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Behavior of alkali minerals in oxyfuel co-combustion of biomass and coal at elevated pressure

Keywords: Oxyfuel co-combustion; Equilibrium calculations; Chemical kinetic reactions; Mineral's identifications; Thermo-gravimetric combustion

Related research projects:

1. Study of the kinetic behaviour of biomass and coal during oxyfuel co-combustion (https://doi.org/10.1016/j.cjche.2020.02.023)
2. Forms of potassium and chlorine from oxy-fuel co-combustion of lignite coal and corn stover (https://doi.org/10.1016/j.crcon.2019.03.003)
3. Alkali release measurement with Laser-Induced Breakdown Spectroscopy and kinetic modeling during Oxy-fuel co-combustion of biomass and coal (https://doi.org/10.1016/j.fuel.2020.119658)

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1.0 Introduction: 课题背景意义



1. Zhundong (ZD) coal

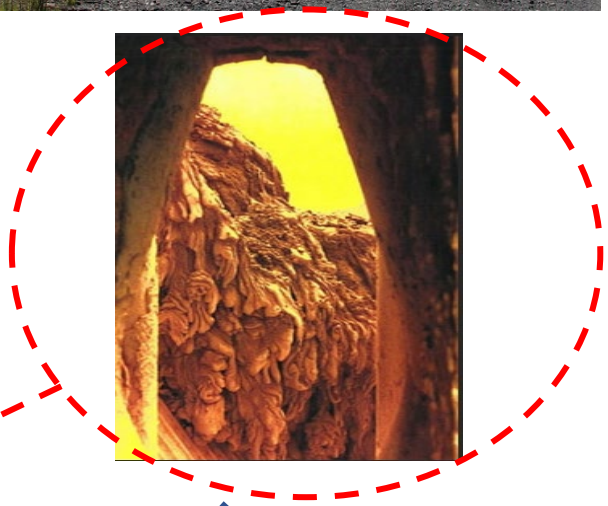
- **Advantage**: Huge reserve (~164Gt)
- **Problem**: Non-renewable and % Na is very high



CFB



Boiler system



2. Biomass corn stalk

- **Advantage**: Available (~39% of total straw) and renewable
- **Problem**: % K very high





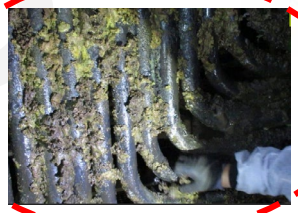
ZD use in power plants limited by:

- Slagging and
- Fouling

Due to high Na %

Corn stalk use in power plants limited by:

- Fouling due to high K%
- Low steam temperature etc.



3. solution: cofiring

4. What are the chemical mechanisms when blended?

1.1 Introduction: Why blend and high pressure?

1.Unlock the potential use of a huge fuel resource

2. Reduce, CO_2, NO_x, SO_X and high temperature corrosion and ultimately maintenance costs



课题背景意义

4.Likely minimize ash, slagging and agglomeration in the boiler

3. Improve heat transfer, char oxidation rate and power cycle time

1.2 Introduction: Objectives

- Under pressurized oxy-fuel co-firing of coal and biomass it was required to investigate influence of co-combustion on ash chemistry and the sulfur-chlorine-alkali transformations.

2.0 Material: Fuels

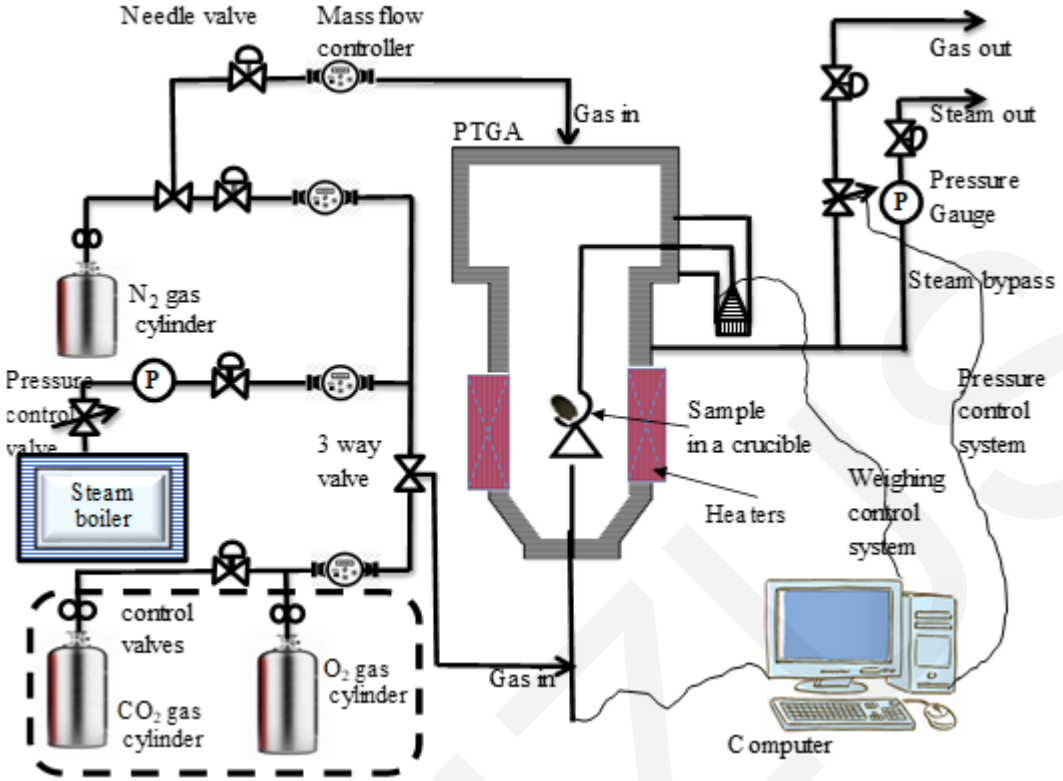
- Coal: Lignite coal from Zhundong region
- Biomass: Corn stalk

2.1 Fuel mixing

- Energy basis: biomass/(coal+biomass)*100 = 20% and 30% blends

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2.2 Experiment: Thermogravimetric analysis of fuel blends ash at high pressure.



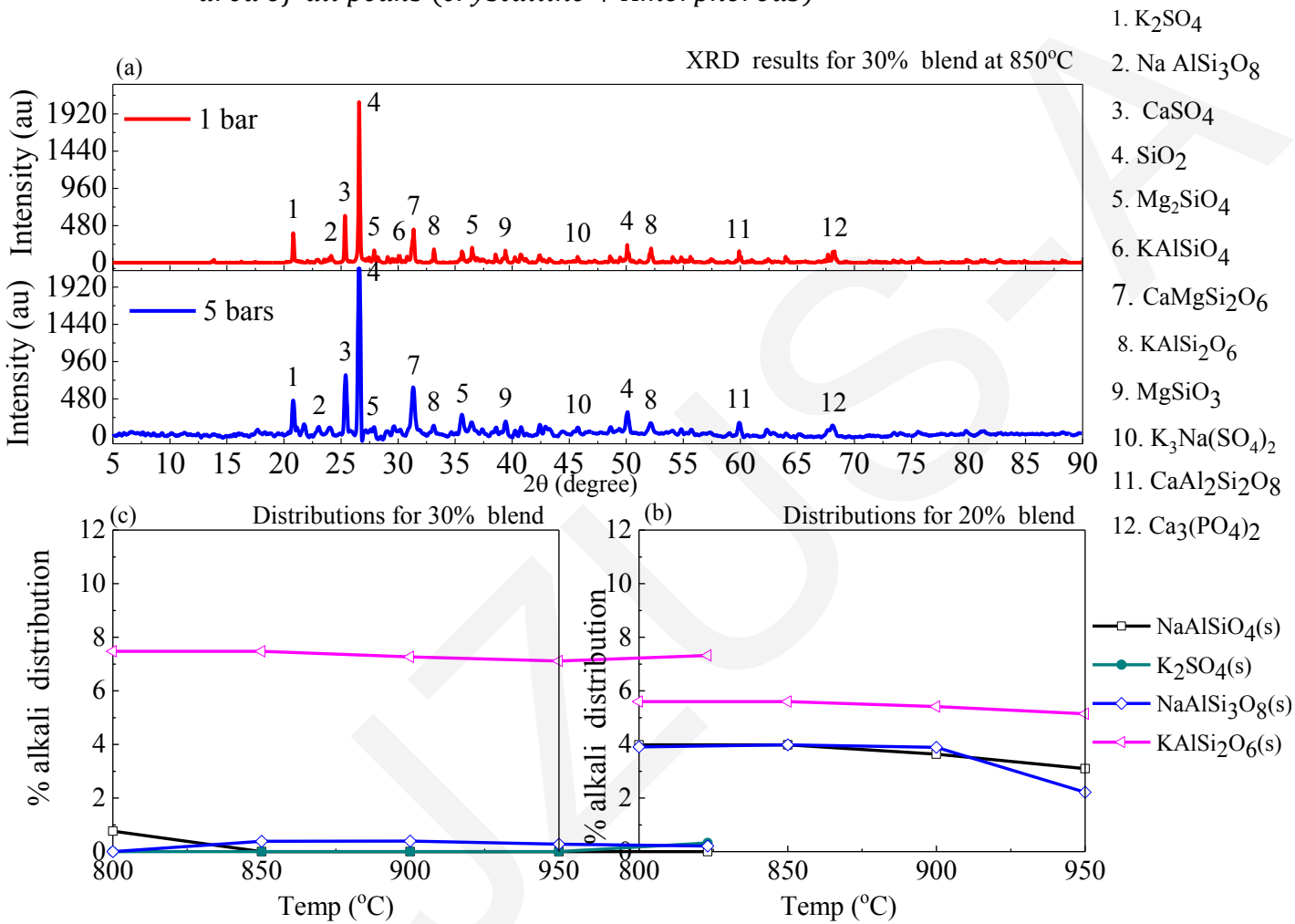
- Feed: 100% coal, 100% biomass 20% and 30% fuel blends
- Gas from cylinders was taken as 80:20 (O_2: CO_2) % vol. and set to flow at 100 $mlmin^{-1}$
- Steady heating rates of 25°Cmin^{-1} until the designated temperatures of 800, 850 and 950°C were reached
- Pressure of 1 and 5 bars were considered

Fig. 1. High pressure (Cahn Thermax 500) thermogravimetric analyzer (PTGA) system

- The ashes were cooled in a N_2 environment and later their mineral contents were determined by XRD and SEM/EDS analyses

3.0 Results: XRD Ash analysis from high pressure combustion

$$\%\ crystallinity = \frac{area\ of\ crystalline\ peaks}{area\ of\ all\ peaks\ (crystalline + Amorphorous)} x100 \quad (1)$$



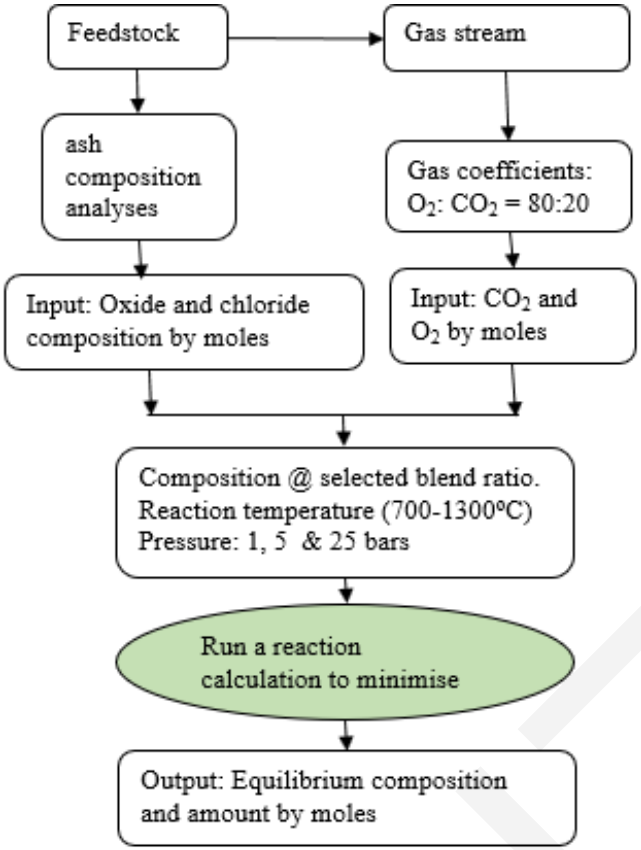
- Crystallinity at 1 bar = 67.4%
- Crystallinity at 5 bars =56.6%
- Pressure reduces the degree of crystallinity in the sample although more results are needed to confirm the outcome

Fig. 4. XRD alkali mineral distribution for the (b) 20% and (c) 30% blends

- Alkali minerals formation and distribution depend strongly on temperature and the blend ratio.

4.0 EQUILIBRIUM AND KINETIC CALCULATIONS

❑ Dynamic equilibrium calculations



❑ FactSage

❑ Algorithm

Fig. 4.2 Algorithm for Dynamic calculation procedure

- ❑ Calculations conducted using FactSage 5.2 software based on minimization of Gibbs free energy
- ❑ software solver based on the input composition and mineral database FACT-SLAGC
- ❑ Inputs to the solver are the fuel ash oxides and chlorides
- ❑ Oxygen required was calculated with inputs from Table 1 using Eq. 1 and applying an excess coefficient of 1.2.

❑ Chemical kinetic calculations

Chemkin

➢ Chemkin is employed to solve the governing Eqs for a cylindrical plug flow reactor.

$$\frac{dT}{dt} = -\frac{1}{\rho \bar{c}_p}\sum_{j=1}^{J} h_j \dot{\omega}_j W_j \qquad (2)$$

$$\frac{dY_j}{dt} = \frac{\dot{\omega}_j W_j}{\rho}, j = 1, \ldots, J \qquad (3)$$

✓ where T, ρ, Yj, cp, hj, ωj and Wj are the temperature, density, mass fraction, mean specific heat capacity, specific enthalpy, molar production rate and molecular weight of species j involved respectively

❑ Alkali sulfation and chlorination schemes for K/Na/O/H/S/C/Cl gas phase kinetic elementary was deployed

❑ 30% blend; pressure is changed to 1, 5 and 25 bars

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5.0 Results and Conclusions: Equilibrium predictions

❑ Equilibrium prediction results for a 20% blend sample as an example

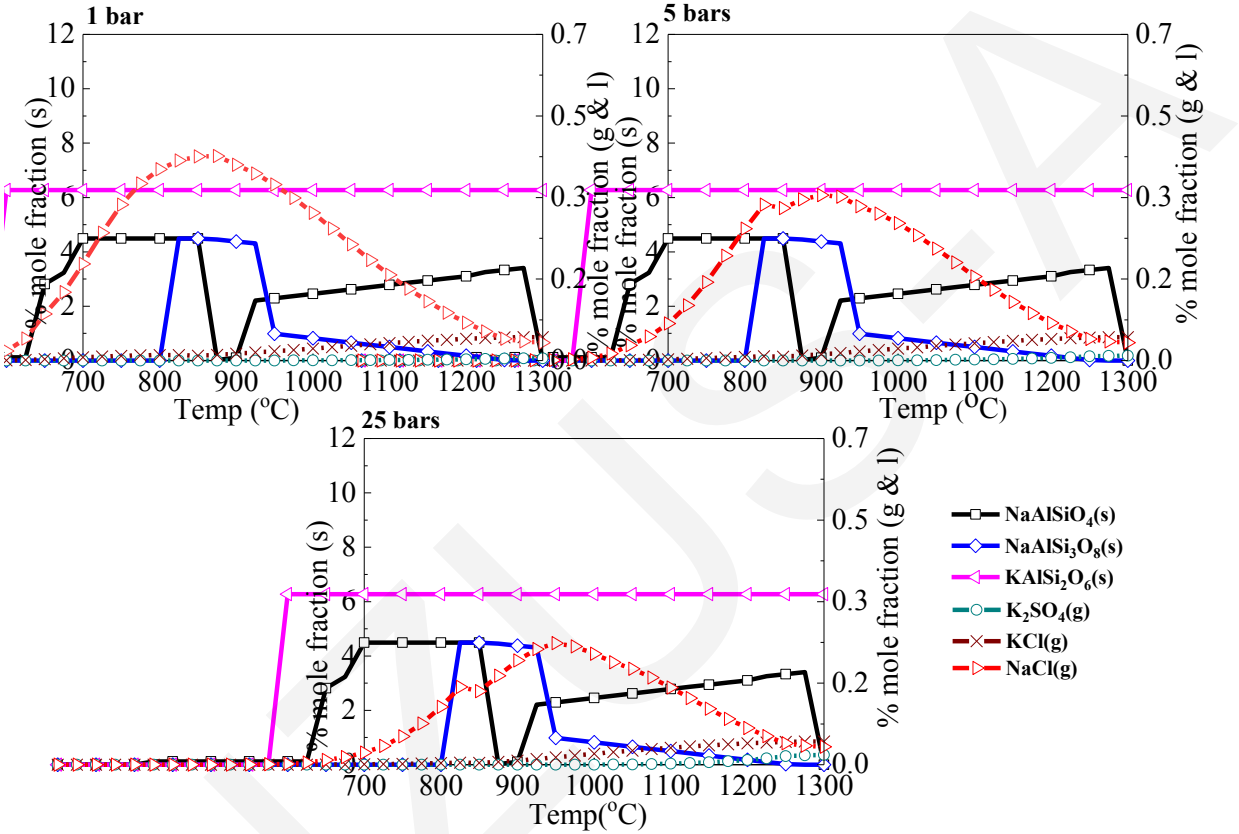


Fig. 7. Equilibrium predictions of K and Na minerals for the 20% blend

- ❑ Increasing the blend ratio, increases the content of K-based minerals and reduces of Na-based minerals
- ❑ Pressure rise increases amounts of all liquid, but not for solid alkali species.
- ❑ Increasing the blend ratio and pressure within 850-900°C, reduces gaseous KCl

5.1 Results and Conclusions: Kinetic predictions

❑ Kinetic prediction results for a 30% blend sample as an example

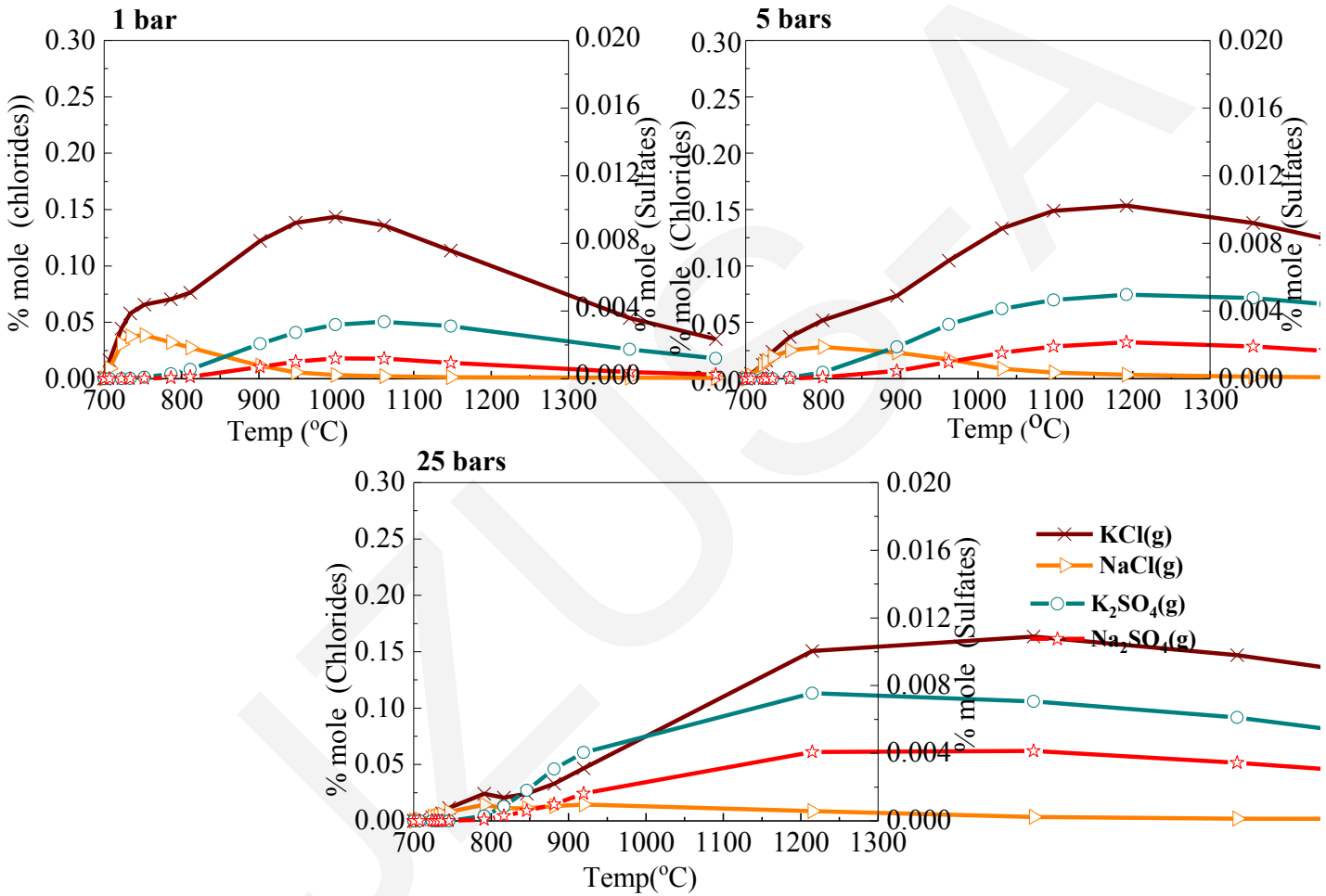


Fig. 9. Kinetic predictions of alkali species for 30% blend

❑ Increasing the pressure within 850-900°C, reduces gaseous KCl

5.2 Results and Conclusions: Gas phase alkali reactions from Chemkin

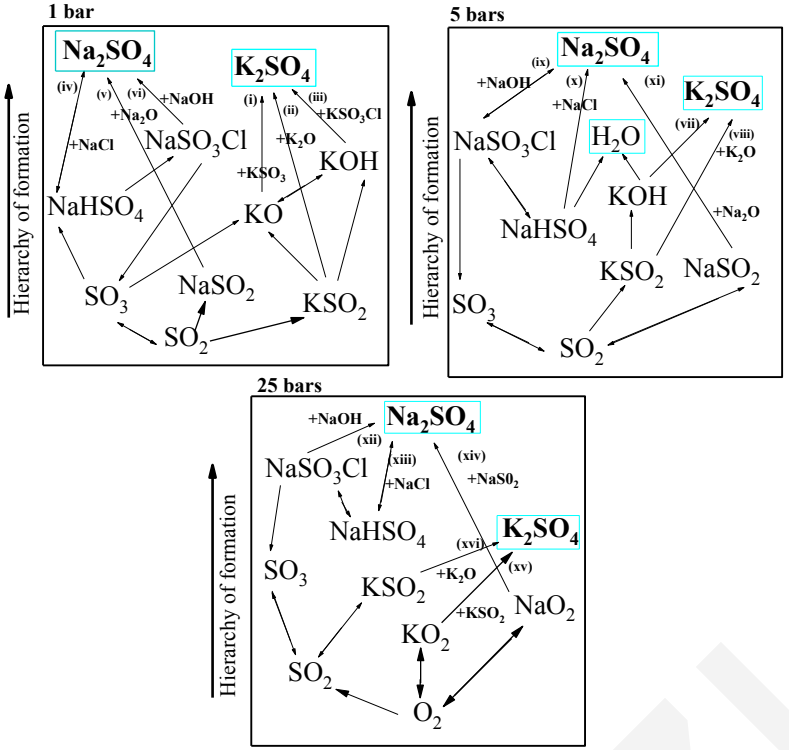


Fig. 10. Pathways for the formation of K_2SO_4 and Na_2SO_4 at 850°C

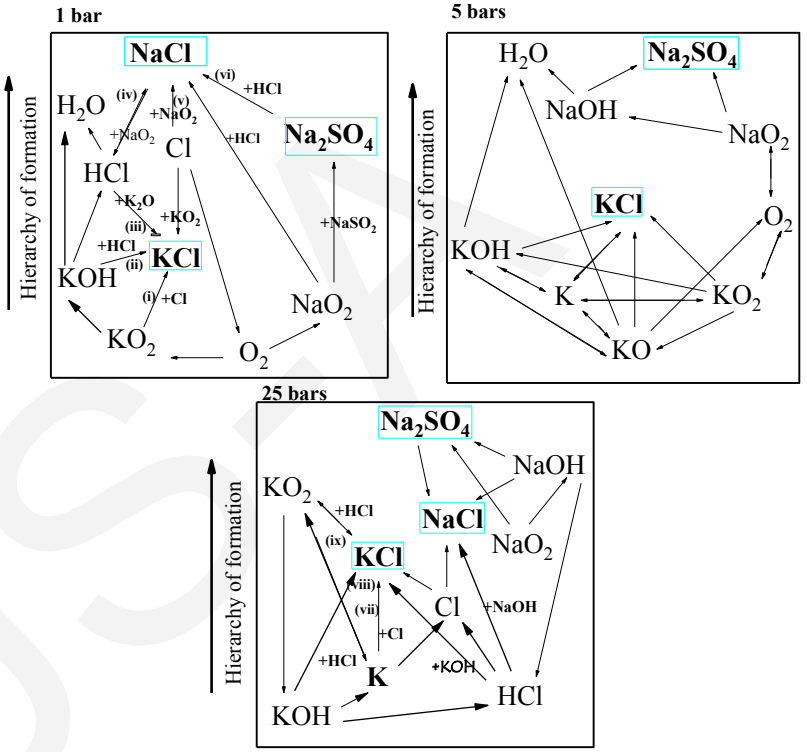


Fig. 11 Pathways for the formation of KCl and NaCl at 850°C

- $SO_2 \rightarrow SO_3$ is limiting at low pressure but its influence reduces with increasing pressure

6.0 Main innovations: 论文创新点

- An increase in pressure and biomass blend to coal can reduce the emission of KCl aerosol and inhibit the corrosion of boilers heat exchanger.

- Oxidation of SO_2 to SO_3 plays a major role in K_2SO_4 formation but that the contribution of this oxidation decreases with increase in pressure