

# Modeling X-ray Line Shapes from Asphaltenes

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**Abstract.** Structural studies of asphaltene in crude oil have been performed by x-ray diffraction (XRD). The XRD spectra were taken with a Rigaku Dmax 2200V/PC, and built-in Jade<sup>TM</sup> software was used for initial analysis. XRD was performed with Cu-K- $\alpha$  radiation operating at 40 KV and 40 mA, with a scan rate of  $0.001^\circ$   $2\theta$  per second. The XRD data were first fitted with Pearson VII profiles and then with pseudo-Voigt profiles, and then modeled in Mathematica<sup>©</sup> using a generalized Fermi function (GFF). These fits also included several different backgrounds (linear, exponential, and Lorentzian). The results are discussed in terms of their accuracy with different combinations of background and line profile.

## 1. Introduction

Asphalt binder finds many applications such as in asphalt cement pavement for roads and highways, roofing materials, and heavy oil fuel upgrading. The latter application may involve asphaltene removal technology with solvents, or heavy oil catalysis into lighter fuels. So why study asphaltene? Recent history suggests that conventional light oil sources have decreased leaving the more abundant heavy oil sources to be developed. With this trend in mind, there has been a growing interest in further understanding the constituents in heavy oil such as asphaltene [1].

Asphaltene is a chemical constituent of crude oil reservoirs, bitumen and natural sources. Asphaltene chemistry, molecular size and structure are important variables. Crude oils can be separated into saturates, aromatics, resins and asphaltenes (SARA) in the laboratory. The asphaltene component has repeat units consisting of straight or branched chain molecules known as aliphatic or paraffinic; saturated rings with a high hydrogen to carbon ratio; unsaturated ring structures that are aromatic; and additional metals and heteroatoms as part of the ring structures. These repeat units have been previously studied by various analytical techniques including x-ray diffraction (XRD) originally developed for colloids in order to quantify molecular length scales [2-4]. XRD characterization is also useful in the case of asphaltene samples when one or more chemical phases (eg. asphaltene, wax, metal etc.) are present. This paper will focus on analyzing the X-ray line shapes of asphaltenes as measured by XRD for the purpose of further understanding chemical



phases and related structure in these samples with three different combinations of backgrounds (linear, parabolic, 3<sup>rd</sup> order polynomial).

## 2. Experimental

The asphaltene samples were obtained from Canadian crude oil and asphalt by using solvent separation methods [5]. They were then coated onto glass slide holders by heating to 150°C for 10 minutes in a drying oven followed by cooling to ambient (25°C) temperature.

The X-ray diffraction (XRD) system used was a Rigaku Dmax 2200V-PC and Jade™ software (version 6.1) [4-5]. XRD was performed by using Cu-K- $\alpha$  radiation operating at 40 KV and 40 mA, scan rate of 0.001° 2 $\theta$  per second and detector count time of 5 seconds/step. The XRD spectra obtained was then peak searched (screened out K- $\alpha$ -2 peaks) over the angular range of 5° to 110°. The full width at half-maximum (FWHM) and profile fits were obtained by using either Pearson VII and pseudo-Voigt function and three background types (linear, parabolic, 3<sup>rd</sup> order polynomial) over the approximate ranges 5° to 35° 2 $\theta$  and 60° to 110° 2 $\theta$  on the x-ray diffraction line spectra of interest.

The background radiation produced in the XRD spectra is an important aspect in studying asphaltene. Three background types (linear, parabolic, 3<sup>rd</sup> order polynomial; see table 1) were used in the case of the XRD analysis for generating profile fits with Pearson VII and pseudo-Voigt. The XRD spectra modeled in Mathematica© using a generalized Fermi function (GFF) also used three background types. The GFF modeled fits and plots were compared to Pearson VII and pseudo-Voigt. However, the calculations for the aromaticity ( $f_a$ ), and crystallite parameters for interlayer distance between aromatic sheets ( $d_M$ ) and interchain layer distance ( $d_\gamma$ ) are as follows:

$$f_a = C_a/C_{total} = C/C(\text{graphene} + C_\gamma) = \text{Areagraphene}/(\text{Areagraphene} + \text{Area}_\gamma) \quad (1)$$

$$d_M = \lambda/(2\sin\theta) \quad (2)$$

$$d_\gamma = 5\lambda/(8\sin\theta) \quad (3)$$

For each calculation they are all treated differently due to the types of background used and the different mathematical functions for each background.

## 3. Results and discussion

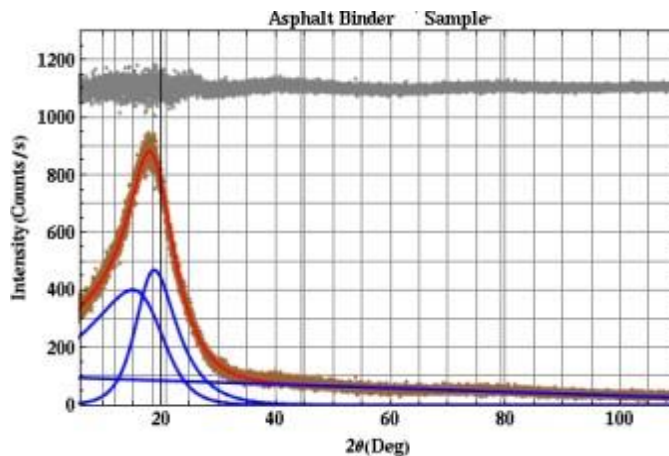
The results in table 1 highlight the effect of background type on accuracy of fit as indicated by the residual error of fit when using two different mathematical functions (Pearson VII, pseudo-Voigt) to fit asphalt binder samples. By inspection it is seen that the residual error of fit is lowest for parabolic, highest for 3<sup>rd</sup> order polynomial and low to intermediate for linear types of background. This trend in accuracy of fit is consistent for both types of mathematical functions used in profile fitting.

The asphaltene XRD patterns consists of four peaks: gamma peak ( $\gamma$ ), (002) graphene, (100), and (110). The first two peaks in the XRD patterns and GF-mathematica© profile fit spectra (figure 1) are the gamma and graphene at about 18-20° 2 $\theta$  while the peaks and planes for (100) and (110) are much broader at higher angles.

The XRD peak profile fitting function of Pearson VII and pseudo-Voigt have different peak shapes. Pseudo-Voigt is a combination of Gaussian and Lorentzian. Pearson VII is an exponential mixing of Gaussian and Lorentzian. The four most commonly used empirical peak shape functions ( $y$ ) and the Generalized Fermi function are expressed mathematically in equations (4) to (8) [6]:

**Table 1.** The effect of background on fit.

Sample	Mathematical Function	Background	Residual Error of Fit %
AT1	Pseudo-Voigt	Linear/Parabolic/3 <sup>rd</sup> Order Polynomial	8.8/5.4/25.3
AT3	Pseudo-Voigt	Linear/Parabolic/3 <sup>rd</sup> Order Polynomial	8.6/5.4/26.4
AT5	Pseudo-Voigt	Linear/Parabolic/3 <sup>rd</sup> Order Polynomial	7.8/5.4/22.3
AT1	Pearson VII	Linear/Parabolic/3 <sup>rd</sup> Order Polynomial	10.0/6.1/23.3
AT3	Pearson VII	Linear/Parabolic/3 <sup>rd</sup> Order Polynomial	9.6/5.8/24.0
AT5	Pearson VII	Linear/Parabolic/3 <sup>rd</sup> Order Polynomial	8.2/5.7/20.5



**Figure 1.** GF-mathematica© profile fit spectra with fixed background.

$$\text{Gauss: } y(x) = G(x) = (C_G^{1/2})/(\sqrt{\pi}H) \exp(-C_G x^2) \quad (4)$$

$$\text{Lorentz: } y(x) = L(x) = (C_L^{1/2})/(\sqrt{\pi}H') (1+C_L x^2)^{-1} \quad (5)$$

$$\text{Pseudo-Voigt: } y(x) = \eta (C_G^{1/2})/(\sqrt{\pi}H) \exp(-C_G x^2) + (1-\eta) (C_L^{1/2})/(\sqrt{\pi}H') (1+C_L x^2)^{-1} \quad (6)$$

$$\text{Pearson: } y(x) = \text{PVII}(x) = \Gamma(\beta)/(\Gamma(\beta)-1/2) (C_P^{1/2})/(\sqrt{\pi}H) (1+C_P x^2)^{-\beta} \quad (7)$$

$$\text{Generalized Fermi: } y(x) = A/[\exp(-a(x-c))+ \exp(b(x-c))] \quad (8)$$

Where:  $H$  and  $H'$  are the full widths at half maximum (FWHM),  $x = (2\theta_i - 2\theta_k)/H_k$ , where  $x$  is the XRD Bragg angle of the  $i^{\text{th}}$  point in the diffraction pattern with its origin in the position of the  $k^{\text{th}}$  peak divided by the peak's FWHM;  $2\theta_i$  is the Bragg angle of the  $i^{\text{th}}$  point of the diffraction pattern;  $2\theta_k$  is the Bragg angle of the  $k^{\text{th}}$  Bragg reflection [6].

A Gauss function is taller at the top with little to no side tails at the bottom relative to the Lorentz that has a shorter sharp top with long tails at the bottom. Both functions are symmetric since  $G(x)$

$= G(-x)$  and  $L(x) = L(-x)$ . These distributions can vary in XRD results. In pseudo-Voigt the ratio of  $\eta$  and  $\eta-1$  varies for Gaussian to Lorentzian behavior, while in Pearson VII exponent ( $\beta$ ) varies [6].

The determination of x-ray background intensity can be an issue in line profile analysis. When line profiles have long tails (at high  $2\theta$  angles in our data) there is always overlap of profiles leading to apparent background intensity [7]. These conditions can create errors in structural parameters obtained from line profile analysis. Usually a linear background under the profile is assumed from the height and slope as calculated by a fixed straight line from the extremities of the profile over a specified measuring range. For relative determinations this is usually not a serious problem. However, in the case of comparing profiles using Jade<sup>TM</sup> software to modeling in Mathematica© the determination of x-ray background intensity can differ thus leading to mixed results in aromaticity and structure (crystallite parameters) as indicated by the values of residual error of fit in table 1. The lowest to highest residual error of fit was parabolic<linear<3<sup>rd</sup> order polynomial using the methods defined in this research paper.

**Table 2:** Aromaticity ( $f_a$ ), crystallite parameters (interlayer distance between the aromatic sheets ( $d_M$ ), and interchain layer distance ( $d_\gamma$ )) for Pearson VII (P), pseudo-Voigt (V), and Generalized Fermi Function (GF).

Sample AT5	$f_a$			$d_M(\text{\AA})$			$d_\gamma(\text{\AA})$		
Background	P	V	GF	P	V	GF	P	V	GF
Linear	0.4	0.6	0.7	4	4	5	5	5	5
Parabolic	0.5	0.7	0.7	4	4	5	5	5	5
3 <sup>rd</sup> Order	0.5	0.6	0.7	4	4	5	5	5	5

The XRD results modeled in GFF (GF) provided a smooth shape (Figure 3), however analysis of aromaticity and crystallite size parameters (Table 2) using the XRD data were sometimes mixed due to asymmetry in the GFF data and differences in calculating background intensity (Table 1).

#### 4. Conclusions

XRD pattern profile fits by Pearson VII and pseudo-Voigt using Jade<sup>TM</sup> software compared to generalized Fermi function data modeled in Mathematica© showed mixed correlation. The results are explained in terms of the calculation of x-ray background intensities, peak shape function, profile fitting, and asymmetry of XRD data.

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