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Thermodynamic behavior of volatile species during high temperature and pressure gasification of Pakistani lignite char

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Abstract

Thermal conversion of coal especially at elevated temperature and pressure during gasification released of some volatile species (Na-,K-,Cl-, and S).These species badly affected in the colder part of heat recovery systems, on super heaters and gas turbines by causing severe problems such as fouling, slagging and corrosion. Thermodynamic study of released inorganic compounds is helpful to carry out experimental work. Therefore thermodynamic equilibrium has been calculated using Fact Sage 5.2, simulating gasification conditions at elevated temperature (1000,1400 and 1600°C) and elevated pressure (5, 10 and 15 bar).Their releasing order of various volatile species was estimated by plotting mole fraction of each species at temperature 1000°C and pressure 1 bar. These calculations predict that H_2S is the most stable species for gasification. The release of SO_2, NaCl, KCl, and HCl is lowest at all pressure than temperature. The volatilization of NaCl, KCl, and HCl is depends on the amount of Cl- present in LKH and THR lignite char.

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

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1 INTRODUCTION

Pakistan is currently facing huge crises of energy due to severe shortage of power about 5,000MW and natural gas which badly affected the industrial and social sectors as well as economy of Pakistan. [1],[2]. Pakistan has 33.0 trillion tons world third largest coal resources in south-eastern part of the country.i.e Thar [3]. Thar coal(THR) is a cheap source for production of affordable electricity for domestic, commercial, and industrial purpose [2,[4] but its mining, power generation and gasification due to low ash, high moisture, volatility and sulfur require some special techniques. Unfortunately high volatile species like Na,K,S,Cl during high temperature and pressure gasification are released and penetrate hot gas filtration unit and gas turbine blades. The efficiency of power plant may be achieved by hot gas cleaning [5].

Therefor the comprehensive knowledge of released volatile species during high temperature and pressure gasification is required prior to carryout experiment by utilization of Pakistani lignite char. 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 temperature (1000°C to 1600°C) at 1bar pressure and high pressure 5 to 15) bar at 1000°C and also predict the release of volatile species for Pakistani lakhra(LKH) and Thar (THR) lignite chars using equilibrium calculations by Fact sage 5.2.

2 MATERIAL AND METHOD

Two kinds of Pakistani Thar(THR) and Lakhra (LKH) lignite from Fuel Research Center, PCSIR, Karachi, Pakistan, are mainly used. Their proximate and ultimate analysis is given in Table 1. Char was made by following procedure. Firstly, the 60 or 76.06 g by weight of raw THR or LKH coal was loaded twice with some ceramic beads in fixed bed inserted in an electric furnace with sufficient heat and it underwent a carbonization in nitrogen atmosphere under temperature 750°C and ambient pressure with heating rate 15°C/min and flow rate 664.675 L/h for one hour. Then these chars removed from ceramic beads were respectively pulverized with particle size 0-0.154 mm (< 100 mesh). The composition of the above chars and ashes are listed respectively in Table 1 and 2

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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 lignite char. The thirteen 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 Temperature (1000 to 1600°C) at 1 bar pressure and Pressure (5 to 15 bar) at 1000°C for gasification process as shown in Figure 1 to 10 and calculated mole fractions are listed in Table 4 and 5. The chemical composition of Pakistani chars is included in Table 3.

Table: 1 Proximate and ultimate analysis of Pakistani LKH and THR Lignite and char

Coal Type	Proximate analysis				Ultimate analysis				
	M_{ad}%	A_{ad}%	V_{ad}%	$FC_{ad\%}$	$S_{t,ad}$%	H_{ad}%	C_{ad}%	N_{ad}%	O_{ad}%
LKH lignite	10.24	14.66	44.54	30.56	5.15	3.07	52.44	0.85	13.6
THR lignite	8.5	19.37	48.52	23.66	4.02	2.94	49.93	0.98	14.31
LKH lignite char	6.07	28.19	4.82	60.92	5.62	1.71	54.77	0.89	2.75
THR lignite char	3.88	36.25	6.18	53.69	3.46	1.36	51.78	0.74	2.53

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

Char sort		LKH char	THR char
A_{ad} %		28.19	36.25
Ash	SiO_2/ Al_2O_3	1.32	2.13
Composition analysis of ash, %	SiO_2	27.98	39.01
	Al_2O_3	21.21	18.31
	Fe_2O_3	24.85	22.46
	CaO	9.44	9.82
	MgO	4.77	2.66
	TiO_2	1.53	1.95
	SO_3	8.08	4.10
	k_2O	0.15	0.05
	Na_2O	1.16	0.96
	P_2O_5	0.53	032
Fusion temperature ℃	DT	1228	1188
	ST	1234	1216
	FD	1239	1226

Table: 3 Chemical composition of Pakistani Chars %

Coal Type	Si	Al	Fe	Ca	Mg	Ti	K	Na	P	Cl
LKH lignite Char	3.69	1.58	2.45	1.90	0.812	0.26	0.031	0.12	0.042	0.000012
THR lignite Char	6.61	1.76	2.83	2.55	0.58	0.42	0.015	0.131	0.033	0.000015

Table: 4 Calculated mole fraction at Temperature 1000 to 1600°C and pressure 1 bar for gasification

Alkali Species	T °C	Mole Fraction LKH Char	Mole Fraction THR Char
H_2S	1000	1.9630E-02	8.9919E-03
	1400	1.2553E-02	6.9720E-03
	1600	7.8662E-03	5.3351E-03
SO_2	1000	6.8706E-08	1.6737E-10
	1400	2.2205E-05	5.6568E-08
	1600	1.0836E-04	6.1109E-07
NaCl	1000	8.9924E-09	2.9839E-08
	1400	3.9318E-08	6.4600E-08
	1600	3.8966E-08	5.7303E-08
KCl	1000	2.3634E-09	7.8423E-09
	1400	7.9099E-09	1.2996E-08
	1600	1.2593E-08	1.4109E-08
HCl	1000	5.0855E-08	4.6805E-08
	1400	1.4711E-08	6.6614E-09
	1600	1.0115E-08	1.2515E-08

Table: 5 Calculated mole fraction at Pressure 5 to 15 bar and Temperature1000°C for gasification

Alkali Species	P bar	Mole Fraction LKH Char	Mole Fraction THR Char
H_2S	5	1.9830E-02	9.5100E-03
	10	1.9851E-02	9.8184E-03
	15	1.9850E-02	1.0073E-02
SO_2	5	1.4058E-08	8.5873E-10
	10	7.2635E-09	1.7097E-09
	15	5.0831E-09	2.5452E-09
NaCl	5	4.4758E-09	9.7226E-09
	10	3.2527E-09	5.5180E-09
	15	2.6902E-09	3.9640E-09
KCl	5	1.1763E-09	2.5553E-09
	10	8.5489E-10	1.4503E-09
	15	7.0703E-10	1.0418E-09
HCl	5	5.6593E-08	7.4333E-08
	10	5.8217E-08	8.2001E-08
	15	5.9049E-08	8.6068E-08

4 DEFINITION OF CONDITION

To simulate the condition of gasification of LKH lignite Char excess air, O2=1.6733 g or (167.33%) and at highest syngas amount from (0.1 to 1) the O2= 0.8367 g or (83.67%) and for THR lignite char excess air, O2=1.5411 g or (154.11%) and at highest syngas amount from (0.1 to 1) the O2= 0.7706 g or (77.06%) was added to system.

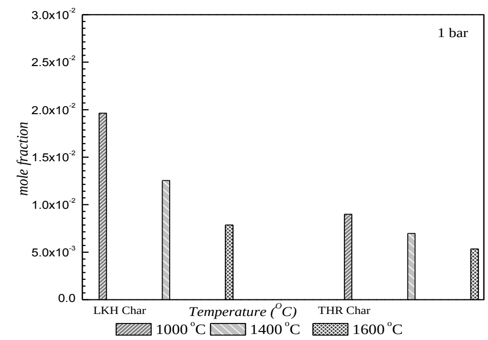
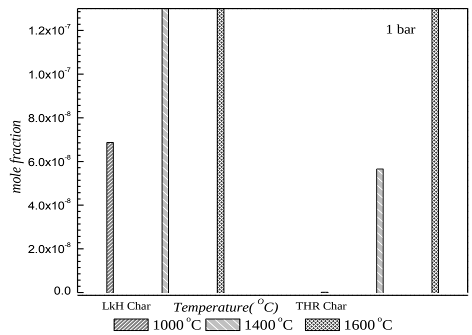


Fig: 1 Pridicted results of H_2S at high temperature gasification



Fig; 2 Pridicted results of SO_2at high temperature gasification

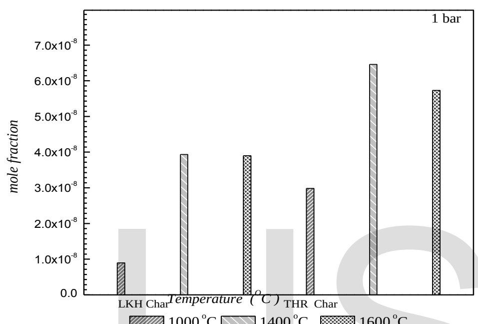
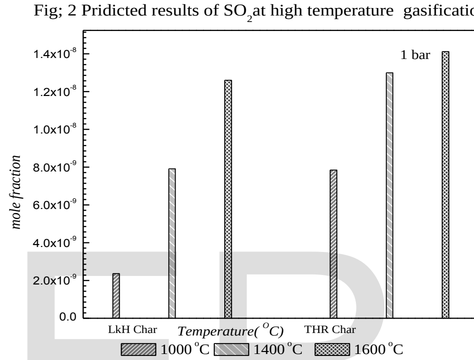


Fig: 3 Pridicted results of NaCl at high temperature gasification



Fig; 4 Pridicted results of KCl at high temperature gasification

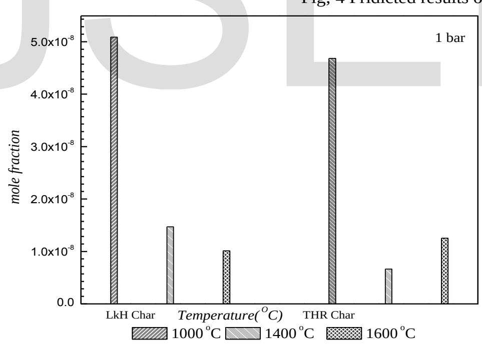


Fig: 5 Pridicted results of HCl at high temperature gasification

5 RESULTS AND DISCUSSION

5.1 Release of volatile species during high temperature gasification

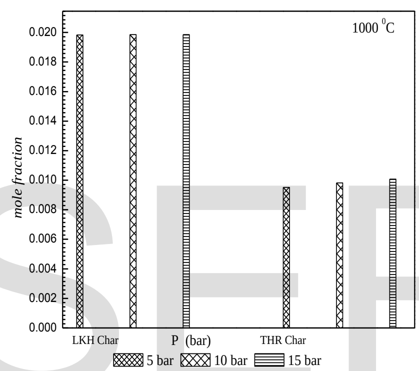
The predicted results regarding the release of volatilization species i.e H_2S, SO_2, NaCl, KCl and HCl during high temperature gasification are listed in Table 4. Figure 1, consider the mole fraction as the base for release of H_2S for two samples: It gradually decreases with increasing temperature 1400 to1600°C for LKH and THR char may be the formation of H_2S is shifting equilibrium to the left side therefore strong decrease is observed at 1600°C [8] .The predicted results of SO_2 are depicted in Figure 2. It strongly increases with increasing temperature for both LkH and THR char may be increase in volatilization of SO_2 is shifting the equilibrium to the right therefore strong increased is observed for LKH char at 1600°C [8]. The release of NaCl and KCl is increasing with increases of temperature as clearly indicated in Figures 3 and 4. The high release of NaCl and KCl is observed at 1400°C and 1600°C this may be due to the fact that in thermodynamic equilibrium system the influence of high temperature increases the partial pressure of the species so volatilization increases [6] but little decrease of NaCl is observed at 1600°C in both LKH and THR Char may be high temperature shift the equilibrium to the left side, so volatilization decreases [8]. The predicted results of HCl are shown in Figure 5. The release of HCl decreases with increasing temperature and this strong decrease HCl is observed for THR char at 1400°C may be because of the equilibrium shifts to the left, decreases the volatilization of HCl [7].

5.2 Release of volatile species during high pressure gasification

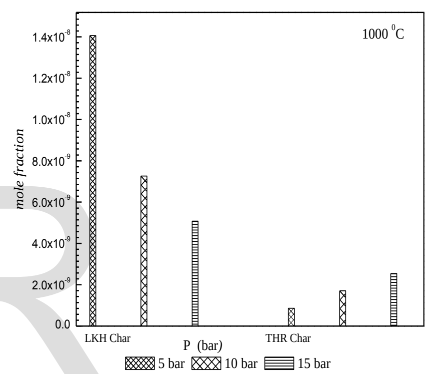
The release of H_2S, SO_2, NaCl, KCl and HCl as computed under pressurized gasification, the predicted results are listed in Table 5. On the basis of the calculated mole fraction the release of H_2S gradually increases with increasing pressure during gasification and high increase is observed at 15 bar in both LKH and THR char as indicated in Figure 6 .The increase in volatilization of H_2S may be high pressure shift the equilibrium to the right side of the fewer molecules of the product [8].The volatilization of SO_2 is gradually decreases with increase of pressure from 5 to 15 bar as shown in Figure 7, but H_2S increase is higher than SO_2 due to higher gasification product because chemically bonded organic sulphur compounds on coal matrix easily decompose to H_2S[6]. Therefore volatilization of SO_2 is observed lower at 15 bar in LKH char.

$$Na+Cl \rightarrow NaCl \quad (1)$$
$$K+Cl \rightarrow KCl \quad (2)$$
$$H+Cl \rightarrow HCl \quad (3)$$

The results of volatilization of NaCl and KCl as clearly indicated in Figure 8 &9. The release of NaCl and KCl is gradually decreases with increasing pressure in LKH and Thar Char & even sharp decrease of KCl is observed at15 bar in LKH char. The release of HCl is increases with increasing of pressure as depicted in Figure 10.The strong increase is observed at 15 bar in THR char. The decrease and increase volatilization in LKH and THR Char may be lower content of Cl in LKH Char and little high content in THR Char 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 [8] as clearly indicated in equation [1,2.3]



Fig; 6 Pridicted results of H_2S at high pressure gasification



Fig; 7 Pridicted results of SO_2 at high pressure gasification

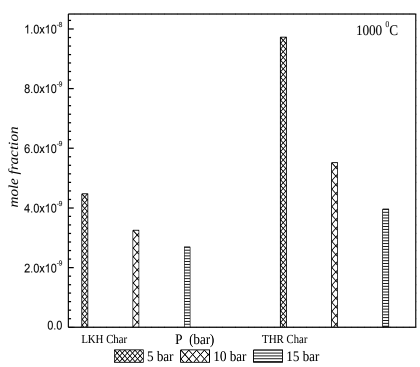
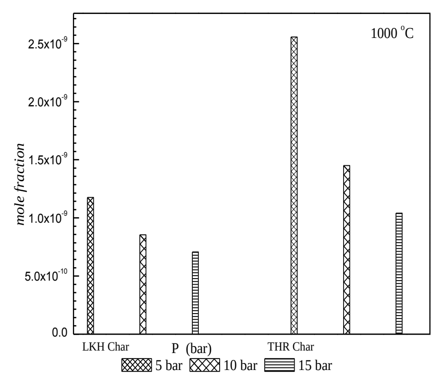
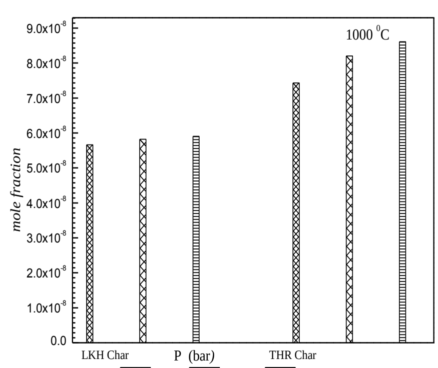


Fig: 8 Pridicted results of NaCl at high pressure gasification



Fig; 9 Pridicted results of KCl at high pressure gasification



Fig; 10 Pridicted results of HCl at high pressure gasification

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6 COMPARISON OF PREDICTED GASIFICATION RESUTS AT ELEVATED PRESSURE WITH HIGH TEMPERATURE

The predicted gasification results have been compared using thermodynamic equilibrium calculations both at elevated pressure and temperature. The comparison of predicted gasification results at elevated temperature with high pressure as shown in Figure 11.It is found that the release of H_2S is sharply reached at maximum value for LKH Char at 15 bar in Figure 11 (B),(a) as compared to temperature 1600°C in Figure 11 (A),(a), moreover 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 LKH and THR lignite char during gasification at elevated temperature and pressure are predicted as follows:

1. **Releasing order of species at elevated temperature:**
   LKH Char (H_2S>SO_2>NaCl>KCl<HCl)
   THR Char (H_2S>SO_2>NaCl>KCl>HCl)
2. **Releasing order of species at elevated Pressure:**
   LKH Char(H_2S>SO_2>NaCl>KCl<HCl)
   THR Char (H_2S>SO_2<NaCl>KCl<HCl)

Consider the releasing order the H_2S release is higher at elevated pressure than elevated temperature.

The release of H_2S is highest for LKH Char at 10 bar and lowest for THR Char at 1600°C, the order of release at elevated temperature and elevated pressure is LKH Char >THC Char.

The KCl release is higher for THR char at 1600°C and lower for LKH char at 15 bar the order of release is THR char >LKH char. The order of release at elevated temperature and elevated pressure is THC char > LKH Char.

The HCl release is higher for THR char at 15 bar and lower at 5 bar for LKH char than elevated temperature, the order of release is THR char > LKH char. The order of release at elevated temperature is LKH char > THR char.

7 CONCLUSION

The high volatilization of H_2S for both at elevated temperature and pressure can be predicted that H_2S is the most stable specie for gasification

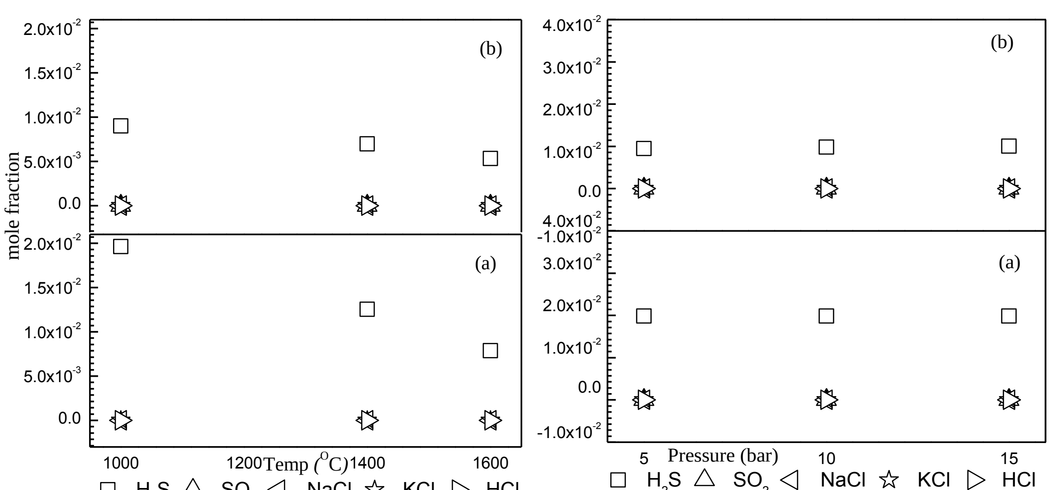
The volatilization of H_2S is predicted higher for LKH char (10 bar)) at elevated pressure and lowers for THC char (1400°C) at elevated temperature during combustion.

The volatilization of SO_2 is predicted higher for LKH char (1600°C) and lowers for THR Char (1000°C) at elevated temperature .

The release order of NaCl, KCl and HCl species at elevated temperature is not similar with elevated pressure.

The predicted release of NaCl, KCl is higher for THC char at elevated temperature while volatilization of HCl for THC char is higher at elevated pressure.

The volatilization of NaCl, KCl and HCl is dependent on Cl content present in the LKH and THR char



(a) LKH Char (b) THR Char
(A) Elevated Temperature
(B) Elevated Pressure

Fig:11Comparision of predicted equiliberium calculation results of gasification at elevated temperature and pressure

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