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In-situ catalytic upgrading of coal pyrolysis tar with CO_2 reforming of methane

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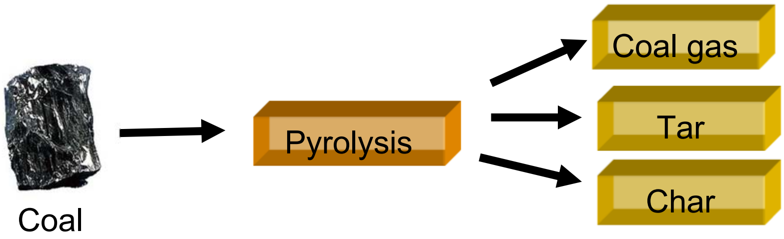


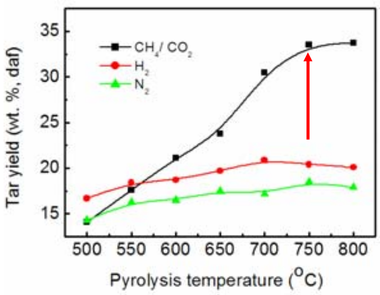
Coal tar, an important resource from coal pyrolysis

- contains many valuable chemicals
- coal tar pitch is the main feedstock for carbon materials
- could be converted to liquid fuel

In conventional pyrolysis process, tar yield is low (less than 7 to 8%)

Introduction

Integrated Process of Coal Pyrolysis with Methane Activation (POM, SRM, CRM, …)



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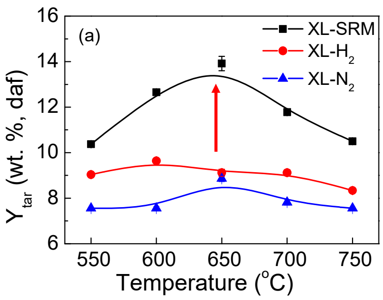
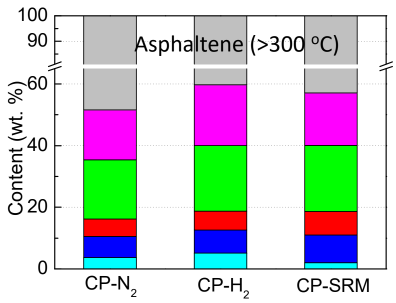


Dong C. et al., Energy Fuels 2014, 28, 7377–7384



At 750 °C, PS coal, the tar yield under CH_4/CO_2 is 1.6 and 1.8 times as that under H_2 and N_2
At 650 °C, XL coal: tar yield under CH_4/H_2O is about 1.57 and 1.44 times those in N_2 and H_2

Heavy component (asphaltene) in tar is still higher than 40%. Upgrading of tar is necessary for further processing.

Introduction

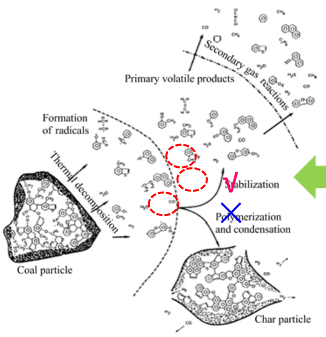
Methods of catalytic upgrading of tar

Decarburization —catalytic cracking→ increase of light tar content, but **drastic decrease** of tar yield

Hydrogenation → H_2: **too expensive**

Hydrogenation → CH_4: wide resource & high H/C ratio

Hard to be activated → CO_2 reforming of methane (CRM)

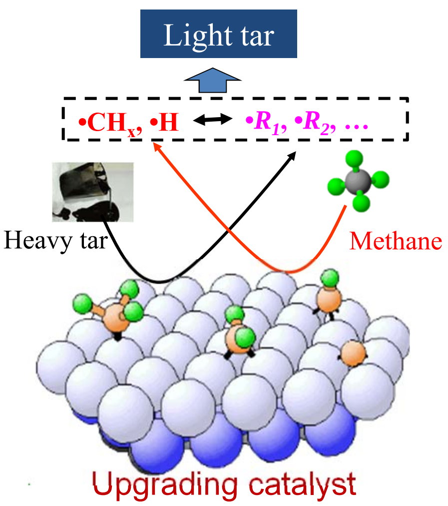


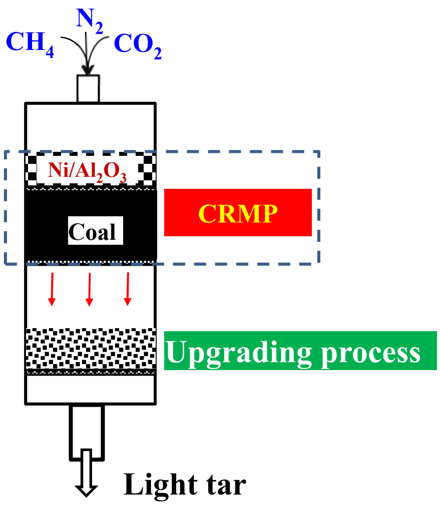
·CH_x
· H

CRMP can improve tar yield.
Conversion of CH_4 and CO_2 is 50%.

Using **the remaining CH_4** to upgrade pyrolysis tar

Main objective of this work





Aim of this work is to find a good catalyst for both heavy tar cracking and methane activation.

Results & discussion

Table 1. Proximate and ultimate analyses of Baliangou coal

Proximate analysis (wt.%)			Ultimate analysis (wt.% daf)				
M_{ad}	A_d	V_{daf}	C	H	N	S	O^*
2.11	15.05	37.68	77.50	4.62	1.27	0.84	15.77

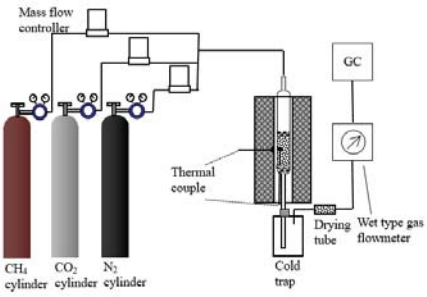


Figure 1. Schematic of the experimental apparatus

Experimental conditions:

- $CH_4/CO_2/N_2$ =120/120/60 mL/min
- Retention time: 40 min
- BLG coal: 5 g
- Reforming catalyst: commercial Ni/Al_2O_3
- Upgrading catalyst:

Ni-based or carbon-based catalysts

Results & discussion

Ni-based catalysts as upgrading catalysts

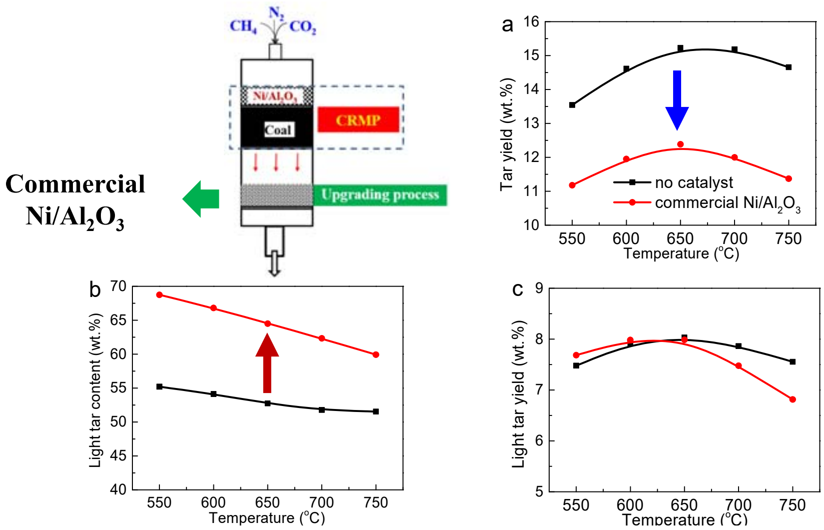


Figure 2. Upgrading effect of commercial Ni/Al_2O_3

- Light tar content increases
- Tar yield decreases
- Light tar yield decreases

Results & discussion

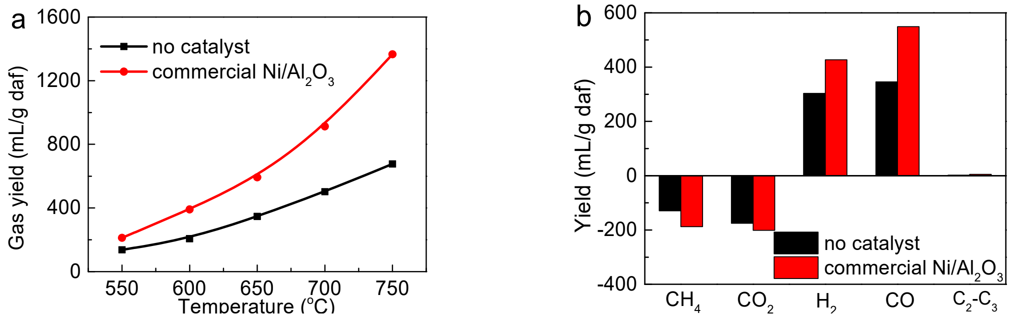
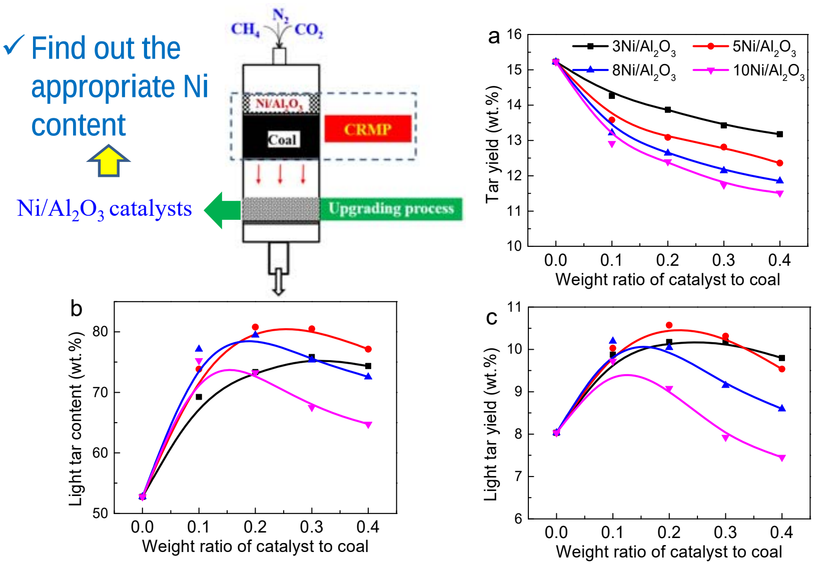


Figure 3. Gas variation with or without commercial Ni/Al_2O_3 as the upgrading catalyst

- ✓ Gas yield increases with rising temperature, because CRM and tar cracking are both endothermic reactions.
- ✓ With the commercial Ni/Al_2O_3 added in upgrading zone, the yields of CH_4 and CO_2 further decrease, and yields of H_2 and CO increase significantly, indicating the CRM happens in the upgrading zone.

Results & discussion

✓ Find out the appropriate Ni content



- High Ni content in the upgrading catalyst could lead to excessive cracking of tar
- $5Ni/Al_2O_3$ with 0.2 weight ratio of catalyst to coal has an appropriate activity for tar upgrading

Figure 4. Upgrading effect of different Ni/Al_2O_3 catalysts at 650 °C

Results & discussion

Table 2. Boiling Point Range for Classifying Tar Fractions

light oil	phenol oil	naphthalene oil	wash oil	anthracene oil	pitch
<170 °C	170-210°C	210-230 °C	230-300 °C	300-360 °C	>360 °C

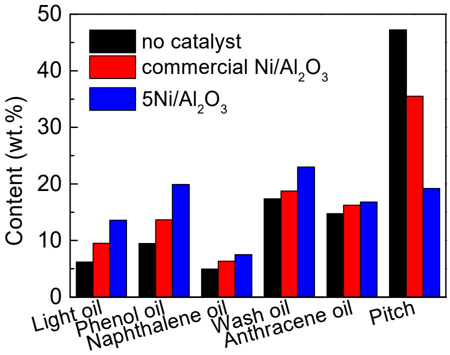


Figure 5. Tar components with or without Ni-based catalysts at 650 °C (Simulated distillation)

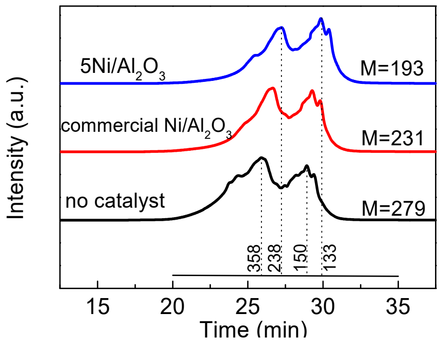


Figure 6. Molecular weight distribution of tars with or without Ni-based catalysts at 650 °C (GPC)

- **$5Ni/Al_2O_3$ could promote pitch cracking, and •H and $•CH_x$ generated from CRM can stabilize the free radicals of tar cracking to form light tar components effectively.**

Results & discussion

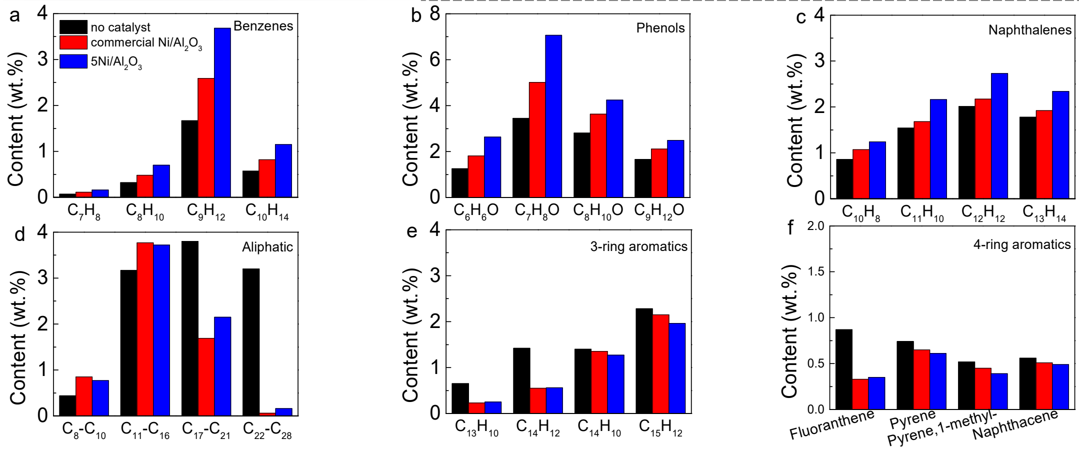


Figure 7. Tar compositions with or without Ni-based catalysts at 650 °C

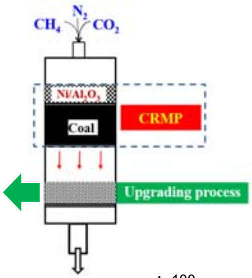
- Benzenes, phenols and naphthalenes increase during catalytic upgrading;
- Alkanes with long chains crack into short chains;
- Ring-opening reaction can happen, and the contents of fluorene and fluoranthene decline more.

Results & discussion

Carbon-based catalysts as upgrading catalysts

- ✓ Char
- ✓ Modified char (MC)
- ✓ Activated carbon (AC)

Carbon-based catalysts



- Low cost, easy availability and sulfur resistance
- With carbon-based catalyst, tar yield decrease, but light tar content increase significantly.
- Compared with non-upgrading tar, yield of light tar over AC increases from 8.0 to 11.6 wt %.

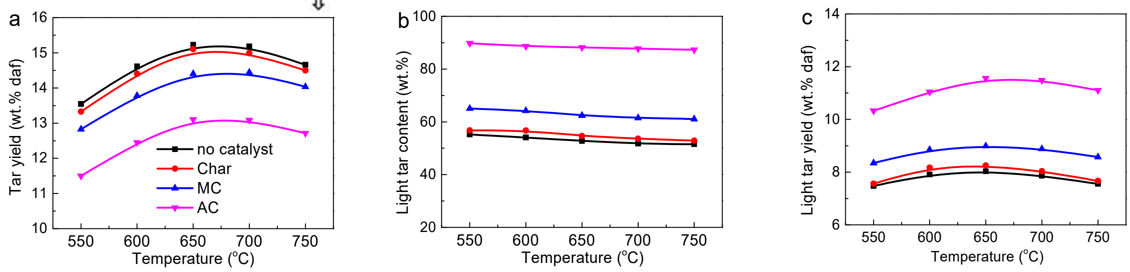


Figure 8. Upgrading effect of different carbon-based catalysts

Results & discussion

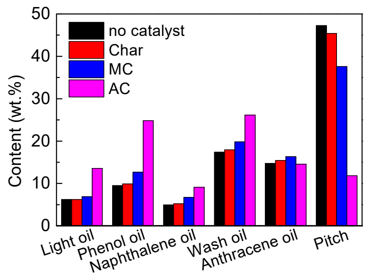


Figure 9. Tar components with different carbon-based catalysts at 650 °C

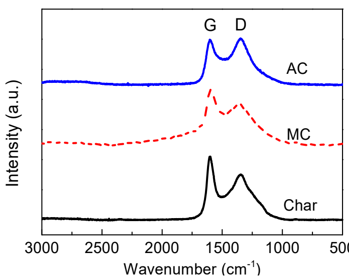


Figure 10. Raman spectra of three carbon-based catalysts

- AC has high surface area, more active sites
- AC has much higher I_D/I_G than MC and char
- I_D/I_G is usually used to determine the quantifying defect

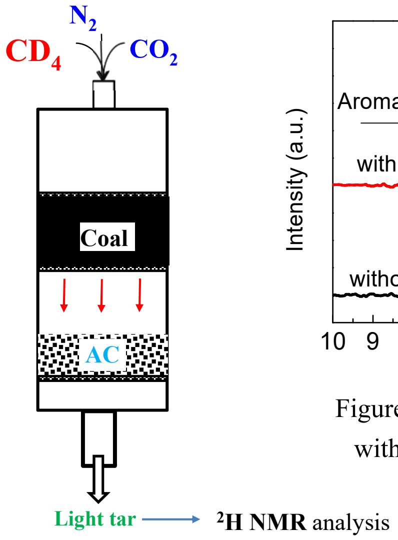
Table 3. Textural properties of carbon-based catalysts

Sample	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	V_t (cm^3/g)	V_{mic} (cm^3/g)	D_{ave} (nm)
Char	11	5	6	/	/	3.61
MC	758	426	332	0.39	0.19	2.08
AC	1533	1086	447	0.75	0.48	2.11

AC catalyst exhibits a better upgrading effect because of **its more disordered structure and higher surface area and pore volume**

Results & discussion

Mechanism of catalytic upgrading



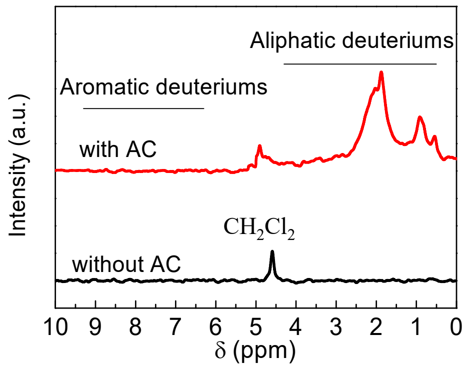


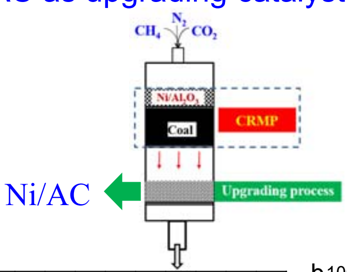
Figure 11 ^{2}H NMR spectra of tar with or without AC at 650 °C

- without AC, **CD_4 does not take part in the formation of tar**.
- With AC, mainly aliphatic deuteriums were determined.

We believe Some active species (such as •D and •CDx) generated from the reforming reaction are produced over the carbon catalyst, and these •D and •CDx participate in the upgrading process via stabilizing the radicals from catalytic cracking of pyrolysis tar.

Results & discussion

Ni/AC as upgrading catalysts



Prepared 5%Ni/AC catalyst

- The light tar content in the upgrading tar is more than 95%;
- Light tar yield increased by 51% over Ni/AC at 650 °C compared with that without catalyst

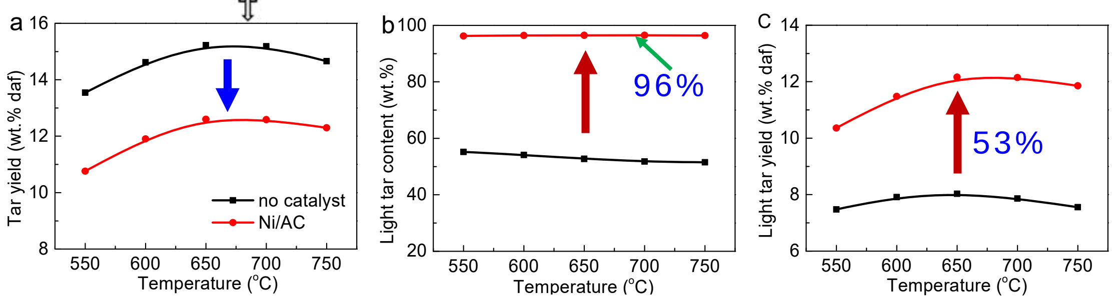


Figure 12. Upgrading effect of Ni/AC

Results & discussion

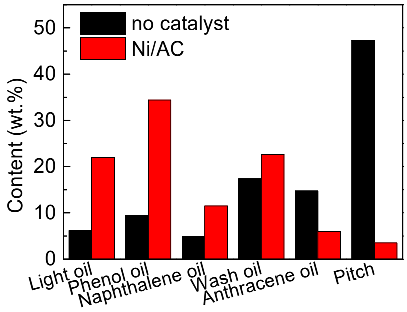


Figure 13 Tar components with or without Ni/AC at 650 °C

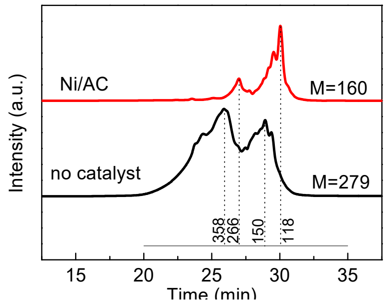
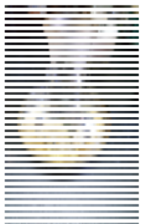


Figure 14. Molecular weight distribution of tars with or without Ni/AC at 650 °C

- The upgrading tar has high contents of light oil, phenol oil, naphthalene oil and wash oil
- The average molecular weight of tar over Ni/AC decreases from 279 to 160.
- The color of tar becomes shallow

Catalytic upgrading over Ni/AC



Color change of tar

Summary

- A new method for tar upgrading by integrating in-situ catalytic cracking of coal pyrolysis tar with CO_2 reforming of methane was developed.
- •H and •CH_x produced in CRM combine with the radicals from catalytic cracking of tar to result in the high content and yield of light tar.
- Light tar content and yield increase by 53% and 32% at 650 °C when 5%Ni/Al_2O_3 was used as the upgrading catalyst.
- Light tar content increase to 88 wt.%, and light tar yield increase by 45% at 650 °C when AC was used as the upgrading catalyst.
- Light tar content increases to 96 wt.% over Ni/AC, and the average molecular weight decreases from 279 to 160.

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