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Thermodynamic analysis of release volatile species during high pressure gasification of biomass

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Abstract

Biomass gasification released high level of volatile species (e.g. Na-,K-,Cl-, and S).These gaseous species may deposited on super heater tubes leading to strong damage by acceleration of oxide formation moreover also causes of eventual problems such as agglomeration, fouling, slagging and corrosion. Thermodynamic Study of high released volatile species is informative prior to carry out experimental work. Therefore, thermodynamic equilibrium was calculated using FactSage 5.2, simulating gasification conditions at elevated pressure (6, 12 and 18 bar) at 1000 °C. Their releasing order of various volatile species was estimated by plotting mole fraction of each species at elevated pressure (6, 12 and 18bar) at 1000 °C . These calculations predict that H_2S is the most stable species for gasification. At all pressure the lowest amount of SO_2 volatilized for Rice husk while lowest volatilization of kCL for Bagasse. Evolution of NaCl, KCl and HCl depends on the amount of Cl present in both biomass (e.g. Bagasse and Rice husk).

Index Terms: Fact sage, Equilibrium calculations, Gasification, Biomass, release of volatile species

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1 INTRODUCTION

Pakistan is facing serious problem of load shedding [1] because the supply of energy is far less than the actual demand [2]. Pakistan is needed 22000-24000 MW electricity but difference between demand and supply has been reached 6000 MW in 2018, Therefore circular debts have increased up to level of 400 billion [1]. Which badly affected the industry and economy of Pakistan [2][3]. There is only one way to overcome this chronic energy crises is to shift of non-renewable energy sources to renewable energy sources which are cheapest and environmentally friendly [3]. Livestock and Bagasse are two major biomass energy sources of Pakistan [4]. The annual production of bagasse is 65,451 million tons and its utilization in mills is 76.45 [5] and rice husk production is about 1,78 million tons [6][4]. Biomass indirect gasification and combustion may convert biomass energy into 15000MW electricity through biomass-based power plant [3] and also found that biomass gasification technologies as most feasible, environmentally sound and economically viable [7] than electric power generation of coal, wind and disel [6][8].

Unfortunately, the biomass firing power plants at high temperature may cause of high corrosion rate of super heaters due to the formation of complex eutectics which have low melting point and deposit as slag on boiler heating surfaces [9][10] in consequence of higher gas temperature released from boiler which reduce the steam generation and efficiency of power plants [10]. To achieve the requirements for different end application and for environmental regulations the gaseous products and particulate impurities may be removed before the gas product qualify as fuel for gas engine or gas turbine purpose [11][12]

Therefor the comprehensive knowledge of released volatile species during high temperature and pressure gasification is required prior to carryout experiment by utilization of bagasse and rice husk biomass. Thermodynamic equilibrium calculations is the basis for obtaining such information and its method is capable of identifying species that are stable only at high temperature and pressure especially those employed in commercial combustors. The results are useful guidance for predicting the trends occurring during gasification. Therefore the present study simulates the gasification at high pressure (6, 12 & 18) bar at 1000°C and also predict the release of volatile species for bagasse and rice husk using equilibrium calculations by Fact sage 5.2.

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2 MATERIAL AND METHOD

Two kinds of biomass i,e bagasse and rice husk from Thatta sugar Mill and Hyderabad Rice Mill are mainly used. Their proximate and ultimate analysis and ash analysis is given in Table 1 and 2.

3 CALCULATION PROCEDURE

Thermodynamic equilibrium calculations were performed using Fact sage 5.2. The initial model composition is based on the data of elementary and chemical composition relate to 1 g of biomass. The fifteen (15) elements C, H, N, S, O, Cl, Al, Ca, Fe, K, Mg, Na and Si were included in the computation, as listed in Table 1 and 3. The results were calculated by plotting mole fraction of each species Vs pressure and Pressure (6 to 18 bar) at 1000°C for gasification process as shown in Figure 1 to 5 and calculated mole fractions are listed in Table 4. The chemical composition of Pakistani chars is included in Table 3.

4 DEFINITION OF CONDITION

To simulate the condition of gasification for bagasse excess air O_2= 2.1319 g or (213.19 %) and highest syngas amount from (0.1 to 1) the O_2=0.8528 (85.28%) and for rise husk excess air O_2= 2.2426g or (224.26%) and highest syngas amount from (0.1 to 1) the O_2= 0.897 g or (89.7%) was added to the system.

Table: 1 Proximate and ultimate analysis of Bagass and Rice husk

Biomass Type	Proximate analysis				Ultimate analysis				
	M_{ad}%	A_{ad}%	V_{ad}%	$FC_{ad\%}$	$S_{t,ad}$%	H_{ad}%	C_{ad}%	N_{ad}%	O_{ad}%
Bagasse	9.58	3.07	70.05	17.3	0.25	6.21	61.068	0.18	19.642
Rice husk	5.75	20.6	57.36	16.29	0.063	6.924	59.01	5.004	2.65

Note：O_{ad}%=100-A_{ad}%-$S_{t,ad}$%-C_{ad}%-H_{ad}%-N_{ad}%- M_{ad}%

Table: 2 The ash composition and fusion temperature of Pakistan chars

Biomass sort		Bagasse	Rice husk
A_{ad} %		3.07	20.6
Ash	SiO_2/ Al_2O_3	1.32	2.13
Composition analysis of ash, %	SiO_2	45.71	52.5
	Al_2O_3	16.42	10.5
	Fe_2O_3	15.15	5.25
	CaO	5.55	3.23
	MgO	4.44	1.54
	TiO_2	3.62	0.58
	SO_3	0.18	10.55
	k_2O	5.65	11.65
	Na_2O	0.95	1.15
	P_2O_5	1.73	2.53

Table: 3 Chemical composition of Pakistani Chars %

Bagasse Type	Si	Al	Fe	Ca	Mg	Ti	K	Na	P	Cl
Bagasse	0.66	0.133	0.16	0.12 2	0.08	0.07	0.12	0.01	0.015	0.00004
Rice Husk	5.05	0.57	0.37	0.47	0.191	0.075	1.7	0.09	0.145	0.00002

5 RESULTS AND DISCUSSION

5.1 Release of volatile species during high pressure Gasification

The computed release of H_2S , SO_2, NaCl, KCl and HCl under pressurized gasification is listed in Table 4.

On the basis of the calculated mole fraction the release of H_2S is gradually increases with increasing the pressure from 6 to 18 bar, and highest increase is observed at 18 bar both in Bagasse and Rice husk as shown in Figure 1, but higher than SO_2 due to higher gasification product. The increase in volatilization of H_2S may shift the equilibrium to the right side of the reaction, Such changes are mainly as a consequence of the law of Le Chatelier-van't Hoff Law [13]. Therefore the release of SO_2 gradually decrease with increasing pressure and strong decrease is observed at 18 & 12 bar in Bagasse and Rice husk during gasification, as indicated in Figure 2. The results of NaCl and KCl are depicted in Figures 3 and 4. The release of NaCl, KCl is strongly decreases with increasing pressure from 6 to 18 bar for Bagasse and Rice husk. The sharp decrease of NaCl, KCl was observed in Bagasse & Rice husk at 18 bar. The release of HCl gradually increases with increasing pressure 6 to 18 bar for Bagasse and Rice husk as obviously indicated in Figure 5. The sharp increase in mole fraction of Bagasse and Rice husk was observed at 18 bar while the sharp decrease was observed at 6 bar both in Bagasse and Rice husk but volatilization of Bagasse is higher than Rice husk ,this increase and decrease volatilization in Bagasse and Rice husk may be higher content of Cl in Bagasse and lower content in Rice husk but the system is in equilibrium and no effect on reaction will takes place because no of moles of the gas are same on each side of chemical equation of NaCl, KCl and HCl (Lechatelier Principle).

$$Na + Cl \rightarrow NaCl \quad (1)$$

$$K + Cl \rightarrow KCl \quad (2)$$

$$H + Cl \rightarrow HCl \quad (3)$$

Table:4 Calculated mole fraction at pressure 6 to 18 bar and temperature 1000°C for gasification

Alkali Species	Mole Fraction		
	P(bar)	Bagasse	Rice Husk
H_2S	6	9.0243E-04	2.2159E-04
	12	9.0539E-04	2.2495E-04
	18	9.0973E-04	2.2950E-04
SO_2	6	8.9595E-10	1.2414E-11
	12	4.7303E-10	9.4924E-12
	18	3.4194E-10	1.1089E-11
NaCl	6	2.3273E-09	7.0065E-09
	12	1.6541E-09	6.0944E-09
	18	1.3522E-09	5.3995E-09
KCl	6	6.1167E-10	3.0081E-08
	12	4.3473E-10	3.3159E-08
	18	3.5539E-10	2.9378E-08
HCl	6	1.3532E-07	2.1566E-08
	12	1.3667E-07	2.8548E-08
	18	1.3781E-07	3.4460E-08

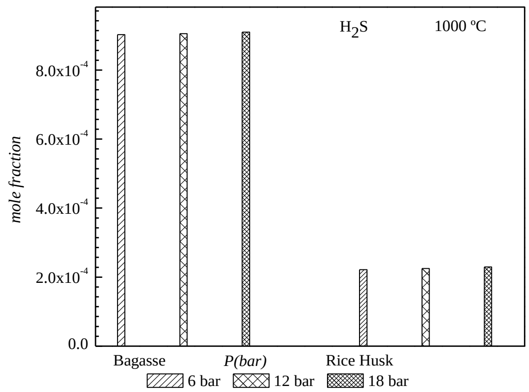

Fig:1 Pridicted results of H_2S at high pressure gasification

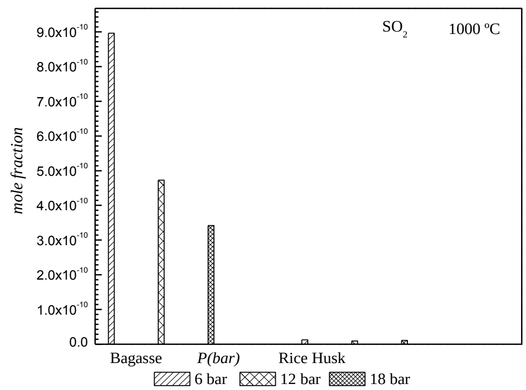

Fig:2 Pridicted results of SO_2 at high pressure gasification

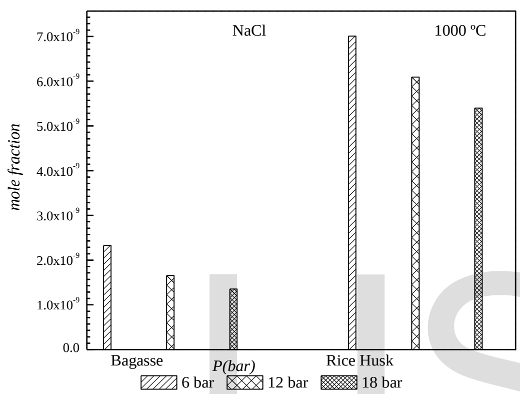

Fig:3 Pridicted results of Nacl at high pressure gasification

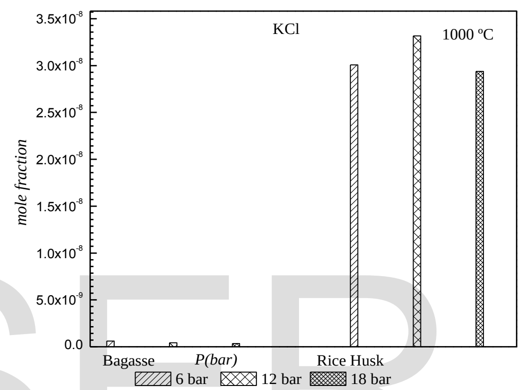

Fig:4 Pridicted results of KCl at high pressure gasification

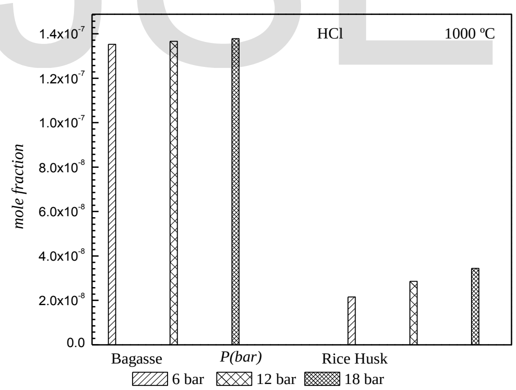

Fig:5 Pridicted results of HCl at high pressure gasification

6 COMPARISON OF PREDICTED GASIFICATION RESUTS OF BAGASS AND RICE HUSK AT ELEVATED PRESSURE

Thermodynamic equilibrium calculations were used to compare the predicted results of gasification both Bagasse and rice husk at elevated pressure. The comparison of predicted gasification results at elevated pressure as shown in Figure 6. It is found that the release of H_2S is very sharply reached at maximum value at 18 bar for Bagasse in Figure 6(A), as compared to pressure 18 bar for Rice husk in Figure 6 (B), moreover the release of H_2S at 18 bar is also greater than the release of SO_2, NaCl, KCl and HCl at elevated pressure.

On the basis of calculated mole fractions, the order of release species, H_2S, SO_2, NaCl, KCl and HCl for Bagasse and Rice husk during gasification at elevated pressure are predicted as follows:

6.1 Releasing order of species at elevated pressure:

Bagasse ($H_2S > SO_2 < NaCl > KCl < HCl$)

Rice Husk ($H_2S > SO_2 < NaCl < KCl < HCl$)

On the basis of releasing order, the release of H_2S is higher at elevated pressure both in Bagasse and Rice husk. The release of H_2S is higher for Bagasse than Rice Husk at 18 bar, the order of release at elevated pressure is **Bagasse > Rice husk.**

For SO_2 the higher release at 6 bar for Bagasse and Rice husk and lowest at 12 bar for Rice husk. The order of release is **Bagasse > Rice husk** at elevated pressure.

The higher and lower release of NaCl is observed at 6 & 18 bar for Bagasse and Rice Husk. The order of release at elevated pressure is **Rice Husk > Bagasse**.

The KCl release is higher for Rice Husk at 12 bar and lower for Bagasse at 18 bar, the order of release is **Rice husk > Bagasse** at elevated pressure.

The HCl release is higher for Bagasse at 18 bar and lower at 6 bar for Rice husk, the order of release is **Bagasse > Rice husk** at elevated pressure.

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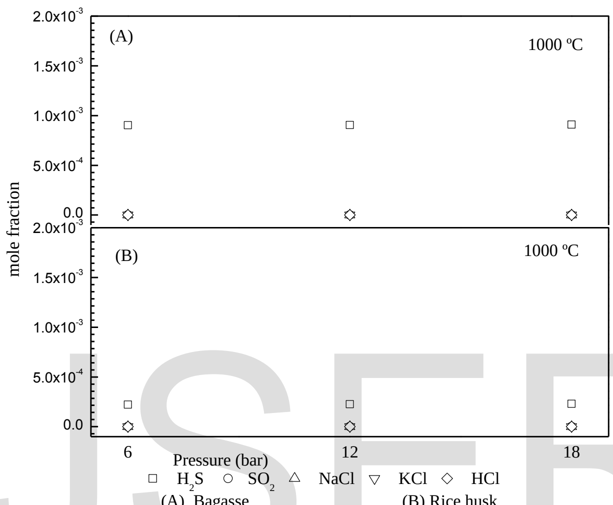

Fig: 6 Comparision of predicted equilibrium calculation results of Gasification at elevated pressure.

7 CONCLUSION

1. The high volatilization of H_2S at elevated pressure can be predicted that H_2S is the most stable specie for gasification. The volatilization of H_2S is predicted higher for Bagasse & Rice husk (18 bar) and lowers for Bagasse & Rice husk (6 bar) at elevated pressure during gasification.
2. The volatilization of SO_2 is predicted lower for rice husk & Bagasse (12 &18 bar)) at elevated pressure than NaCl, KCl and HCl.
3. The predicted release of NaCl, KCl is lower for Bagasse (18 bar) at elevated pressure while volatilization of HCl for Bagasse is higher (18 bar) at elevated pressure.
4. The volatilization of NaCl, KCl and HCl is dependent on Cl content present in the Bagasse and Rice husk.

8. References

[1] Sirajul Haq, "The Crises of Electricity" https://nation.com.pk/23-Jun-2018

[2] K.Perveen, "Energy Crises hurting Economy"http://nation.com.pk/business/18-May-2016

[3] Renewable energy's condition in Pakistan, http://icece.kics.edu.pk/6-Sept-2018/renewable- energys-condition-in-pakistan/

[4] M.J.S.Zuberi,S.Z.Hasany,M.A.Tariq and M.Fahrioglu, "Assesment of biomass energy resources potential in Pakistan for Power generation" *Proc, IEEE 4th International Conference on Power engineering, energy and electrical drives (POWERENG)*,pp.1301-1306, 2013. **DOI:** 10.1109/PowerEng.2013.6635801

[5] M.K.Iskander, “Annual Review of Pakistan Sugar Mills Association, 51st Annual General Meeting”, pp.1- 12,Oct: 2016. http://www.psmacentre.com/aboutus.php?id=6&type=annual_review&status=1#top

[6] A.A.Mirani, A.Munir, K.A.Shabbir and A.Tanveer, “ A Rice Husk Gasifier for Paddy Drying”*J.Sci.Tech and Dev.vol.*32,no,2,pp.120-125,2013. docsdrive.com/pdfs/std/std/2013/120-125.pdf

[7] R.B Mahar, “Report on assessment of environmentally sound technologies (ESTs) for Waste Agricultural Biomass in District Sanghar Pakistan” in collaboration with UET Jamshoro and UNEP Osaka/Shiga, Japan, 2011. docsdrive.com/pdfs/std/std/2013/120-125.pdf

[8] M.A.Saeed, A.Irshad,H.Sattar,G.E.Andrews, H.N. Phylaktou & Gibbs B.M, “Agricultural Waste Biomass Energy Potential in Pakistan”. Proc, International Bioenergy (Shanghai) Exhibition and Asian Bioenergy Conference Shanghai, P.R.China. Oct, 2015. http://dx.doi.org/10.5071/BSCE2015-ICO.1.2

[9] S.C.Okoro, M. Montgomery, F.Jappe Frandsen, K.Pantleon, “ Alkali Chloride induced corrosion of superheaters under biomass firing conditions :improved insights from laboratory scale studies.” Proc, The Nordic Flame Days. 2015. http://orbit.dtu.dk/files/117326655/Okoro_et_al_1_.pdf

[10] V.Ganapathy, “ High Temperature Corrosion Problem in Waste Heat Boiler” http://vganapathy.tripod.com/htcorr.html

[11] W.Zhang, H.Liu,I.U.Hai, Y.Neubauer, P.Schroder, H.Oldenburg, A.Seilkopf and A.Kolling, “Gas cleaning strategies for biomass gasification product gas.” *J. International Journal of Low-Carbon Technologies*,Vol.7, pp.69-74, 2017. http://dx.doi:10.1093/ijlct/ctr046 Advance Access Publication 8

[12] L. H.Anders , “Hot gas cleaning in biomass gasification” Review of activities within EC Sponsored R&D Programs. February 2012. https://web.anl.gov/PCS/acsfuel/.../Files/40_3_CHICAGO_08-95_0657.pdf

[13] LeChatelier-van’tHoffLaw. (https://www.chemguide.co.uk/physical/equilibria/lechatelier.html)