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## Comparison of the fluorescence behavior of a biocrude oil and crude petroleum oils.

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### Abstract

The production and characterization of biocrude and petroleum like products from natural, renewable resources such as oil-bearing plant seeds is an interesting area of research at the moment. The present article discusses the results of a comparative fluorescence study in relation to the composition of a biocrude with petroleum crude oil of Assam, India (Assam-A), and some other crude oils around the world. It has been observed that biocrude has a very different lifetime-wavelength plot when compared to that of Assam-A and other petroleum crude oils. Although biocrude has a normalized lifetime-wavelength profile similar to that found in light crude petroleum oils, the magnitude of the lifetimes are dramatically reduced by the presence of a high concentration of polar compounds (~16.11%). The study of TSFS plots shows that Assam-A has a profile similar to most light-medium crude oils, but the biocrude plot is totally different from any of the crude oils for which we have TSFS data. This indicates that the biocrudes have a radically different distribution compared to crude oils. This might also explain the "pinch point" of the biocrude at an excitation wavelength below ~300 nm.

### Introduction

The fluorescence behavior of crude petroleum oils is very dependent on the chemical composition, and therefore offers a very sensitive method for analysing different oils.<sup>1-9</sup> The fluorescence of crude petroleum oils derives largely from the aromatic hydrocarbon fraction, and this fluorescence emission is strongly influenced by the chemical composition (e.g., fluorophore and quencher concentrations) and physical characteristics (e.g., viscosity and optical density) of the oil.<sup>2,3</sup> To date, most oil fluorescence studies have either involved the analysis of crude oils,<sup>1-6,9</sup> refined petroleum oils,<sup>7,8</sup> or edible oils,<sup>11,12</sup> and to the best of our knowledge, there have been no fluorescence studies of biocrudes. This is an area, which deserves attention since biocrudes are being advanced as renewable replacements or supplements to petroleum crude oils, especially in developing nations. In particular, the development of non-contact analytical methods for characterizing the composition of biocrudes during production is necessary. Methods such as Total Synchronous Fluorescence Scan (TSFS) and fluorescence lifetimes offer an inexpensive, sensitive, and non-destructive method suitable for oil characterization.<sup>9</sup> In this article we make a preliminary attempt to compare the fluorescence behavior (lifetime and TSFS) of a biocrude to that with various crude petroleum crude oils and try and correlate this to chemical composition.

### Experimental Section

The biocrude (B) was prepared by thermocatalytic cracking of *Mesua ferrea* L seed oil and has been previously reported.<sup>12</sup> A typical high-wax crude oil, Assam-A, was supplied from the Numaligarh Refinery, Assam, India while the provenance and composition of the other crude oils are described in earlier publications.<sup>2, 3</sup> °API gravity was measured for the biocrudes using an ASTM procedure<sup>13</sup> while the gross chemical composition (alkane, aromatic, polar, and asphaltene components) were determined using column chromatography methods (gravity method). The column was made with 6-20 mesh silica gel and was eluted overnight with n-hexane followed by crude oil to be analyzed for 2 hours. The solvent used for the recovery of different fractions were: n-hexane for alkane, toluene for aromatics, 1:1 v/v of chloroform and methanol for polars, and the remainder was removed using dichloromethane for the asphaltene fraction.

All optical measurements were made using the undiluted, non-degassed oil in sealed triangular quartz cuvettes using front surface excitation at room temperature. Fluorescence lifetime data was collected on a time correlated single photon counting (TCSPC) system, (Fluotime 200, PicoQuant, Germany) using a 405 nm laser diode excitation. The lifetimes used throughout are the intensity average lifetime ( $\bar{\tau}$ ) calculated by deconvolution of the decay data using the FLUOFIT program (ver 3.1, PicoQuant).<sup>2, 3</sup> The error in  $\bar{\tau}$  is typically less than 0.2 ns. TSFS data was obtained from a Perkin-Elmer LS-50B in front surface excitation mode, with the excitation and emission slits set to 15 and 20 nm respectively, a scan speed of 1500 nm.min<sup>-1</sup>, and a wavelength interval step size of 20 nm. For comparison purposes, each TSFS plot was normalized to the point of maximum fluorescence intensity, and then plotted with 9 equally stepped contour lines from 0.1 to 0.9.<sup>9</sup>

## Results and Discussion

Fluorescence data were collected under similar conditions to that employed in previous studies to enable comparisons to be drawn between the biocrude and the Assam-A with data already obtained from a wide-ranging sample of crude oils.<sup>2, 9</sup> Figure 1-A shows that the Biocrude has a very different lifetime-wavelength ( $\tau$ - $\lambda$ ) profile when compared to Assam-A, with its longest lifetime at a shorter wavelength (550 versus 610 nm) and the lifetimes are shorter at longer emission wavelengths. This is the opposite of what one would expect since the lighter biocrude has a high alkane concentration. However, the biocrude also has a much higher polar concentration, causing more quenching leading to the shorter lifetimes. The shape of the  $\tau$ - $\lambda$  profile is largely determined by energy transfer (ET) processes with emission in the red largely resulting from secondary emission (i.e. ET from small to larger fluorophores). Plotting the normalized  $\tau$ - $\lambda$  plot (Figure 1-B) for the biocrude, Assam-A and oil 7098; we see that the profiles overlap very well. This could indicate that the fluorophore distributions should be reasonably similar; however one would expect that the specific identities of the fluorophores would be widely different. However there is a very large difference in  $\bar{\tau}$ , with the biocrude having a maximum  $\bar{\tau}$  of 4.3 ns at 550 nm and 7098 a  $\bar{\tau}$  of 8.8 ns at 560 nm. We surmise that the dramatic reduction in  $\bar{\tau}$  across the emission spectrum is due to the very high concentration of polar species in the biocrude (~16.11%).

For Assam-A the  $\tau$ - $\lambda$  profile (Figure 1-A) matches closely that of a medium mature crude oil (7193) and it is interesting to note that even with a relatively large differences in API gravity

(~8 units), aromatic content (~12 %), and asphaltenes (5.8 %), the plots are almost identical. The only comparable compositional element between the two oils is the alkane content (48.1 % vs. 50.73 %). However, other oils with alkane concentrations in this range have much different lifetimes.<sup>2</sup> In summary, the lifetime data tends to indicate that the biocrude has a similar distribution of emitting fluorophores to that found in light crude petroleum oils, but that the lifetimes are dramatically reduced by the presence of a high concentration of polar compounds. However, since we do not get a perfect overlap in the  $\tau$ - $\lambda$  profile, we have to further probe the identity and nature of the fluorophores in the biocrude using TSFS which give a good fingerprinting method for the analysis of crude oil.<sup>9</sup>

The TSFS plots (Figure 2) show quite clearly the differences between the oil samples, and it is evident that the differences are more significant than that suggested by the lifetime data. Comparing Figure 2 with the TSFS plots from our oil library we see that while the Assam-A shows a similar profile to most light-medium crude oils, the Biocrude (B) plot is totally different from any of the crude oils for which we have TSFS data. Our TSFS data set covers an extensive range of crude oils and this would suggest that the composition of the biocrude (B) is fundamentally different from most crude oils.<sup>9</sup> This is not surprising since the biocrude has been formed by entirely different processes, and is relatively immature when compared to crude petroleum oils that have been aged underground.

Returning to the similarity of the lifetime data between the high-wax Assam-A and oil 7193, when we compare TSFS plots (Figure 2) we see that this degree of similarity is not maintained. While the TSFS plots follow the same general trend with high relative intensity extending from short excitation wavelength/long wavelength interval (corresponding to ET from blue absorbing to red emitting fluorophores, high Stokes shift) to longer excitation wavelength/short wavelength interval (corresponding to emission from directly excited fluorophores, short Stokes shift). However we do get a relatively good match with oil 7058, which is a little lighter (API = 40.1). The 7058 oil has however, longer lifetimes than Assam-A or 7193. From this one might conclude that Assam-A has a similar composition to 7058, but with a higher polar concentration, which would account for the shorter lifetime.

## Conclusions

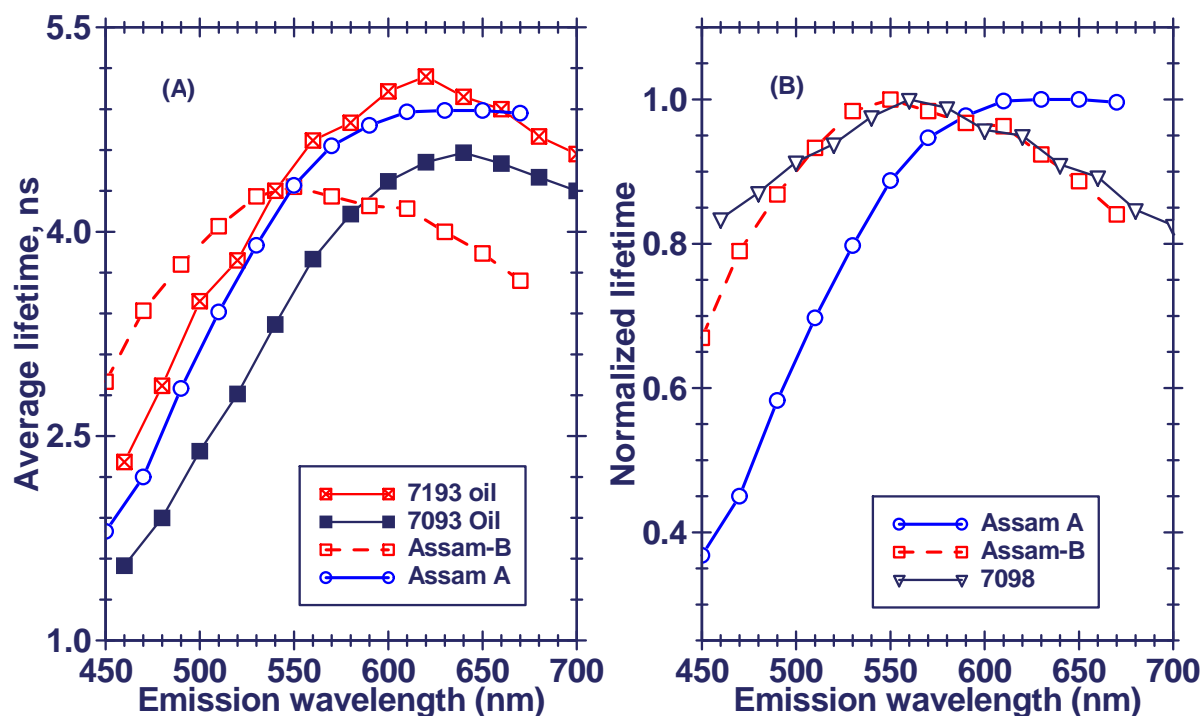
This represents the first attempt to correlate the fluorescence behavior of a biocrude oil with that of crude oils, with a view to developing rapid fluorescence based methods for characterizing biocrudes. Fluorescence lifetime data can be used to explain broad trends in the fluorescence behavior of biocrudes relative to crude petroleum oils, but without an exact overlap in the  $\tau$ - $\lambda$  profiles a quantitative relationship is not possible. This lack of overlap in the  $\tau$ - $\lambda$  profiles is due to the radically different nature of the fluorophores present in the biocrudes as evidenced in the TSFS plots. Our tentative suggestion for explaining the TSFS profile of the biocrude is that there are two almost distinct classes of fluorophores involved which don't overlap and this hinders the smooth ET processes that we observe in normal crude oils. This might explain the "pinch point" at an excitation wavelength below ~300 nm. However, it is clear that a wide range of fully characterized biocrudes is required in order to develop a quantitative model for biocrude composition based on fluorescence measurements

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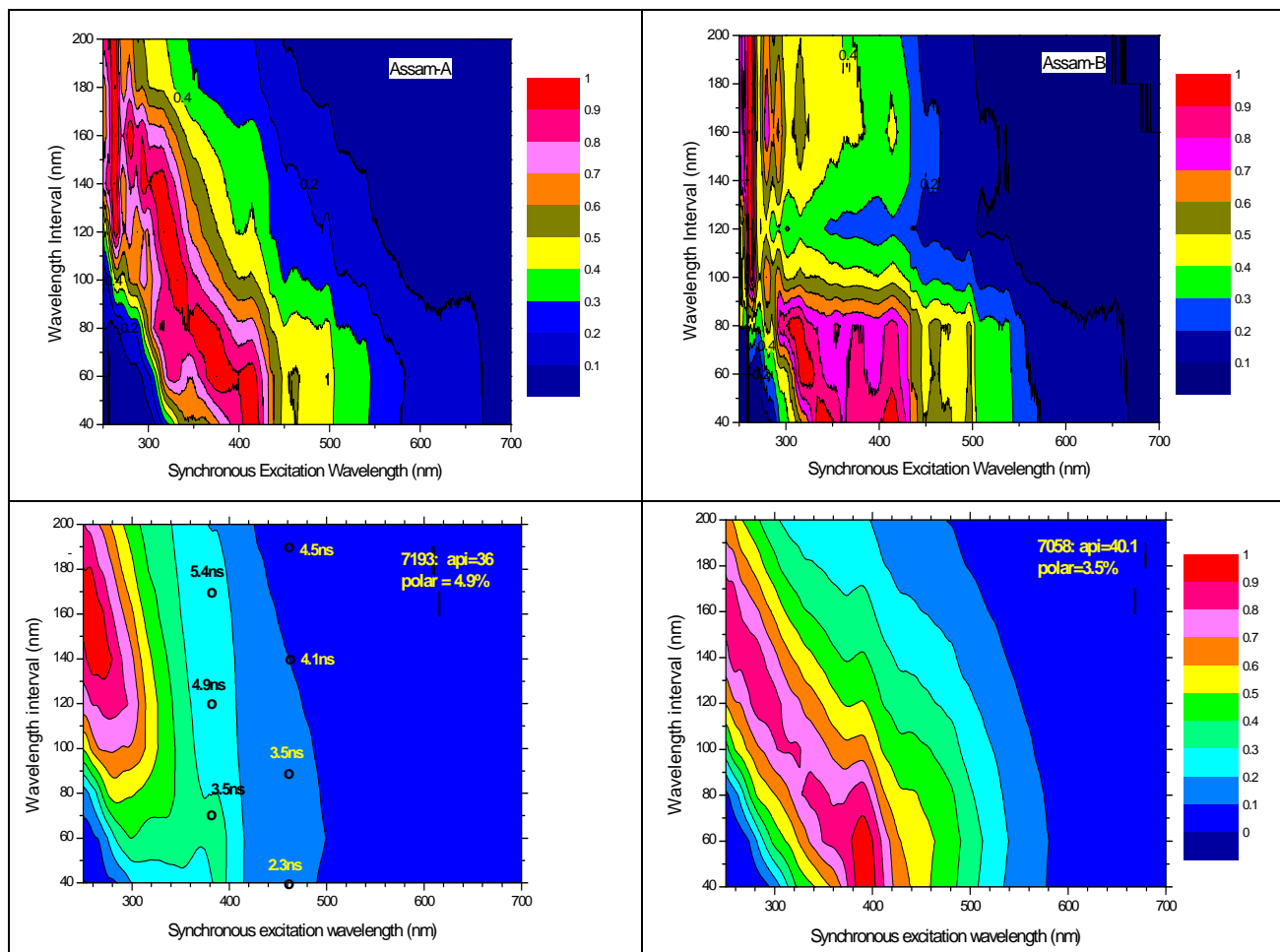
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**Table 1:** Fractionation data for the crude petroleum oils and the biocrude discussed in this work. The corr. Refers to data that has been corrected for column losses. \* Data from references [2, 3].

<i>Oil ID</i>	<i>API</i>	<i>Alkanes</i>	<i>Aromatics</i>	<i>Polars</i>	<i>Asphaltenes</i>	<i>Column Loss</i>
Assam-A	<b>28.0</b>	<b>48.10</b>	<b>24.22</b>	<b>8.23</b>	<b>7.51</b>	<b>11.94</b>
<i>Corr</i>	-	59.71	30.07	10.22	-	-
Biocrude (B)	<b>34.4</b>	<b>79.91</b>	<b>1.01</b>	<b>16.11</b>	<b>1.80</b>	<b>1.17</b>
<i>Corr</i>	-	82.36	1.04	16.6	-	-
7193*	36.0	50.73	12.37	4.89	1.7	32.02
<i>Corr</i>	-	74.61	18.19	7.2	-	-
7058*	40.1	34.08	18.15	3.45	0.04	44.32
7093*	30.9	33.86	19.35	11.47	3.5	35.32
7098*	44.6	42.18	4.61	0.70	-	52.51
<i>Corr</i>	-	88.82	9.70	1.47	-	-



**Figure 1:** (A) Plot of intensity averaged fluorescence lifetime ( $\bar{\tau}$ ) versus emission wavelength for the typical high-wax Assam-A crude oil(A) and Biocrude(B) recorded using 405 nm excitation. (B) Plot of normalized  $\bar{\tau}$  versus emission wavelength for the Biocrude, and Assam A. Also included for comparison in both plots purposes are  $\bar{\tau}$  data from various crude oils previously studied.



**Figure 2:** TSFS plots for Assam-A and Biocrude. TSFS plot of oil 7193 (Left) and oil 7058 (right), adapted from Ref. 9.