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Optimization of the Operating Conditions for Tailored Syngas Generation from Biomass Gasification under Simulated Reactive Media

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Abstract **-** The present study is contributed to developing a numerical model using the Aspen Plus process simulator to investigate the influence of reactive media on biomass gasification systems. The energy performance of the biomass gasification system was examined at 900ºC. A parametric examination is conducted to study the influence of the critical parameters. The equilibrium modeling approach concluded that the theoretical carbon conversion rate was nearly constant at 75% in both cases: oxy-steam and steam-CO_2 gasification. The theoretical cold gas efficiency is enhanced by increasing the input percentage of CO_2 in steam, whereas it shows a declining trend with an increase in O_2 content in steam. Nevertheless, oxy-steam gasification promotes hydrogen-rich syngas by assisting combustion reactions facilitating auto thermal gasification. This analysis is pivotal to studying the effect of reactive gas agents on syngas quality and its utilization purpose.

Keywords**:** Biomass, oxy-steam gasification, CO_2 utilization, syngas, H_2/CO ratio, renewable fuels.

1. Introduction

In recent decades, the major challenge for mankind has been to fulfil the ever-increasing energy demand. To procure this energy, fossil fuels have been used as the conventional energy sources, which generate CO_2 in the atmosphere and lead to global greenhouse gas emissions. As these conventional energy sources are depleting faster and are disadvantageous in environmental sustainability, future energy sources may be found from renewable energy sources (viz., solar, wind, biomass, geothermal, etc.). One such energy source, bioenergy, has gained considerable attention in the research field of energy production. Biomass being in global abundance and a carbon-neutral energy source makes it the best alternative to fossil fuels [1].

Several thermochemical conversion routes can generate fuel gas from biomass. Yet, the most promising thermochemical technique yielding high conversion efficiencies and meeting the terms with the noxious emissions international policies is biomass gasification. In gasification, feedstock elemental composition and reactive gas agents play a significant role, and there is a need to look for the feedstocks and input reactive media that are appropriate for commercial energy growth. Steam gasification is a widely conferred technology for generating syngas with a moderate range heating value [2]. The major syngas components are H_2 and CO with some amounts of CO_2, CH_4, and H_2O and higher hydrocarbons (HHCs). Using discrete reactive agents in steam can be rewarding in hydrogen production, achieving carbon negativity, and generating syngas with flexible H_2/CO ratios for various chemical syntheses.

Steam used as a reactant along with oxygen stimulates higher hydrogen yields. Hydrogen is a promising fuel for clean energy technology [3]. Approximately 49% of hydrogen is utilized only in ammonia production for the agriculture sector [4]. Also, to improve air quality, the use of hydrogen fuel is growing in the automobile sector and power generation. On the contrary, CO_2 gasification facilitates CO gas generation, which is useful in producing various chemicals such as organic acids, polycarbonates, and agricultural chemicals. These processes require a controlled H_2/CO ratio. The inclusion of CO_2 in steam will also inhibit H_2 concentration and increase CO formation via the Boudouard reaction that enhances the energy performance of the gasifier. It is also an essential process if the goal is to produce syngas with a low H_2/CO ratio to meet the availability of fuel gas for petrochemical applications that can be more easily transported than hydrogen.

Modeling and simulation of biomass gasification have gained substantial momentum in recent times. The computational analysis benefits from studying the result of different operating conditions and input parameters, escaping costly and time-consuming experimentations. In order to avoid gasification process intricacies and develop the simplest model that could incorporate the primary reactor operating conditions and principle gasification reactions, the Aspen Plus process simulator is an optimum simulation program [5, 6].

In the present study, a numerical model using the Aspen Plus process simulator is developed to investigate the influence of reactive media on biomass gasification. The energy performance of the gasification system is examined at 700ºC for SBR=0.9, 1. The equilibrium model is validated against the experimental results of Fremaux et al. [7] for syngas composition. Moreover, a parametric examination is conducted using an equilibrium modeling approach to study the influence of the critical parameters such as reactive gas agents, H_2 production, CO_2 and CO conversion, syngas heating value, and gasification efficiency with O_2-steam and steam-CO_2 as discrete gasifying agents. The simulation results specified optimum operating conditions for the reactive oxy-steam and steam-CO_2 gasification process to obtain tailored H_2/CO ratios intended for chemical synthesis.

2. Methodology Opted

Aspen plus process simulator is opted for the gasification analysis employing Gibbs free energy minimization approach. The reactor is assigned into discrete unit blocks for drying, pyrolysis, and gasification. Peng Robinson with Boston Mathais (PR-BM) function is incorporated from the fluid package as it can suitably handle the higher hydrocarbons (HHCs). HCOALGEN and DCOALIGT models are used to determine the enthalpy and density of non-conventional components; biomass and ash. The primary assumptions considered in the modeling approach are: (1) reactors operating at atmospheric conditions; (2) adiabatic and isothermal thermodynamic conditions; (3) ideal gas laws are followed by all the elements and gaseous compounds; (4) char is solid carbon and ash is an inert residue material; (5) insignificant formation of tar and HHCs.

To validate the model against the experimental data, root mean square deviation (RMS) was calculated using the following formula:

$$RMS = \sqrt{\frac{\sum_i^N (\exp erimental_i - \mathrm{mod}\, el_i)^2}{N}} \tag{1}$$

Where N depicts the number of data points taken for comparison.

The LHV of syngas and HHV of biomass (MJ/Nm^3) was calculated from the following formulae [6, 9]:

$$LHV_{syngas} = 12.62 y_{CO} + 10.79 y_{H_2} + 35.81 y_{CH_4} \tag{2}$$

$$HHV_{biomass} = 0.312(\%FC) + 0.1534(\%VM) \tag{3}$$

The carbon conversion and cold gas efficiencies of syngas are calculated from the following formulae:

$$CCE(\%) = \frac{Carbon\ in\ gas\,(mol/h) - Input\ carbon\ in\ CO_2\,(mol/h)}{Input\ carbon\ in\ biomass\,(mol/h)} \times 100 \tag{4}$$

$$CGE(\%) = \frac{m_{syngas} LHV_{syngas} \times 100}{(m_{biomass} H_{biomass} + m_{steam} H_{steam})} \tag{5}$$

The chief gasification reactions used in the thermodynamic modeling are demonstrated in Table 1. The elemental and proximate analysis of the legume straw used in the sensitivity analysis is summarized in Table 2. Findings from the open literature were incorporated into the study for model validation and justification of the analysis.

Table 1. Gasification reactions exercised in the equilibrium modeling [6].

Reaction symbol	Gasification reactions	Reaction name
R1	$C+1/2O_2 \rightarrow CO$	Partial oxidation
R2	$C+O_2 \rightarrow CO_2$	Char combustion
R3	$C+CO_2 \leftrightarrow 2CO$	Boudouard reaction
R4	$C+H_2O \leftrightarrow CO+H_2$	Char reforming reaction
R5	$CO+H_2O \leftrightarrow CO_2+H_2$	Water gas-shift reaction
R6	$C+2H_2 \leftrightarrow CH_4$	Methanation reaction
R7	$CH_4+H_2O \leftrightarrow CO+3H_2$	Steam-methane reforming reaction

Table 2. Ultimate and proximate analysis of legume straw [9]

Ultimate Analysis	(wt. %)	Proximate Analysis	(wt. %)
Carbon	43.30	Ash	1.62
Hydrogen	5.62	Volatile Matter	73.74
Nitrogen	0.61	Fixed Carbon	14.84
Oxygen	50.35	Moisture content	9.80

The Aspen Plus modeling scheme for the biomass gasification process is demonstrated in Fig.1. The elemental and proximate analysis of biomass is specified in non-conventional feed and; feedstock of 10 kg/h feed rate, WETFEED is delivered into the unit operation model DRIER to separate moisture from the feedstock via calculator block employing FORTRAN code. The dried biomass is then forwarded to the PYROL unit, which is RYIELD reactor. The PYROL model uses another FORTRAN calculator block that converts non-conventional biomass components into the conventional elements, viz. carbon, oxygen, hydrogen, nitrogen, sulphur, moisture, and ash on a mass basis. The ash is separated from the pyrolysis products via the SOLIDSEP separator. The VMATTER stream leaving the PYROL unit enters the GASIFY unit model, a GIBBS reactor that works on the principle of Gibbs free energy minimization. The chief gasification reactions are incorporated in the GASIFY module, and simulated gas (O_2-steam/ steam-CO_2) is fed in the unit block. The gasification products are cooled via COOLER, and then syngas is obtained in the GAS stream.

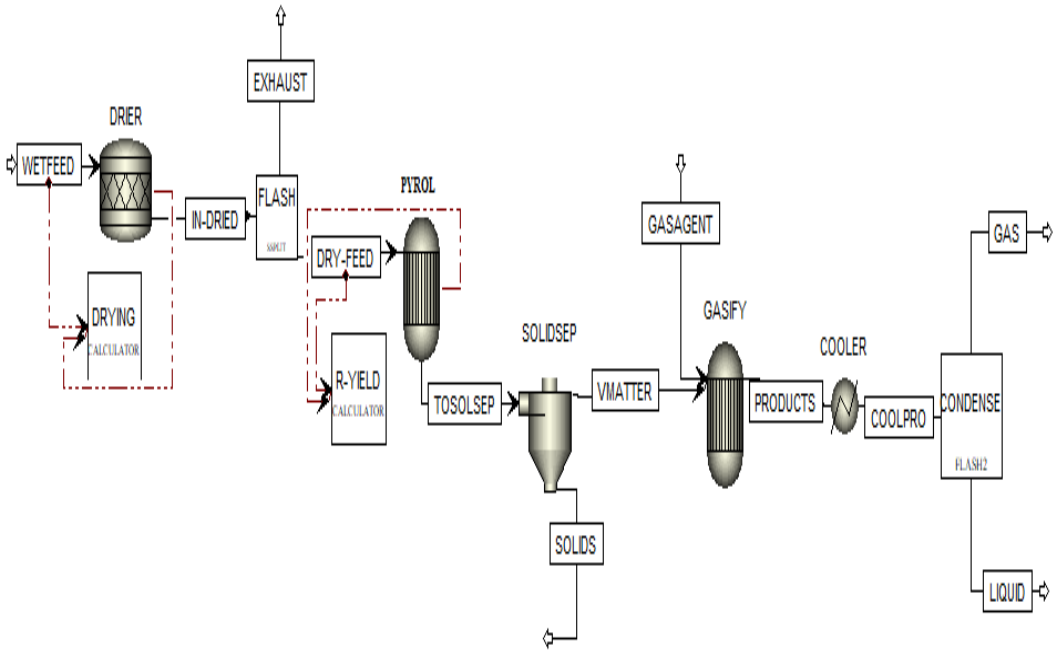

Fig.1. Process description of biomass gasification via aspen plus simulator.

4. Results and discussion

4.1 Model validation

The syngas compositions are predicted using the thermodynamic equilibrium approach and validated against the experimental data of Fremaux et al. [7]. Table 3 depicts the comparative analysis of the steam gasification of simulation and experimental data at 700ºC and steam to biomass range (SBR) values of 0.9 and 1. Since the biomass steam gasification model is based on the equilibrium approach, it is assumed that the maximum number of reactants are converted into products in a sufficient reaction time. Yet, equilibrium is not attained in a gasifier working under practical operating conditions.

With increase in SBR from 0.9 to 1, the CO concentration is slightly decreasing while CO_2 concentration is rising, both experimentally and numerically. This is due to the enhanced steam flow rate that triggers steam-methane reforming reaction (R7). The model results show underprediction of CH_4. Similar numerical trends of CH_4 underprediction has been reported in literature also and the possible reason of high CH_4 formation in a real working gasifier may be due to the partial thermal cracking of the pyrolysis products [5, 8,11]. The remaining syngas volume fractions were reasonably predicted by the model. The overall root means square deviation (RMSD) of 4.99 validates the good agreement between simulation and experimental results.

Table 3. Comparison of model with experimental results [7].

Gas vol. fraction (%)	**SBR=0.9**		**SBR=1**		**RMSD**
	Exp.	Model	Exp.	Model	
H_2	49.60	48.20	51.0	47.40	2.73
CO	19.70	19.63	18.86	17.84	0.72
CO_2	16.0	12.50	16.31	12.93	3.44
CH_4	11.45	0.93	12.40	0.72	11.15
RMSD		5.58		6.36	

4.2 Sensitivity analysis

The devised model is further employed to perform sensitivity analysis. The process optimization is performed for the CO_2-steam and oxy-steam gasification of legume straw as feedstock [9]. The effect of reactive agents in steam on gas composition, LHV, cold gas efficiency, and carbon conversion efficiency at 900ºC is investigated. The feed rate of biomass and input steam is kept at 10kg/h and, the effect of replacement of steam by CO_2/O_2 is studied.

4.2.1 Influence of CO_2 inclusion in steam

The effect of the replacement of steam by CO_2 on the syngas composition and LHV at 900 ºC is depicted in Fig.2 (a). H_2 and CO are the two major syngas constituents that sway the heating value of syngas. As the amount of CO_2 in steam increases to 50%, CO concentration increases due to the triggering of the Boudouard reaction (R 3). The LHV of the syngas in pure steam gasification is 8.865 MJ/Nm^3 and it fairly becomes consistent at 50% of CO_2 inclusion.

Fig. 2(b) represents the carbon conversion efficiency and cold gas efficiency of the syngas using steam-CO_2 as co-gasifying media. The equilibrium modeling results reported that the carbon conversion remained constant, i.e., 75% irrespective of the change in gasifying media. This suggests that the replacement of H_2O by other oxidizing media neither enhanced nor depreciated the conversion of carbon into gas. The cold gas efficiency (CGE) demonstrated the useful energy in the syngas for the input biomass energy. As the CO_2 concentration is enhanced, the CGE of the syngas enhanced from 45% to 59%. This rise in CGE may be attributed to the more CO formation due to the dominance of Boudouard reaction (R3) due to the reaction of char with CO_2 in the gasifying media.

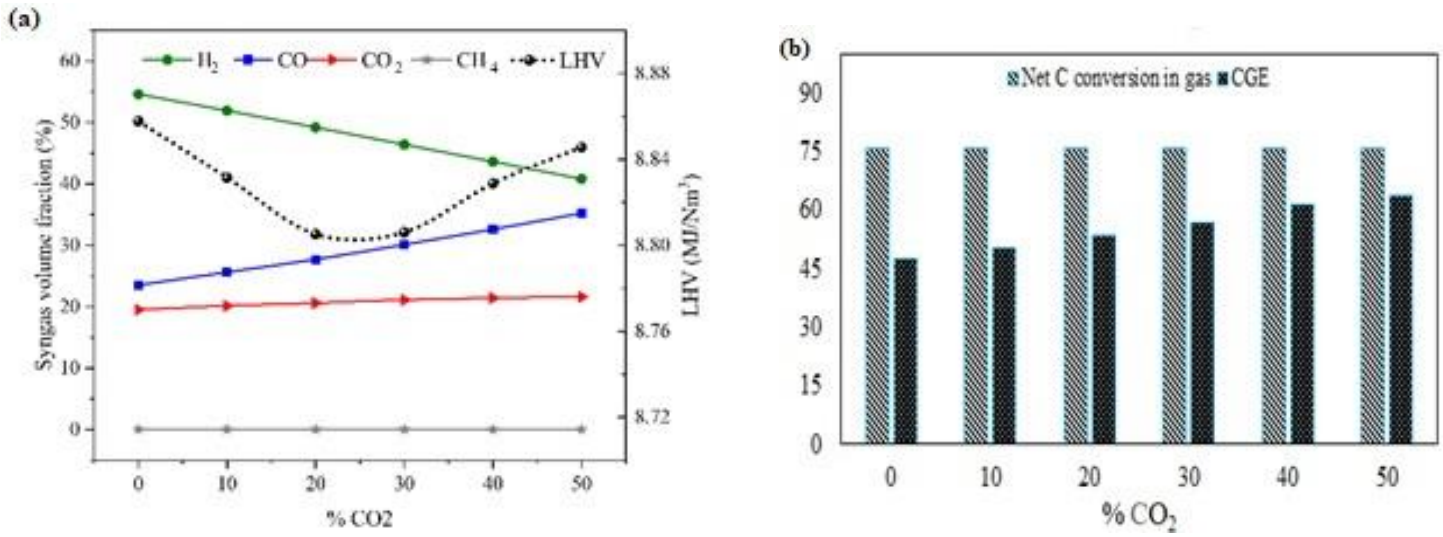

Fig 2. Effect of CO_2 concentration on (a) syngas composition and LHV and, (b) CCE and CGE

4.2.2 Influence of O_2 inclusion in steam

Fig. 3(a) demonstrates the effect of O_2 inclusion in steam. Increase in O_2 concentration in steam favours combustion reactions that lead to more formation of CO_2 and H_2O. Therefore, in this case, it is required to vary and optimize the composition of steam and oxygen simultaneously to generate maximum H_2. In Fig. 3(a), O_2 inclusion up to 15% generates nearly 55% of H_2, nearly same composition as in steam gasification. Pure steam gasification is an energy-intensive and uneconomical process. Therefore, to sustain the flame in the combustion zone and conduct auto-thermal gasification, oxygen in a small amount with steam facilitates hydrogen-rich syngas. The volumetric concentration of CO in oxy-steam gasification declines as the O_2 concentration rises due to oxidation reactions. This hydrogen-rich syngas may be utilized in hydrogen generation as green fuel or in ammonia synthesis.

Fig. 3(b) depicts the syngas' carbon conversion and cold gas efficiency. Since the LHV of syngas declines with an increase in O_2 concentration in steam, the cold gas efficiency of the syngas declines from 47.48% in pure steam gasification to 36.77% in an equal mass proportion of steam and oxygen. From this point of view, the primary purpose of oxy-steam gasification is to generate hydrogen-rich syngas usable in ammonia synthesis and hydrogen fuel in the transport sector [12]. This derived hydrogen energy can find applications in fuel cells to promote cleaner energy production. Moreover, H_2/CO ratio can also be tailored via oxy-steam gasification for various chemicals synthesis. Table 4 depicts the temperature and concentration range of the reactive media to tailor the H_2/CO ratio between 1 and 2.

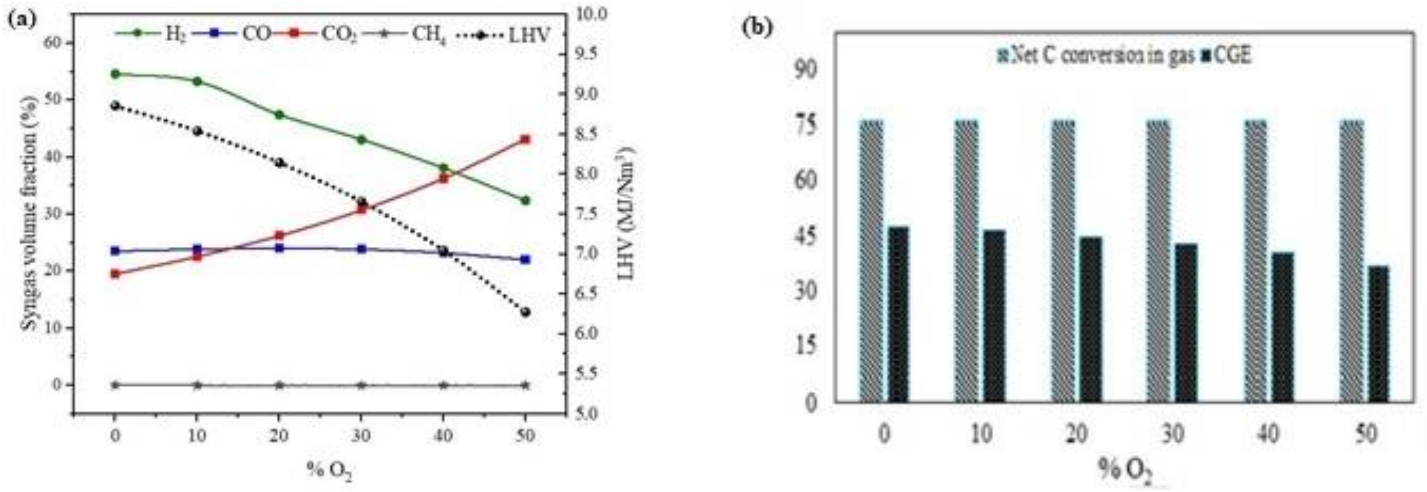

Fig. 3. Effect of O_2 concentration on (a) syngas composition and LHV and, (b) CCE and CGE

Table 4. Optimization of H_2/CO ratio for petrochemical applications.

Chemical application	H_2/CO ratio	Temperature range	Pressure (bar)	O_2 /steam range	CO_2/steam range
Oxo-synthesis	1	900 ~950 ºC	~1	~0.67-1.0	~0.11 - 1.0
Fischer-tropsch synthesis	2	800-950 ºC	~1	~0.11-0.67	~0.11- 0.25

Conclusion

The simulation results reported that steam-CO_2 gasification aided in the adjustment of H_2/CO ratio in syngas intended for downstream chemical synthesis applications. CO_2-steam gasification also enhanced the biofuel energy from biomass and further contributes toward utilizing captured CO_2 as a gasifying input agent to mitigate global greenhouse gas emissions. O_2 in steam gasification facilitated autothermal gasification and stimulated hydrogen-rich syngas production up to O_2 concentration of 15% in steam. This derived hydrogen energy can find applications in fuel cells to promote cleaner energy production and, as an automobile fuel. Thermodynamic modeling results for steam gasification concluded that the optimum reactive agents to biomass ratio and operating temperature favor rich quality syngas production.

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