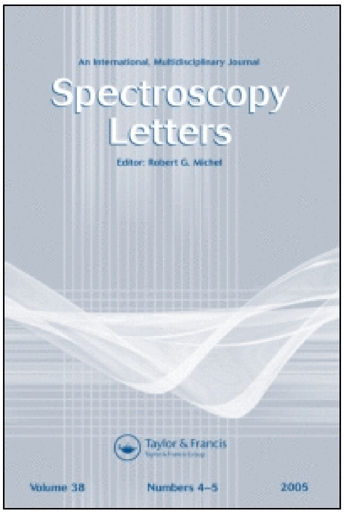

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IN-SITU DIFFUSE REFLECTION FT-IR SPECTROSCOPIC STUDY OF PYROLYSIS OF LIGNITE

Key words: Infrared spectra, Diffuse reflection, Lignite, Pyrolysis

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ABSTRACT

Pyrolysis of lignite coal has been investigated ***in-situ*** by diffuse reflectance infrared spectroscopy. The diffuse reflectance spectrum of lignite coal is concluded to be made of Gaussian bands. The increase of aromaticity factor with temperature could be clearly evidenced from the C-H stretching region. Although quantitative analysis of the structural modification can not be performed at the moment, qualitative information can be provided at least from the peak intensity variations. This work demonstrates that the temperature and atmospheric effects on the physicochemical properties of powdered materials can be readily studied by interfacing the reflectance optics with a controlled environment reaction chamber.

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INTRODUCTION

The need for efficient utilization of fossil fuel reserves has made stringent demands on chemists to better elucidate and understand the chemical and physical properties of coals. Although various spectroscopic techniques can be applied to the characterization of coal, infrared spectroscopy has been utilized as the most important tool because most organic and mineral components in coal absorb in the infrared region.[1] However, infrared spectra of coals has been traditionally obtained by the transmission method after dispersing the sample in an infrared transparent medium (usually KBr) and then pressing into a glassy pellet.[2] Owing to its inherent disadvantage requiring mechanical mixing with other matrix, the infrared spectroscopic method has thus been regarded inappropriate for ***in situ*** studies. This changed with the pioneering work of Fuller and Griffiths,[3] who successfully developed diffuse reflectance technique for infrared spectroscopy and demonstrated its usefulness in coal characterization studies. In this paper, we wish to report the usefulness of diffuse reflectance Fourier transform (DRIFT) infrared technique for ***in situ*** studies of coal by interfacing the DRIFT optics with a reaction chamber. In this regard, the pyrolysis of lignite has been investigated by recording the infrared spectra at various temperature.

EXPERIMENTAL

Diffuse reflectance infrared spectra were measured with a vacuum-purged Bruker Model IFS 113v FT-IR spectrometer. The source was a water-cooled Globar and a liquid nitrogen cooled mercury-cadmium-telluride detector was used. The diffuse reflection attachment (Harrick Model DRA-2CO) designed to use the 6:1, 90° off-axis ellipsoidal mirrors subtending 20 % of the 4π solid angles was fitted to the sampling compartment of the FT-IR spectrometer. A reaction chamber made of stainless steel (Harrick Model HVC-DR2) was located inside the reflection attachment. The position of sampling cup was adjusted to match with the focal point of incident radiation. CaF_2 crystals were used as the infrared transparent windows. The temperature of sampling cup was regulated by a

TABLE 1.

Proximate, Ultimate, and Ash Analyses of Lignite Coal[a]

Proximate Analysis[b]		Ash Analysis[d]	
Moisture (ad)	4.56	SiO_2	47.51
Ash (ad)	4.81	Al_2O_3	32.59
Volatile Matter (daf)	45.9	Fe_2O_3	6.73
Elemental analysis[c]		TiO_2	3.74
		MnO	0.11
Carbon (dmmmf)	69.1	CaO	2.88
Hydrogen (dmmf)	5.17	MgO	1.29
Oxygen (dmmf)	23.9	K_2O	1.18
Nitrogen (dmmf)	1.13	Na_2O	0.24
Sulfur (dmmf)	0.66	P_2O_5	3.94

[a]Wt %, [b]ad: as analyzed (air dry) basis, daf: dry, ash free basis, [c]dmmf: dry, mineral free basis, [d]High temperature (1023 K) ashes.

home-made temperature controller, and the chamber was flushed continuously with dry nitrogen (ca. 100 ml/min) during the pyrolysis of lignite.

The spectra were measured at a nominal resolution of 4 cm^{-1} by co-adding 128 scans. The temperature of sampling cup was raised at a rate of 3°C/min and kept for 4 min at each specified temperature to take the spectra. Diffuse reflectance spectra at infinite depth were calculated by taking ratio of the single-beam spectrum of the sample to that of the KBr reference placed in the same cup at room temperature. The spectrum was then converted to the Kubelka-Munk (K-M) function.[4] The triangular squared function was used in the apodization of measured interferograms.

The proximate and ultimate analyses of the lignite sample, originating from Indonesia, are given in TABLE 1. The mineral contents of high temperature (1023 K) ashes analyzed by X-ray fluorescence method are also included in the

TABLE 1. The samples having particle sizes less than 111 μm (115 mesh) were exclusively used to record the reflectance spectra without any other treatment.

RESULTS AND DISCUSSION

Prior to applying the DRIFT technique to the pyrolysis of lignite, it was tested whether the diffuse reflectance spectrum would contain the same type of information for powdered coal samples as the conventional transmittance spectrum. As reported by Fuller and Griffiths,[3] the spectral pattern of the diffuse reflectance spectrum of powdered lignite taken at room temperature was observed, in fact, barely different from that of the transmittance spectrum of pelletized lignite with KBr. The peaks appearing in both spectra could be adequately assigned by referring to the literature.[2,5]

FIG. 1 shows the DRIFT spectra of lignite taken during the pyrolysis under dry nitrogen atmosphere. It can be seen that a noticeable spectral change takes place at around 673 K. Below 573 K, the removal of moisture content appears to be the dominant process since the spectral variation occurs only in the 3000-3500 cm^{-1} region. At 923 K, any distinct peak is hardly observable indicating that most of the organic functional groups are converted to volatile matter leaving char as the resulting residue.

It is seen from FIG.1 that the aliphatic C-H stretching bands in the 2800-3000 cm^{-1} region weaken significantly as the temperature is raised from 573 K to 673 K. At the same time, the aromatic C-H stretching band at near 3050 cm^{-1} is, on the other hand, intensified. This can be evidenced more clearly from the expanded spectra of C-H stretching region shown in FIG. 2. At 723 K, the C-H stretching band of aromatic group becomes as strong as those of aliphatic groups. The present observation can be understood by invoking that aromatic rings existing originally as highly substituted or cross-linked states convert to simple aromatics by pyrolysis. Similar aromaticity increase has been observed previously by Williamson[6] from the ^{13}C nuclear magnetic resonance spectroscopy. Differently from the earlier work, we could identify the same phenomenon under ***in-situ***

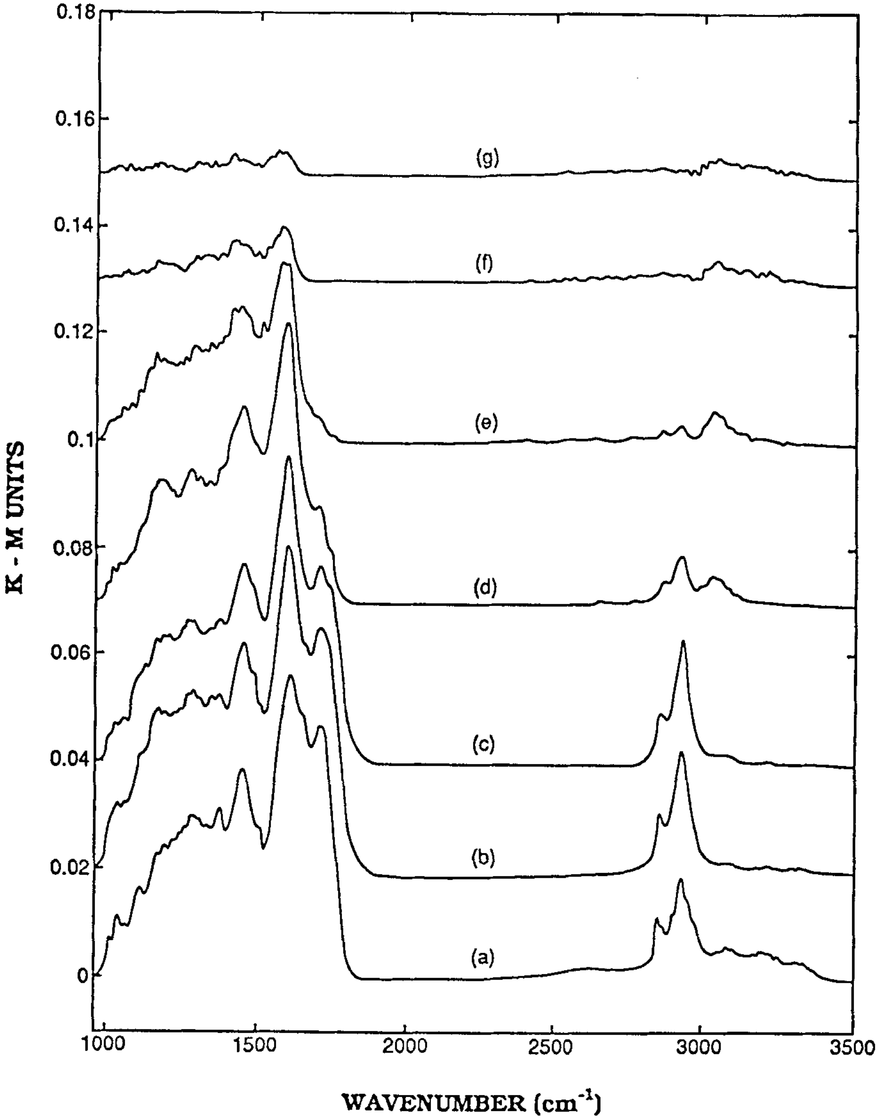

FIG 1. Diffuse reflectance infrared spectra of lignite during pyrolysis under dry nitrogen atmosphere. Spectra were obtained at (a) 298, (b) 473, (c) 573, (d) 673, (e) 773, (f) 873, and (g) 923 K.

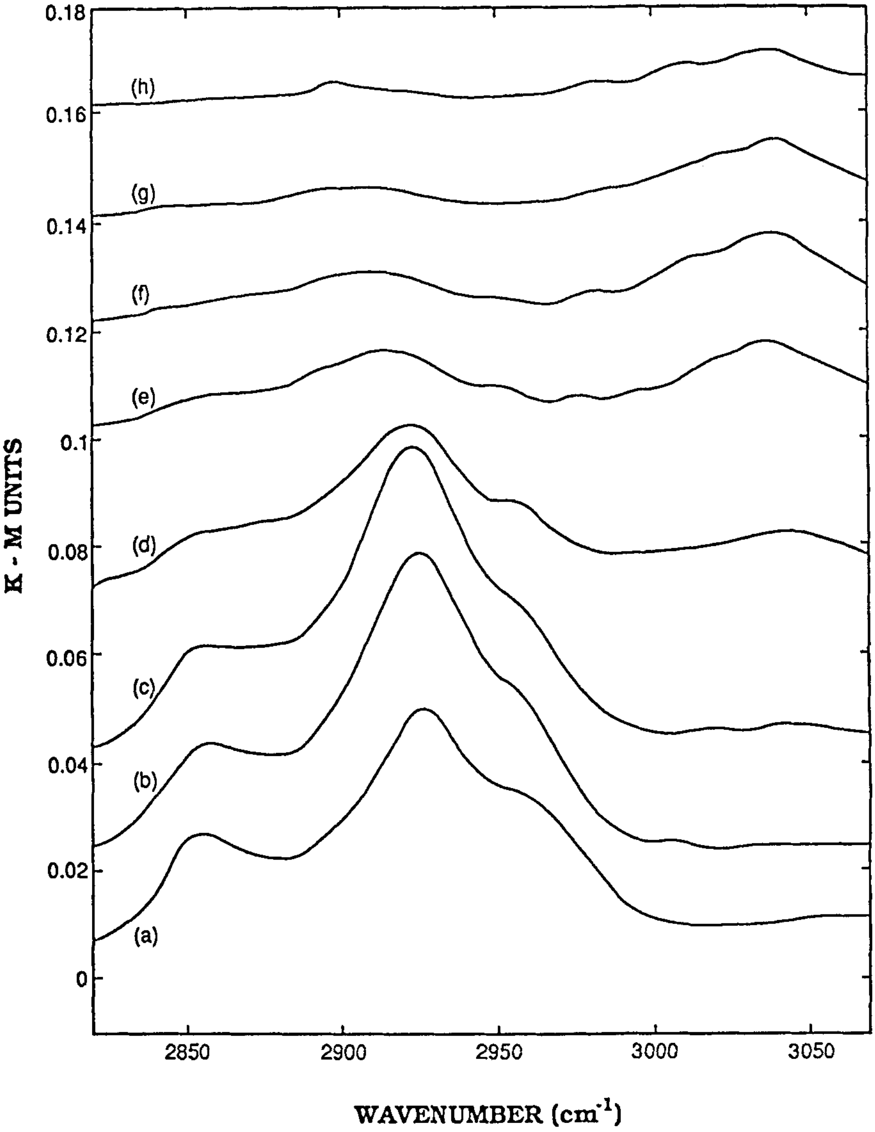

FIG 2. Diffuse reflectance infrared spectra of lignite in the C–H stretching region. Spectra were obtained at (a) 298, (b) 573, (c) 623, (d) 673, (e) 723, (f) 773, (g) 823, and (h) 873 K.

condition. In order to get more quantitative information on the aromaticity increase, we have attempted to curve-fit the C-H stretching profiles.

Although curve-fitting can be used to determine the spectral parameters (number of peaks, peak shapes, positions, widths, and amplitudes), its success depends on the quality of the information used in the calculation. It has been generally accepted that curve-fitting should be attempted only if the number of bands is known, and the accuracy of the calculation relies on the correctness of the models for the band shapes.[7,8] In this regard, we have attempted firstly to get the information on the number of peaks, peak positions and band shape from the analysis of the DRIFT spectrum of lignite at raw state obtained by co-adding 4096 scans for the signal-to-noise ratio to be better than 300:1. By applying the second derivative[8] and the Fourier self-deconvolution[9] technique, we could identify the presence of several peaks in the aliphatic C-H stretching region, for instance, at 2853 [$\nu_s(CH_2)$], 2872 [$\nu_s(CH_3)$], 2893 [$\nu(CH)$], 2920 [$\nu_{as}(CH_2)$], 2953 [$\nu_{as}(CH_3)$], and 2975 cm^{-1}. The latter very weak shoulder peak at 2975 cm^{-1} seems to be assigned to methyl groups in a different environment. The initial estimates for the bandwidths were determined also from the second derivative spectra. The curve-fitting calculation to obtain the refined bandwidths and amplitudes was performed by minimizing the squared difference between the measured and fitted spectra. To minimize the difference, the linear constrained optimization algorithm (Nelder-Mead downhill simplex fitting algorithm[10]) was employed. Gaussian, Lorentzian, and Voigt (1:1 Gaussian-Lorentzian sum) functions were used as possible models for the band shape. It was found that Gaussian function should be the most probable band shape. The suitability of Gaussian band shape was verified further by deconvoluting the fitted spectrum with the same parameters as for the measured spectrum.

Above mentioned curve-fitting process was applied also to the spectra shown in FIG. 2. The relative peak intensities of the aromatic C-H stretching band at 3050 cm^{-1} and the asymmetric CH_2 stretching bands at 2920 cm^{-1} were then evaluated. Their temperature dependence is presented in FIG. 3(a). It is clearly seen that aromaticity increases abruptly at above 723 K. On the other hand, when

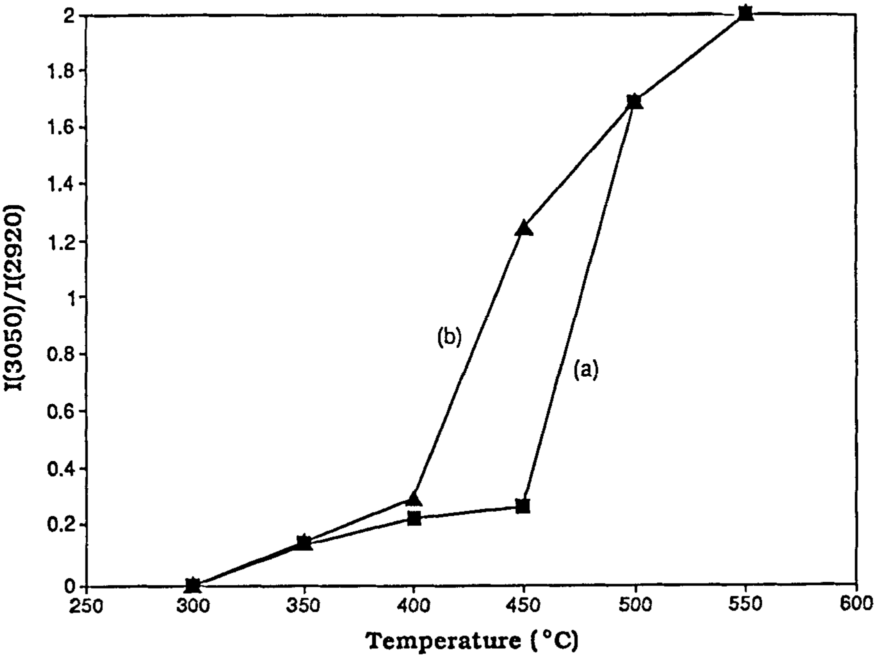

FIG 3. Temperature dependence of aromaticity factor defined as the intensity ratio of aromatic C-H stretching band at 3050 cm^{-1} and the asymmetric CH_2 stretching band at 2920 cm^{-1}. Under dry nitrogen (a) and wet nitrogen (b) environment.

water vapor was injected into the pyrolysis chamber, such an abrupt aromaticity increase occurred at around 673 K as shown in FIG. 3(b). In that case, spectral pattern in other regions was observed also nearly the same as that obtained at temperature higher than 50 K under dry nitrogen atmosphere. Namely, the pyrolysis temperature becomes lowered by the presence of water vapor. As reported by Minkova et al.,[11,12] water vapor should have facilitated the thermal conduction as well as the formation of porous structure rendering the increase of adsorption capacity. Considering that the spectral pattern was barely affected by the presence of water vapor except the lowering of pyrolysis temperature, any

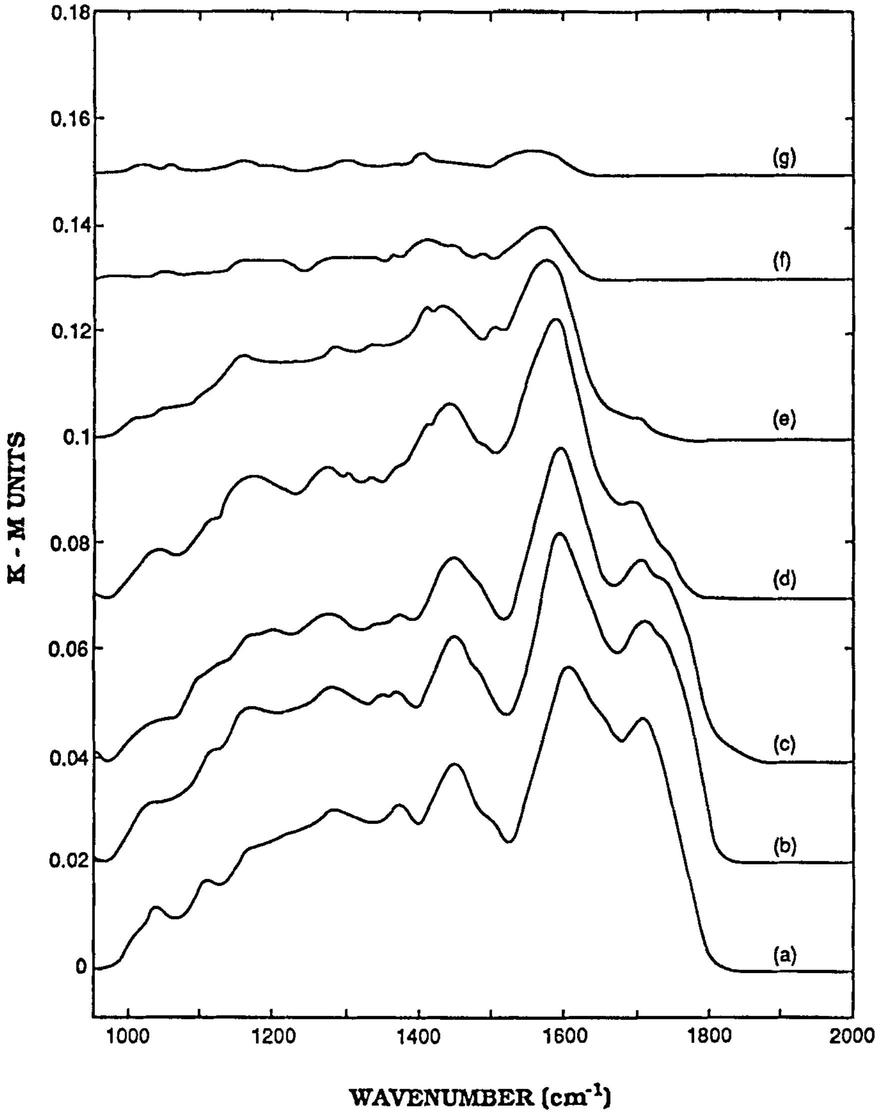

FIG 4. Diffuse reflectance infrared spectra of lignite during pyrolysis under dry nitrogen atmosphere in 1000–2000 cm^{-1} region. Spectra were obtained at (a) 298, (b) 473, (c) 573, (d) 673, (e) 773, (f) 873, and (g) 923 K.

steam gasification reaction seemed not to have occurred, however, in the temperature region below 873 K. Hence, the major role of water vapor during the pyrolysis is thought to enhance the efficiency of thermal conduction.

In contrast with the C-H stretching region, the spectral variation in lower spectral region was rather difficult to be quantified. A reliable curve-fitting is not successful, and thus only a qualitative explanation can be presented at the moment. FIG 4 shows the expanded DRIFT spectra in the 1000-2000 cm^{-1} region. It can be evidenced from the Figure that the bending vibrational bands of CH_2 and CH_3 groups at 1460 and 1375 cm^{-1} become weakened as the pyrolysis temperature increases as likely in the C-H stretching region. The peaks at near 1700 cm^{-1} can be attributed to the C=O stretching vibrations of ketones, aldehydes, and carboxylic acids.[2,5] On the other hand, the peaks at near 1600 cm^{-1} can be assigned to the carbonyl stretching vibrations of highly conjugated C=O groups and the aromatic ring stretching vibrations. All of these peaks weaken also by the increase of temperature. Nonetheless, the peaks at around 1600 cm^{-1} is less sensitive to the temperature than the peaks at 1700 cm^{-1}. This may indicate that decarboxylation is more difficult to occur for the highly conjugated C=O groups. The survival of the 1600 cm^{-1} bands at higher temperatures may also have some relevance with the aromaticity increase with temperature. Even for the bands at near 1700 cm^{-1}, subtle spectral variation can be notified. It can be seen from the spectra taken at 573 and 673 K that the peaks at 1735 and 1765 cm^{-1}, which can be attributed, respectively, to ester and lactone species, diminish more rapidly with temperature than the peak at 1708 cm^{-1} assignable to ketone species. This can be understood by invoking that decarboxylation should take place more readily for esters than for ketones. It can be seen also from Fig. 4 that the 1000-1300 cm^{-1} region experiences comparatively less variation with temperature. Considering that the peak at near 1157 cm^{-1} can be attributed to the C-O stretching vibrations of ether species,[2,5] its sustenance at higher temperature seems to reflect the bonds of R-O-R' compounds to be substantially strong.

In summary, it is shown in this work that the *in-situ* pyrolysis of coal can be studied by diffuse reflectance infrared spectroscopy. The diffuse reflectance spectrum of lignite coal is concluded to be made of Gaussian bands. The increase of aromaticity factor with temperature is clearly evidenced from the C-H stretching region. Although quantitative analysis of the structural modification can not be performed at the moment, qualitative information can be provided at least from the peak intensity variations. To get a quantitative information on the chemical modifications of coals during pyrolysis, spectral manipulating routines for strongly overlapping bands are certainly needed. Nevertheless, the present work reveals that the temperature and atmospheric effects on the physicochemical properties of powdered materials can be readily investigated by interfacing the reflectance optics with a controlled environment reaction chamber.

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