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Chemical transformation of inherent sodium and calcium species during direct liquefaction of two typical lignites rich in alkali and alkaline earth metals

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ABSTRACT

Lignite, a suitable feedstock for direct coal liquefaction (DCL), is usually rich in sodium and calcium species. To better understand chemical transformation of inherent sodium and calcium species during DCL, two lignites rich in sodium and calcium species were liquefied in this work. The results show that both Australia lignite (AU) and Hami lignite (HM) are preferred raw materials for DCL. After DCL, mineral matters were obviously enriched in residues (DCLR). Under all the temperatures, retention ratios of sodium species were lower than those of calcium species. One obvious transformation of calcium species was reflected in changes of organic-bound calcium species (AS-Ca) and hydrochloric acid-insoluble calcium species (HIS-Ca) in HM. During direct liquefaction of HM, the amount of AS-Ca decreased significantly and the amount of HIS-Ca increased sharply. XRD analyses of low temperature ashes of DCLR confirmed that when temperatures reached above 400 °C, kaoline in HM gradually decomposed and came to react with AS-Ca, which resulted in formation of HIS-Ca. Due to the low ash content, transformation of calcium species in AU showed unobvious tendency and only $CaCO_3$ was detected in DCLR.

1. Introduction

As an efficient way to convert solid coals into liquid products [1,2], direct coal liquefaction (DCL) is of strategic importance to relieve the demand for oil and it has attracted much interest worldwide [3–7]. Generally, the suitable raw materials for DCL are low-rank coals that include subbituminous coal and lignite. For the coals with higher carbon contents and lower hydrogen contents are usually more difficult to be liquefied [8]. However, the low-rank coals, especially lignite, are typically featured by high contents of sodium and calcium species which can be present in several chemical forms [9,10], such as water-soluble and organic-bound species. It has been demonstrated that these metallic species acted actively during DCL and could reduce oil yield [11–13], which has posed a barrier for further thermal utilization of lignite during DCL. Therefore, a deep understanding on chemical transformation of sodium and calcium species during DCL is really necessary for increasing oil yield and optimizing operations in commercial DCL plants.

While the total amounts of sodium and calcium species in lignites are relatively lower than other mineral elements, the presence of these species is a non-negligible issue in efficient utilization of lignites [14]. Previous investigations mainly focused on volatilization and catalytic effects of sodium and calcium species in thermal conversion. For instance, sodium species were found to volatilize more easily than calcium species in pyrolysis. Sodium species that can be dissolved in moistures are even more volatile [15]. At temperatures higher than 800 °C, volatilization ratios of sodium species from pyrolysis of sodium-rich coals were as high as ca. 35 wt% [16]. As for calcium species, the amount of organic-bound calcium species in coals was verified to decrease with the pyrolysis temperature rising, but they still existed in chars after 900 °C [17]. Moreover, during gasification of a sodium-rich coal, sodium species were found to have excellent gasification performance and could catalyze the conversion of gaseous hydrocarbons to syngas [18], which indicated catalytic roles of sodium species.

During DCL, though catalytic roles of sodium and calcium species were investigated previously [11–13], chemical transformation (chemical form changes) of sodium and calcium species has been rarely reported. Compared with those in coal pyrolysis and gasification,

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Table 1
Proximate and ultimate analyses (wt%) of AU and HM.

Sample	Proximate analysis				Ultimate analysis (daf)				
	M_{ad}	A_d	V_{daf}	FC_{daf}	C	H	N	O[a]	S
AU	8.39 ± 0.11	1.38 ± 0.06	54.00 ± 0.41	46.00 ± 0.41	69.41 ± 0.21	4.67 ± 0.03	0.66 ± 0.11	24.95 ± 0.36	0.31 ± 0.01
HM	7.24 ± 0.05	9.24 ± 0.09	53.96 ± 0.56	46.04 ± 0.56	75.98 ± 0.12	5.78 ± 0.05	1.03 ± 0.10	16.15 ± 0.35	1.06 ± 0.08

daf: dry and ash-free base; M_{ad}: moisture (air dried base); A_d: ash (dry base); V_{daf}: volatile matter (dry and ash-free base); FC_{daf}: fixed carbon (dry and ash-free base).

[a] By difference.

Table 2
Chemical compositions (wt.%) of coal ashes from AU and HM.

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	K_2O	Na_2O	SO_3	P_2O_5
AU	21.87	23.43	9.37	11.71	10.93	0.78	0.78	7.03	14.06	0.04
HM	17.19	9.85	19.35	26.03	1.43	0.25	0.20	3.65	21.84	0.21

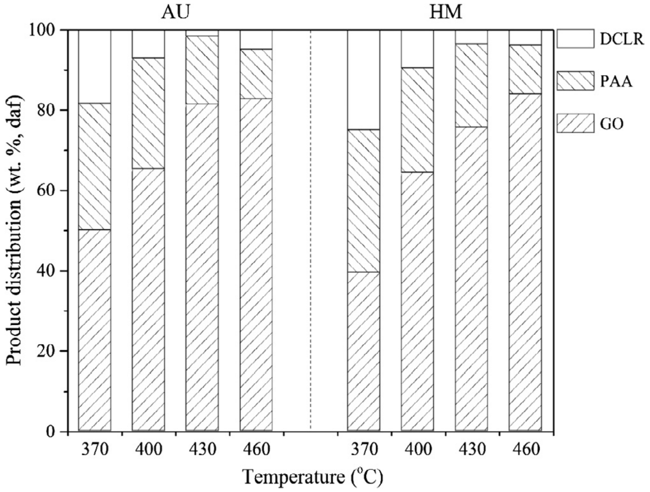

Fig. 1. Product distribution during direct liquefaction of AU and HM at different temperatures.

chemical transformation of sodium and calcium species during DCL is more complicated. For the operating temperatures are lower and the reactors belong to batch systems. Just as indicated in the previous work, volatilization of sodium species during DCL was nearly negligible and most of the sodium species would be reserved during direct coal liquefaction residue (DCLR) [13]. Since enrichment of sodium and calcium species in DCLR tends to result in accumulation of solid particles and deterioration of devices [19], it is rather essential to evaluate chemical transformation of these species during DCL and their occurrence mode distributions in DCLR. Hence, in this work, Australia lignite (AU) and Hami lignite (HM) were liquefied to investigate chemical transformation of sodium and calcium species during DCL. To characterize the chemical transformation as a function of liquefaction temperature, XRD and sequential chemical extraction method were jointly used. Currently, the main challenges in understanding these chemical transformation processes during DCL lie in the precise determination of mineral matters in DCLR, as the unconverted organic matters can interfere determination of mineral matters. In view of this key issue, low temperature ashing (LTA), which is the most efficient method to remove the organic matters in coals with inducing the least structural changes in mineral matters [20,21], was carried out to probe the possible chemical transformation mechanisms. After LTA, the mineral matters will high likely stay in their original chemical forms. This investigation may provide some references for better understanding the chemical transformation of sodium and calcium species during DCL.

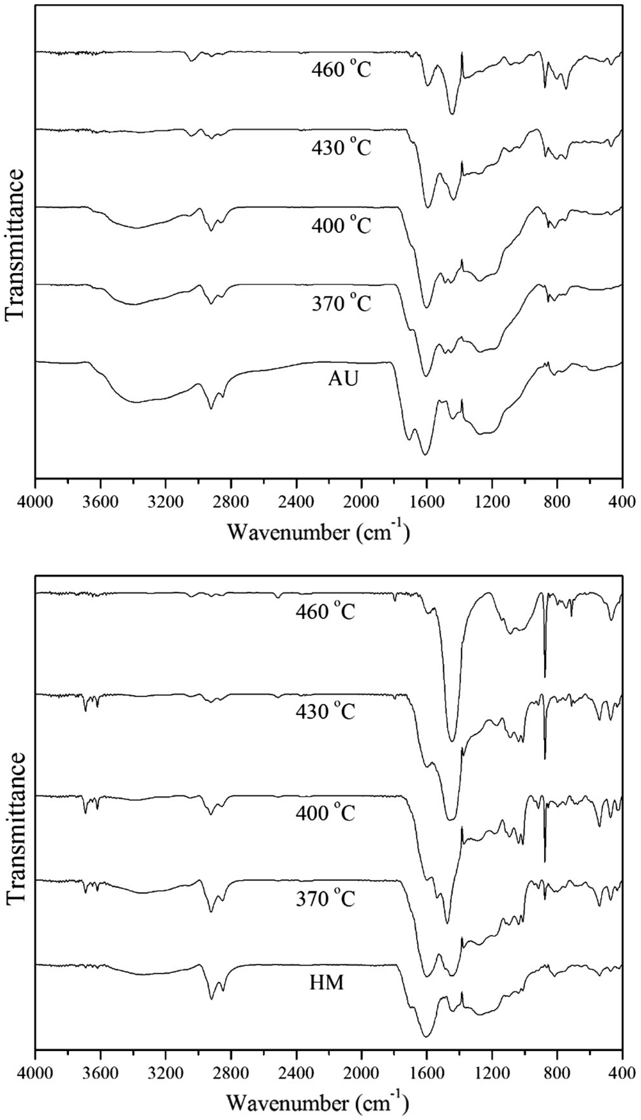

Fig. 2. FTIR spectra of AU, HM, and DCLR obtained at different temperatures.