



## Second-order Raman spectroscopy of char during gasification

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### ABSTRACT

Raman spectroscopy has been widely used in the structural characterization of various carbonaceous materials. Through spectral deconvolution, FT-Raman spectroscopy has been used to gain insights into the transformation of char structure during gasification, providing new evidence to understand the char gasification mechanisms. These studies have mainly focused on the first-order Raman spectra in the range between 800 and 1800  $\text{cm}^{-1}$ . Additional information can be gained from the second-order Raman spectra. This study aims to develop a new spectral deconvolution scheme for the second-order Raman spectra of chars from the gasification of coal and biomass. As our initial attempt, the second-order Raman spectra of chars in the range between 2000 and 3300  $\text{cm}^{-1}$  were deconvoluted into 7 bands representing the main structural features in the chars. Both total Raman peak area and band area ratios are used to gain information about the structural features of char. Using chars from the gasification of WA Collie sub-bituminous coal in  $\text{CO}_2$  and  $\text{H}_2\text{O}$  as examples, the implication of the first-order and second-order Raman spectral data in terms of gasification mechanisms is discussed.

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### 1. Introduction

Gasification is an effective method to convert a solid fuel into a high value gaseous fuel [1]. An important aspect of gasification is the reaction between char and gasifying agents to produce syngas [2]. This is a heterogeneous gas–solid reaction and is very complicated as a result of changes in the char structure during gasification [2,3]. Therefore, understanding the transformation of structural feature of char during gasification and the effects of char structure on its gasification reactivity is critically important for a better understanding of the gasification mechanisms [4–7].

Raman spectroscopy has been widely used as a powerful tool to characterize various carbonaceous materials due to its ability to response to symmetric vibration of less or non-polar bonds [8,9]. A Raman spectrum represents the scattering due to many types of distinctly different bonds in the char. There are two Raman spectral regions, in the ranges of  $\sim 800$  to  $1800 \text{ cm}^{-1}$  (first order) and  $\sim 2000$  to  $3300 \text{ cm}^{-1}$  (second order), that are of interests in understanding the structural features of a carbonaceous material. Much has been done to investigate the char structure through deconvolution and analysis of various bands in the first-order Raman spectra [10–15]. Like a first-order Raman spectrum, a second-order Raman spectrum is also the summation of scattering from many bonds. If deconvoluted properly, a second-order spectrum can also provide additional detailed information about the skeletal structure of a carbon-based material. However, second-order Raman spectroscopy has been mainly used for

the characterization of highly ordered carbon materials such as graphite [9,16,17]. Little study has been carried out on the highly disordered carbon materials such as chars from the pyrolysis and gasification of coal and biomass. Even for some research that analyzed the second-order Raman spectra of some highly disordered carbon materials [18–25], most samples have undergone a high temperature treatment (higher than  $1000 \text{ }^\circ\text{C}$ ) [18,19,24,25], resulting in the samples to have higher degree of crystallisation and graphitization. Therefore, the second-order Raman spectra of such samples were simply deconvoluted into three or four bands and the interpretation of these bands followed the bands assignment of highly ordered carbon materials [19–25].

Obviously, the second-order spectra of chars from the pyrolysis and gasification process ( $<1000 \text{ }^\circ\text{C}$ ) differ considerably from that of highly ordered materials or highly graphitized materials. A simple adoption of the concept of bands in the second-order spectra for highly ordered carbon materials would be very inappropriate for the analysis of char structure. Unlike the second-order spectra of graphite-like materials that exhibit a clearly-resolved strong peak of 2D (overtone of D band) and a peak of D + G (combination of D band and G band) [9,16,17], the second-order spectrum of a char could show a very broad band. The overlaps between the 2D and D + G bands as well as the shoulders at the two sides of the 2D and D + G broad bands in the second-order Raman spectrum of a char could contain much information about the structural feature of the char. Therefore, instead of just considering the 2D and G + D bands, the second-order Raman spectrum could be deconvoluted into more bands in order to acquire detailed information about the chemical structure of the char. In addition, because of the differences in crystal structure between graphite and amorphous carbon,

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simple applications of the interpretation of the second-order Raman spectra of highly ordered materials to chars would result in some misleading information and miss some important information about the skeletal carbon structures.

In our previous study [26], a WA Collie sub-bituminous coal was gasified at different temperatures (800, 850 and 900 °C) in atmospheres containing steam and CO<sub>2</sub>. The Raman spectra of char samples collected after varying extents of gasification were acquired by using a laser with a wavelength of 1,064 nm [11,26]. In this study, the same spectra in the second-order region have been analyzed. Compared with our previous work [4,6,7,11–15,26] which mainly focused on the analysis of the first-order Raman spectra, a new spectral deconvolution method for the Raman spectra in the second-order region was established in order to acquire detailed information about the changes in char structure during gasification. The information about char structure from the second-order region is compared with that of the first-order region and complementary or additional information was found through analysis of the second-order Raman spectra.

## 2. Experimental

### 2.1. Gasification of coal

The details of the gasification experiments have been presented previously [26]. Briefly, Collie sub-bituminous coal, supplied by the Muja Power Station in Western Australia, was used. It has an ultimate composition of 75.7% C, 4.5% H, 1.4% N, 0.5% S and 17.9% O [26]. The gasification experiments were carried out in a fluidized-bed/fixed-bed reactor [26,27] with coal particles being heated up rapidly.

### 2.2. Char characterization

The acquisition of Raman spectra of chars was detailed before [26]. The same spectra were used in this study. Briefly, a Perkin-Elmer Spectrum GX FT-IR/Raman spectrometer with an excitation laser of 1064 nm was used to acquire the Raman spectra of chars [11,26]. A char sample was firstly ground into powder and then diluted and ground with spectroscopic grade KBr [11,26]. The char concentration of 0.25 wt% in KBr-char mixture exhibited the plateau total Raman intensity in the first-order Raman region [26]. The total Raman peak area in the second-order Raman region had also reached the plateau with this char concentration as shown in Fig. 1. An InGaAs detector was used to collect Raman scattering using a back scattering configuration [11,26]. Each spectrum represents the average of 200 scans and the spectral resolution was 4 cm<sup>-1</sup> [11,26]. Baseline correction was carried out on each spectrum using the software provided by Perkin-Elmer with the spectrometer [11,26]. The first-order and second-order regions had different baselines.

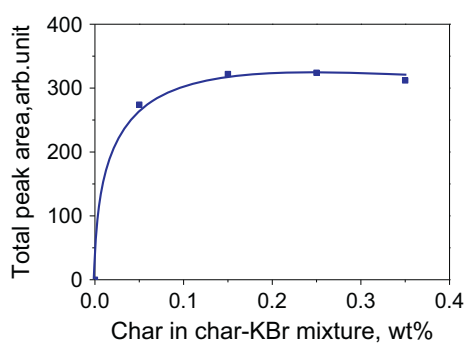


Fig. 1. Effects of char concentration in char-KBr mixture on the total second-order Raman area (2000–3300 cm<sup>-1</sup>). Char was prepared from the gasification of the Collie sub-bituminous coal in 15% H<sub>2</sub>O balanced with Ar at 900 °C.

### 3. Deconvolution and band assignment of the second-order Raman spectra

The second-order Raman spectra of chars in the range between 2000 and 3300 cm<sup>-1</sup> were curve-fitted with 7 mixed Gaussian and Lorentz bands using the GRAM/32 software. The position and assignment of these 7 bands are briefly summarized in Table 1, which we believe represent the typical structural features of chars from the pyrolysis and gasification of coal and biomass.

In the second-order spectra of sp<sup>2</sup> carbon materials, there is a strong Raman feature appearing in the range of 2500–2700 cm<sup>-1</sup>, and it is called the 2D band to mean that it is the overtone of D band in the first-order region [9,16,17]. In the study of the second-order Raman spectra of highly ordered carbonaceous materials, the 2D band was considered to originate from a double resonance, involving two iTO phonons near the K point of the unit cell [9]. The intensity of the 2D band was believed to be related to the number of grapheme layers and the stacking order [9,16,17]. Unlike the defect-induced D band in the first-order region, the 2D band does not indicate any kinds of disorder or defect for the graphite-like material [9,16,17,28,29]. However, the “crystal” structure of char is quite different from the graphite-like carbon materials. Chars from the pyrolysis and gasification of coal and biomass are highly disordered carbonaceous materials with a wide variety of O-containing groups and sp<sup>2</sup>–sp<sup>3</sup> or sp<sup>3</sup>–sp<sup>3</sup> cross-linking structures [11]. According to the bands assignment for the highly disordered materials [11], the D band mainly represents aromatics with not less than 6 rings. For graphitic materials, the D band and 2D band come from two different physical scattering processes so there is no direct relationship in band intensity between these two bands [9,16,17,28,29]. However, a char from the gasification of coal or biomass does not have similar lattice structure and therefore its D and 2D bands do not necessarily originate from two scattering processes. Based on the vibrational theory of the overtone process for chemical structures [8,30], it is believed that the D band and the 2D band come from the same vibration mode for the amorphous carbon materials. Therefore, the interpretation of the 2D band in the second-order spectra of char should be the same as the D band in the first-order [11], i.e. representing the large aromatic ring systems (no less than 6 fused rings). It is also expected to have close relationship with the D band in term of the band intensity in the second-order Raman spectra.

Another main band in the second-order spectra of carbonaceous materials is the D + G band located in the range of 2800–2950 cm<sup>-1</sup> with an exciting laser in the visible range [16,17,24,25]. In the study of the highly ordered carbon materials, this band is considered as a disorder-induced band and would disappear with increasing crystallinity [16,24]. Amorphous carbon materials such as char from gasification would not have a band of the same nature in their second-order spectra. Instead, in this study, the D + G band is assigned to the aromatic ring structures of amorphous carbon materials.

Different from the graphite-like materials, vast amounts of spectral residue would be left if only 2D and D + G bands were considered to deconvolute the second-order Raman spectra of chars. Based on the spectra of some model aromatic compounds [30] and considering the structure of char from coal/biomass gasification process [11–15], two bands have been assigned in the region between the 2D band and D + G band. One is the overtone of the fundamental vibrations of aryl methyl functional groups at around 2750 cm<sup>-1</sup> [30] and named as 2V<sub>R</sub> (in order to correspond with the band name V<sub>R</sub> in the first-order [11]). The other is the (2D)<sub>L</sub> band (standing for 2D left) at around 2650 cm<sup>-1</sup>. These two bands are mainly found in amorphous carbon materials [24,25,30]. In this case, 2V<sub>R</sub> + (2D)<sub>L</sub> can represent the small aromatic ring systems, and it is believed to decrease with the condensation of aromatic ring systems according to some Raman spectra of amorphous carbon materials that have been heat-treated at high temperature [24,25].

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