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Hydro-treatment of a direct coal liquefaction residue and its components

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Abstract

Direct coal liquefaction residue (DCLR) contains a significant fraction of heavy liquids. Better use of DCLR is an important task to overall economy of direct coal liquefaction. This paper studies hydro-treatment of a DCLR and its solvent-extraction components under typical direct coal liquefaction conditions. The DCLR is found hydro-treatable, resulting in more light products and less heavy products. In one case, 40 wt% heavy fractions in the DCLR are converted into light fractions. Hexane soluble fraction (HS) is the most stable while pre-asphaltene fraction (PA) is the most active during the hydro-treatment. Some synergetic effect can be observed when DCLR is treated as whole. The fractions of DCLR, before and after the hydro-treatment, are subjected to FTIR and NMR analyses, which show increase in hydrogen content and decrease in oxygen content in HS fractions after the hydro-treatment. GPC analysis reveals that the hydro-treatment results in slight decreases in molecular weight of HS fraction. The data seem to suggest that separation and hydro-treatment of liquid fractions from a DCLR is a viable option for high oil yield.

Keywords: Direct coal liquefaction; Residue; Heavy oil; Hydro-treatment

1. Introduction

Direct coal liquefaction (DCL) aims to convert coal into valuable liquid products, but generates also light hydrocarbons and bottom residues (DCLR). The DCLR usually accounts 20–30 wt% of the feed [1,2]. The residue contains not only solids (un-reacted coals, minerals and catalyst) but also a large amount (about 30–50 wt%) of heavy liquids to maintain its flow in and discharge from the system [3]. Historically DCLR is difficult to be used due to presence of a large amount of poly-aromatics, but this needs to be changed due to economical reasons. Currently, the usage of DCLR is feed stock for gasification, coking or combustion. Use of the liquid fraction in the DCLR as a source of high-value fuels has been a subject considered in some of the direct coal liquefaction designs, but only limited information is available in the open literature.

Some researches have been done to extract or convert the heavy liquids in the residue to lighter products. One example is co-hydrogenation of the heavy liquids with waste tire, where carbon blacks and inorganic constituents of the tire were pronounced to be beneficial to the process [4]. Another example is pre-treating a DCLR with H_2O_2 to promote its decomposition in hydrogenolysis [1]. It should be noticed that "heavy liquids" in DCLR is a very general term, which often refers to different materials. A liquid fraction defined by distillation may be a solid fraction defined by solvent extraction, or vice versa. To have a broad understanding on upgradeability of a DCLR, reactivity of all its components, liquids and solids, should be studied regardless of its definition. From the solvent fractionation point of view, the upgradeable components in a DCLR may include all the soluble fractions as well as a portion of non-soluble materials. This paper presents recent work on hydro-treatment of a laboratory-produced DCLR and all of its fractions with emphases on products yields and characteristics of *n*-hexane soluble fractions.

2. Experimental

2.1. Samples

A DCLR sample used in this study was produced from a 0.1 ton/day continues DCL unit at China Coal Research

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Institute. The coal liquefaction was carried out at 450 °C and 19 MPa hydrogen pressure over a Chinese bitumen coal (SH coal) in the presence of an iron-based catalyst [5]. The products from the DCL unit were separated by passing through two separators, atmospheric and vacuum distillation columns. The DCLR was discharged from the bottom of the vacuum distillation column which is operated at <100 Pa and 350 °C. The DCLR is solid at room temperature with initial boiling temperature of 420 °C.

The DCLR was also extracted with *n*-hexane, toluene and tetrahydrofuran (THF) in a Soxhlet apparatus sequentially and separated into four fractions. The extraction time used for each solvent is 48 h. After extraction the insoluble in the thimble was dried and weighed. The yield was calculated based on the weight of the insoluble. The soluble was collected after distilling out the solvent by rotary evaporation. To eliminate the solvent effect all the insoluble and soluble fractions have been dried in a vacuum oven for 48 h. The fractions obtained were *n*-hexane soluble, *n*-hexane insoluble/toluene soluble, toluene insoluble/THF soluble and THF insoluble and named as heavy oil (HS), asphaltenes (A), pre-asphaltenes (PA) and THFIS, respectively. Properties of the DCLR and its four fractions are listed in Table 1.

2.2. Hydro- or thermal treatment

The hydro- or thermal treatment of the DCLR was carried out batch-wise in a 25 ml tubing bomb reactor. After loading the sample (1 g for each run), the reactor was purged and pressurized to a designated H_2 pressure, and sealed. The reactor was then immersed into a preheated fluidized sand bath and continuously shaken horizontally. The reactor content reached the reaction temperature in less than 2 min. The hydro-treatment was carried out at temperatures of 250, 350, 400, 425 or 450 °C and initial H_2 pressures of 1.5, 3, 5, 6 or 7 MPa. 1 wt% of iron-based catalyst, which is same as that used in the DCL process, is added for catalytic hydro-treatment. Thermal treatment was carried out at 400 °C and 7 MPa N_2 pressure (initial). Since the main purpose of this study is to investigate the hydrogenation ability of DCLR and the effects of temperature and pressure, 1 h duration time was selected to reduce the kinetic effect and keep the test comparable. After the reaction, the reactor was quenched in cold water and gases in the reactor were vented. The solid and the liquid in the reactor were washed out using about 200 ml *n*-hexane and followed by the same solvent extraction procedure mentioned early for raw DCLR fractionation. A, PA and THFIS defined as above. Their yields were calculated based on the weights of *n*-hexane, toluene and THF insoluble, and defined as the percentage of A, PA and THFIS on daf coal basis, respectively. HS + gas yield was calculated based on hexane insoluble and defined as the percentage of HS + gas on daf coal basis. In some cases gas yield was calculated based on the weight of reactor + sample before and after treatment. All the reactions were duplicated to ensure accuracy with average error less than 2%.

2.3. Products analyses

HS fractions were analyzed by FTIR, ^{1}H-NMR spectroscopy and gel permeation chromatography (GPC). FTIR spectrometer used is Digilab FTS-3000 with attenuation total reflection (ATR) accessory. The spectra were recorded at a resolution of 4 cm^{-1}.

^{1}H-NMR spectra were recorded on a Bruker DRX-300 at 300.1 MHz. $CDCl_3$ was used as solvent.

GPC analysis was carried out on Shimadzu LC-3A high-performance liquid chromatography with an UVD-2UV detector ($\lambda = 254$ nm). A Shimpack GPC-801 (30 cm length, 0.8 cm i.d., polystyrene 6 μm) separation column was operated isothermally at 25 °C. THF was used as the mobile phase with a flow rate of 1.2 ml/min. Aromatic hydrocarbon and polystyrenes were used as standards to establish the GPC calibration curve, which is expressed as:

$$\log M = 5.3058 - 0.3958 \times t \tag{1}$$

in which t represents the retention time (min). The number-averaged molecular weight (M_n) is used and defined as:

$$M_n = \frac{\sum H_i}{\sum H_i/M_i} \tag{2}$$

where M_i represents the molecular weight of i fraction and H_i represents its peak height.

3. Results and discussion

3.1. Reactivity of DCLR

The sequential extraction experiments show that the DCLR consists of 37% HS, 27% A, 8% PA and 28% THFIS. The

Table 1
Proximate and ultimate analyses of the DCLR and its components HS, A, PA and THFIS

Sample	Content in DCLR (wt%, daf)	Proximate analysis (wt%)			Ultimate analysis (wt%, daf)					
		M_{ad}	A_d	V_{daf}	C	H	O[a]	N	S	H/C
DCLR		0.39	11.96	50.81	86.46	5.67	5.12	1.06	1.69	0.79
HS	37	–	–	–	88.09	7.78	3.32	0.71	0.10	1.06
A	27	–	–	–	87.78	6.16	5.04	0.93	0.10	0.84
PA	8	–	–	–	80.95	5.50	12.06	1.36	0.13	0.82
THFIS	28	0.63	29.78	19.37	84.70	4.64	4.45	1.25	4.96	0.66

[a] By difference.

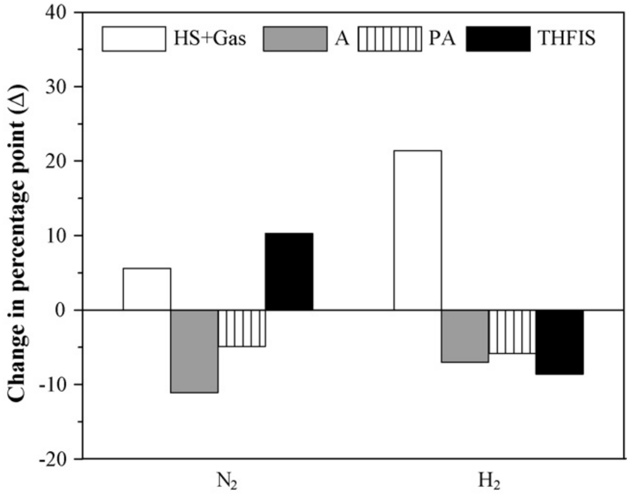

Fig. 1. Change in percentage point on separated fractions due to thermal and hydro-treatments; 400 °C, 7 MPa N_2 or H_2 pressure (initial), 1 h.

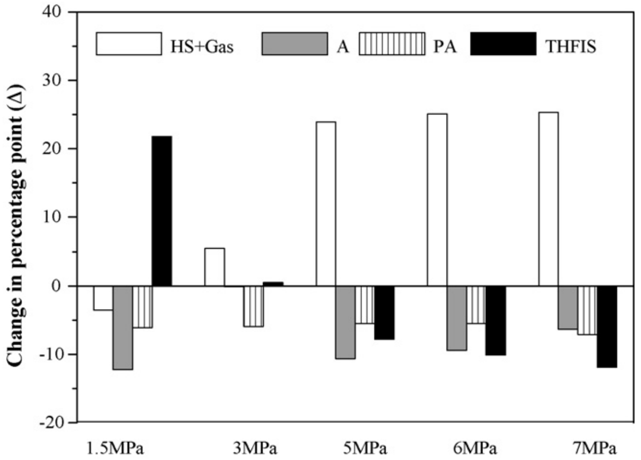

Fig. 3. Change in percentage point on separated fractions due to hydro-treatment at various pressures; 450 °C, 1 h.

treatments will alter this composition. The change in percentage point of each fraction before and after treatment, labeled with a prefix Δ, is used to characterize extents of the treatments. The results are shown in Figs. 1–4, where a negative value indicates a decrease in specified fraction while a positive value indicates an increase in specified fraction due to the treatment. The gas fractions are combined with HS fractions in the figures.

The thermal treatment, without a catalyst, results in 5 and 10 percentage point increase in ΔHS + gas and THFIS fractions, and decrease in A and PA fractions (Fig. 1, left). This indicates an occurrence of condensation reaction, which convert the DCLR into light and heavy fractions. Hydrogenation of the DCLR in the absence of a catalyst results in an increase in HS + gas fraction and decrease in A, PA and THFIS fractions (Fig. 1, right). This indicates a conversion of A, PA and THFIS to HS + gas. Apparently, the DCLR can be hydrogenated further to yield more valuable products under the hydro-treatment conditions. This is agreed with the mechanism of coal liquefaction, in which A, PA and THFIS fractions could be an intermediate to produce light products. It is understandable that the incomplete reacted coal could be further treated even under mild conditions.

Fig. 2 shows effect of temperature on hydro-treatment. Clearly a higher temperature in a range of 250–450 °C promotes cracking and hydrogenation of A, PA and THFIS to HS + gas. It appears that ΔA has the lowest value at 425 °C, indicating conversion of A to HS + gas and formation of A from PA and THFIS simultaneously during the treatment. The effect of temperature seems to be more significant between 400 and 425 °C while less pronounced between 425 and 450 °C, which agrees with the result reported earlier [6].

Fig. 3 shows effect of H_2 pressure. It is clear that the main reaction involved is condensation reaction under lower H_2 pressure (1.5 MPa H_2). As the pressure increased to 3 MPa the condensation reaction was significantly restricted and the light products began to increase. At 5 MPa, 24 percentage points increase in HS + gas and 10 percentage points decrease in THFIS were observed. In the range of 5–7 MPa the effect of the H_2 pressure became insignificant with small increase in

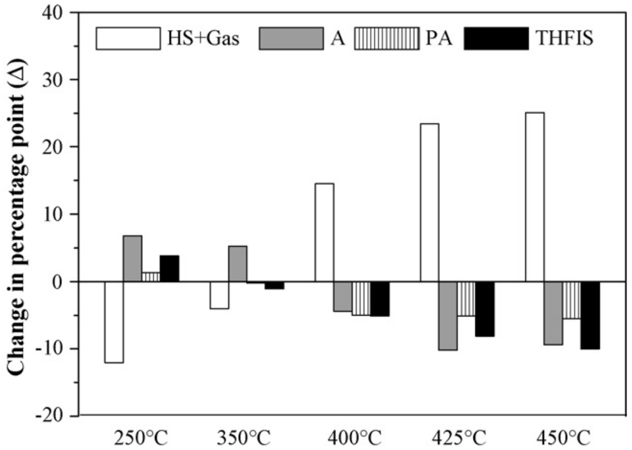

Fig. 2. Change in percentage point on separated fractions due to hydro-treatment at various temperatures; 6 MPa H_2 pressure (initial), 1 h.

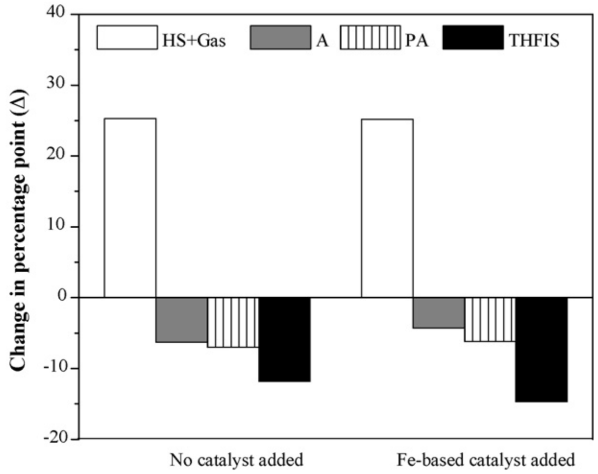

Fig. 4. Effect of catalyst addition on hydro-treatment of DCLR; 450 °C, 7 MPa H_2 pressure (initial), 1 h.

HS + gas and small decrease in PA and THFIS. However, the extent of decrease in A lessened with the increasing of H_2 pressure, suggesting more PA and THFIS being converted to A at higher H_2 pressures. The data also show that an initial H_2 pressure of 5 MPa is sufficiently high for hydrogenation of the DCLR, which is similar to the data reported in co-processing of a coal and a FCC slurry [7]. The data also seem to suggest that hydrogenation of A to HS + gas is mainly determined by temperature at a higher H_2 pressure range.

Fig. 4 shows effect of the Fe-based DCL catalyst on hydrotreatment of the DCLR. As mentioned in Section 2.2 the iron-based catalyst used is same as used during DCL process. It is highly dispersed ultra-fine FeOOH as reported in the literature [8]. Compared with non-catalyst addition case, ΔHS is roughly constant, the negative value of ΔA and ΔPA are slightly decreased. On the other hand, the negative value of ΔTHFIS is slightly increased with the addition of the catalyst. The differences, however, are insignificant. The remaining of the used DCL catalyst in DCLR could be one of the reasons enshrouding the activity of the catalyst added. More detailed study is necessary to clear up the activity of the catalyst.

3.2. Reactivity of individual fractions separated from the DCLR

Among the four fractions separated from DCLR, HS is the lightest fraction and termed oil traditionally. A and PA are mid-fractions of DCLR and contain mainly asphalt-type materials, including poly-aromatic hydrocarbons containing heteroatoms especially in PA fraction. THFIS includes highly condensed poly-aromatic hydrocarbons and mineral matters. To understand the behavior of each of these fractions, they are hydrotreated separately at 450 °C under an initial H_2 pressure of 7 MPa for 1 h with 1 wt% of the iron-based catalyst. Results in Fig. 5 show that HS is stable with a conversion of only 7 wt% to gas. The conversion of A is about 56 wt%, with the main products being HS and gas. PA is the most active fraction with a conversion of 94 wt% and a broad products distribution, from the lighter to the heavier fraction. The conversion of THFIS is about 40%, with 8% to gas, 20% to HS, 8% to A and 4% to PA. Generally HS is the most stable fraction while PA is the least stable fraction during the hydro-treatments.

To study synergetic effect among the fractions, the products distribution experimentally obtained from the hydrogenation of the DCLR as whole (labeled experimental) were compared with the products distribution calculated from the hydrogenation of the individual fractions (labeled calculated) in Fig. 6. The calculated values are arithmetic summation of the theoretical contribution from the individual fractions shown in Fig. 5 and weighted by their fraction in raw DCLR (37% HS, 27% A, 8% PA and 28% THFIS).

The experimental HS + gas yield is 62 wt% while the calculated is 61 wt%. The experimental A yield is 23 wt% while the calculation shows 16 wt%. The experimental PA yield is 1.8 wt% while the calculation shows 1.6 wt%. The experimental THFIS yield is 13 wt% while the calculated THFIS yield is 21 wt%. The significant higher A yield and lower THFIS yield indicate some synergism occurred during hydro-treatment.

3.3. Characteristics of fractions of DCLR

FTIR spectra of HS, A and PA fractions are shown in Fig. 7. The bands between 3000 and 2800 cm^{-1} are assigned to aliphatic C–H stretching vibration mode and used to measure aliphatic hydrogen content [9-13]. The bands between 3100 and 3000 cm^{-1} are assigned to aromatic C–H stretching vibration mode and used to measure aromatic hydrogen content. Fig. 7 shows that the order of intensities of both aliphatic and aromatic C–H stretching modes is HS > A > PA, which agrees with the element analysis data in Table 1. The band near 1600 cm^{-1}, assigned to aromatic ring stretching vibration modes [14], moved from 1609 cm^{-1} in HS and A to 1638 cm^{-1} in PA, indicating more poly-aromatic or heterocyclic compounds in PA [15,16]. This is supported by the appearance of carbonyl vibration band at 1710 cm^{-1} [17–19] for PA. The band near 3370 cm^{-1} for PA, assigned to OH stretching mode [11,19], is much stronger than that for A and HS, suggesting presence of

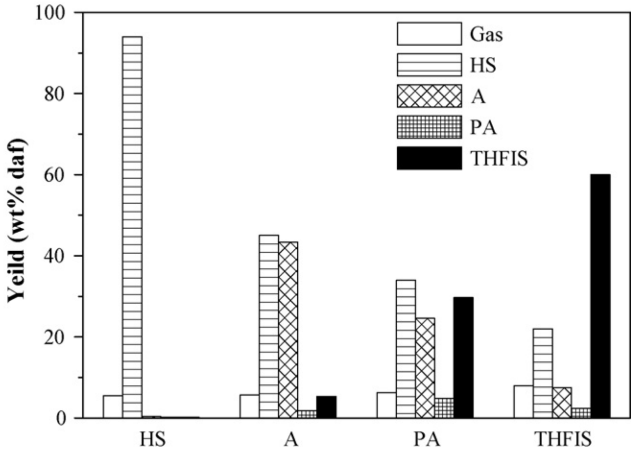

Fig. 5. Products distributions from hydro-treatment of each DCLR components; 450 °C, 7 MPa H_2 pressure (initial), 1 h, with 1 wt% iron catalyst addition.

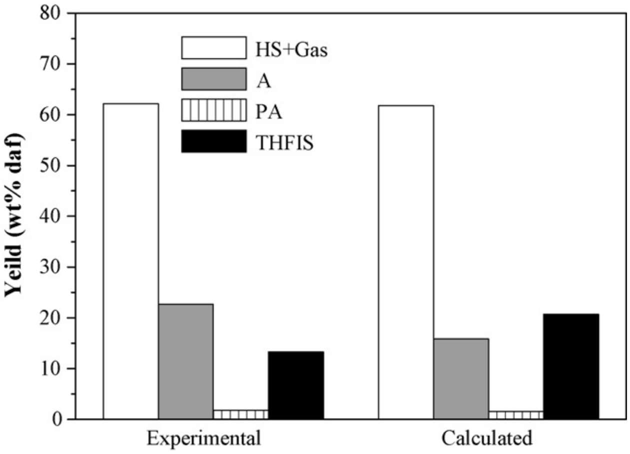

Fig. 6. Comparison of experimental and calculated results; 450 °C, 7 MPa H_2 pressure (initial), 1 h, with 1 wt% iron catalyst addition.

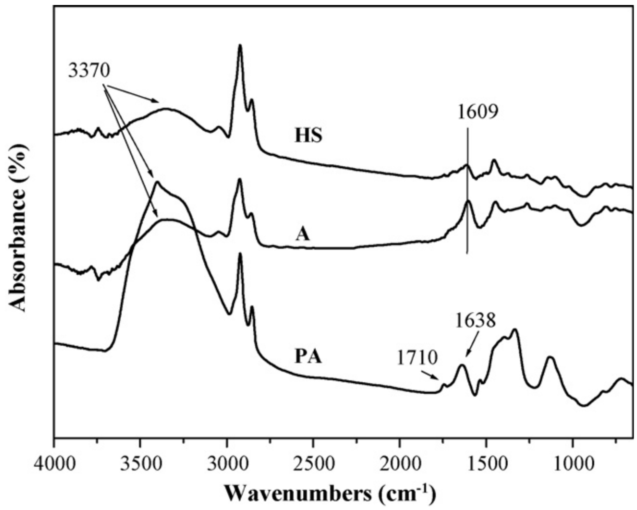

Fig. 7. FTIR spectra of HS, A and PA fractions obtained directly from DCLR.

more phenol group in PA, corresponding to higher oxygen content in PA compared to HS and A (see Table 1).

Fig. 8 shows FTIR spectra of HS fractions obtained from hydro-treated HS, A, PA and THFIS along with that directly from DCLR. It is obvious that the band intensities of the aliphatic and aromatic C-H stretching modes of the HS obtained from hydro-treated HS, A and PA are slightly stronger than that of obtained directly from the DCLR. The HS obtained from hydro-treated THFIS shows no band for aromatic C–H stretching modes but enhanced bands for aliphatic C–H stretching modes compared also to HS obtained directly from DCLR. All these indicate an increase in HS' hydrogen content by the hydro-treatment. The HS from hydro-treated fractions show increased bands at 2955 and 2855 cm^{-1}, assigned to methyl group, indicating increased aliphatic hydrogen content possibly resulted from opening of aromatic rings. A comparison of spectra a and e shows reduction in HS' OH content by the hydro-treatment.

Fig. 9 shows the molecule weight distributions of the HS fractions obtained. In general, the distributions are similar, especially for HS from DCLR, hydro-treated DCLR and hydro-treated THFIS. It is logical to see that HS from hydro-treated A (A/H) contains more higher molecular weight compounds while HS from hydro-treated HS contains more lower molecular weight compounds than other HS. These behaviors are quantified in Table 2, where the number-averaged molecular weight (M_n) of these HS fractions varies from 250 to 310. With experimental error this apart is not sufficient to distinguish the difference between them. However, it shows that the molecular weights of HS fractions are very much similar. Considering the closed properties for the tested samples, the trend that they directed may be used as a reference. In addition it should be mentioned that although THF is commonly used as GPC solvent it has limitations used for coal-derived liquids. The results showed here are only for comparison.

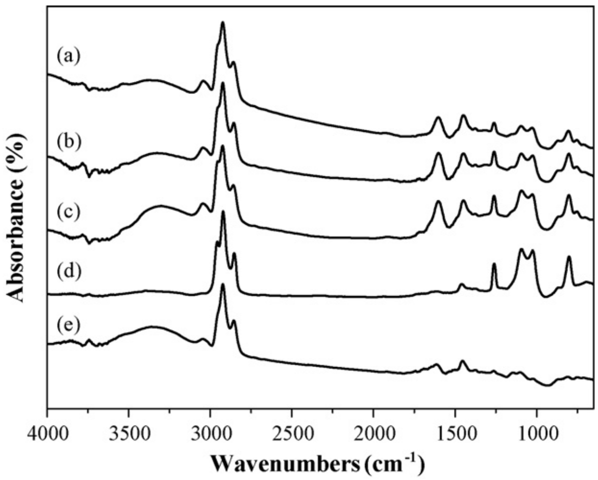

Fig. 8. FTIR spectra of HS fractions obtained from hydro-treatment of HS (a), A (b), PA (c) and THFIS (d) and from DCLR (e).

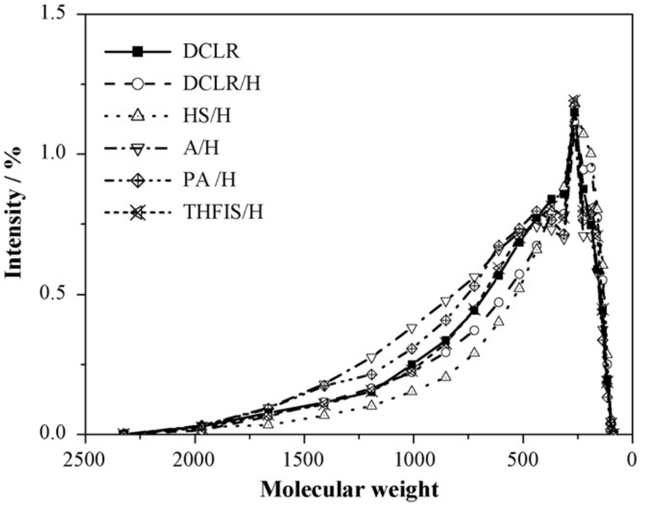

Fig. 9. Molecular weight distributions of HS fractions obtained from DCLR, hydro-treated DCLR (DCLR/H), and hydro-treated HS (HS/H), A (A/H), PA (PA/H) and THFIS (THFIS/H) fractions.

To evaluate extent of the hydro-treatment and changes in atomic hydrogen distribution, HS fractions obtained from DCLR and hydro-treated DCLR are subjected to ^1H NMR analysis. The results are shown in Fig. 10. The peak at 2.7 ppm is assigned to naphthenic hydrogen α to aromatic rings, the peaks at around 1.7 and 0.9 ppm are assigned to hydrogen at β and γ positions more distant to ring, the peak at 1.3 ppm is assigned to $–CH_2–$, and the bands between 6.5 ppm and 9.5 ppm are assigned to aromatic C–H. All these peaks seem to increase by the hydro-treatment. The peaks at 1.9 and 3.8 ppm,

Table 2
Number-averaged molecular weight (M_n) of HS fractions obtained from DCLR (DCLR), hydro-treated DCLR (DCLR/H) and hydro-treated HS (HS/H), A (A/H), PA (PA/H) and THFIS (THFIS/H) fractions

Origin of the HS	Number-averaged molecular weight (M_n)
DCLR	288
DCLR/H	273
HS/H	254
A/H	309
PA/H	310
THFIS/H	283

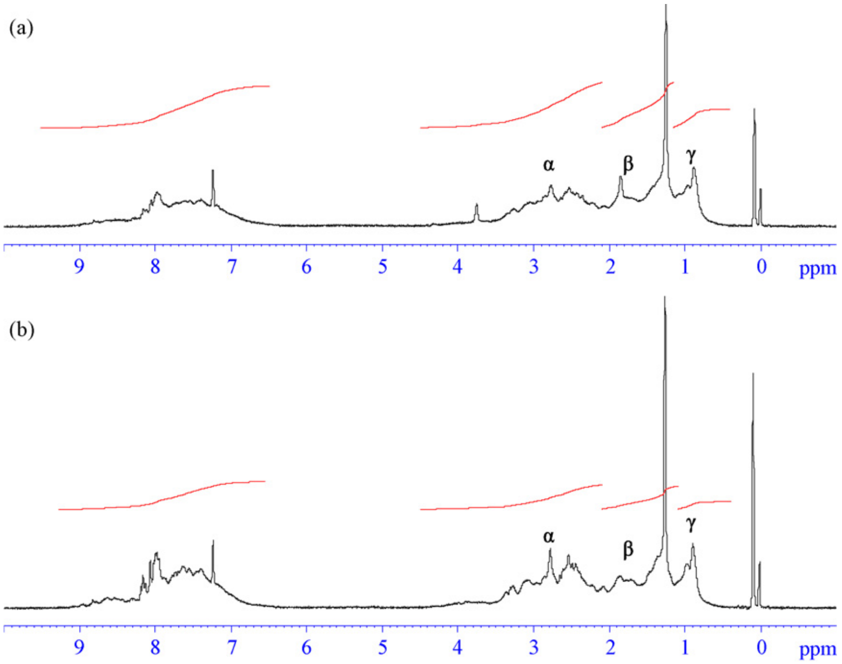

Fig. 10. 300 MHz ^{1}H NMR spectra of HS fractions of DCLR (a) and hydro-treated HS (b).

assigned to hydrogen α to $C=C–CH_3$ and hydrogen α to carboxyl [20], respectively, however, are reduced by hydro-treatment. Clearly, these results are consistent with that of FTIR analysis.

4. Conclusion

A direct coal liquefaction residue, containing 37 wt% *n*-hexane soluble materials (HS), is found hydro-treatable. Under a typical direct coal liquefaction conditions, a significant heavy fraction of the DCLR, about 40 wt%, can be converted into light products. The DCLR's HS fraction itself is stable during the hydro-treatment, with only a 7 wt% conversion to gas. A 56 wt% conversion of asphaltenes fraction (A) is observed with main products being lighter fractions. Pre-asphaltenes (PA) in the DCLR is the most active fraction with a conversion of 94 wt%, but about 30 wt% to THFIS. THFIS is the heaviest fraction and also convertible to lighter fractions. Synergetic effect can be observed when DCLR is treated as whole. FTIR and NMR analyses reveal that the hydro-treatment increases HS' hydrogen content and decreases its oxygen content. GPC analysis reveals that the hydro-treatment reduces the HS' average molecular weight. All the results indicate that separation and hydro-treatment of liquid fractions of DCLR is a viable option for higher oil yield.

Acknowledgments

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