and erosion of the reactor body. Because fluidized bed reactors operate at pressures slightly above atmospheric, their design and construction must prevent leakage. Other drawbacks of the fluidized bed gasifier lie in the rather high tar content of the product gas and the incomplete carbon burn out [17].

Fluidized bed gasification has been extensively used for coal gasification for many years, its advantage over fixed bed gasifiers being uniform temperature distribution achieved in the gasification zone. The uniformity of the temperature is achieved using a bed of fine grained material into which air is introduced, fluidizing the bed materials and ensuring intimate mixing of the hot bed materials, the hot combustion gas and the biomass feed.

Fluidized bed gasifiers can be classified on the basis of their configuration and the gasifying agent velocity into bubbling fluidized bed, circulating fluidized bed and spouted fluidized bed.

Bubbling fluidized bed gasifier
The bed is termed a bubbling fluidized bed when granular material are lifted in a vessel through which an upward flow of gas is passing at a flow rate where the pressure drop across the particles is sufficient to support their weight. In bubbling fluidization, low fluidization velocity just above the minimum fluidization passes through the bed in the form of bubbles.

Bubbling bed gasifiers consists of a vessel with grate at the bottom through which the air is introduced. Above the grate the moving bed of fine grained material into which the prepared biomass is introduced. Regulation of the bed temperature to 700-900 °C is maintained by controlling the air biomass ratio. The biomass is pyrolysed in the hot bed to form char with gaseous compounds, the high molecular weight compounds being cracked by contact with the hot bed materials, giving a product gas with a low tar content typically 1-3g/ m^3.

The bubbling bed gasifiers can be categorized according to the number of the bed, which can be applied to all fluidized bed as single fluidized bed and multi fluidized bed [12] .

Single fluidized bed gasifiers: The system consists of one bed only, into which the feedstock and the gasifying agent enter and out of which the produced gas and char exit. The advantage of the system include, a low cost compared to the multi bed, less maintenance due to the use of one bed only, the produced gas is ready for utilization. On the other hand the system has some disadvantages. These include; the produced gas heating value is lower than that produced by the dual bed, the separation of the inorganic materials in the feedstock is impossible, pyrolysis occurs in the combustion zone at the bottom of the gasifier which leads to non unifiorm temperature distribution.

Dual and muti fluidized bed gasifiers: the system consist of more than one bed and usually the first bed is used to burn some of the char to produce the energy for the second bed in which the pyrolysis occurs. The advantage of the dual bed system were reported by many Authors [18]. These include the gas heating value is larger than that produced by the single bed gasifiers because the combustion of the char occurs in a sepearte reactor and hence the combustion gas does not dilute the pyrolysis gas, separation of the inorganic material in the feed is possible. The disadvantages, high construction cost and more maintenance requirement as compared to the single bed.

Keiich Tomishige et al [18] have studied the gasification of the biomass by using single bed and double bed gasifier. It was found that in the dual bed system combined with suitable catalyst, almost the tar can be converted to syngas at lower temp. than that needed by the conventional method with high energy efficiency.

Circulating fluidized bed gasifiers
If the gas velocity in a bubbling bed is further increased, more particle will be entrained in the gas stream and leave the reactor. Eventually, the transport velocity for the most of the particle is reached and the vessel can quickly be empty of the solid unless additional particles are fed to the base of the reactor. If the solid leaving the vessel are returned through an external collection system, then the system is called a circulating or fast fluidized bed system. The circulating fluidized bed have high processing capacity compared to the conventional reactor , better gas solid contact and the ability to handle cohesive solids that other wise be difficult to fluidize in a bubbling fluidized bed.

Despite these advantages, the circulating fluidized bed are still less common than the bubbling ones because of their height which restrict their application in terms of cost analysis [19].

Spouted bed gasifier

A spouted fluidized bed consists of a bed of a coarse particle partially filling the vessel which is provided with a relative large control opening at its base. Gas is injected through this aperture. With sufficient flow of the gas, the particle in the gas can be made to rise in fountain at the center of the bed and develop cyclic motion on the bed as whole. The bed motion can be assisted by the additional air at the base to produce a spouted bed. Spouted bed gaifiers have been used to gasify the coal of various ranks.

Abdul Salam [20] has studied the gasification of solid fuels in a spouted bed, which has certain potential advantages over the fluid bed configurations. The effect of spouting velocity and the type of distributor on the gasification performance were discussed. They found that at a higher velocity, the gasification efficiency of circular slit spouted bed was slightly more compared with that of central jet spouted·

3.3.3 Entrained flow gasifier (EFG)

The materials that might be proceed in the co-current flow EFG include dry pulverized solid, atomized liquid fuel or a fuel slurry with employing oxygen as the gasification agent - the gasified material particles shall be well separated from one another. The advantages: higher throughput, tar and methane are not present in the product. These advantages are mainly obtained due to using high temperature and pressure.

The disadvantages of EFG: High operating temperature and pressure. More energy than for the other types of gasifier for milling of the gasified materials, as the fuel particles must be much smaller than for other types of gasifiers. This means the fuel must be pulverized which consumes more energy [11].

3.4. Operation and performance of gasifiers

The performance of the gasifier depends on the design of the gasifier, type of the fuel used and the air flow rate. In general fixed bed gasifiers have the advantage of a simple design but the disadvantage of producing a low CV gas with a high tar content. The product gas composition is typically 40-50 N_2, 15-20 H_2, 10-15% CO, 10-15% CO_2 and 3-5% CH_4 with a net CV of 4-6 MJ/Nm^3. When using air as the gasifying medium, the resulting high N_2 content doubles the volume of the produced gas and increases the size of the downstream gas cleaning equipment. To obtain high CV gas the moisture content of the feed should be 15-20% so that the pre-drying of the biomass feed stocks is usually required. Waste heat from the gasifier can be used to assist with pre-drying the feed materials. The energy content of the produced gas is up to 75% of the biomass energy content, the losses being accounted for by the sensible heat in the produced gas, the heat content of the ash and radiation losses.

In addition of the initial release of volatiles, a solid char produced. The char can be reacted further to produce additional gas, making a high char content indicative of considerable gas producing potential. The char produced from straw and wood biomass is typically in the range 22-29 wt % but the reactivity of the char varies greatly [21, 22].

Improvement to gas quality have been proposed by operating a two stage. pyrolysis of the biomass takes place in the first stage using external heating at 600 °C. The gases formed in the first stage are then reacted with steam to crack the tars. In the second stage the gas react with the char from the first stage to produce the final product gas. After clean up the gas quality is sufficient for use in a spark ignition gas engine.

In fluidized bed, the major operational difficulty experienced with fluidized bed gasifiers is the potential for slagging of the bed materials due to the ash content of the biomass. Of particular importance is the alkali metal content of the biomass, which is a problem with biomass derived from annual plants. To avoid the slagging, the bed temperature can be lowered but this result in an increase loss of char with the ash removal. The gas formed in the gasifier contains a number of impurities; Particulates, tar, nitrogen, sulphur and alkali compounds [12].

The end use of the gas determines the degree of clean up required and can be achieved either by hot or cold gas cleaning. The benefits of the hot gas cleaning is that more energy is gained from the gas but the process posses significant technical challenges, while cold gas cleaning is technically simpler but produce a waste water contaminated with tar, which is likely pose disposal problem.

Criteria for the comparison of gasifiers: Many criteria for such a classification can be imagined but the analysis led to five main criteria such as: Technology, use of material, use of energy, environment and economy.

Every main criterion is divided by sub-criteria. To be objective, the numerical evaluation should be independent of relative relations [23].

3.5. Process parameters and their effects on the gasification process

The process parameters affect various performance aspects like efficiency, product gas quality, energy and exergy inputs. Many of studies have been undertaken to investigate the optimum parameters to obtain maximum hydrogen or syngas.

Moghtaaderi [24] conducted a study to gain a fundamental understanding about the catalytic steam gasification of some species under low temperature conditions. His research , in particular focused on the role and relative importance of controlling parameters such as temperature and the heating rate on the composition of the products. In the experimental study temperatures changed from 200 to 800 °C and investigated the catalytic and non catalytic situation. The residence time changed as 20 min to 2 min. Addition of catalyst particle changed the selectivity of gasification reaction enhancing hydrogen production while reducing the level of methane produced at temperature above 500 °C. At lower temperatures the catalysts appeared to have no significant impact of hydrogen yield although they increased the yield of methane. A relatively low reaction temperature of 600°C and a high steam content of about 90% showed the strongest tendency for maximizing the hydrogen production.

Midilli et al. [25] investigated the potential of hydrogen production from hazelnut shells by using a downdraft gasification. The effect of air fuel ratio and oxidation zone temperature on the production of hydrogen gas were discussed. In their study the endothermic and exothermic reactions took place between 821 and 1021 °C at the oxidation zone of downdraft gasifier. The air fuel ratio were between 1.37 and 1.64 m3/kg. The flow rate of hydrogen gas and the temperature of oxidation zone decreased with the increase of the air fuel ratio. The production of hydrogen gas was sufficiently achieved at between 1.44 and 1.52 m3/kg of air fuel ratio. The hydrogen yield obtained in the down draft reactor was almost 2.4 kg/h of hydrogen from 100kg of wet hazelnut shells.

Midilli et al. [26] also studied hydrogen production from sewage sludge via fixed bed gasifier product gas. In their study, the endothermic and exothermic reaction took place at temperatures between 1009 and 1077 °C in the oxidation and reduction zone of downdraft gasifier for all runs. While feed of wet sewage sludge changed from 2.8 to 3.9 kg/h mass flow rate of hydrogen gas range from 0.045 to 0.082 kg/h

The gasification processes is affected by different factors including temperature, pressure, residence time, properties of feed materials, air to steam ratio and presence of catalyst [1]. Theses parameters are quite interrelated and each of them affects the gasification rate, process efficiency, product gas heating value and product gases distribution.

3.5.1 Effect of the temperature

Temperature appears to have the greatest influence on the performance of the gasifiers. The composition of the volatiles produced from a gasifier depend on the degree of the equilibrium attained by various gasification reactions. All the gasification reactions are normally reversible and the equilibrium point of any of the reaction can be shifted by changing the temperature. Based on the equilibrium of the fundamentals char gasification reactions, the gas composition from a gasifier can be predicted using the method presented by Gumz [27].

The temperature of the gasifier affects on the reaction rate and the composition of the product; reduction in CO, CO_2, and CH_4 occurs, yet more H_2 produced with increasing the temperature [28, 29]. On the other side, the char conversion decreases with the temperature increase. Thus the gasification temperature is needed to be selected carefully as a tradeoff between the char conversion and the H_2 output. However, other research [30] shows that high H_2 yield can be obtained at low temperature (600^{o}C) by using 90% steam content.

At high gasification temperature, particularly between 800 and 850°C, produce a gas mixture rich in H_2 and CO with small amounts of CH_4 and higher hydrocarbons. At low temperatures, solid carbon and CH_4 are present in the product gas. In actual gasifiers solid carbon is carried away to the catalytic bed and is deposited on the active catalyst sites thereby deactivating the catalyst. It is necessary to ensure that the product gas is free of any solid carbon. As temperature increase, both carbon and methane are reformed. At about 726 °C both are reduced to very small amount and in the process get converted into CO and H_2. This explains the increase in hydrogen mole numbers. At about 756 °C, the hydrogen yield reaches a maximum values of about 1.33 moles. At higher temperatures the H_2 yield starts reducing. This is attributed to the water gas shift reaction.

Like most chemical reactions, the rate of gasification is highly dependent on the temperature [15]. Scott et al [31] reported that the product gas yield in the flash pyrolysis of maple saw dust increased as the reactor temperature increased whereas the liquid and solid products decreased with increase in the pressure. The decreasing the amount of the char indicated that the conversion increased with increase in the temperature. Elliot and Sealock [32] reported that 10 % and 50% basis conversion of the lignine at 350 and 450 °C, respectively was attained.

Tars are normally produced during the pyrolysis stage and are favoured by the low temperature. Van den Aaresen et al. [33] reported that a drastic decrease in tht tars content from 6290 mg/Nm^3 dry gas at 740 °C to 412 mg/Nm^3 at 850 °C of the producer gas with increase in the temperature during air gasification of beech wood. Beck and Wang [34] found that the tar content of the gas from steam wood gasification is decreased from 3.17% at 504 °C to 0.58 % at 780 °C.

Elevated temperature help to crack tars to simple gases such as CO, H_2,CO_2, hydrocarbons and char by thermal cracking or by steam reforming. Scott et al (34), reported that in the fast pyrolysis of wood , CH_4, C_2H_4, C_2H_2 increased with increases in the temperature over the range tested (500-800 °C). The yield of higher hydrocarbons (C_3-C_8) decreased with increase in the temperature over 650 °C which indicated the commencement of the cracking/ reforming reactions. Other gases (H_2, CO) also, increased with the increase in the temperature.

Carbon dioxide is reported to generally decrease with increasing temperature. Brink [15] found water, CO and H_2 yields to decrease rapidly with increase in the temperature above 600 °C. The decrease in the water content in the producer gas showed that the C-H_2O reaction was occurring and carbon dioxide was consumed by the reaction. Another source of the CO, CH_4, C_2H_4 is the reforming of the tars and higher hydrocarbons. These reactions result in reductions of the solid residue and tars and corresponding increase in the total gas yield and reactor temperature.

The first order constant of the gasification was found to increase with temperature according with Arrhenius equation. Brink [15] pointed that gasification rates are too fast and are controlled by heat and mass transfer rates above 900 °C while in the range of 600-900 °C, the gasification reaction are rate controlling, below 600 °C the gasification reaction are very slow.

The heating value of the producer gas is also, influenced by temperature. Kumar et al [34] found that the calorific value of the crop residue gasification producer gas to increase with temperature steadily up to 700 °C and then decrease. The increase in the gas heating value must be due to the increasing concentration of CO, H_2 and hydrocarbon gases in the gas mixture. The decline at higher temperatures is probably due to the cracking of hydrocarbons.

Beck et al [35] Reported that the off gas from a pilot plant reactor volumetric yield increased from 0.36 nm3/kg at 517 °C to1.15 m^3/kg at 636 °C whereas the gas heating value increased from 9 to 12 MJ/m^3 within the same temperature range. The increase in the heating value was attributed to an increase in ethylene concentration of the off gas. Energy recovery and carbon conversion, also increased from 20 to 60%. An axial temperature gradient as high as 227°C was noted in the reactor [36].

Lv et al [37] have investigated the reactor temperature on the gas composition and gas yield. The results showed that higher temperature contributed to more hydrogen production but too high temperature lowered gas heating value.

3.5.2. Effect of pressure

Pressure increases equilibrium H_2 and CO yields reduce. Simulation carried out to study the effect of reducing pressure below 101.3KPa on equilibrium product yield showed that increase in H_2yield is negligible even for pressures as low as 10.13 KPa.

The role of increased pressure has been investigated on the equilibrium percentage of various species in the dry gas, unconverted char, calorific value of the gas, gasification efficiency, outlet gas temperature and heat absorbed in the reduction zone. It follows that the percentages of CO and H_2 decrease as the pressure increases, as expected from Chateliers principle, while the CH_4, CO_2, N_2 and unconverted char grow with increasing the pressure

The calorific value of the gas decreases as the pressure increases, since the percentage of H_2 and CO decrease significantly, as compared to the improvement in pressure is not so significant on the calorific value of the gas and the gasification efficiency.

Pressure has been reported to have a significant effect on the gasification processes. Nandi et al [37] found that the weight loss during the devolatization of crop residues in N_2 atmosphere at 815 °C, to decrease with increase in the pressure. However, at a constant temperature, the first order rate constant for the char gasification increased with increase in the pressure. Using a gasifying medium at 50:50 H_2O/N_2 at a temperature of 815 °C, the values of the rate constant for wood char were 0.101, 1.212 and 0.201min^{-1} at a pressure of 0.17, 0.79 and 2.17 MPa, respectively.

The gasification rate of crop residues char prepared at atmospheric pressure increased with increase in the pressure. The increase was more significant at high temperature (900-950°C). The increase in the char rate with increase in the pressure was reported by several authors. Increasing the pressure was found to cause a significant increase in the yield of methane. Another advantage of pressurized reactors is the high reaction rate which allows for a smaller reactor vessel. Richard [38] found that the H_2/CO and CO_2/CO molar ratios to increase with increase in the total pressure of a char-steam gasification processes.

3.5.3 Effect of equivalence ratio

The equivalence ratio has the strongest influence on the performance of the gasifier because it affects the bed temperature, the gas quality and the thermal efficiency.

The ratio between the theoretical and practical air demand in steam gasification process utilizing air or O_2 is termed the equivalence ratio (ER). For each kind of biomass, there is a theoretical O_2 demand needed to achieve the combustion based on its contents of combustible materials, yet gasification is based on realizing relatively partial combustion, thus fraction of this ration is the only used, a ratio of 0-0.3 has been investigated, and it comes up that high that ER promotes the gasification by increasing the temperature, meanwhile, decreases the lower heating value of the produced H_2 by having dilute output. High ER decreases significantly the H_2 production, while increases radically the CO_2 output.

Ergudeneler [39] observed that increasing the equivalence ratio resulted in lower pressure drop both in the dense bed and the freeboard regions when the gasifier operated at different fluidization velocities and bed heights.

Beck et al [40] reported that higher equivalence ratios increased in the gas production rate in air gasification. The gasifier temperature was found to increase with increases in the equivalence ratio because of increase in the exothermic reactions. On the other hand, a very low equivalence ratios results in very low bed temperature which produces a lower gas and higher tar yields.

3.5.4 Effect of biomass characteristics

Characteristics of biomass are determined through the physical properties , proximate and ultimate analysis. Physical properties contain the particulate size, absolute density and bulk density. Proximate analysis includes the volatile matter, moisture content, fixed carbon, ash content and gross calorific value and the ultimate analysis comprises the carbon, oxygen, nitrogen and sulfur of the dry biomass on a weight %.

Feed materials moisture content The moisture content affects the reaction temperature due to the energy required to evaporate the water in the fuel and the gasification processes takes place at lower temperature. Gray et al [41] reported a decrease in the gasifier temperature with increase in the fuel moisture content. Elliot and Sealock [32] reported that on the conversion of lignine of lesss than 10 %w basis moisture content at 350 °C and about 40 % w basis 450 °C. They found that the higher moisture content the higher produced char.

Feed material particle size. Agricultural wastes and other materials used as feed stock for the gasification process can be used in different sizes; fractions ranging from 0.075 mm to 1.2 mm have been investigated experimentally; the results reveal the smaller the particle size, the more the hydrogen produce, carbon conversion, and less tar formed [42]. Moreover, smaller particle size affects positively the low heating value (LHV) of the produce gas [43].

Raman et al. [44] reported that the feed particle size fraction of feed lot manure did significantly affect the gasification results. For a given temperature, the produced gas yield increased with a decrease in the manure particle

size. For example, the gas yields for the smallest size fraction increased from 0.51 m^3/kg at 627 °C to 0.81 m^3/kg at 737°C and for the largest size fraction, the gas yield increased from 0.1 to 0.6 m^3/kg for the same temperature range. The heating value versus temperature plots for each particle size fraction were parabolic in shape with the maximum heating value being for the smallest particle size fraction, the heating value increased from 14.3 MJ/m^3 at 627 °C to 19.8 MJ/m^3 at 980 °C and then decreased to 12.0 MJ/m^3 at 737 °C. The produced gas composition was also significantly affected by the manure particle size.

Lv et al [37] have investigated the particle size of biomass (02-0.9) mm on the gas composition and gas yield. The results showed that smaller particle size was more favorable for higher gas composition and yield.

3.5.5 Effect of gasification agents

Biomass can be gasified using different gasifying media, the choice of which depends on the desired product gas composition and energy consideration. Commerical and research gasifers generally use steam or air as the gasifying media. Air gaification is an exothermic process which produce a low heating value rich in CO and having small amount of H_2 and higher hydrocarbons. Steam gasification on the other hand is an endothermic processes, which produce a medium heating value gas rich in H2 and CO.

Tomeczek et al. [45] used air steam mixture in the gasification process of coal in fluidized bed reactor. The results showed that the influence of steam to air ratio on char tied was particularly strong at small ratio due to the fact that the steam released at the devolitization stage contributed to the gasification process even in the case when steam was added. When the steam-air ratio increased the heating value was increased and reached its peak at 0.25 kg/kg.

Schoeters et al [46] investigated the effect of air to steam ratio on the gasification of wood shavings. An increase in the steam flow rate resulted in lowering the gas yield, the heating value and the energy recovery, although the reactor was heated from outside which helped to keep the temperature constant without any adjustment of the flows.

3.5.6 Effect of biomass /steam ratio

Gasification agent role is distinct on the output gas composition, yet there are contrary recorded data about its impact. Some studies [5] records that higher ratio has a positive impact on raising H_2 production ratio, while others [43,44] shows it has adverse effect. This can be accounted for by employing different gasification systems [5] which indicate that this ratio is dependent and pertinent to the entire system configuration.

The steam biomass ratio (STR) refers to moles of steam fed per mole of biomass, like temperature has a strong influence on both product gas composition and energy input. At low values of steam biomass ratio, solid carbon and methane are formed. As more steam is supplied, both of these species are reformed to CO and H_2. For SBR >1 solid carbon and methane moles reduce to very small values and CO and H_2 yields increase monotonically; CO on the other hand reduces monotonically.

3.5.7 Effect of turndown ratio

Turndown is defined as the ability of the gasifier to respond to the changes in the demand for the product gas with different capacity of biomass and at the same time, operated with a stable reaction zone. Turndown is often quoted in the gasifier trade leaflets, but most of these are ambiguous. It was observed that turndown ratio goes up almost linearly with the increase of the capacity of the dry fuel as well as the amounts of the produced gas and combustible gas. So, the Turndown ratio is calculated by the following equation [36]:

$$\mathbf{R_{td}=C_{db}/C_{mdb}}$$

Where R, td,C,db and mdb stand ratio, turndown, capacity dry biomass and maximum dry biomass

3.5..8. Effect of gas hourly space velocity

Tars are undesirable products in biomass thermo-chemical gasification processes for a number of reasons. There are a number of methods to separate or reform tars from the product gas like wet scrubbing, thermal cracking or catalytic cracking. Wet scrubbing does not eliminate tars but merely transfers the problem from gas phase to condense phase. Thermal cracking is a hot gas conditioning option but it requires high temperature to achieve high conversion efficiencies. This process may also produce soot which is unwanted impurity in the product gas stream [36].

The GHSV is defined as the ratio of volumetric flow of reactants at standard conditions to the total catalyst volume and has units of inverse time.

3.5. 9. Effect of catalyst used.

The effect of catalyst on gasification products is very important. Gaseous products leaving the reactor contained mainly CO, CO_2, H_2, CH_4, light hydrocarbons and some other organic vapors. The use of catalyst did not affect the gas yields but the composition of the gases was strongly influenced. The content of hydrogen and CO_2 increased, while that of CO decreased, a drastic reduction in the content of organic compounds could also be observed. Because the char yields almost constant compared to an equivalent non catalytic thermal run, the increase in the content of hydrogen (hydrogen rich gas) was probably due to the influence of catalyst on the shift reaction [47-69]. Three distinct groups of catalysts materials have been mentioned for biomass gasification and are described in the following sections [47]

Effect of dolomite catalysts. Dolomite, a magnesium ore with the general formula $MgCO_3.CaCO_3$ is used in the Pidgeon process for the manufacture of magnesium by thermal reduction.

The use of dolomite as a catalysts in biomass gasification has attracted much attention since it is a cheap disposable catalyst that can significantly reduce the tar content of the product gas from a gasifier. It may be used as a primary catalyst, dry mixed with the biomass or more commonly, in a down stream reactor in which case it is often referred to as guard bed [47, 53]

Aznar et al. [16] investigated the use of dolomite for steam/oxygen gasification. They reported that the H_2 content of the flue gas increased by 7 vol%, while the CO content decreased by 7 % vol. This effect was due to a greater contribution of the water gas shift reaction as a result of a high steam content and high temperature.

Effect of alkali metal and other metal catalysts. Fung and Graham [50] showed that potassium carbonate and calcium oxide increased the gas production in the gasification processes. Rolin et al·[51] reported that for wood gasification at 900 °C, potassium carbonate is the most efficient catalyst of all carbonates (Na_2CO_3, K_2CO_3, $CaCO_3$) tested. Hallen at al. [52] showed that the addition of alkali a cesieum carbonate to crop residue either by solution impregnation or dry mix increased the gas production in the crop residue steam gasification.

Mudge et al. [53] studied the gasification of biomass with steam and CO_2 in the peresene of alkali carbonates at 750 °C. The alkali carbonates K_2CO_3 and Na_2CO_3 were impregnated on the wood at two concentration 8% and 4 % kg/kg for K_2CO_3 and 6%, 3% kg/kg for Na_2CO_3. Both catalyst increased the char gasification rates. Potassium carbonate is more effective than sodium carbonate in this respect. The catalyst increased the total gas yields, enhanced H_2 and CO_2 production and decreased CO concentration in the product gas.

Effect of nickel catalyst. The most significant body of literature published on the area of hot gas cleaning for biomass gasification concerns nickel catalysts. Several groups have investigated system of raw gas cleaning that involves a dolomite or alkali catalyst for the removal of tar. Up to 95 % followed by the adjustment of the gas composition (reforming of methane and the remaining tar) using nickel steam reforming.

Aznar et al [16] investigated several commercially available catalyst for the removal of tars and the adjustment of the product gas composition. Two Haldo Topse catalysts were investigated for the steam reforming of the tar and methane. The catalyst was positioned downstream of the gasifier in a secondary reactor that was maintained at temperatures between 730 and 760 °C, space time of only 0.1s were used.. Catalyst R-67-7H is described as 12-14% Ni on Mg/Al_2O_3 support with a free Mg content of less than 0.5 wt% and SiO_2 of 0.2 wt%. The conversion of tar, methane and C_2 and C_3 were greater for the reduced catalyst.

Modification of nickel catalyst by the addition of promoters have also been investigated. Newly developed Ni on dolomite catalyst exerted high activity and stability under a short contact time of W/F; 0.55gh/mol, for gasification of tar by steam, which was investigated by using toluene as the model compound. Moreover, the performance of the Ni/dolomite catalyst gave negligible carbon deposition, while the conventional supported Ni catalyst gave fairly large carbon deposition. It was found that the calcinations temperature significantly influence the property and the activity of the Ni/dolomite catalyst.

Tomishige et al [64-67] have studied the catalytic gasification of biomass at much lower temperature than the usual methods such as non catalytic and dolomite catalysed gasification. It was found that the $Rh/CeO_2/SiO_2$ with 35% CeO_2 content showed the best performance with respect to the carbon conversion and product distribution. Enough fluidization is very important for the removal of char deposition on the catalyst surface. In addition the introduction of air from the bottom of the reactor is also very important because of the direct contact between the catalyst and the oxygen molecules. The catalyst of this process has the high activity of the combustion and reforming and the smooth redox properties. The fluidized bed reactor plays important roles in the mixing of the catalyst and pyrolysed products of biomass and catalyst circulation between reduced and oxidized states. Almost no tar and char were yielded under the conditions of the feeding rate=12g/h, equivalence ratio=0.12, steam feeding rate=1.8g/h and weight of catalyst/feeding rate of biomass=0.25h at 600 °C and this makes the process useful.

3.6. Over-view on gasification technology

Gasification is a century old technology that flourished quite well before and during the second world war. The technology of gasification disappeared soon after this war, when liquid fuel became easily available. Interest in gasification has undergone many ups and downs during the century. Today as the world supply of the crude oil is decreasing, the fuel price is increasing and environmental concerns, there is renewed interest in this technology of gasification process. Gasification has become more modern and quite a sophisticated technology.

The advantage of gasification technology is a decentralized energy conversion system that operates economically even for small scale. A gas producer is a simple device consisting of a usually cylindrical container with space for fuel, air inlet, gas exit and grate. The design of the gasifier depends upon the type of the fuel used and whether the gasifier is portable or stationary.

Gasification is a thermo-chemical process that convert biomass materials into synthesis gas or hydrogen rich-gas. The producer gas, contains hydrogen, carbon monoxide, methane and some inert gases.

Based on the design of the gasifiers and type of the fuel used, there are different kinds of gasifiers. Portable gasifiers are mostly used for running vehicles. Stationary gasifers combined with engines are widely used in rural areas of developing countries for many purpose including generation of electricity and running irrigation pumps. Technologies such as biomass gasification which allow utilization of biomass fuel are of great importance.

Biomass and coal gasification technology is rapidly advancing and being placed into commercial use. The gasification process is attractive because pollutants such as artificial water gas made in this way can be performed to hydrogen rich gas [48-49].

CONCLUSION

Research and development on new process of gasification is directed towards production of hydrogen rich gas from biomass The parameters has affecting on the gasification of biomasss such as (temperature, gasifying agent/biomass ratio, pressure) and of the materials, type of biomass, type of gasifier) on the performance of the gasification system was clarified which allow to increase yield of hydrogen gas. Key parameters for successful are the feedstock properties and the feedstock pretreatment.

For the third world the use of a simple and robust technology represented by gasification can assist the development of the rural economies by providing the electricity produced from local sources of biomass.

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