Removal of Pollutants in Chemical Looping Gasification of Biomass

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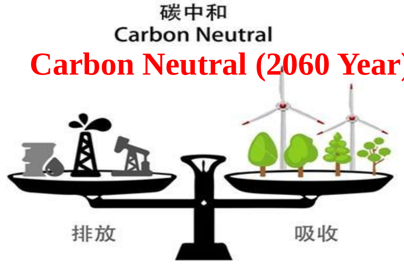
Contents

I. Research Background

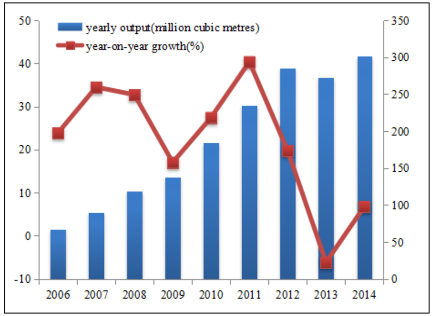
□ Organic Solid Waste from Agriculture and Forestry—(Biomass)

➢ **Energy consumption: 4.86 billion tons; CO_2 emissions: 10.6 billion tons. (2019 Year)**



Industrial Organic Solid Waste—(Sludge/Wood-based panel/Waste plastic)

Municipal sludge **40 million tons per year**, annual growth of about 10%



Wood-based panel output **325 million m^3**, annual growth of about 10%

Environment Pollution

Treatment Principle:

Reduction

Stabilization

Harmlessness

Resource Utilization

Landfill

(Large area, Secondary pollution)

Agricultural Use

(Heavy metal accumulation, Water pollution)

Characteristics of Raw Materials

Table.1 The Characteristics of Industrial Organic Solid Waste

	Proximate Analysis wt./%			Ultimate Analysis wt./%						LHV/(MJ•kg^{-1})
	V_d	FC_d	A_d	C_d	H_d	O_d	N_d	S_d	Cl_d	$Q_{net,d}$
Sludge	51.08	7.80	41.12	28.09	4.58	20.32	4.95	0.94	0.25	11.22
Wood based panel	75.74	22.49	1.77	45.78	6.14	42.63	3.67	0.01	/	18.23
Waste plastic	97.70	0.67	1.54	54.05	7.07	/	/	/	34.97	28.19

- **Industrial organic solid waste is a medium and high heat value solid fuel with high volatile content (Tar), high ash content (Cost), high nitrogen content (NO_x) and high chlorine content (Dioxins)**

Fuel Gasification

- **Incineration**

Many ancillary facilities; High cost;

Large investment

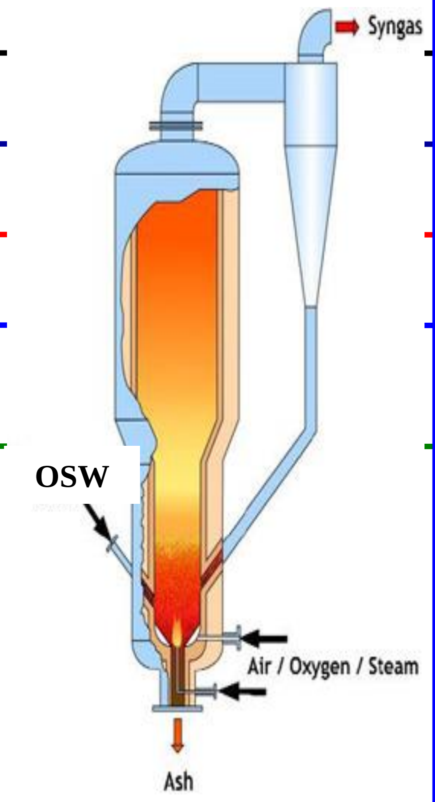
- **Pyrolysis**

Low energy utilization; Low economy

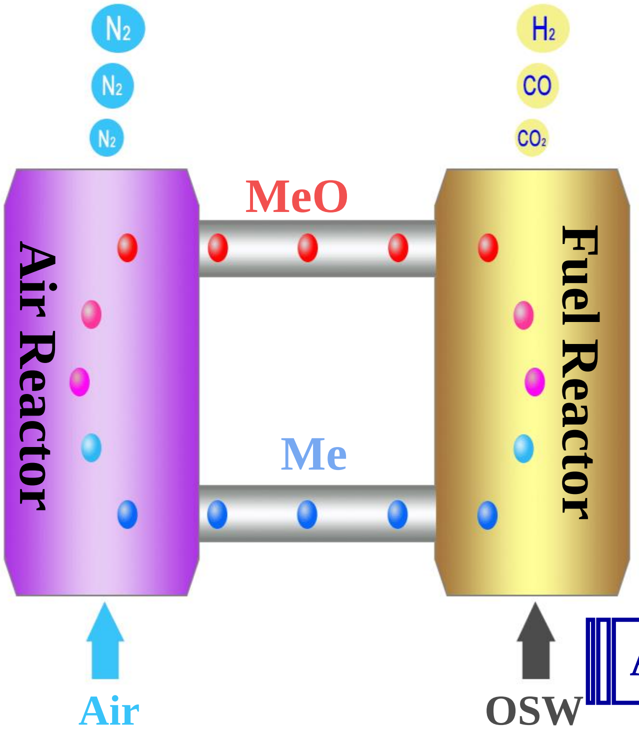
- **Gasification**

Low pollutants emission; Low leaching toxicity; Higher energy utilization; Products with a variety of uses

Air Gasification	Nitrogen dilution Low heating value (5MJ/m^3)
Pure Oxygen Gasification	High cost of producing pure oxygen
H_2O (steam) Gasification	High energy consumption for external heating
Oxygen-enriched H_2O co-Gasification	High cost of producing pure oxygen, Low heat value (~11.5MJ/m^3)
Hydrogen Gasification	High temperature and pressure



Chemical Looping Gasification(CLG)



Fuel reactor：

$$2CH_xO_y + 2(1\text{-}y)MeO \rightarrow 2CO + xH_2 + 2(1\text{-}y)Me + \Delta H > 0$$

Air reactor： $2Me + O_2 \rightarrow 2MeO + \Delta H < 0$

Total response： $2CH_xO_y + (1\text{-}y)O_2 \rightarrow 2CO + xH_2$

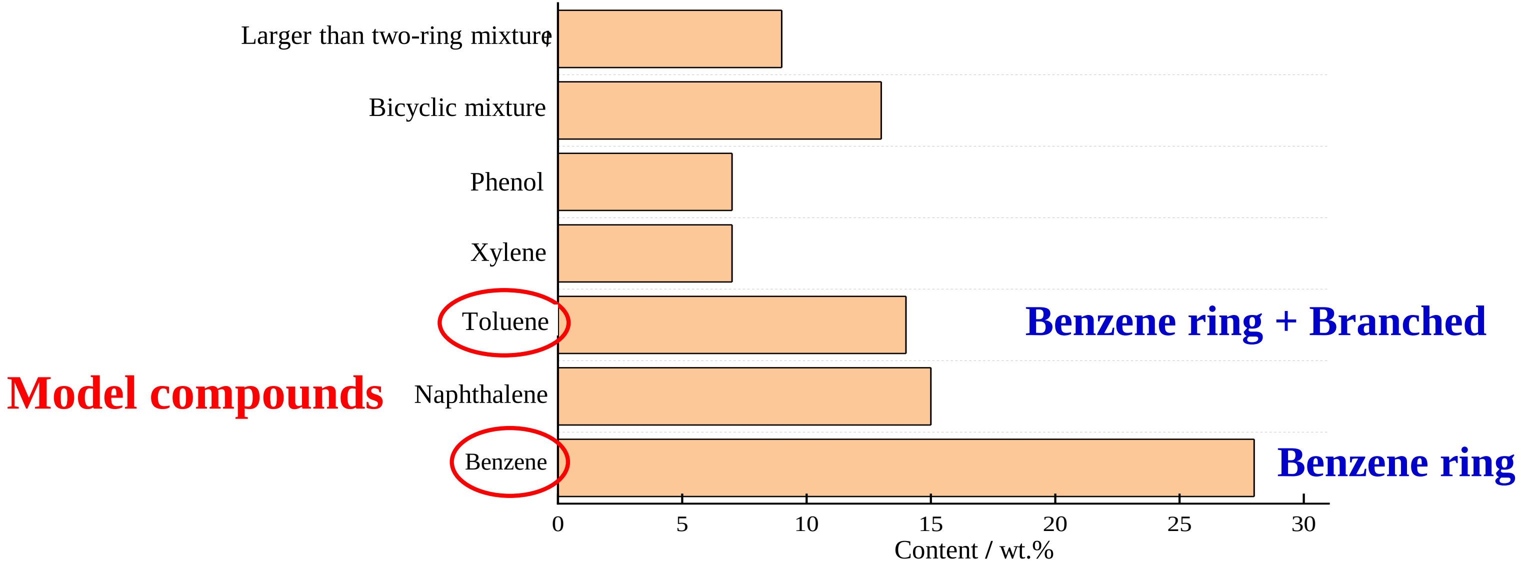
Advantages

- **Low cost**, circulation of oxygen carrier provides the cheap oxygen source, avoiding pure oxygen production；
- Oxygen carrier circulation realizes the self-heating of system **without carbon consumption**；
- **Avoid N_2 dilution**, the lattice oxygen tends to be partially oxidized；
- Oxygen carrier ***in situ* catalytic crack tar**；
- **Low N/S pollutant emissions**；
- Cascade utilization of energy to **reduce exergy loss**；
- **Poly-generation** of high-value products

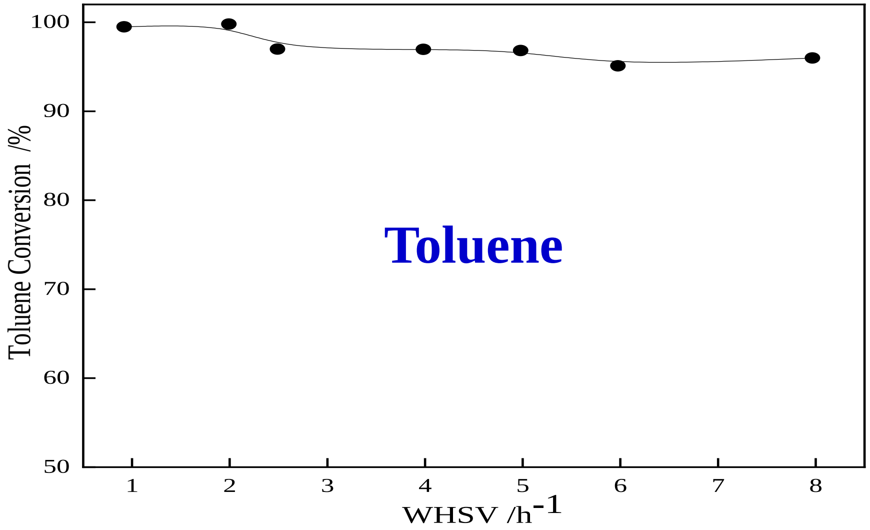
Experimental Device

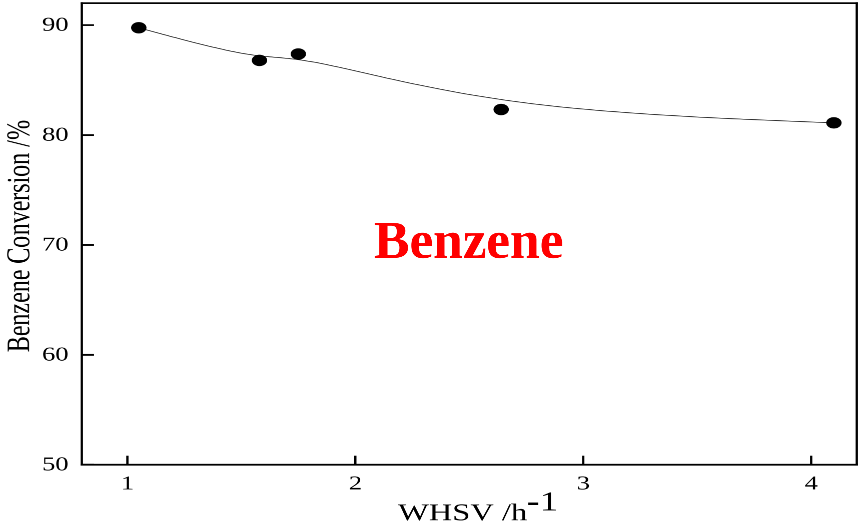
II. Control of Organic Pollutants-Tar

- The tar content is generally between 1~150g/Nm^3, accounting for 5~15% of the total energy of the products.
- Tar is very complex, with hundreds of ingredients.



Weight Hourly Space Velocity (*WHSV*)





- **The toluene conversion decreased from 99.48% of $0.92h^{-1}$ to 95.98% of $7.97h^{-1}$, indicated that *WHSV* increased by 8 times and the toluene conversion only reduced by 3.50%;**
- **The stability of benzene is higher than that of toluene, but the conversion is still higher than 80%;**
- **Ni-based oxygen carrier is a good tar cracking catalyst.**

Oxygen Carrier Phases (Toluene)

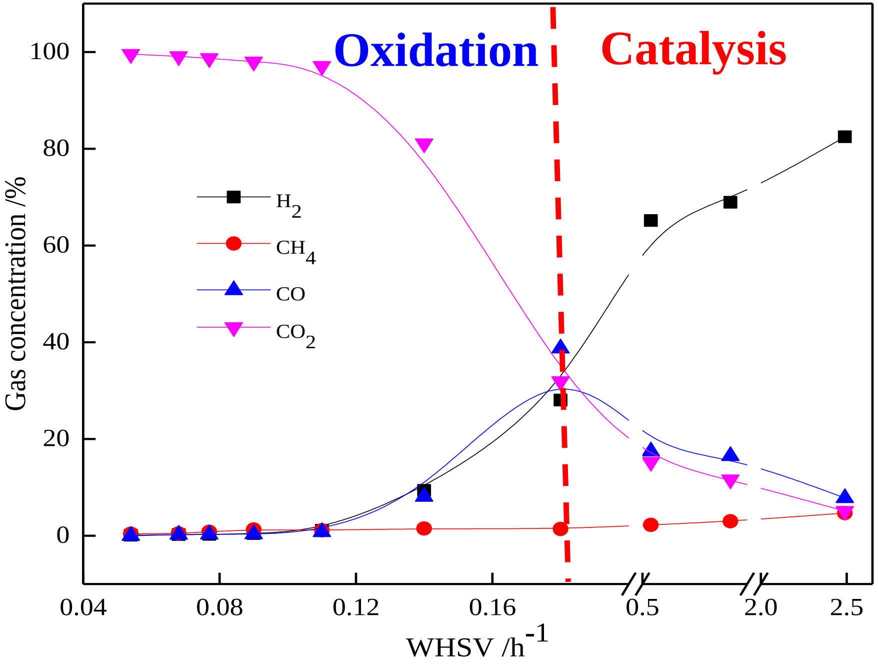
Table.2 Effect of different oxygen carrier phases on toluene conversion

WHSV /h^{-1}	Toluene cracking rate/%	Oxygen carrier phase
0.054	99.86	$Ni_{0.6}Fe_{2.4}O_4$; $Fe_{0.64}Ni_{0.36}$; $Fe_{3-x}O_4$; Fe_xO; C
0.068	99.85	$Ni_{0.6}Fe_{2.4}O_4$; $Fe_{0.64}Ni_{0.36}$; $Fe_{3-x}O_4$; Fe_xO; C
0.077	99.74	$Ni_{0.6}Fe_{2.4}O_4$; $Fe_{0.64}Ni_{0.36}$; $Fe_{3-x}O_4$; Fe_xO; C
0.090	99.86	$Fe_{0.64}Ni_{0.36}$; $Ni_{0.4}Fe_{2.6}O_4$; Fe_xO; C
0.11	99.85	$Fe_{0.64}Ni_{0.36}$; $Ni_{0.4}Fe_{2.6}O_4$; Fe_xO; C
0.14	99.86	$Fe_{0.64}Ni_{0.36}$; C
0.18	99.48	$Fe_{0.64}Ni_{0.36}$; C
0.54	98.80	$Fe_{0.64}Ni_{0.36}$; C
0.92	98.04	$Fe_{0.64}Ni_{0.36}$; C
2.49	97.11	$Fe_{0.64}Ni_{0.36}$; C

Oxidation State

Reduced state

$C_7H_8 + NiFe_2O_4 \rightarrow H_2/CH_4/CO/CO_2 + Fe\ (Ni)$ $C_7H_8 \xrightarrow{Fe(Ni)} 4H_2 + 7C$



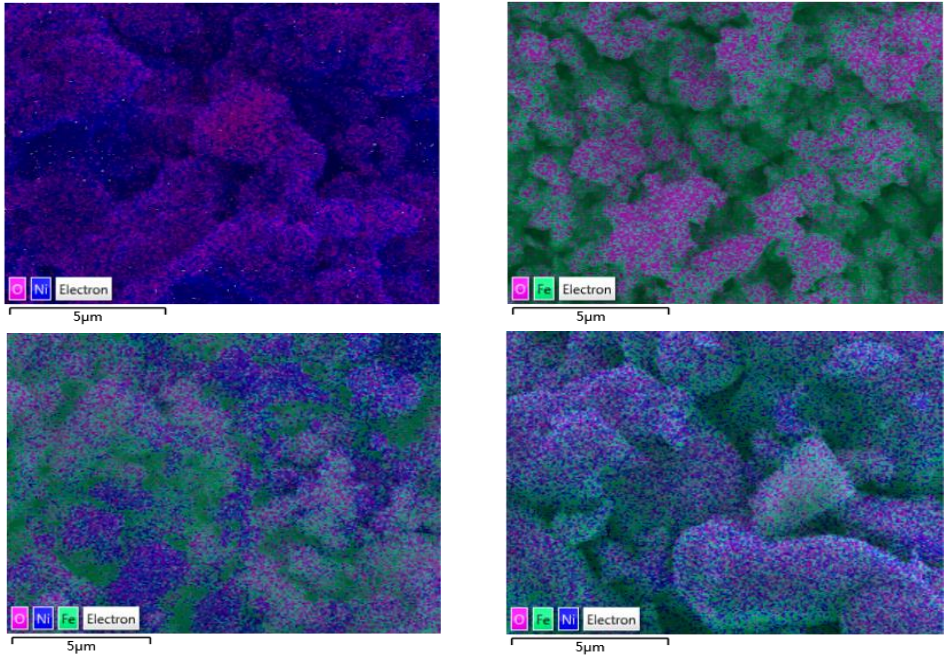
- **Oxidation** or **reduction state** of oxygen carrier has **excellent toluene cracking capacity**.

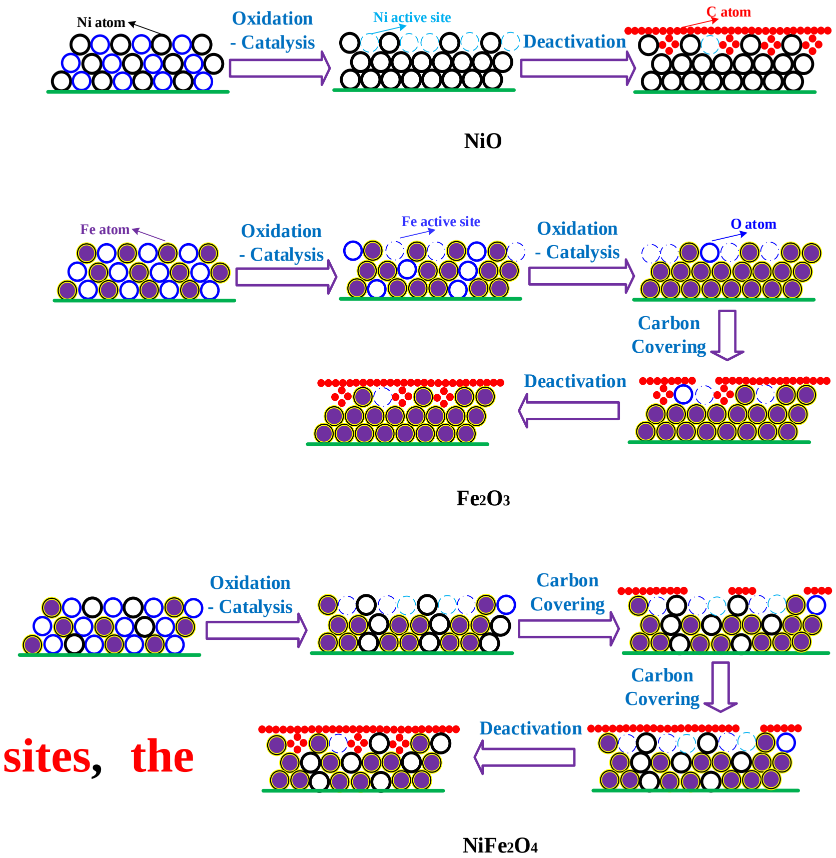
Different Oxygen Carriers (Toluene)

Table.3 Catalytic Cracking Characteristics of Toluene with Different Oxygen Carriers

	H_2	CH_4	CO	CO_2	Toluene cracking rate (%)	H_2 Yield (L/g_{tar})	Theoretical H_2 yield (L/g_{tar})	
Al_2O_3	2.80	1.44	-	-	50.60	0.07	0.49	**Dry Cracking**
NiO	4.81	2.61	0.67	0.77	83.23	0.13	0.81	**Rapid Deactivation/Carbon Deposit Coverage**
Fe_2O_3	14.93	2.56	2.16	0.18	91.06	0.45	0.89	**Gradual Reduction/ O atom Dispersion**
$NiO+Fe_2O_3$	16.14	2.84	1.28	0.43	93.45	0.49	0.91	**Ni atoms are mechanically dispersed by Fe atoms**
$NiFe_2O_4$	27.04	2.17	0.81	0.69	96.83	0.91	0.97	**Fe-Ni Atoms are uniformly dispersed**

□ Different Oxygen Carriers (Toluene)





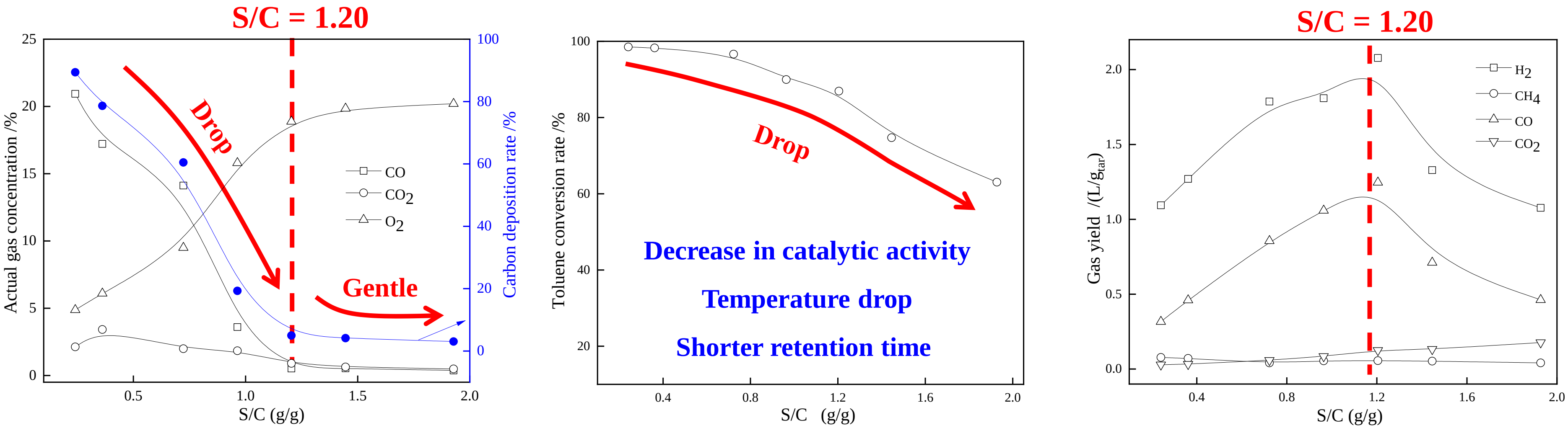
➢ The higher the dispersion of surface active sites, the higher the catalytic activity of OCs.

□ Different Oxygen Carriers (Benzene)

Table.4 Characteristics of Catalytic Cracking of Benzene with Different Oxygen

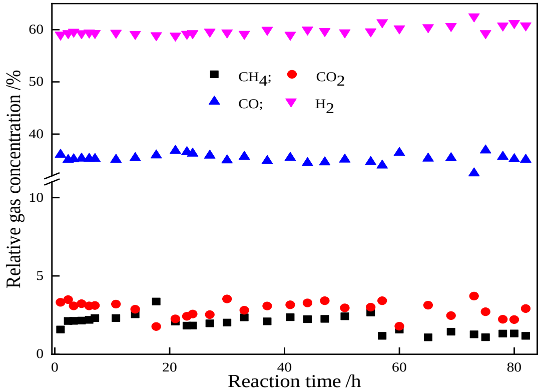
	OCs	Cracking rate (%)	CH_4 (%)	CO_2 (%)	CO (%)	H_2 (%)	C_2H_m (%)	H_2 Yield (%)	Carbon deposition rate (%)	
	SiO_2	60.13	0.13	-	-	7.75	0.03	6.33	1.24	
Transition metal oxides	Ni-	99.27	1.04	1.38	5.80	35.86	0.02	63.68	36.29	Catalysis-Oxidation
	Fe-	80.71	0.52	0.63	4.56	35.61	0.02	76.20	17.50	
	Mn-	74.70	0.16	0.78	0.19	31.08	0.02	43.14	27.99	
	Cu-	84.20	0.11	0.82	5.05	29.92	0.02	40.32	29.18	
AAEMs oxides	Na-	67.26	0.10	0.87	3.54	11.10	0.02	10.20	4.88	Weak Catalysis
	K-	67.30	0.01	1.04	4.21	12.75	-	12.03	6.17	
	Ca-	67.98	0.14	1.03	4.41	26.59	0.02	31.16	7.02	

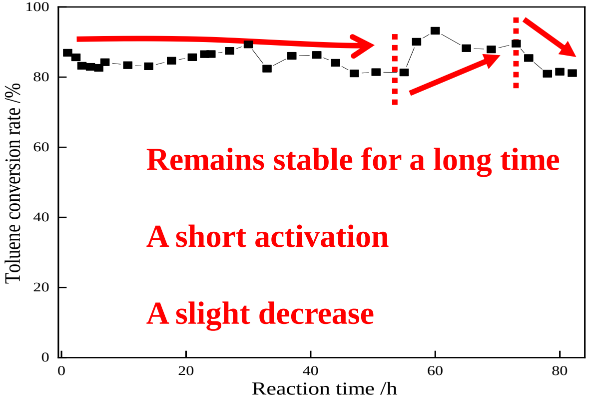
Effect of Steam (Toluene)

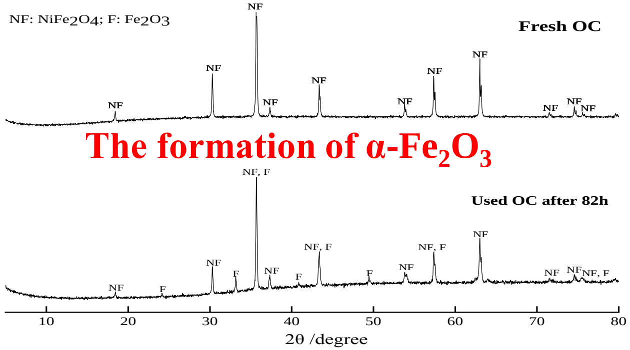


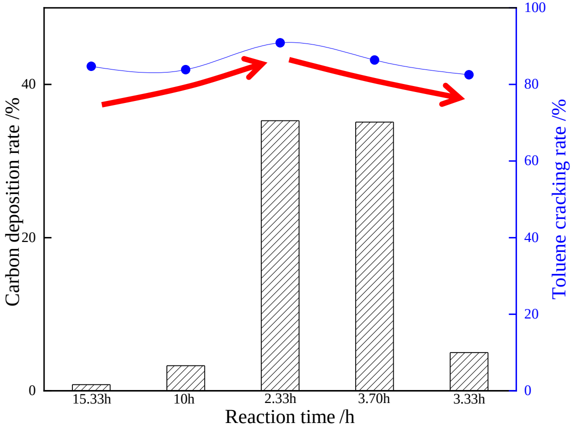
- The addition of steam can inhibit the formation of carbon deposits; $C + H_2O \rightarrow CO + H_2$//$C + 2H_2O \rightarrow CO_2 + 2H_2$;
- Increase of steam inhibits toluene cracking: $(2+y)\ Fe + 4H_2O \rightarrow Fe_{2+y}O_4 + 4H_2$, Decrease the temperature, Shorten the residence time;
- On the one hand, steam promotes the conversion of carbon deposits/toluene into CO and H_2, on the other hand, it inhibits the cracking of toluene, hence, an appropriate ratio of S/C = 1.20 was attained.

Effect of Reaction Time (82h, Toluene)









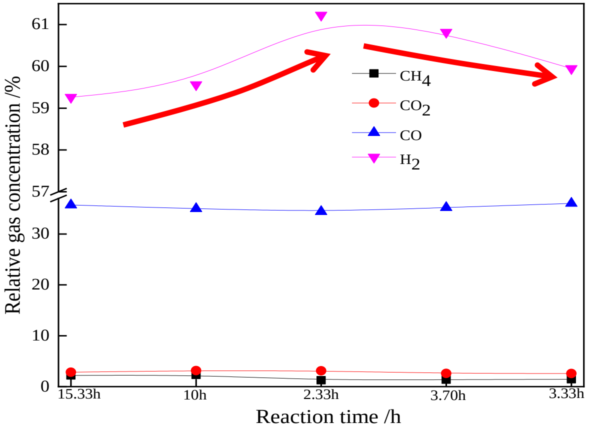


Table.5 Comparisons of Catalytic Cracking of Toluene in the 1h and 82h

Time	Cracking stage (Actual gas concentration, %)				Oxidation stage (Actual gas concentration, %)			Toluene conversion rate (%)	Carbon deposition rate (%)	Specific surface area (m^2/g)
	H_2	CH_4	CO	CO_2	CO	CO_2	O_2			
1st hour	34.27	0.92	20.95	1.92	0.52	0.89	18.88	86.93	4.97	4.12
82nd hour	32.56	0.63	18.80	1.56	1.03	0.90	19.37	81.12	6.85	5.32

Specific surface area increases

Benzene Cracking

Table.6 Effect of OC/Benzene mass ratio

OC/Benzene (g/g)	Benzene conversion rate(%)	Gas concentration(%)					H_2 Yield (%)	Carbon deposition rate(%)
		CH_4	CO_2	CO	H_2	C_2H_m		
0	56.95	0.17	-	-	9.21	0.35	6.33	1.24
0.09	81.51	0.29	0.86	0.14	18.33	0.07	26.53	36.85
0.18	84.60	0.39	1.38	0.74	23.84	0.03	30.11	39.38
0.27	84.71	0.49	1.52	1.11	26.39	0.03	39.63	39.97
0.36	86.05	0.36	1.82	2.95	26.66	0.03	41.93	41.82

Increase

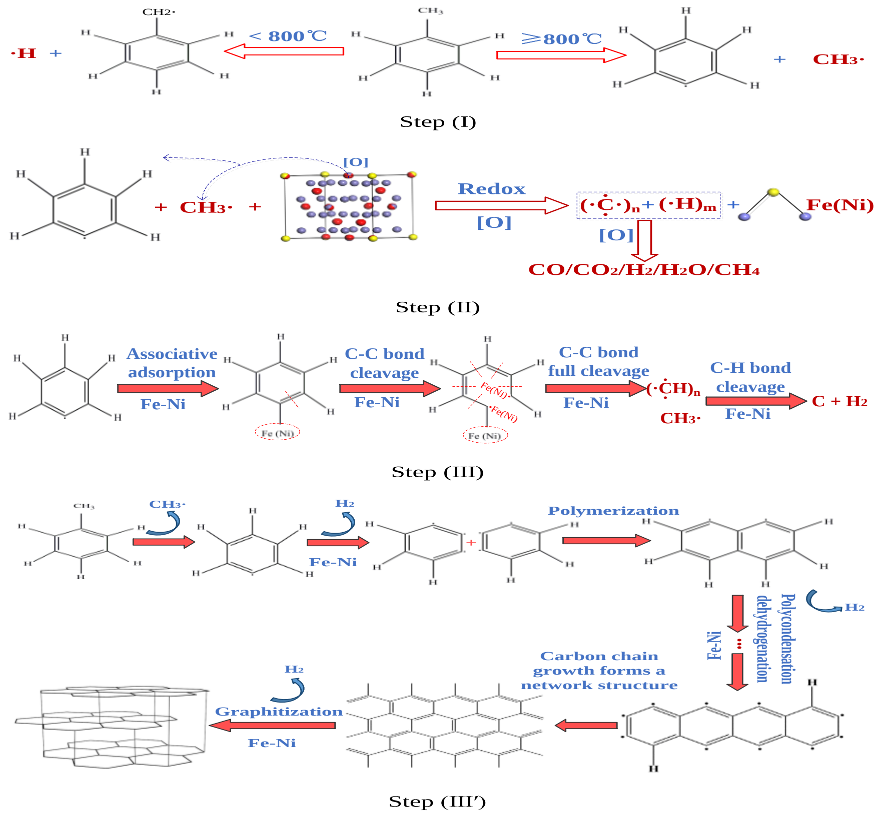
Table.7 Effect of residence time

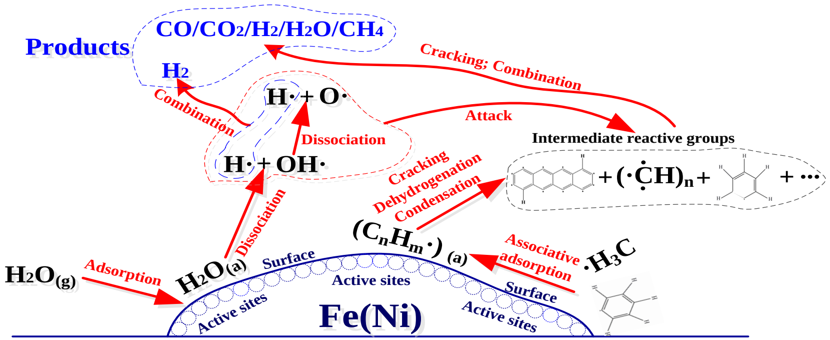
N_2 flow (mL/min)	Benzene conversion rate(%)	Gas concentration(%)					H_2 Yield (%)	Carbon deposition rate(%)
		CH_4	CO_2	CO	H_2	C_2H_n		
40	83.24	0.04	3.56	0.63	11.14	0.01	15.75	18.43
60	46.55	0.03	2.44	0.41	7.92	0.01	15.94	21.29
80	44.12	0.02	1.94	0.29	6.20	0.01	16.17	29.67
100	38.82	0.02	0.02	0.25	4.43	0.01	13.90	13.83

Increase

- **Increase the mass of OC can promote the cracking of benzene**
- **Benzene is more stable than toluene**
- **Extend the residence time can promote the cracking of benzene**

◻ The mechanisms of toluene cracking





Step (IV)

The addition of steam can not only eliminate amorphous carbon deposits, but also inhibit the formation of graphitized carbon

(I) Toluene dry cracking at high temperature;

(II) Reduction of OC;

(III) Formation of amorphous carbon deposits and H_2;

(III′) Formation of graphitized carbon and H_2;

(IV) Steam inhibits the formation of carbon deposits.

Tar Removal in Sludge Gasification

Table. 8 The comparisons of tar content during sludge gasification under different conditions

Sample	Al_2O_3	Al_2O_3+H_2O	1100CS	1100CS+H_2O	NiAl	FeAl	Ni20-CS
Tar yield/ (mg/g)	41	29	23	20	16.4	27.2	13.9
Equivalence factor	Ω =0	Ω =0.16	Ω =0.47	Ω =0.78	Base on Ni20-CS		
Tar yield/（mg/g）	41	22.4	18.6	13.9			
Steam content	0	16.6	27.2	42.7	Base on Ni20-CS		
Tar yield/（mg/g）	18.6	17.6	15.4	14.4	Ω =0.47		

- The OC can oxidize and catalyze the tar cracking, significantly reduce the tar content in the sludge gasification.

Tar removal in Biomass Gasification

Table.9 Effect of hematite OC on biomass gasification

Experimental run	Pyrolysis	CLG	Steam gasification	CLG (H_2O)
LHV (MJ/Nm^3)	16.87	15.52	13.95	11.93
Gas yield (Nm^3/kg biomass, dry-based)	0.75	1.06	1.19	1.53
Carbon conversion efficiency (%)	61.70	86.65	87.21	95.49
Tar content (g/Nm^3, dry-based)	**36.23**	**10.25**	**16.88**	**5.68**

Table.10 Tar content in different gasification model

Gasifying medium	N_2	$NiFe_2O_4$	H_2O/CO_2	$H_2O/CO_2/NiFe_2O_4$
Tar content (g/Nm^3, dry-based)	**22.37**	**3.73**	**14.25**	**2.83**

- **OC can significantly reduce the tar content in biomass gasification, and its performance is much higher than that of conventional oxidization medium.**

III. Control of Inorganic Pollutants-N/Cl Pollutants

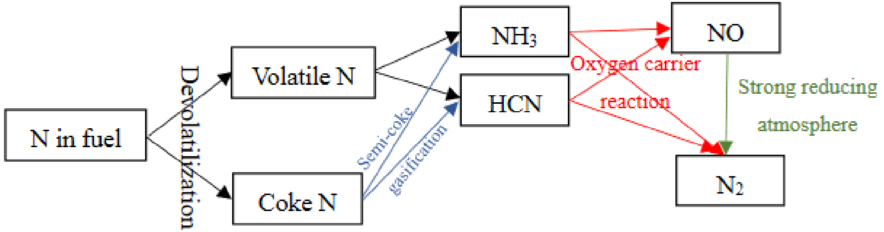
- Removal of N/S/Cl pollutants in CLG of sludge

N pollutants:

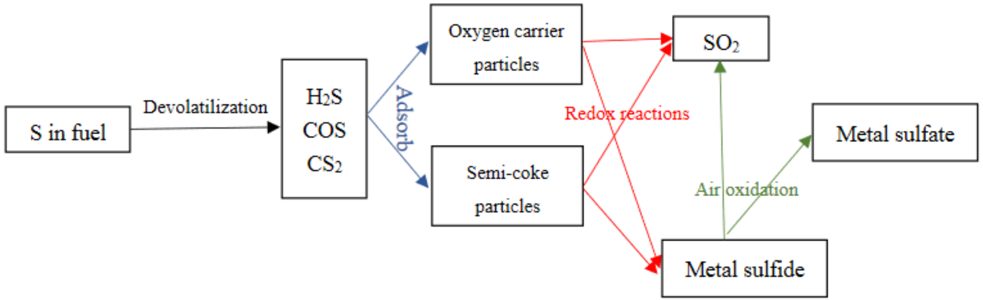
Avoid thermal and rapid NO_x generation

S pollutants:

S element self-fixing



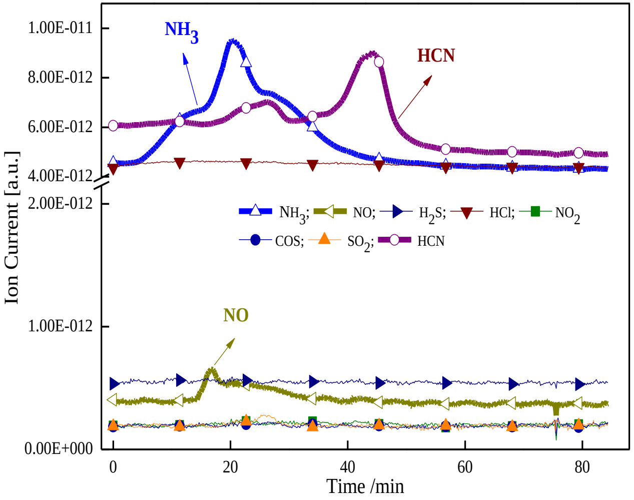
Removal of Fuel-NO_x

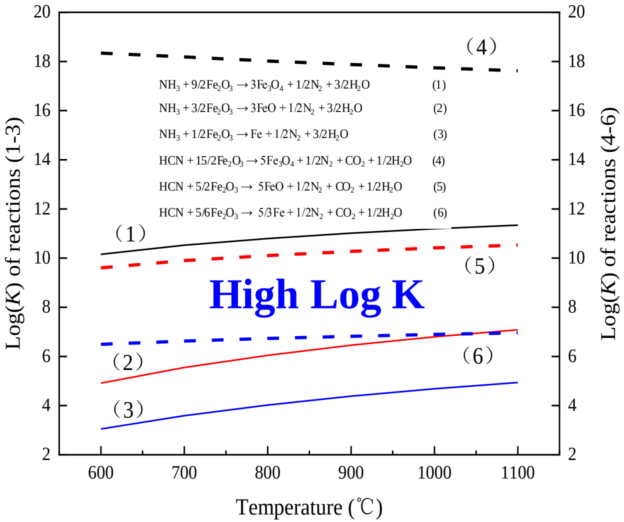


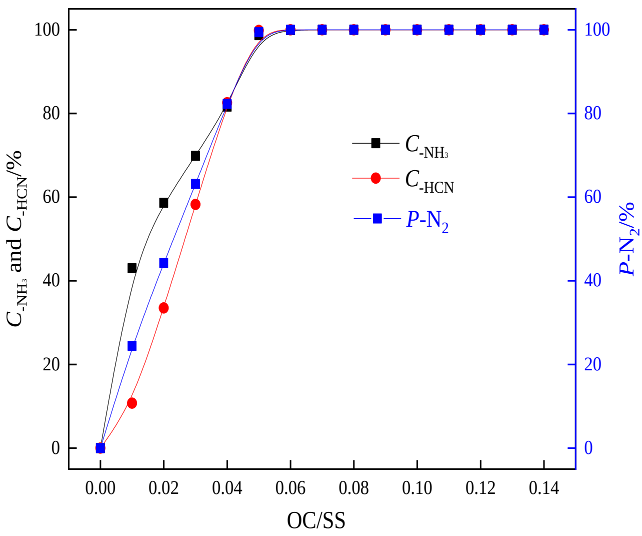
Cl pollutant:

No dioxins formation without gas-phase oxygen

Emission of nitrogenous pollutants during sludge pyrolysis

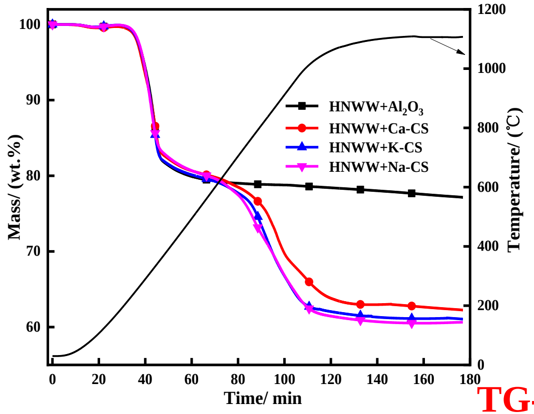


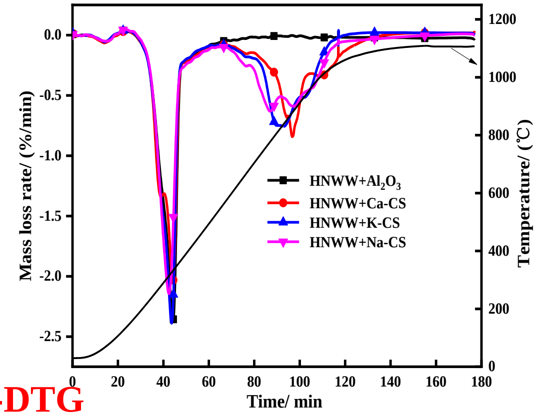




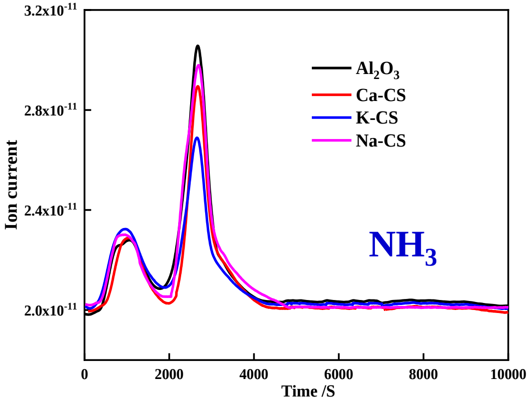
- **The main nitrogen pollutants are NH_3 and HCN in sludge CLG;**
- **NH_3 + [O] = N_2 + H_2O, HCN + [O] = N_2 + H_2O + CO_2;**
- **Reducibility： HCN > NH_3.**

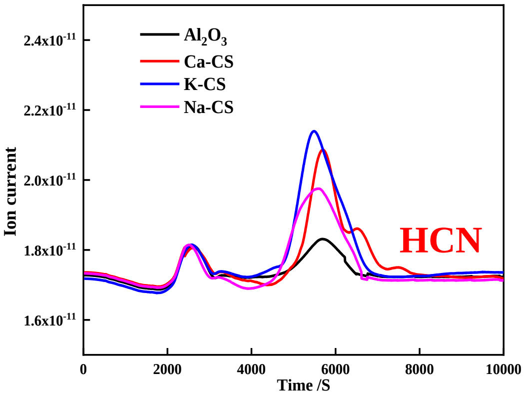
☐ Emissions of nitrogenous pollutants in CLG of wood-based panel waste





TG-DTG





- The OC significantly promotes the char conversion;
- NH_3 is released in devolatilization, and then it is oxidized by the OC;
- HCN is released during char gasification, and the OC promotes the char conversion to release HCN, and then to oxidize HCN.

Nitrogen distributions during sludge pyrolysis and CLG

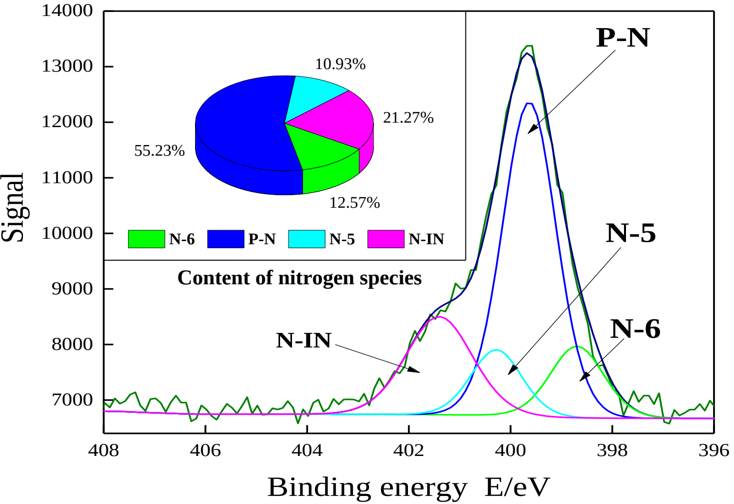
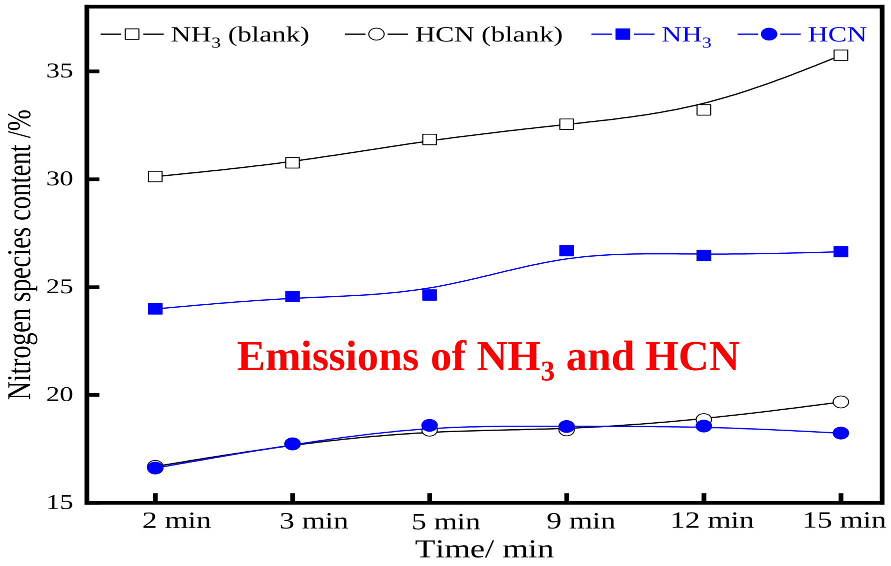


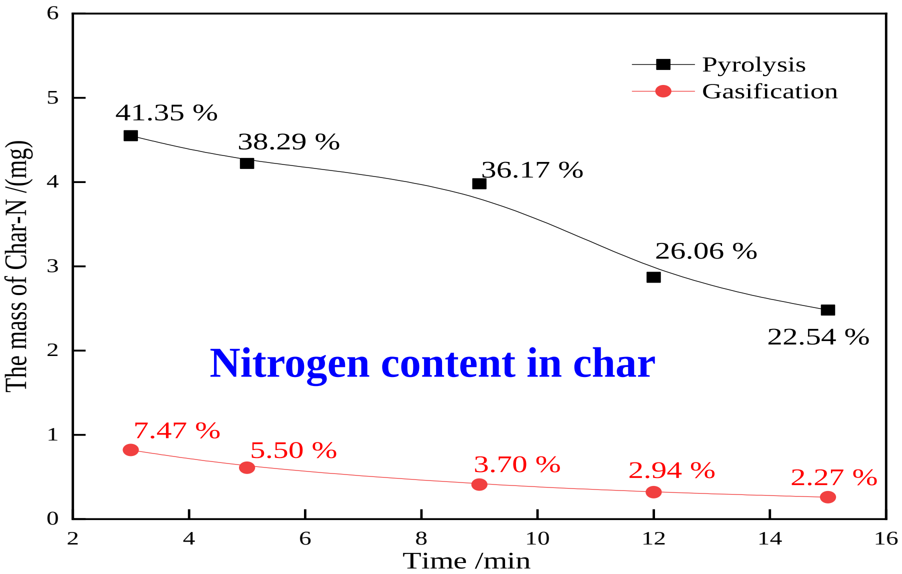
Table.11 Distributions of nitrogen species in sludge pyrolysis and CLG

Mode	η_C	HCN-*N*	NH_3-*N*	Tar-*N*	Char-*N*	N_2-*N*
Pyrolysis	57.03	24.95	20.40	6.27	4.06	44.32
CLG(Cu Slag)	75.06	21.13	14.65	6.52	2.60	55.10
CLG(Ni-Cu Slag)	82.65	3.39	2.22	3.39	1.76	91.98

- **Sludge sample：** 55% (Protein nitrogen/P-N), 21% (Inorganic ammonium/N-IN), 13% (Pyridine nitrogen/N-6), 11% (Pyrrole nitrogen/N-5);
- **A large amount of NO_x precursors (NH_3/HCN) are generated during sludge pyrolysis;**
- **OC can significantly promote the generation of N_2 to reduce the N-pollutants.**

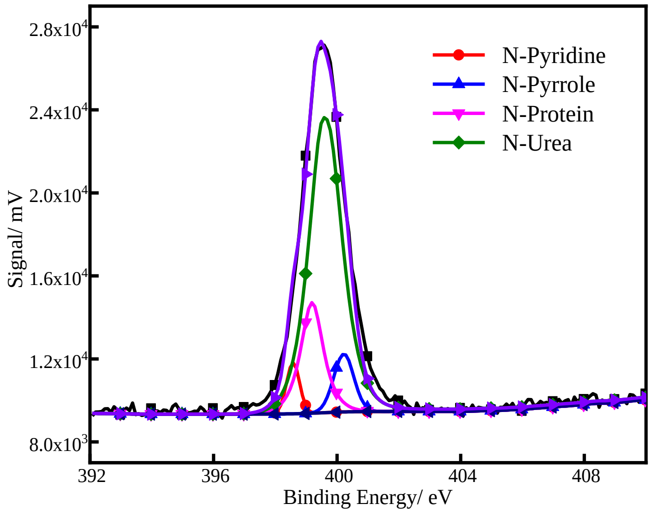
Emissions of N-pollutants during pyrolysis and CLG of wood-based panel waste

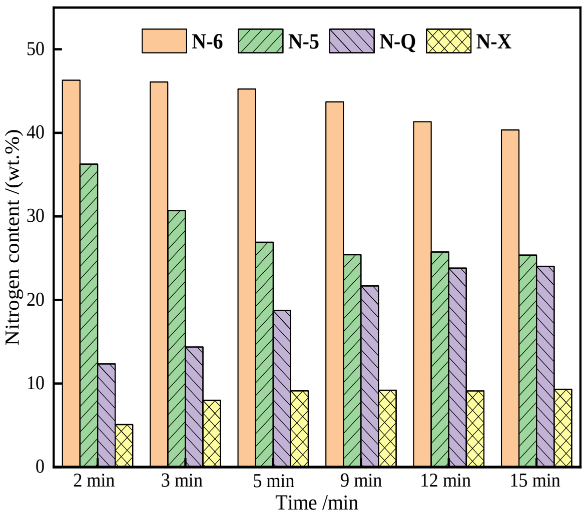


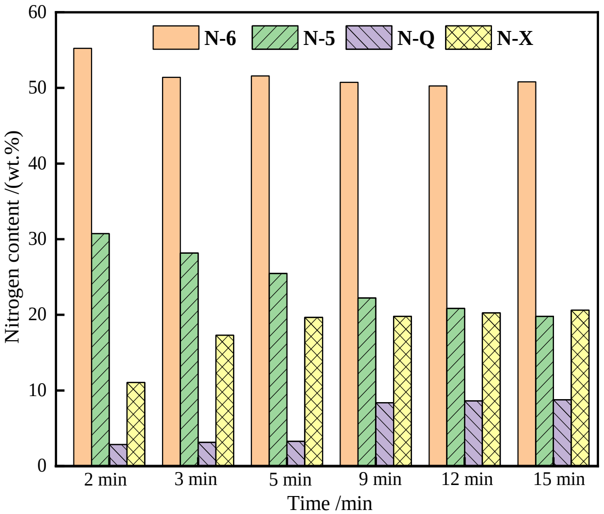


- The **nitrogen pollutants are significantly reduced** in CLG, especially NH_3;
- More **N elements remain in char** during pyrolysis;
- NH_3 **is quickly oxidized**, while HCN **is first released from the char and then oxidized by the OC**.

Evolutions of nitrogen-containing functional groups in char

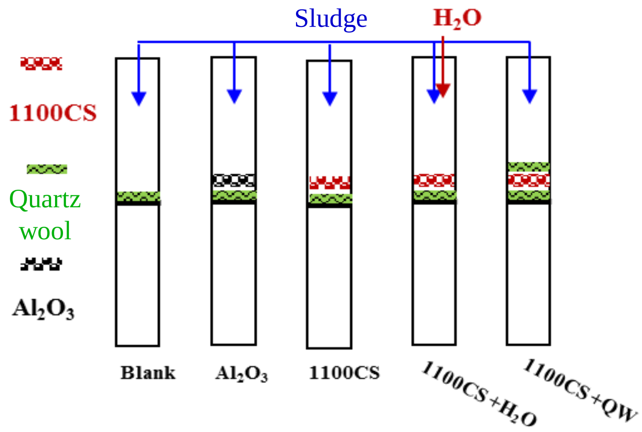


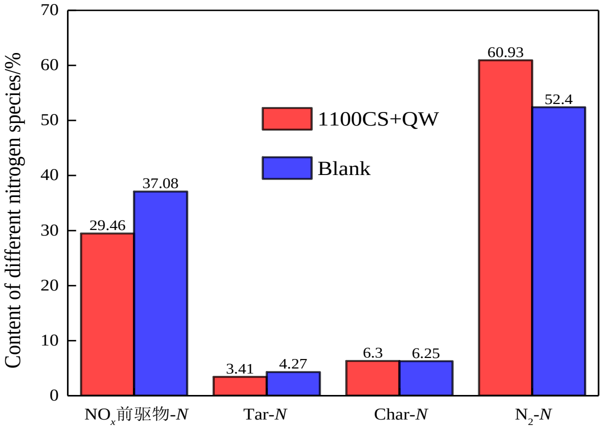


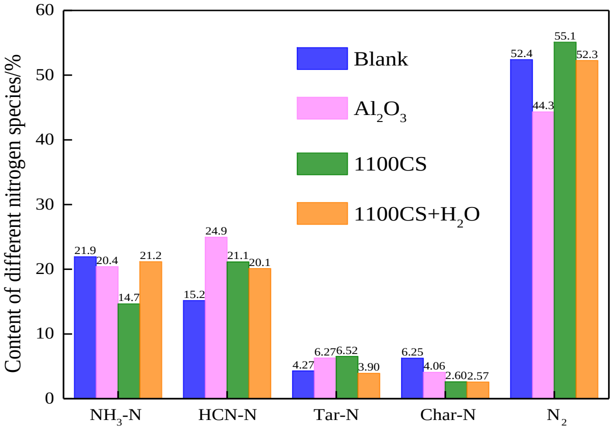


- **Wood-based panel waste: N-U, 70%; N-P, 18%; N-5, 8%; N-6, 4%.**
- **Pyrolysis process: N-6, N-5, N-Q, N-X.**
- **CLG process: N-6, N-5, N-X, N-Q.**
- **Nitrogen-containing functional groups are more stable in CLG.**

Distributions of nitrogen species under different conditions (Sludge)

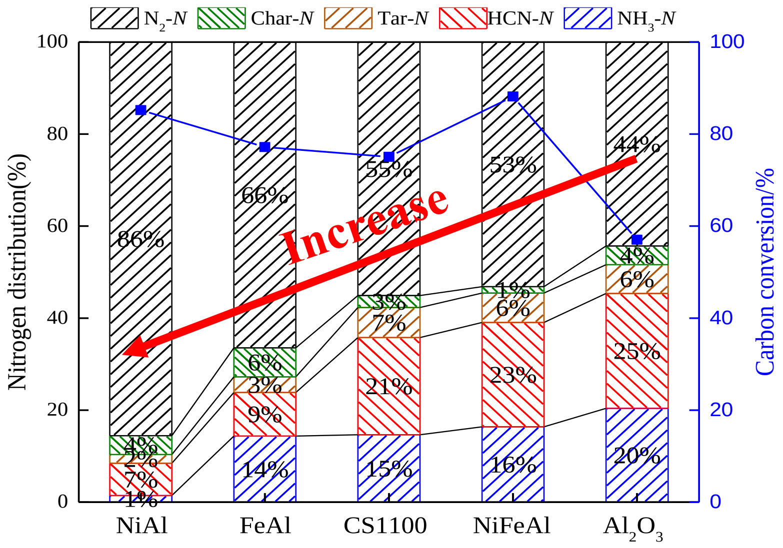


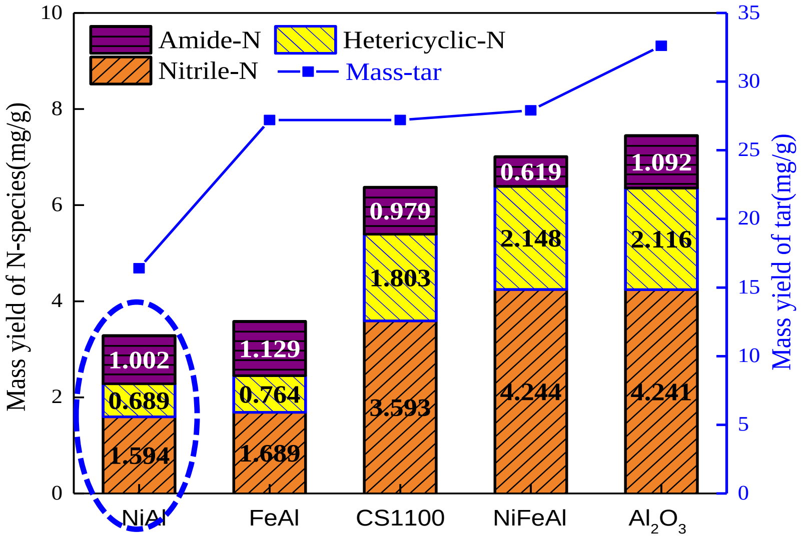




- **The solid carrier enhances the heat and mass transfer, promoting the conversion of nitrogen in the sludge into N_2;**
- **The copper slag OC can further promote the conversion of nitrogen-containing compounds of sludge pyrolysis (NO_x precursors, char nitrogen, tar nitrogen) into N_2;**
- **The steam can promote the conversion of char nitrogen and tar nitrogen, but increases the content of NO_x precursors, especially NH_3-N, $HCN + H_2O \rightarrow NH_3 + CO$.**

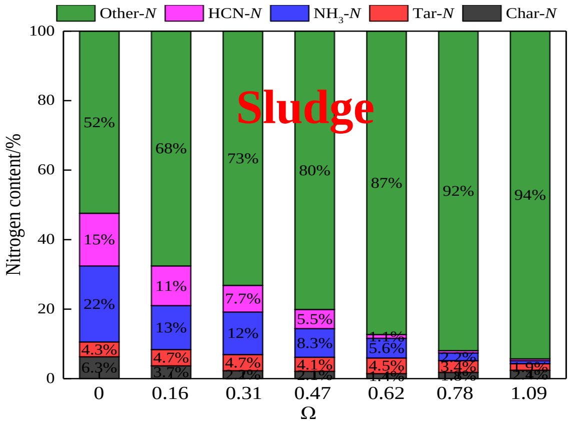
Effect of different OCs on the distributions of nitrogen species (sludge)

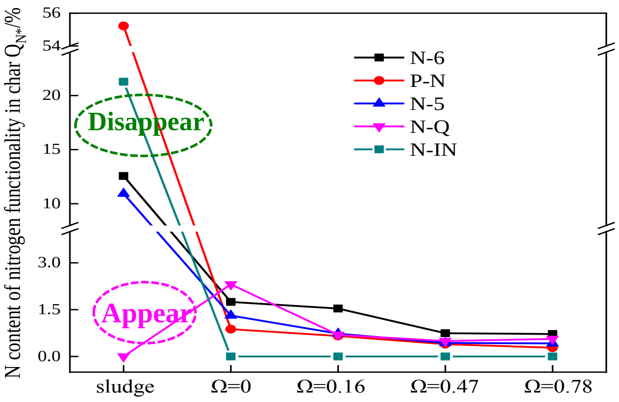


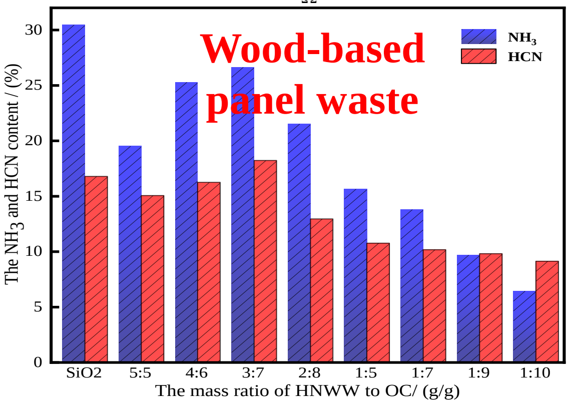


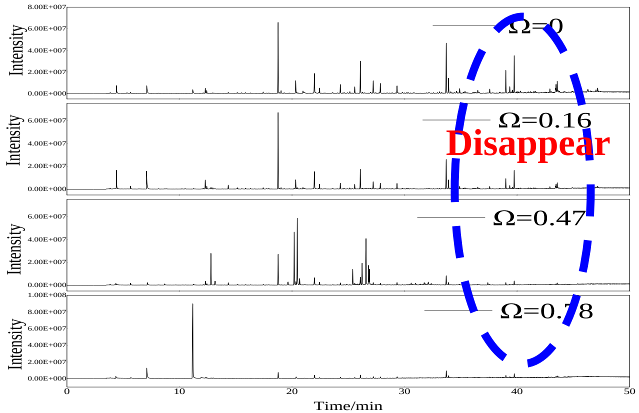
- **OC with higher oxidation performance is facilitated to the conversion of NO_x precursors, char nitrogen, and tar nitrogen into N_2, and NiO OC has the best performance;**
- **Tar N contains Nitrile-N, Hetericyclic-N and Amide-N, and NiO can significantly promote the conversion of Hetericyclic-N and Nitrile-N in tar.**

Effect of equivalent coefficient (*Ω*) on the migration and transformation of Nitrogen



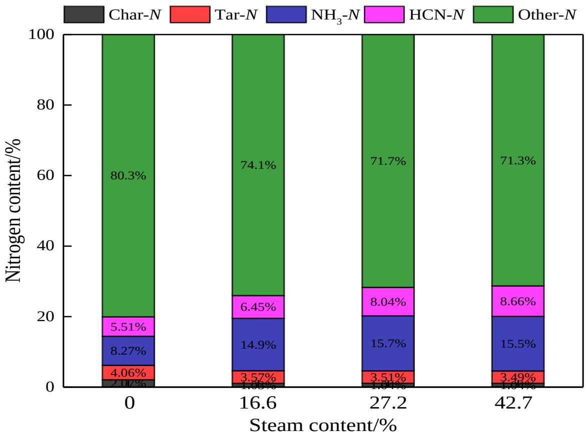


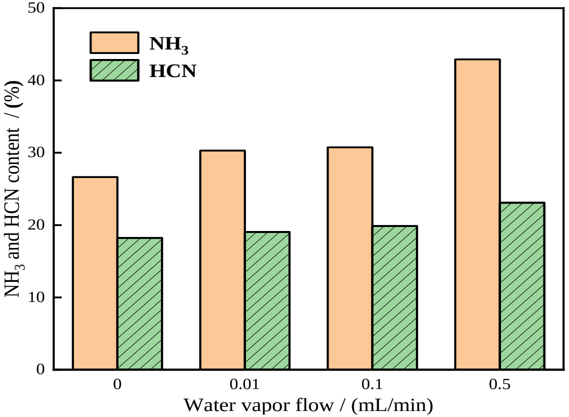


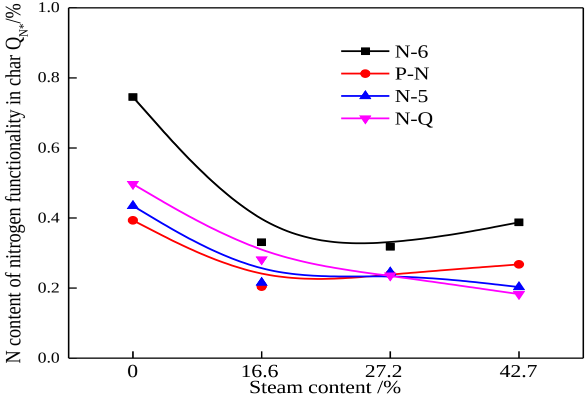


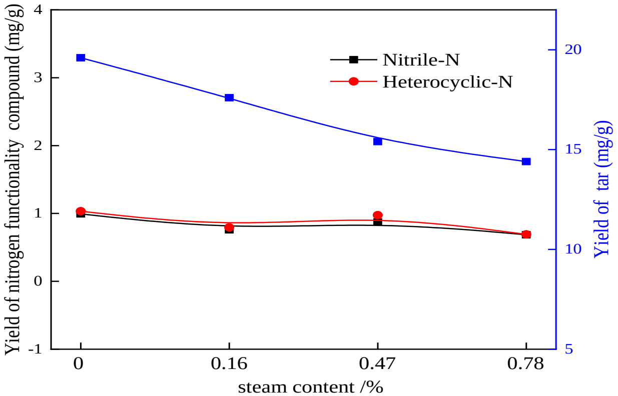
- Increasing the *Ω* is conducive to the conversion of nitrogen in sludge into N_2, and the removal of HCN is higher than NH_3;
- The protonated nitrogen (N-Q) appears in the char, and the stability of the nitrogen-containing functional group: N-Q ＞ N-5 ＞ N-6>P-N> N-IN, N-IN is directly decomposed into NH_3;
- Increasing the *Ω* can significantly promote the ring-opening cracking of the Nitrile-N, Hetericyclic-N in tar, converted into N_2.

Effect of steam content on the migration and transformation of nitrogen



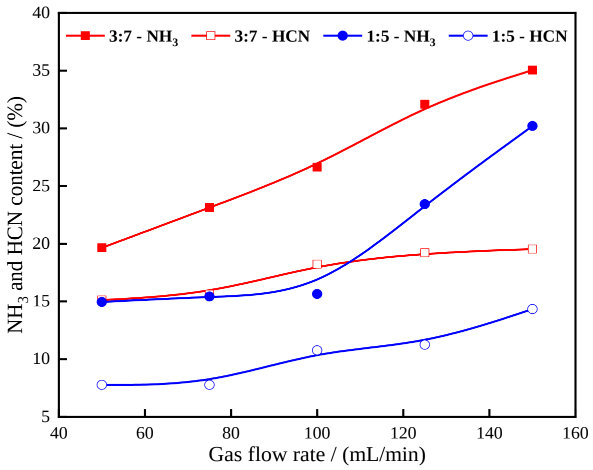


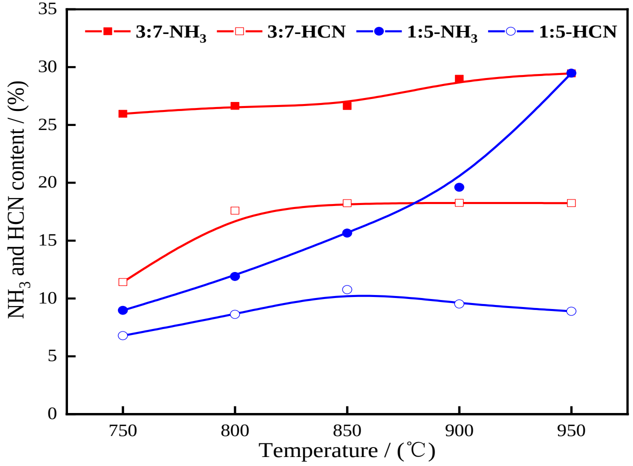


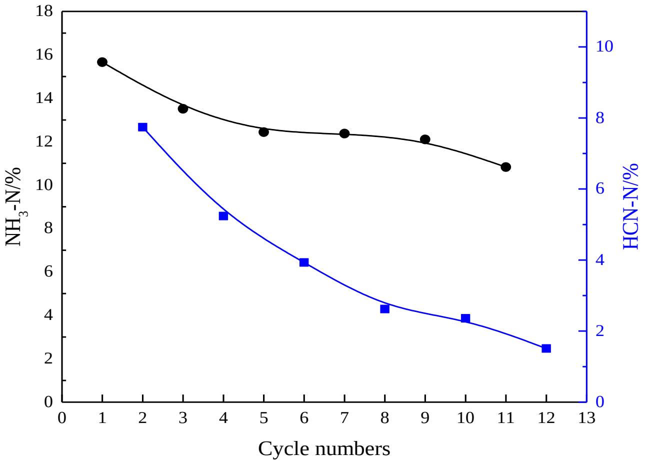


- The **increase of steam is not conducive to** the conversion of N element in the fuel to N_2, and the increase of **NH_3-N** is higher than **HCN-N: $HCN+H_2O \rightarrow NH_3+CO$**
- Steam **can promote the ring-opening cracking of char nitrogen and tar nitrogen;**
- Effect of steam on the **removal of tar nitrogen and char nitrogen is not obvious.**

Effect of residence time, temperature and cycle numbers on NO_x precursors

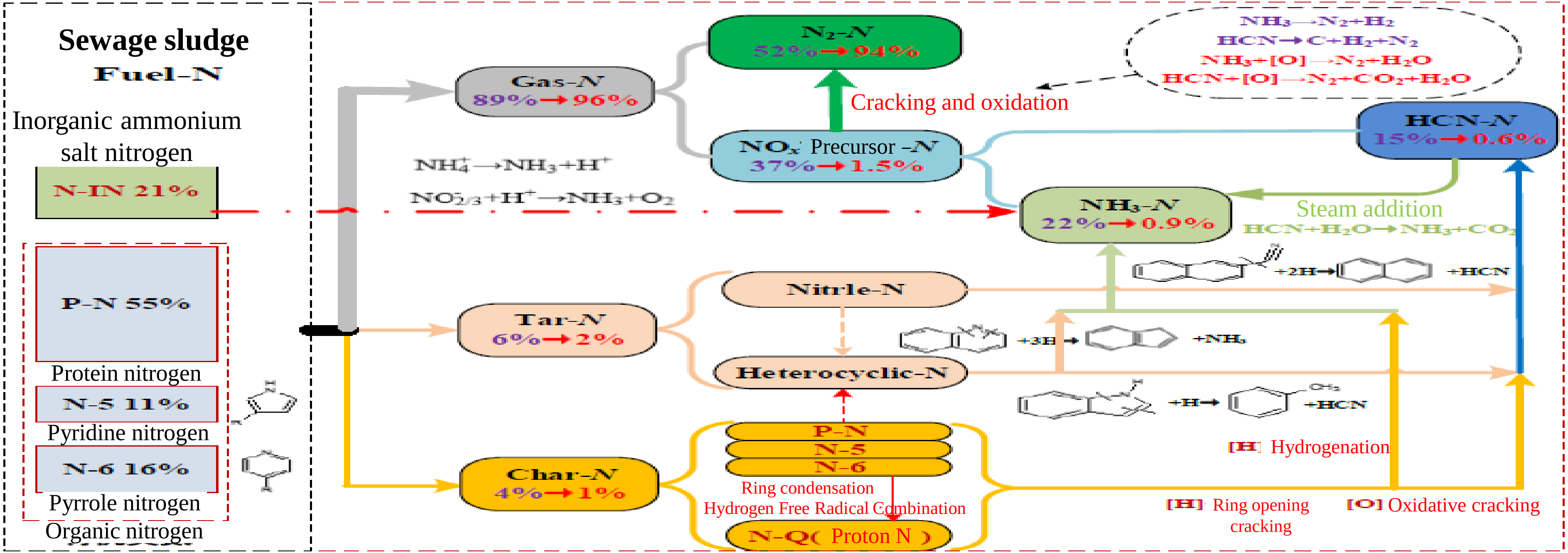






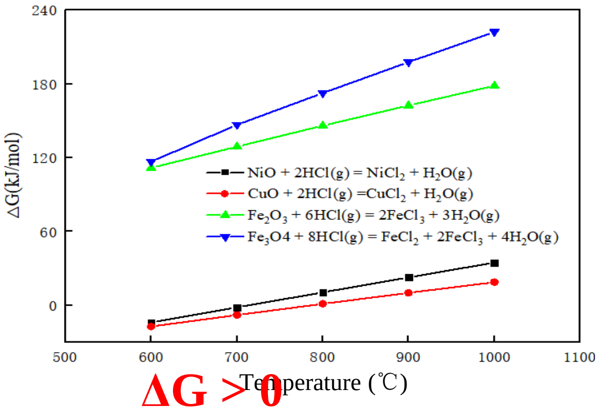
- The **shortening** of residence time and **the increase** of temperature **are not conducive to the control of N-pollutants**;
- The **increase in the number of cycles is beneficial to the control of NH_3 and HCN** in the sludge gasification, and the content of **HCN is lower than that of NH_3**.

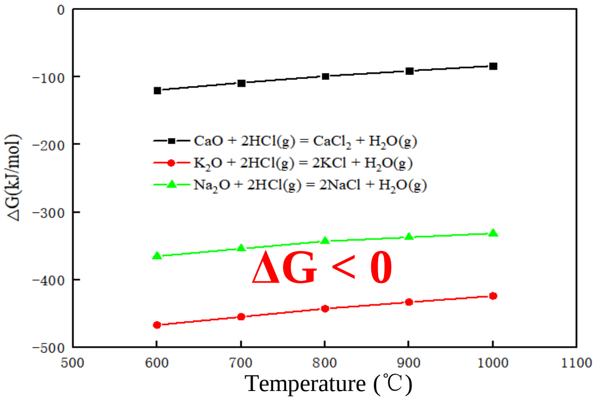
Migration and transformation paths of nitrogen in sludge

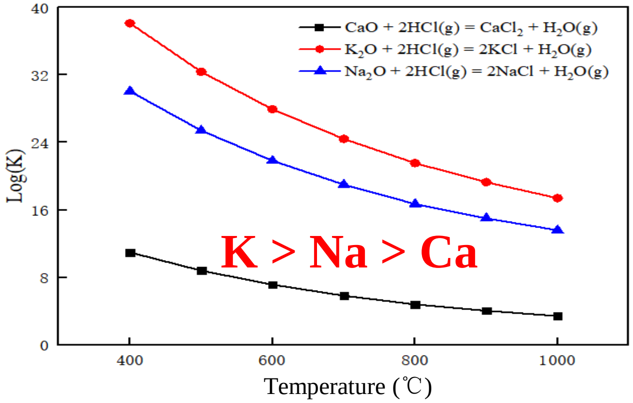


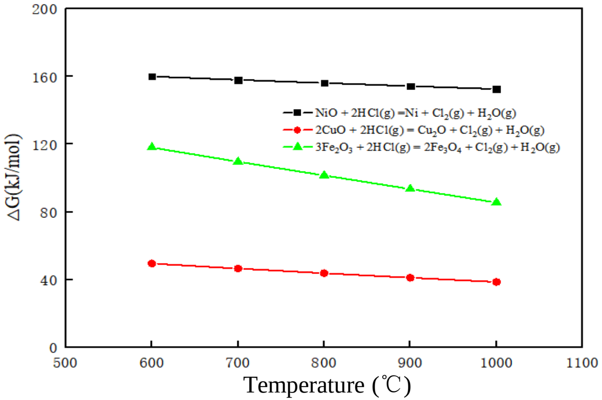
The OC in the dense phase zone can be used as an oxidizing medium to oxidize the reducing nitrogen-containing pollutants (NH_3/HCN) to N_2; since there is no molecular oxygen in the dilute phase zone, the strongly reducing atmosphere in chemical looping can reduce the oxidizing pollutants(NO_x) to N_2, further to achieve the high-efficiency removal of fuel-type nitrogen-containing pollutants.

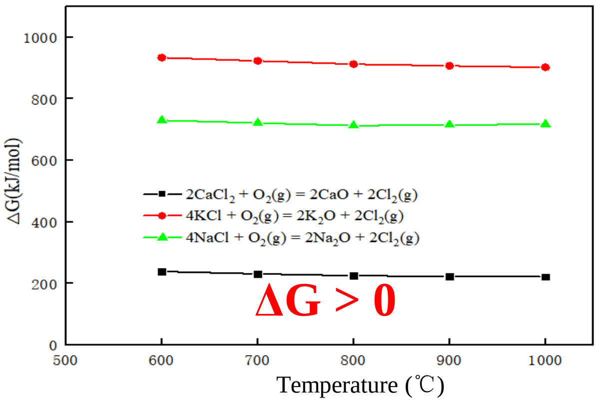
Thermodynamic predictions of chlorine element





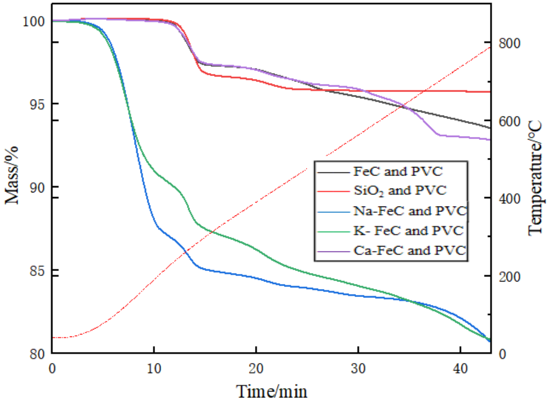


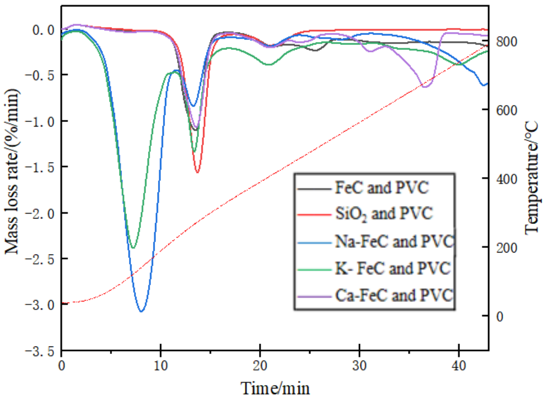


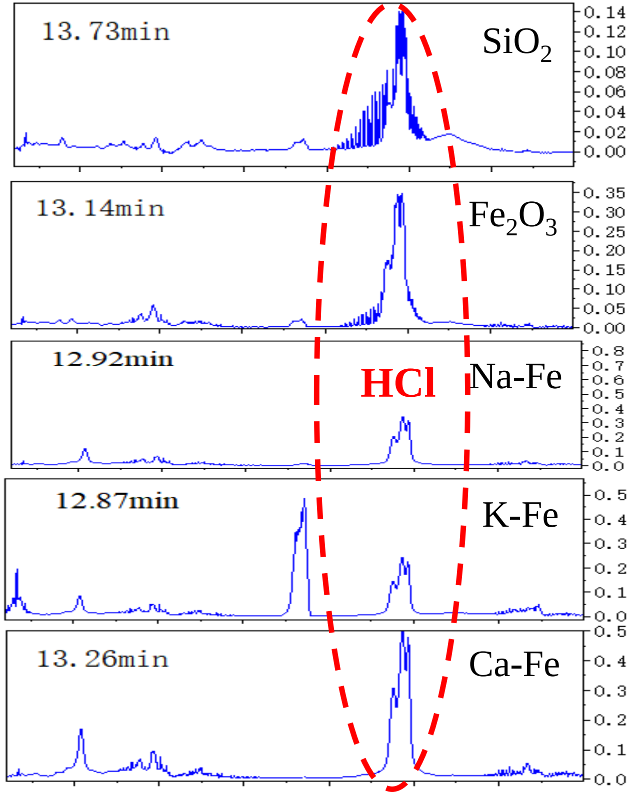


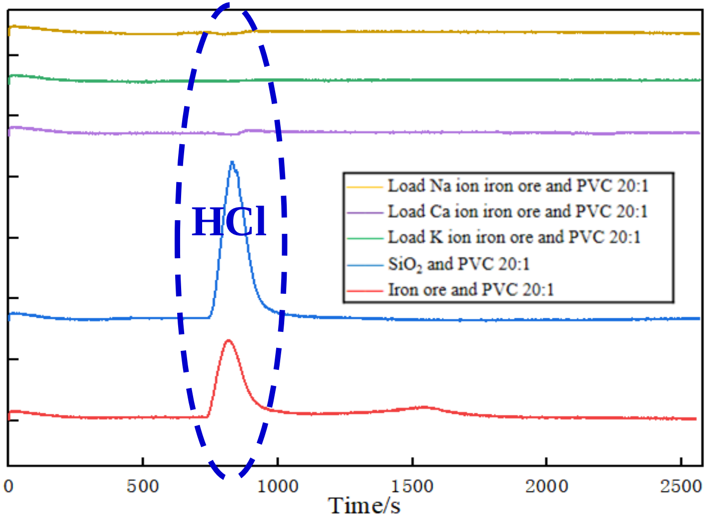
- **Transition metal oxides are difficult to react with HCl(g);**
- ***AAEMs* oxides react easily with HCl(g);**
- **Dioxin precursor Cl_2 is difficult to generate in air reactor;**
- ***AAEMs* dechlorination sequence, K>Na>Ca.**

De-chlorination of waste PVC gasification with different OCs



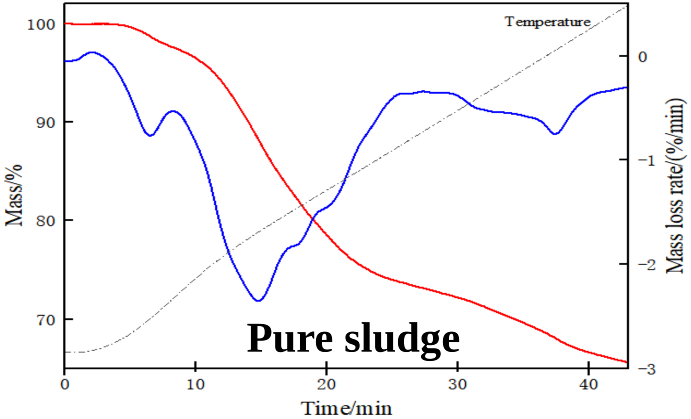




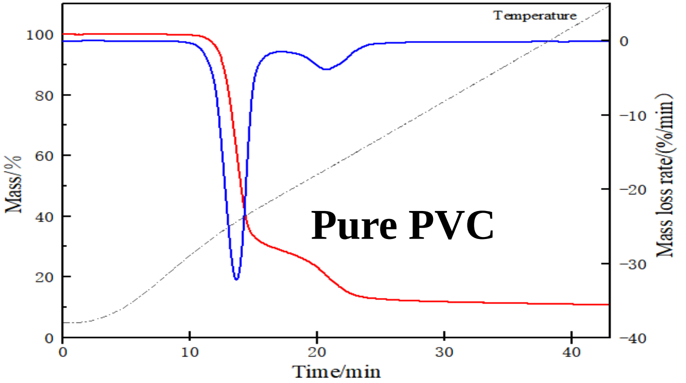


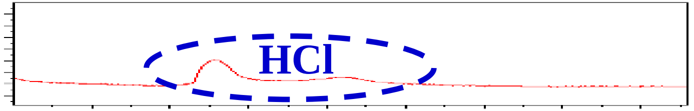
- **The *AAEMs* modified iron ore OCs have excellent de-chlorination performance.**

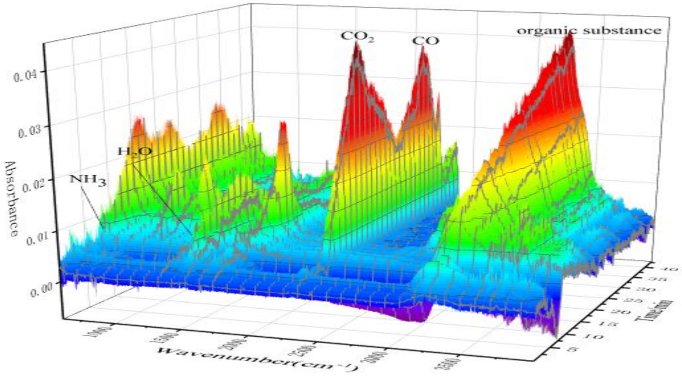
Co-conversion of sludge and waste PVC



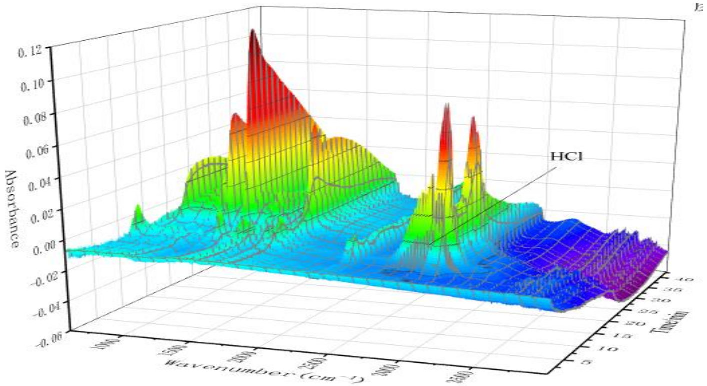
- HCl content is low in sludge pyrolysis



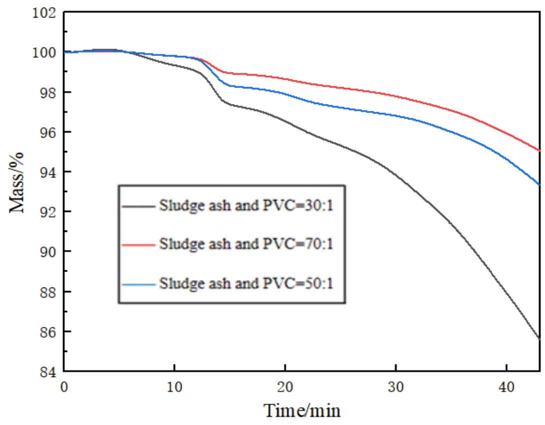


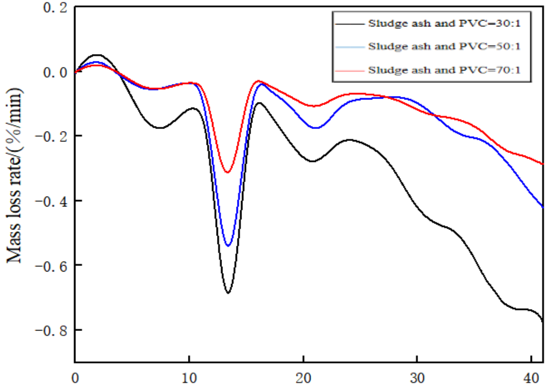


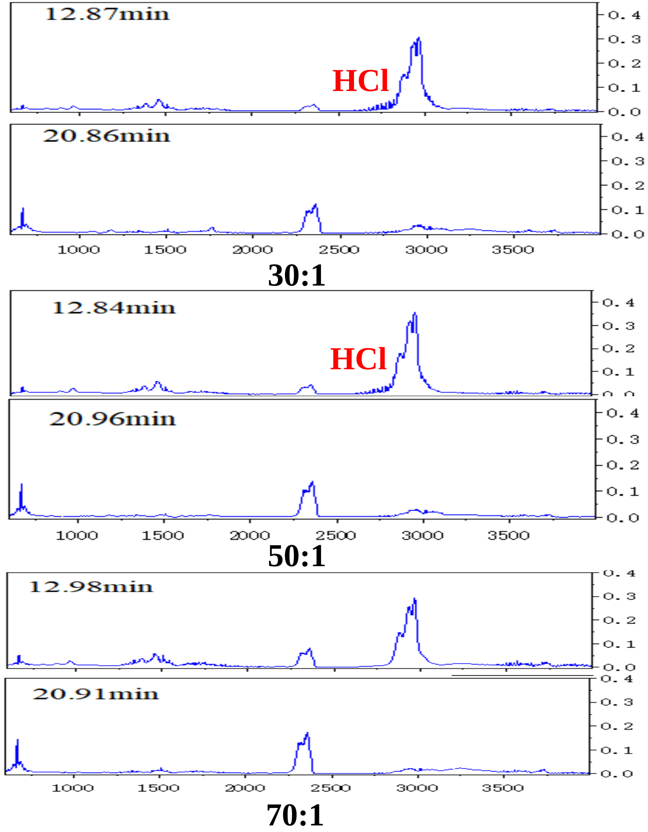
- A large amount of **HCl is generated** in PVC pyrolysis

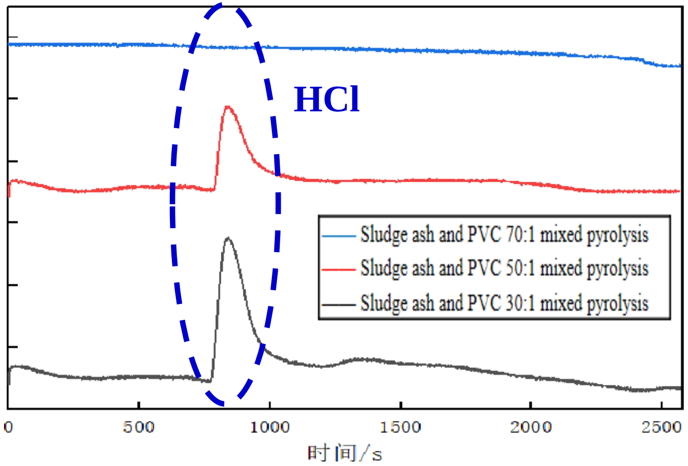


De-chlorination of waste PVC using sludge ash



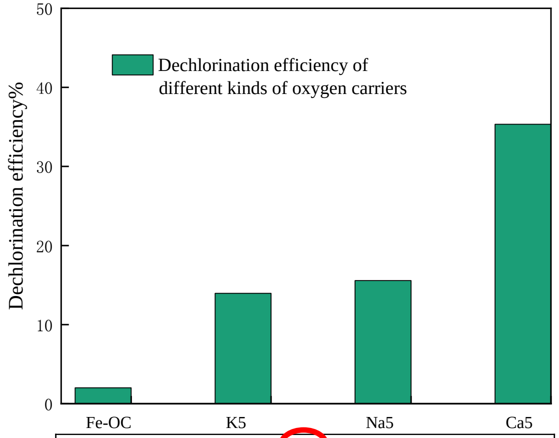


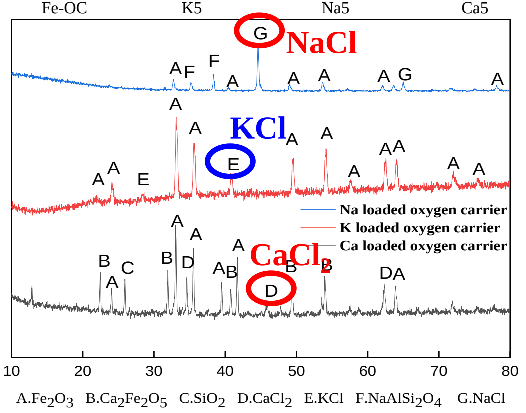




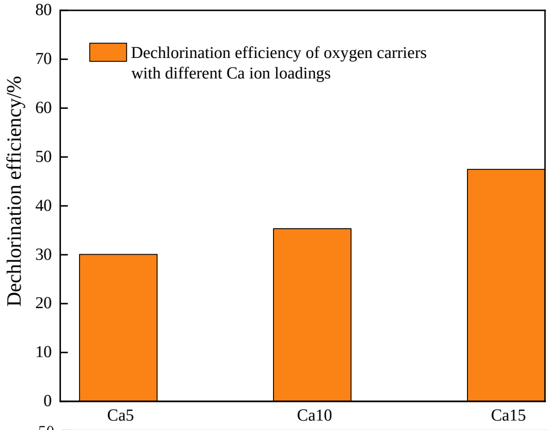
- The sludge ash contains **$CaO/K_2O/MgO$ other *AAEMs* oxides**, which have **good** dechlorination performance

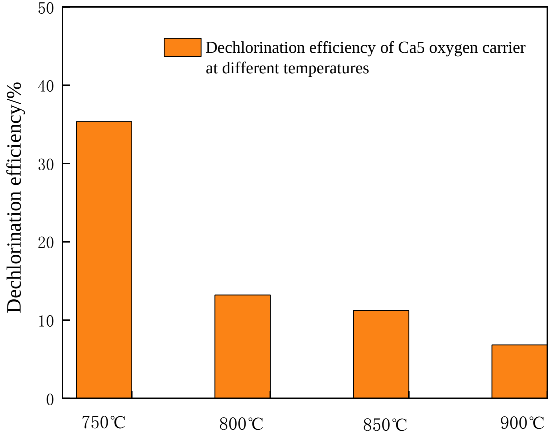
Removal of HCl using different OCs



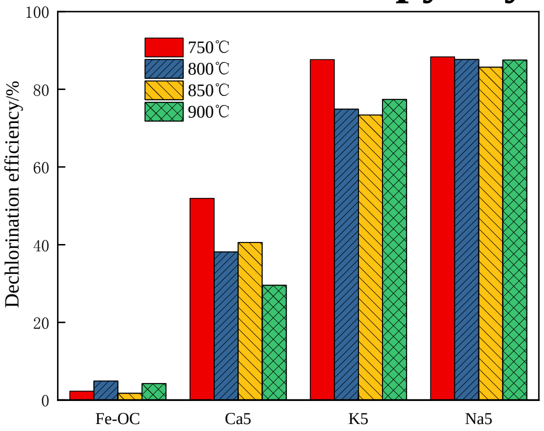


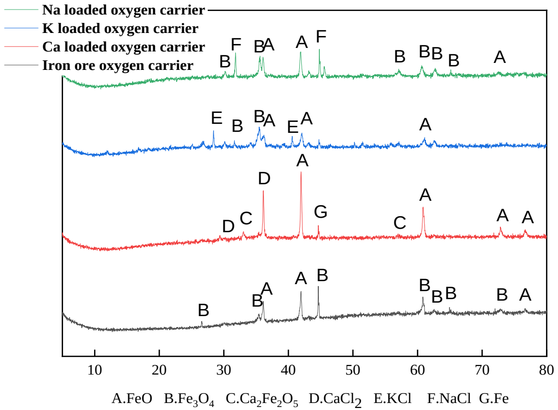
- Calcium ion (Ca^{2+}) has the **highest HCl** removal efficiency;
- The removal efficiency of HCl **increases** with the **increase of Ca^{2+} loading amount**;
- The **low temperature facilitates** the removal of HCl.





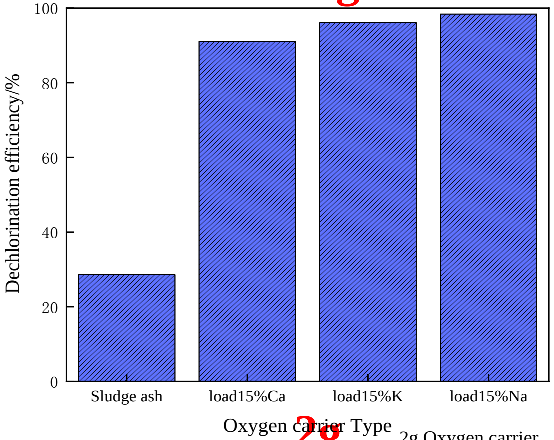
Removal of HCl in pyrolysis gas of sewage sludge



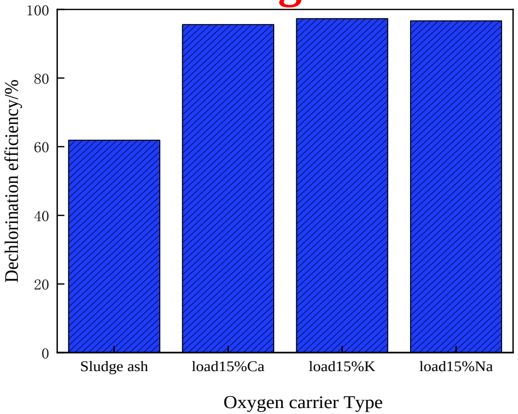


- **Na ion (Na$^+$) shows the best dechlorination performance;**
- **The increase of OC facilitates the removal of HCl.**

0.5g 0.5g Oxygen carrier



2g 2g Oxygen carrier



Co-conversion of sewage sludge and PVC waste

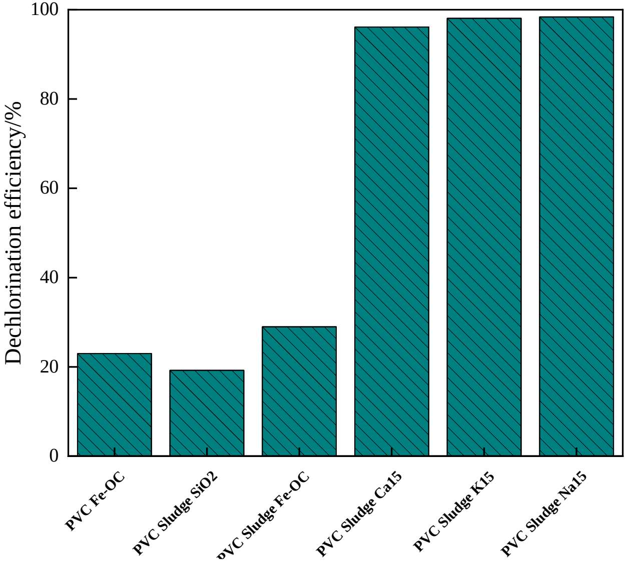
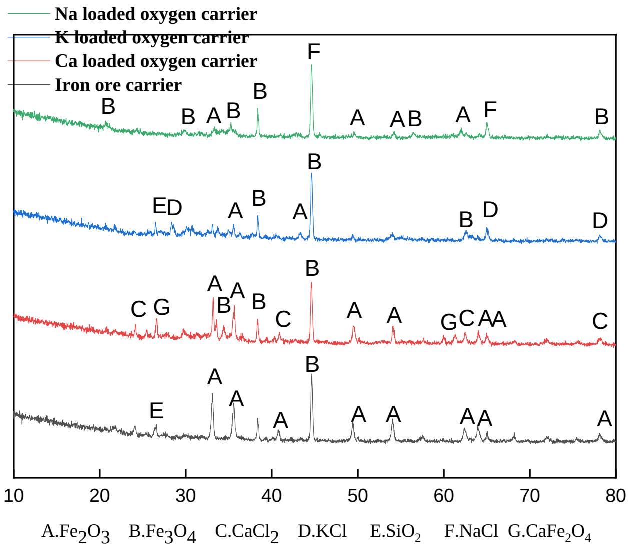


Table.12 Effect of PVC/Sludge ash mass ratio on dechlorination efficiency

PVC/Sludge ash mass ratio	Dechlorination Efficiency
0.2g/1g	15%
0.2g/2g	50%
0.2g/3g	81.3%
0.2g/4g	98.3%
0.2g/5g	97.3%



➢ **Chemical looping co-conversion of sludge and waste PVC can achieve the high-efficiency de-chlorination**

☐ Cheap OCs

- The ash content in organic solid waste is high (~**50 wt.%**), and the **OC is easily lost** during the ash discharge;
- The multiple **impurities** may also cause **irreversible inactivation** of OC;
- The **low-cost**, **widely-sourced** OC is particularly important in CLG of organic solid waste.

Table.13 The main components of calcined copper slag

Item	Fe_2O_3	SiO_2	CaO	Al_2O_3	CuO	MgO
Content (%)	35~60	25~40	2~10	3~15	0.3~2.1	0.7~3.5

Active component **Inert component**

✓ **Modification of Ni/Cu/Fe/Mn and other transition metal oxides**

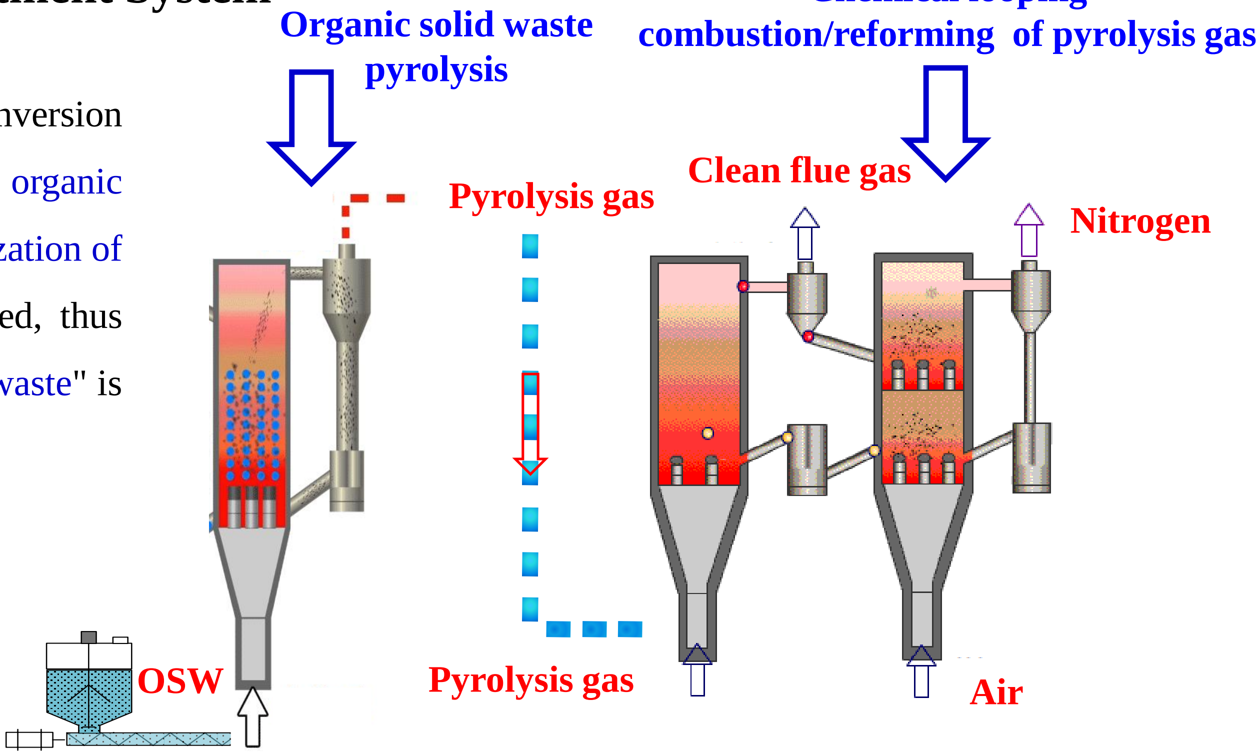
Improve Oxidation Ability

Improve Catalytic Ability

✓ **Modification of K/Na/Ca and other *AAEMs* oxides**

Organic Solid Waste Treatment System

- Using the chemical looping conversion method, the energy utilization of organic solid waste and the resource utilization of inorganic solid waste are realized, thus the goal of "using waste to treat waste" is achieved.



Decentralized, Clean, Low cost

Thank You

Questions?