Effects of low molecular weight compounds on the catalytic upgrading of coal gaseous tar

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by Shanxi Province and the Ministry of Science and Technology
Taiyuan University of Technology
Shanxi province, China

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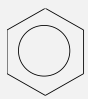
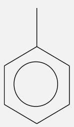
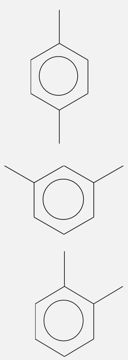
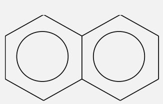
Introduction

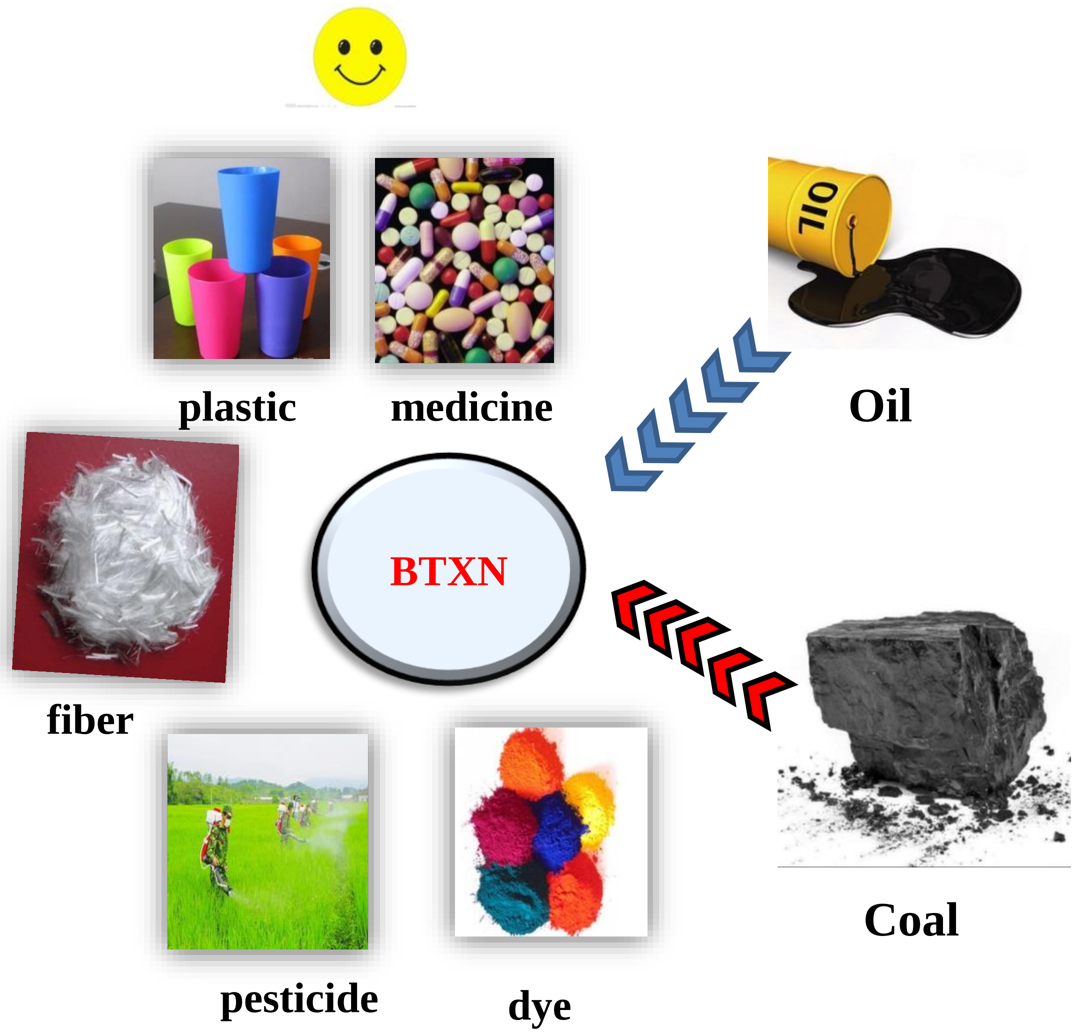
High value–added chemicals


B: Benzene


T: Toluene


X: Xylene (m, p-xylene, o-xylene)


N: Naphthalene



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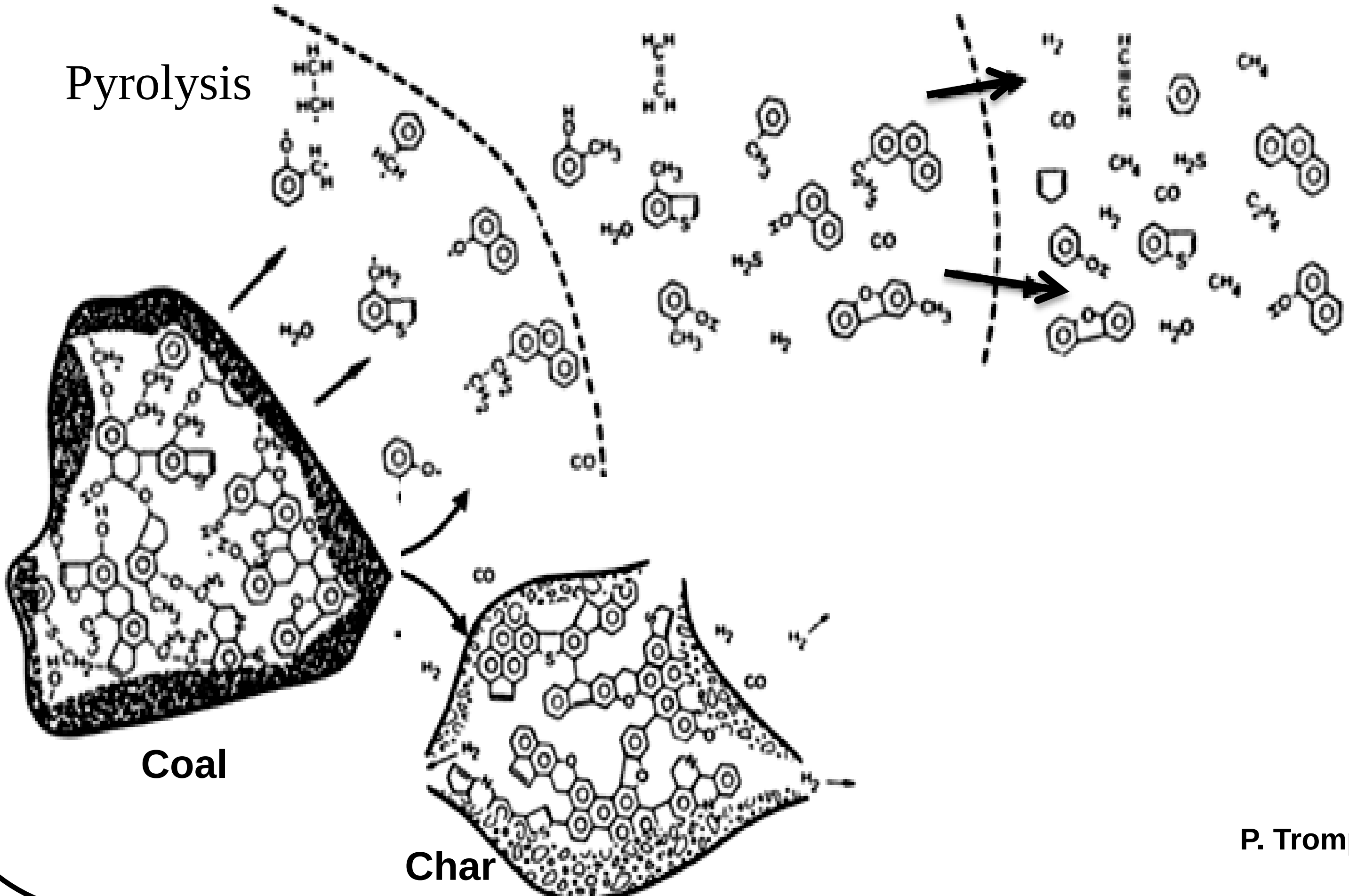
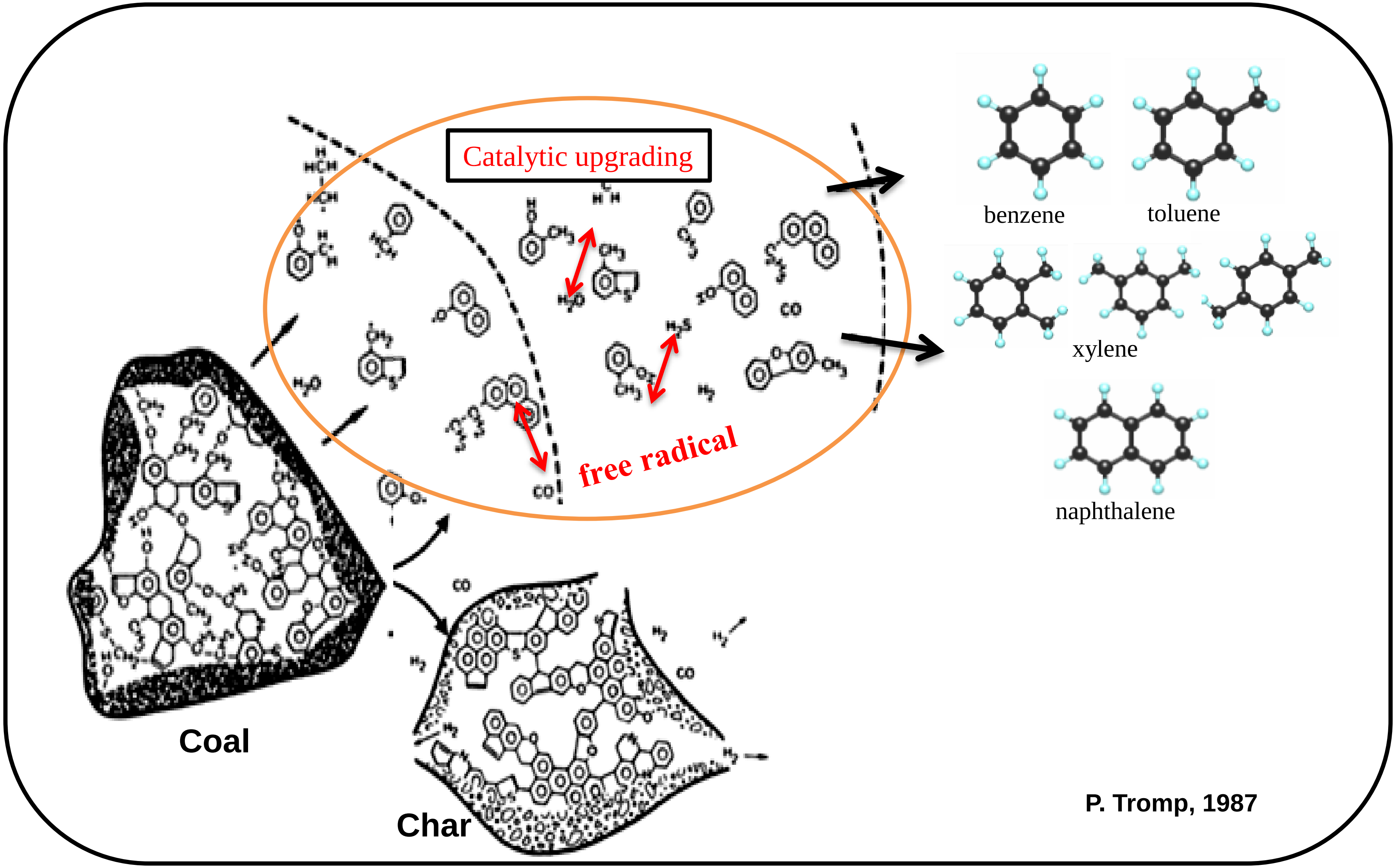


P. Tromp, 1987

Introduction



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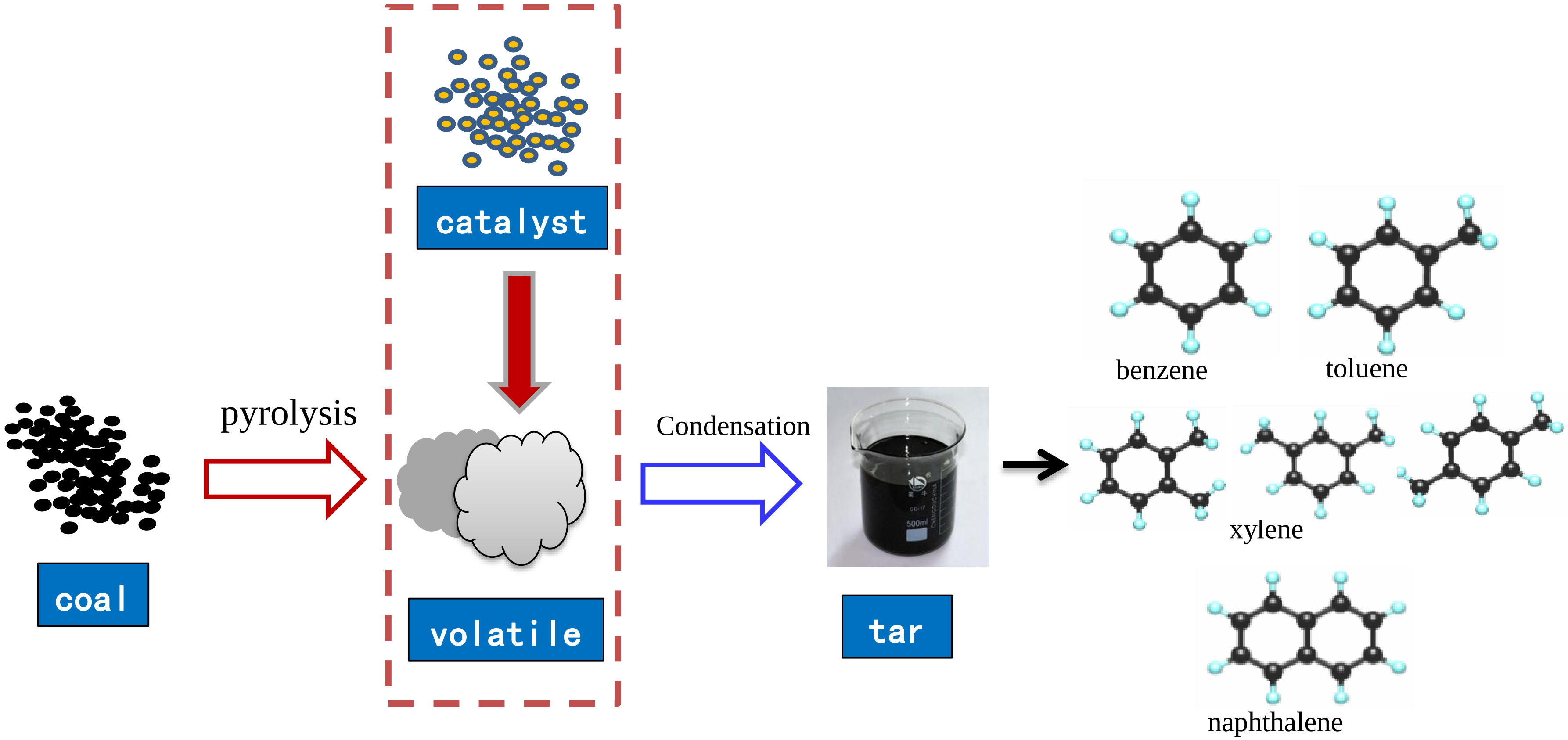
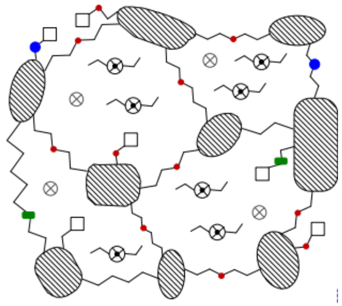
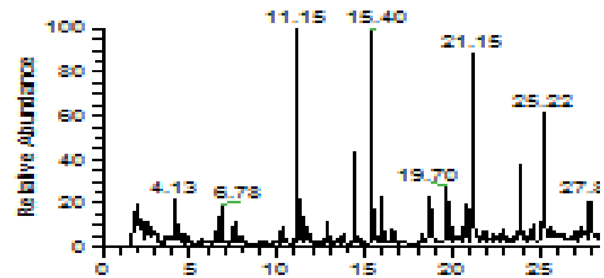


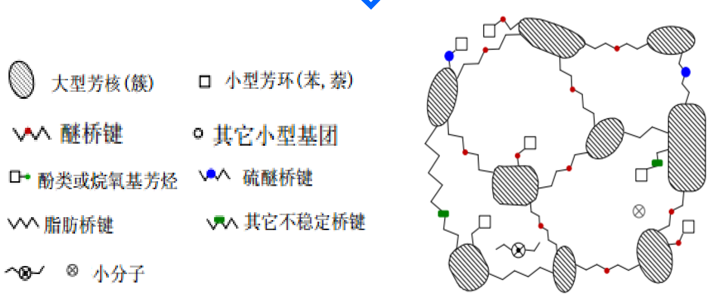
Introduction

Coal

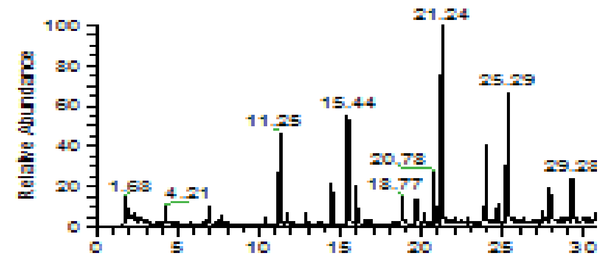


Catalytic upgrading





Catalytic upgrading



Role of low molecular compounds in coal on the catalytic upgrading of coal gaseous tar

Experimental

✓ Coal samples

Table 1. Proximate and ultimate analyses of the coal samples used in the experiments

Samples	Proximate analysis (wt/%)			Ultimate analysis (wt/%, daf)				
	M_{ad}	A_{ad}	V_{daf}	C	H	O*	N	S
Coal DA	11.7	15.3	46.5	69.0	4.3	24.7	1.2	0.7
Coal DB	0.5	9.0	22.9	86.1	4.7	7.1	1.7	0.4

Note: ad, air-dried basis; daf, dry and ash-free basis; *by difference

✓ Extraction experiments

Fig 1. Soxhlet extractor

solvent : pyridine

Extract yield:

$$wt\% = \frac{100 \times (m_1 - m_2)}{m \times (100 - M_{ad} - A_{ad})} \times 100\%$$

where m_1 and m_2 (g) was the weight of mineral-free coal samples before and after pyridine extraction, and m (g) was the weight of raw coal, respectively.

Raw coal	Residual coal		Solution
Coal DA ⟷	Coal DAR	+	AE
Coal DB ⟷	Coal DBR	+	BE

Experimental

✓ Pyrolysis-GC/MS conditions

Fig. 2 The pictures of Pyrolysis-GC/MS

Pyrolysis conditions:

- Pyrolysis temperature: 800 ^{o}C
- Heating rate: 10 ^{o}C/ms
- Residence time: 15s

GC conditions:

- Column: DB-5MS (30m×0.25mm×0.25μm)
- Inlet temperature: 250 ^{o}C
- Temperature program:

$$50\ ^{o}\text{C(3min)} \xrightarrow{3\ ^{o}\text{C /min}} 300\ ^{o}\text{C (1min)}$$

MS conditions:

- Carrier gas: He (>99.999%)
- Ion source temperature : 250 ^{o}C
- Ionization mode : EI
- Transfer line temperature: 310 ^{o}C

Experimental

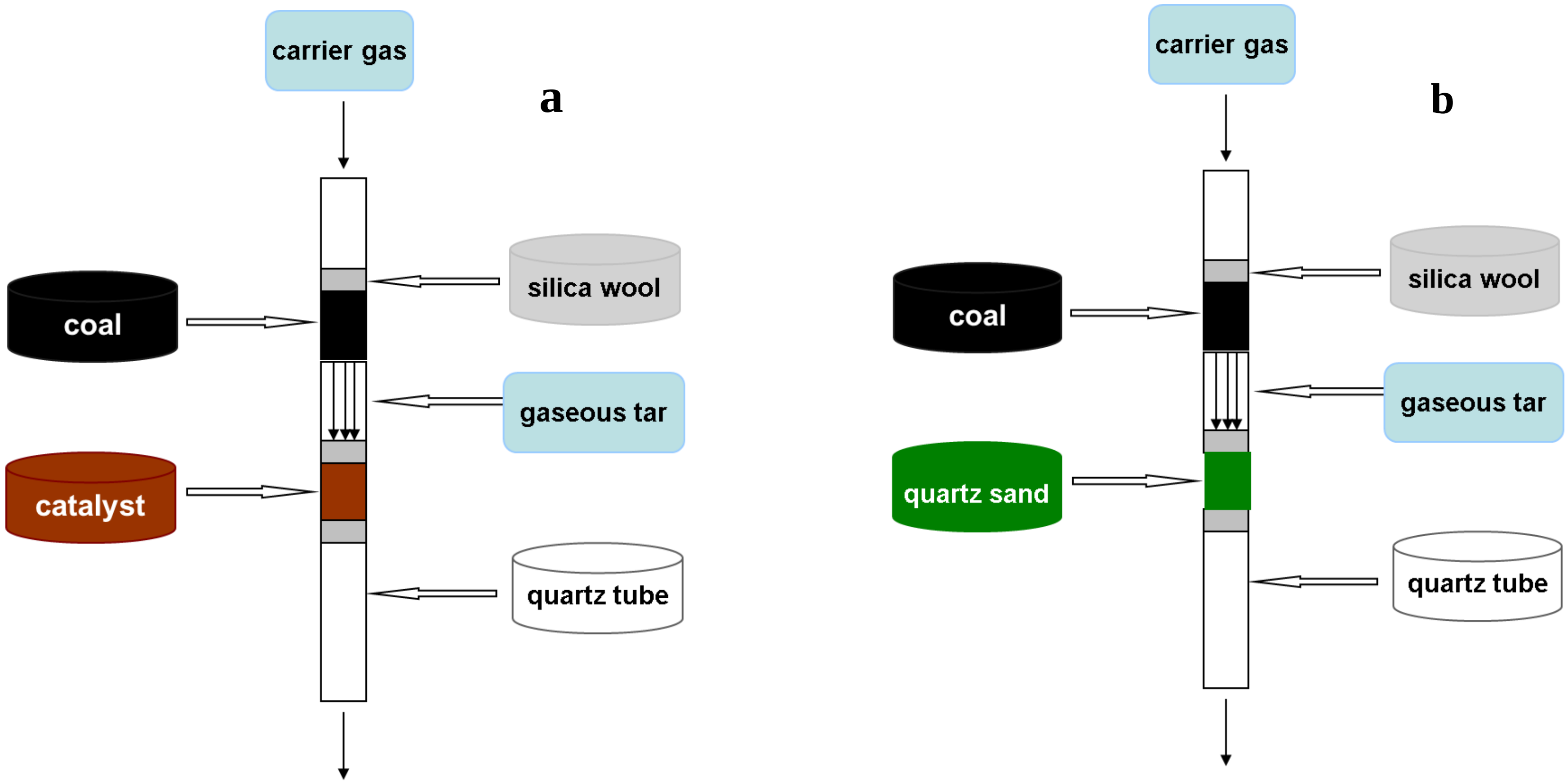


Fig. 3 Sample placement of experiments (a: pyrolysis b: catalysis)

Experimental

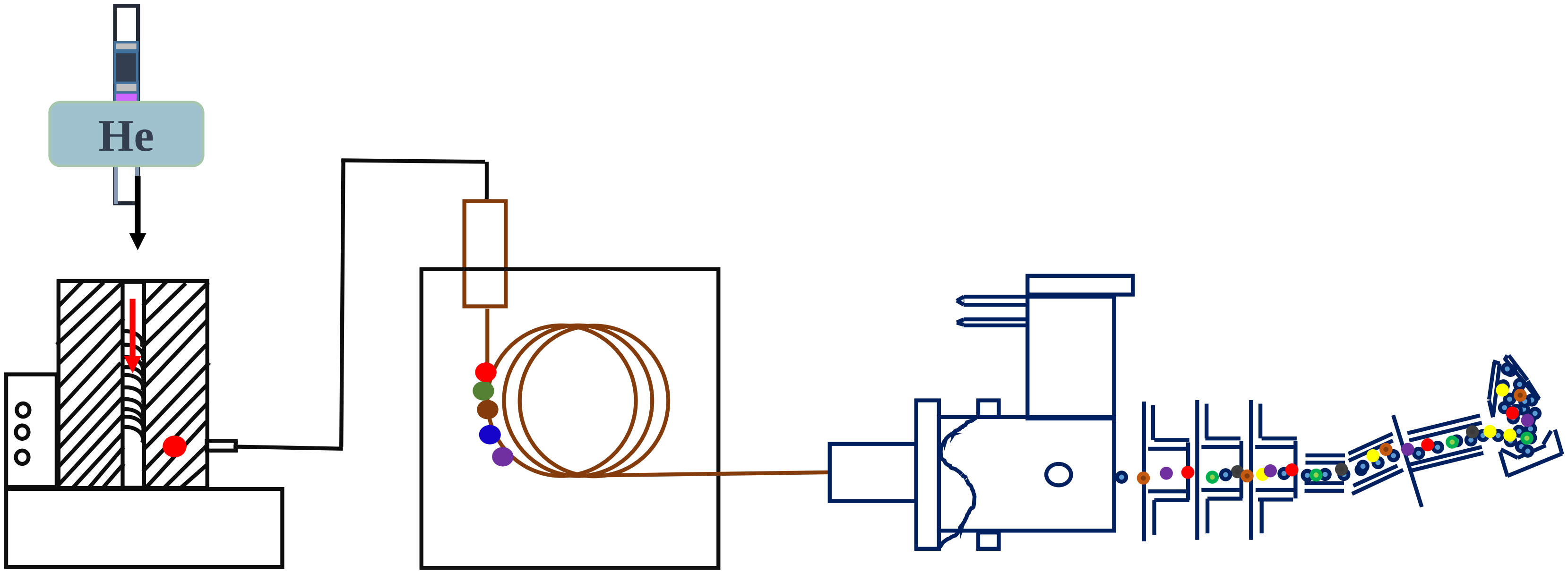


Fig. 4 Schematic diagram of Py-GC/MS

Results and Discussions

➢ **Distribution of pyrolysis products**

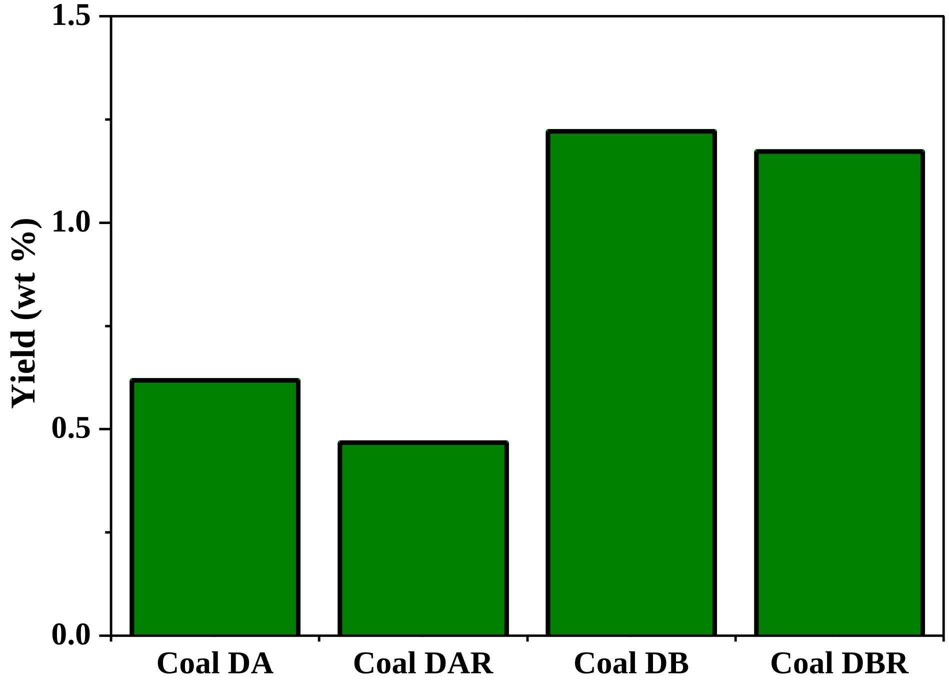


Fig. 5 The BTXN yield obtained from the pyrolysis of different coal samples

❖ Low molecular weight compounds can facilitate the formation of BTXN during coal pyrolusis. However, this effect varies significantly among coals with different metamorphic grades.

Results and Discussions

Role of low molecular compounds in the catalytic processs

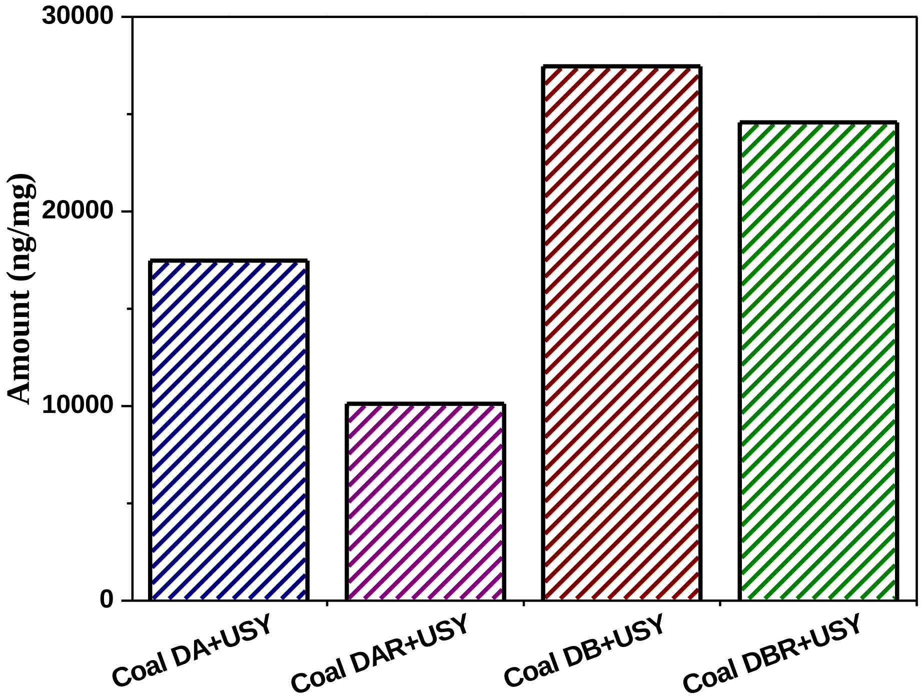


Fig. 6 The BTXN yield after catalytic reforming

- Low molecular weight compounds have a more significant effect on the formation of BTXN in the catalytic reforming.

Results and Discussions

- **Role of low molecular compounds in the catalytic processs**

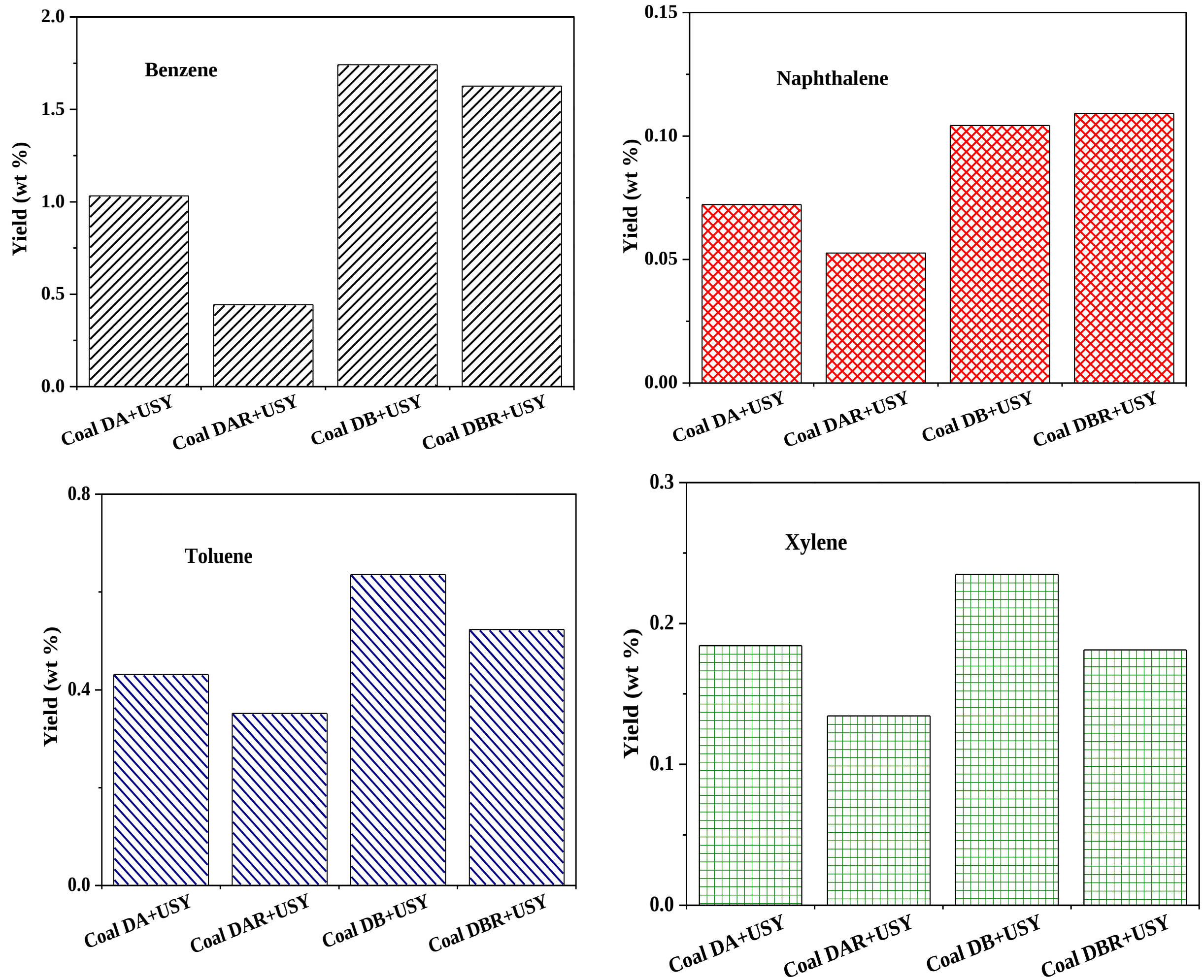
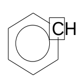
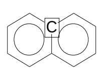
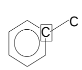
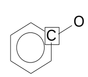


Fig. 7 The distribution of BTXN after catalytic reforming

Results and Discussions

Structural analysis of raw coal and residual coal

Table 2. The chemical shifts of coal carbons in CP/MAS ^{13}C NMR spectra

Chemical shift (ppm)	Functional groups	Carbon functionality	Symbols
0-25	$-CH_3$	Methyl	f_{al}^{1}
25-50	$-CH_2-$ (H–C–H)	Methylene	f_{al}^{2}
50-67	CH_3O-	Methoxy	f_{al}^{o1}
67-90	(C)(C)CHO–C, CHOH, CH_2OH	Oxy-methine ,Saccharide, Alcohol, Ether	f_{al}^{o2}
90-129		Aromatic atoms bound to hydrogen	f_{a}^{1}
129-137		Bridging ring junction aromatic carbon	f_{a}^{2}
137-148		Branched aromatic carbon	f_{a}^{3}
148-171		Oxy-aromatic carbon	f_{a}^{o1}
171-187	–COOR/H	Carboxyl, Ester, Quinone	f^{co}
187-220	(C/H)(C)C=O	Ketone, Quinine, Aldehyde	f^{co}

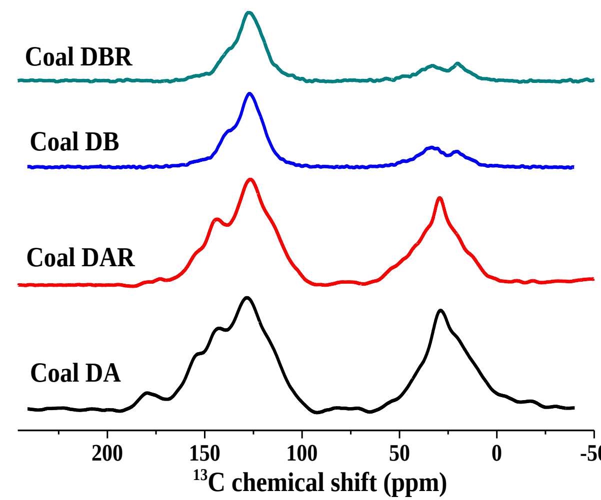


Fig. 8 The CP/MAS ^{13}C NMR spectra of col samples

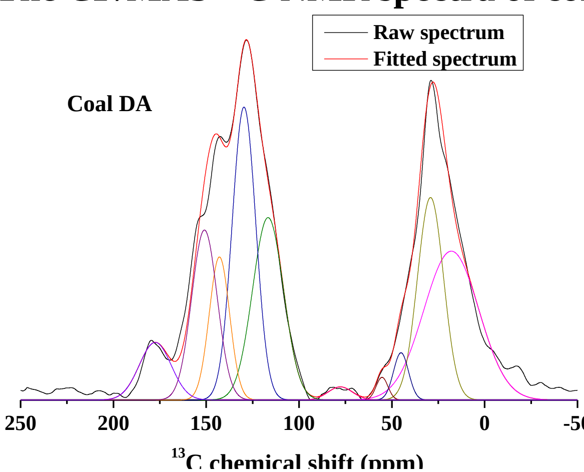


Fig. 9 The fitted CP/MAS ^{13}C NMR spectrum

Results and Discussions

➤ Structural analysis of raw coal and residual coal

Table 3. The distribution of different types of carbons in raw coal and residual coal

Symbols	Carbon type (%)						
	f_{al}^{1}	f_{al}^{2}	f_{al}^{o1}	f_{al}^{o2}	f_{a}^{1}	f_{a}^{o1}	f^{co}
Coal DA	22.5	16.5	0.7	0.9	42.5	11.9	5.0
Coal DAR	18.7	19.7	—	0.7	53.8	5.7	1.5
Coal DB	13.1	14.1	—	—	70.6	2.0	—
Coal DBR	12.0	12.7	—	—	72.8	2.5	—

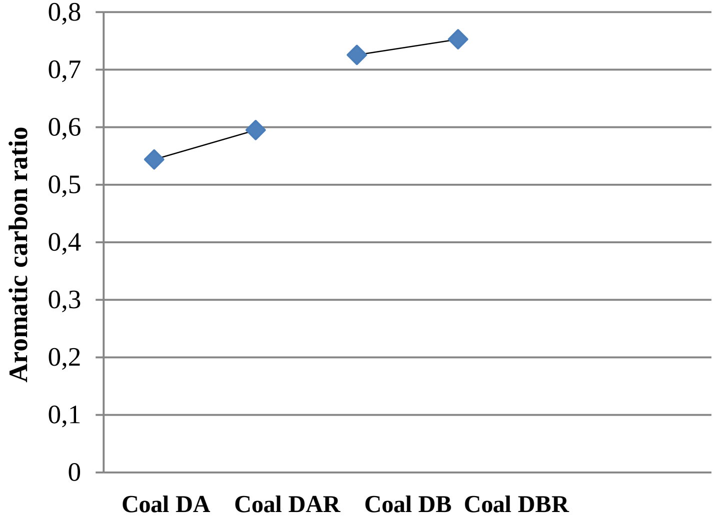
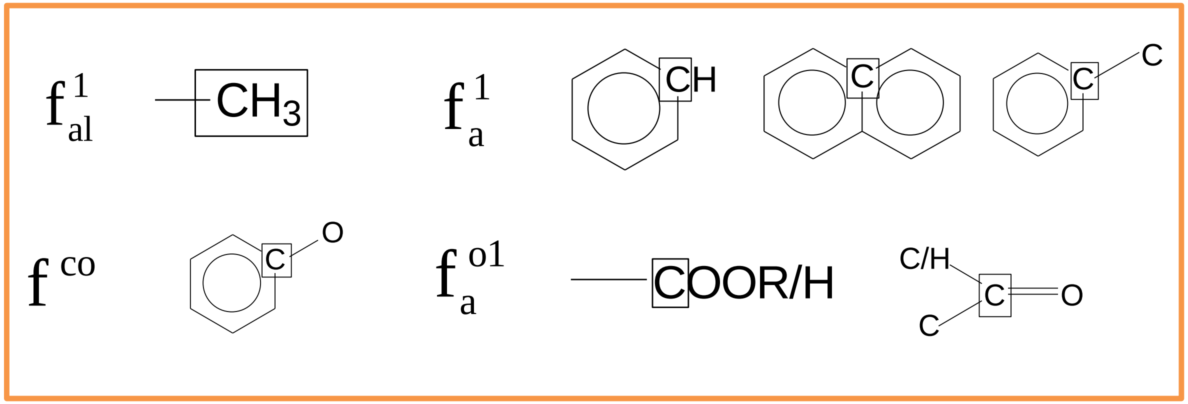
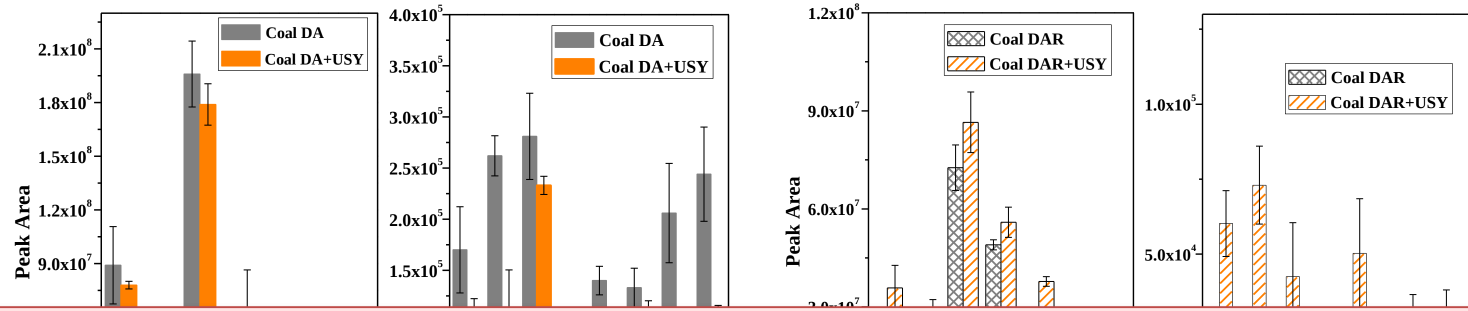


Fig. 10 The aromaticity in raw coal and their residual coal



Results and Discussions

➢ Effects of low molecular weight compounds



> ➢ **Low molecular weight compounds could provide low molecular weight free radicals for catalytic reforming of coal tar, thus contributing to the stabilization of fragments and subsequently the formation of light aromatics.**

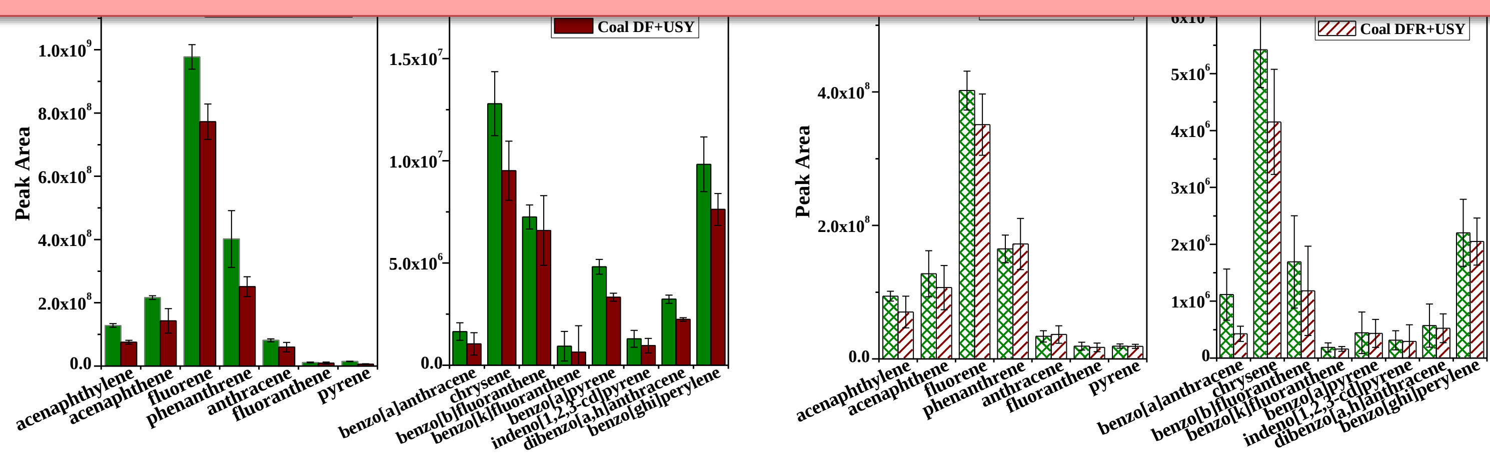


Fig. 11 PAHs yield before and after catalytic reforming

Results and Discussions

➢ Effects of low molecular weight compounds

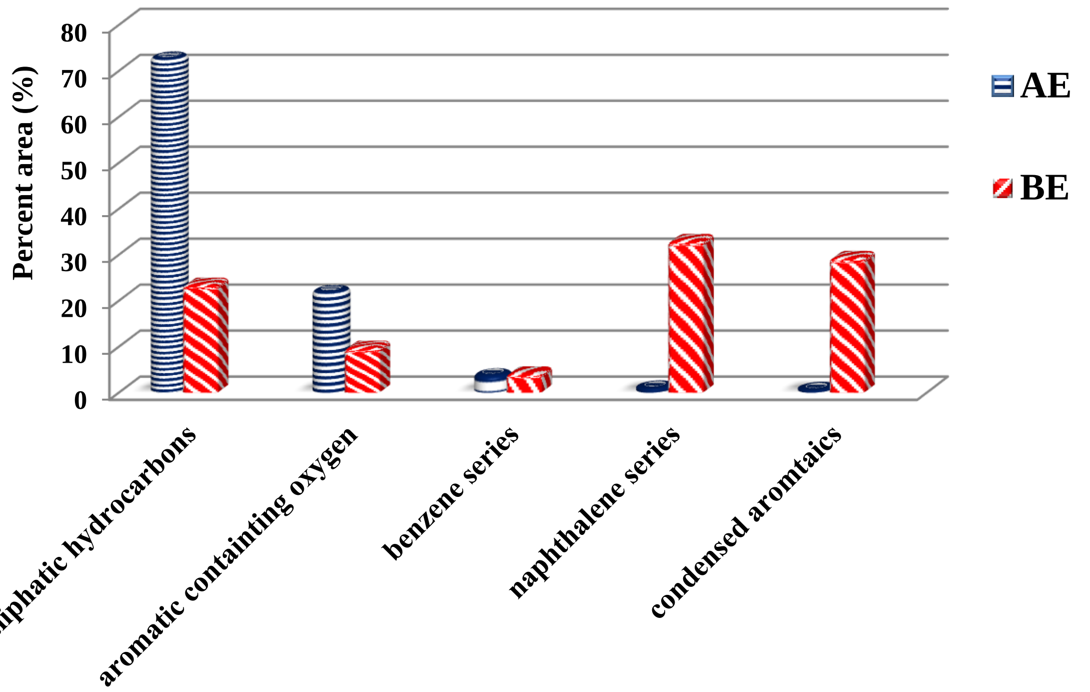


Fig. 12 Components of low molecular weight compounds in Coal DA and Coal DB

❖ The effect of low molecular compounds on the formation of BTEXN is closely related to their content and composition in coal.

Conclusions

- ✓ **The BTXN yield in Coal DAR and Coal DBR is 42% and 10% lower than that in Coal DA and Coal DB, respectively, indicating that the extraction of low molecular weight compounds results in a significant decrease in the BTXN yield.**

- ✓ **Low molecular weight compounds could provide low molecular weight free radicals for catalytic reforming of coal tar, thus contributing to the stabilization of fragments and subsequently the formation of light aromatics.**

- ✓ **Pyridine extracts accounts for 23.7% of Coal DA and 7.2% of Coal DB, respectively. The low molecular weight compounds in Coal DA are predominantly aliphatic compounds (72.7%) and O-containing aromatics (21.9%), whereas that in Coal DB are predominantly naphthalene series (33.1%) and condensed aromatics (29.4%). Thus, low molecular weight compounds have a more pronounced effect on the catalytic reforming of tar from pyrolysis of low-rank coal.**

Acknowledgement

Thank You for your attention !