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COMPOSITION AND SOLIDS  
VOLUME FRACTION

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# FIBRE-OPTIC PROBE FOR THE SIMULTANEOUS MEASUREMENT OF GASEOUS SPECIES COMPOSITION AND SOLIDS VOLUME FRACTION

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## Abstract

A novel infrared fibre-optic probe was developed to measure quantitatively and simultaneously solids volume fraction ( $1-\varepsilon$ ) and gaseous species composition ( $Y_i$ ) in a gas/solid fluidized bed. The fibre-optic probe was used with a FT-IR spectrometer to perform real-time and in-situ measurements of absorbance in the fluidized bed. The effect of  $(1-\varepsilon)$  and  $Y_i$  on the absorbance spectra were additive and could be independently calibrated. To calibrate the probe, fuel mole fractions and  $(1-\varepsilon)$  were varied between 1.8 - 10.1 mol% and 0 - 0.45, respectively. A proof of concept for a novel application in fluidized beds was completed: the fibre-optic probe was used to measure the molar fraction of a tracer gas inside the emulsion and bubble phases during gas tracer experiments.

**Keywords:** solids volume fraction, FT-IR spectroscopy, fibre-optic probe, gaseous species composition, fluidization, bubble, emulsion

## 1. Introduction

Gas/solid fluidized bed processes are characterized through the measurement of gaseous species composition and solid volume fraction. These two parameters are dependent parameters that are coupled through the reaction kinetics and hydrodynamics. Solids volume fraction affects chemical reactions through catalytic and/or inhibitive effects as well as through the thermal balance. For example, the chemical products from fast reactions, such as oxidation, are greatly affected by the gas/solid mixing at the tip of injectors. Furthermore, at the hydrodynamic level, fluidized beds are characterized by the emulsion and bubble phases: determining the species composition in these two regions is key to the process characterization.

Current measurement methods are incapable of measuring gas-phase chemical composition and solids volume fraction simultaneously and in-situ in a gas/solid fluidized beds. Gas-phase chemical composition is usually measured with sampling probes connected to analyzers. Furthermore, solids volume fraction is generally measured with capacitance probes and fibre-optic probes that record the forward- or back-scattering of visible light [1-4].

It may be possible to use a fibre-optic probe with infrared (IR) light to measure solids volume fraction and gas-phase chemical composition simultaneously and in-situ. IR fibre-optic probes used with IR spectroscopy have been previously used to measure chemical composition in multiphase systems [5-14]. However, current IR spectroscopic applications do not measure solids volume fraction and rely on the uniformity of the solid samples with time (between measurements) since the solid phase has been shown to affect the IR absorbance spectra. The solids volume fraction and particle size influence the interaction between the light and the solids, which affect the path length of the IR beam and the effective sample size [15-16]. However, since multiphase systems are generally characterized by solids volume fractions that are heterogeneous in space and time, in-situ and real-time measurement of species concentrations in the different regions of a multiphase system requires the simultaneous determination of solids volume fraction. The measurement volume can be made independent of the solid properties by

inclining the emitting and receiving fibres to form a convergent scheme [17] and this principle can be applied to an IR fibre-optic probe to measure species concentrations.

In multiphase systems, the movement of powders can make spectroscopy measurements and interpretation more complex. Studies have shown that the movement of the particles produced artefacts on the measured spectrum at certain wavenumbers that depended on the timescale of the spectral scan compared to the rate of movement of the particles. The wavenumber at which the artefact appeared increased with increasing modulation frequencies such that the effects of moving particles could be completely eliminated at the wavenumbers of interest with a sufficiently high modulation frequency [18-20].

In the present study, a IR fibre-optic probe was constructed to perform in-situ and real-time measurements in a gas/solid flow of methane/nitrogen and FCC particles ( $d_p = 83 \mu\text{m}$ ). The fibre-optic probe was connected to a near- and mid-IR Fourier transform transmission spectrometer ( $6000\text{-}1000 \text{ cm}^{-1}$ ). Absorbance spectra were recorded at a frequency of 4.5 Hz for a period of 75 seconds and both  $Y_i$  and  $(1-\varepsilon)$  were evaluated from each spectrum. Methane molar fractions in nitrogen were measured over a range of 0-10.1 vol%. Furthermore, the solids volume fraction was varied between 0-0.45.

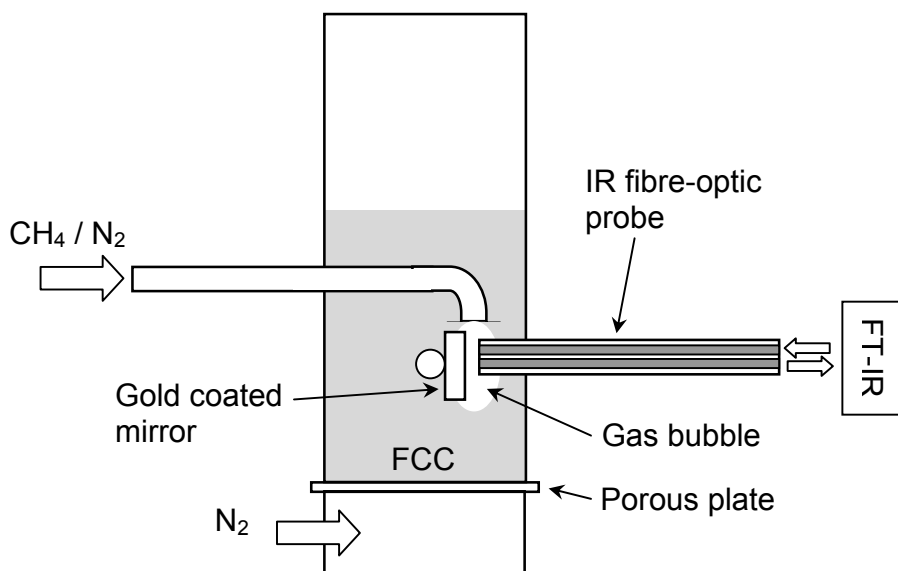


Figure 1: Fluidized bed apparatus

## 2. Experimental

Experiments were conducted with a mid-IR fibre-optic probe connected to FT-IR (Varian Excalibur series 3100). The probe was composed of two parallel fluoride glass fibre-optics (an emitting and a receiving fibre-optic) with a numerical aperture of 0.2 and a core diameter of  $600 \mu\text{m}$ . The fibre-optic probe was connected to the FT-IR with a Harrick Fibremate™. A planar gold-coated mirror was positioned perpendicularly to the probe tip at a distance of 5 mm. The mirror reflected the emitted IR beam to the receiving fibre-optic, which resulted in a measurement volume between the probe tip and the mirror. Experiments were conducted by first measuring a background spectrum - a  $\text{CH}_4/\text{N}_2$  mixture was injected inside the measurement and a background spectrum was obtained from the co-addition of 20 spectra. Then, the measurement volume was flushed with air and the funnel was filled with sand particles to initiate a flow of solids. Absorbance spectra were measured at a frequency of 4.5 Hz (temporal

resolution of 0.22 s) and the methane molar fraction was measured simultaneously to the solids volume fraction.

Gas tracer experiments were conducted in a small scale fluidized bed reactor (I.D. = 5 cm) illustrated in Figure 1 and the fibre-optic probe was used to measure the tracer molar fraction inside the bubble and emulsion phases. The reactor was filled with FCC particles ( $d_p = 83 \mu\text{m}$  and 14% fines ( $d_p \leq 44 \mu\text{m}$ )) and was fluidized with nitrogen at a superficial gas velocity of 2.6 mm/s ( $U_{mf} = 2.5 \text{ mm/s}$  and  $U_{mb} = 2.7 \text{ mm/s}$ ). The expanded bed height was 12.5 cm and the fibre-optic probe was inserted in the bed at a height of 7 cm. A mirror was positioned perpendicularly at the probe tip and gas bubbles were produced in the fibre-optic probe measurement volume by injecting a mixture containing 10.1%  $\text{CH}_4 + 89.9\% \text{N}_2$  through a downward facing sparger. The  $\text{CH}_4/\text{N}_2$  mixture was injected at a flow rate of 10 mL/s by manually opening a toggle valve for roughly 0.5 s at an interval of approximately 11 seconds.

### 3. Results and discussion

Both solid particles and gaseous species contribute to the absorbance spectrum during transmission spectroscopy in a gas/solid sample: the total absorbance at wavelength  $\lambda$  has a contribution from the solids volume fraction and from the gaseous species composition. Solid particles reduce the incident beam intensity by absorption, reflection and diffusion. Solids can also influence the path length and sample volume such that the absorbance due to the chemical species is a function of solids volume fraction:

$$A_{Total, \lambda} = A_{(1-\varepsilon), \lambda} + A_{Y_i, \lambda} [fn(1-\varepsilon)] \quad (1)$$

In the specific case of transmission spectroscopy where the effect of solids fraction on path length and sample volume can be neglected, equation (1) can be simplified to:

$$A_{Total, \lambda} = A_{(1-\varepsilon), \lambda} + A_{Y_i, \lambda} \quad (2)$$

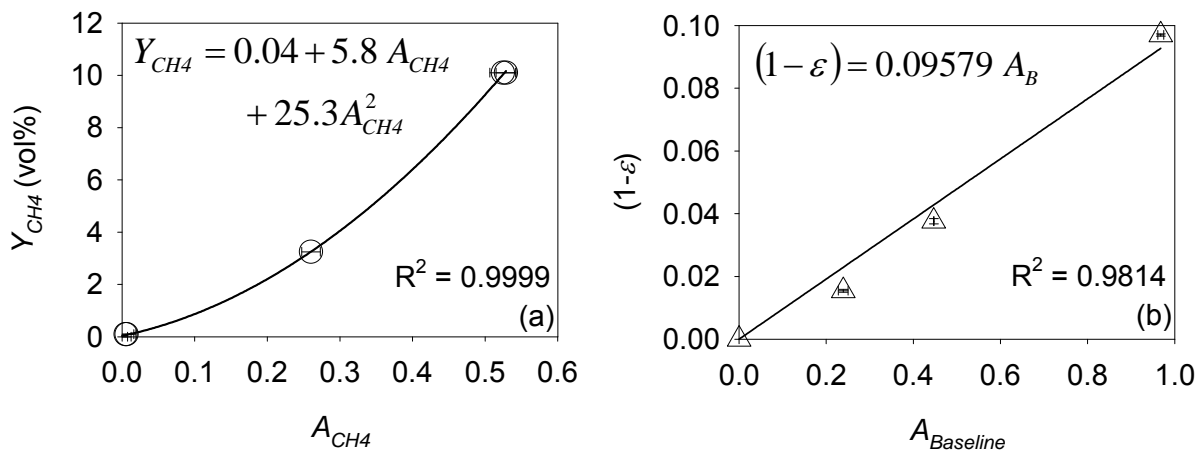


Figure 2: IR fibre-optic probe calibration

Equation (2) is valid when the reflected or diffused beam intensity measured is negligible compared to the transmitted light intensity. In equation (2), the effects of solids volume fraction and gaseous species composition on the absorbance spectrum are independent. Therefore, the effect of  $(1-\varepsilon)$  and  $Y_i$  can be calibrated independently. In the present experiments, the IR light

intensity from diffused reflectance was negligible such that equation (2) was valid. This was verified experimentally by removing the mirror facing the probe tip.

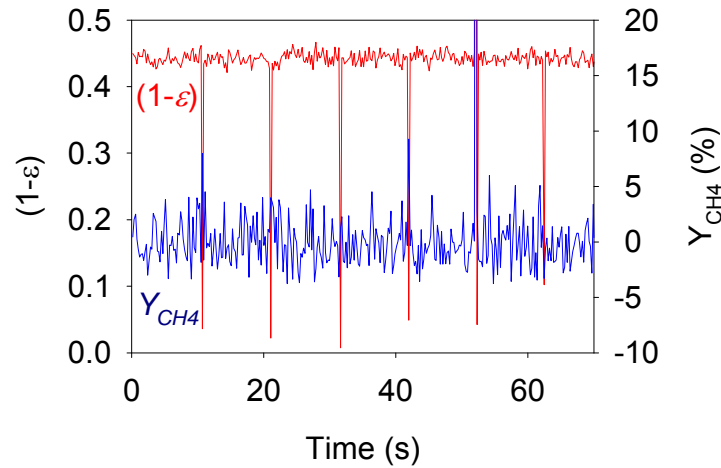


Figure 3: Time-history of  $(1-\varepsilon)$  and  $Y_{CH_4}$  at the fibre-optic probe tip

A calibration was first performed with the fibre-optic probe to evaluate the effect of methane molar fraction and solids volume fraction on the absorbance spectrum. The effect of methane molar fraction ( $Y_{CH_4}$ ) was calibrated with four mixtures containing 0, 0.1, 3.25 and 10.1 vol% of methane in nitrogen. The average absorbance of the methane peak ( $A_{CH_4}$ ) was measured in the region of  $3018.96\text{-}3016.86\text{ cm}^{-1}$  and it is shown as a function of methane molar fraction in Figure 2(a).

The effect of solids volume fraction was calibrated by producing a flow of solids in the fibre-optic measurement volume with a funnel. The solids flow rate and solids volume fraction were varied by modifying the diameter of the funnel throat. Four solids volume fractions were used (0, 0.015, 0.038 and 0.097) and the average baseline absorbance ( $A_{(1-\varepsilon)}$ ) was measured in the regions of  $2997.73\text{-}2992.04$ ,  $3036.70\text{-}3030.72$  and  $3045.87\text{-}3040.39\text{ cm}^{-1}$  during 75 seconds at a frequency of 4.5 Hz. The average baseline absorbance is shown in Figure 2(b) as a function of solids volume fraction and the relationship is close to linear. Cutolo et al. [21] previously reported a linear relationship between absorbance and solids volume fractions. In the present case, solids volume fraction was measured by a conventional back-scattering fibre-optic probe with a different measurement volume than the IR fibre-optic probe. Since the flow of particles was heterogeneous, this may explain the observed deviation from the linear relationship.

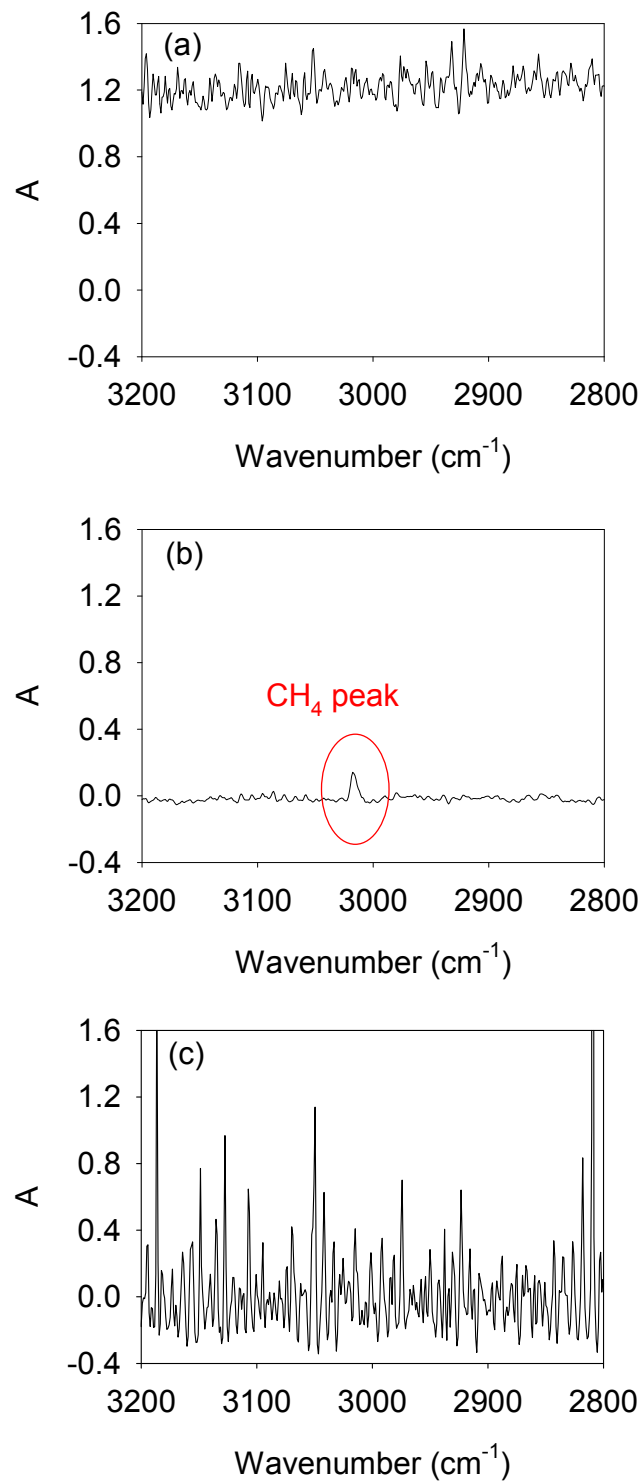


Figure 4: Measurement of  $Y_{CH_4}$  in the fluidized bed

Gas tracer experiments were conducted in the fluidized bed of Figure 1 and the fibre-optic probe was used with the spectroscopic method to measure the molar fraction of a CH<sub>4</sub> tracer inside the bubble and emulsion phases. The bed of FCC particles was incipiently fluidized with nitrogen and bubbles were produced at the tip of the fibre-optic probe by the injection of a nitrogen/methane mixture (10.1% CH<sub>4</sub>) through a sparger. Figure 3 shows the history of solids volume fraction and methane molar fraction measured by the fibre-optic probe during a typical experiment: the solids volume fraction was 0.45 in the emulsion phase and decreased significantly to 0.05-0 when gas bubbles of CH<sub>4</sub>/N<sub>2</sub> were injected at intervals of approximately 11 seconds. The measured methane volume fraction in the emulsion phase fluctuated significantly (5% to -5%) due to the low intensity of the transmitted IR beam and the resulting low S/N. Figure 4(a) shows a typical absorbance spectrum measured in the emulsion phase: the low intensity of reflected signal resulted in a high absorbance throughout the spectrum. However, the time-average methane molar fraction was measured accurately as 0.0% (100% nitrogen).

Figure 4(b) shows an absorbance spectrum measured inside a bubble: a methane peak was observed at 3017.63 cm<sup>-1</sup>. However, the injection of bubbles produced gas/solids movement, which caused noise in most recorded absorbance spectra: 5 spectra out of the 27 measured in the bubble phase were sufficiently clear to make a measurement of  $Y_{CH_4}$ . Figure 4(c) shows a typical absorbance spectrum where noise was observed and the methane peak was indistinguishable. This noise could be eliminated in the wavelengths of interest by using a FT-IR with a higher modulation frequency.

The average peak height measured in the bubble phase corresponded to a methane molar fraction of 5% compared to the injected 10.1% CH<sub>4</sub> in nitrogen. This discrepancy may be due to mixing at the injector tip between the gas injected through the sparger and the fluidizing gas. Furthermore, the small number of clear spectra that were measured in the bubble phase could also explain the low value of  $Y_{CH_4}$  measured since time-average measurements were more accurate than instantaneous measurements. During the present study, the measured absorbance spectra had to be exported and analyzed manually, which greatly reduced the number of spectra that could be considered to measure  $Y_{CH_4}$  in the bubble phase. However, these results clearly show that the developed spectroscopic method with a fibre-optic probe can measure the gas composition in the bubble phase.

### 3.1 Limitation of the technique and future work

The fibre-optic probe used in this study is limited to ambient temperature applications: fluoride glass fibre-optics used can be exposed to temperatures below 150°C. However, fibre-optic probes have been developed with plastic fibre-optics for temperatures up to 1000°C [22]. Therefore, it is reasonable to assume that the measurement technique could be used to perform in-situ measurements in high temperature multiphase systems with an adequately designed fibre-optic probe.

This measurement technique is also limited by the modulation frequency of the spectrometer: the modulation frequency needs to be sufficiently high to avoid noise in the absorbance spectrum due to movement in the gas/solid system. The FT-IR used in the present study was purchased in 2001 and had a maximum modulation frequency of 80 kHz. New models are currently available with significantly higher modulation frequencies.

Another limitation of the technique is the IR beam intensity transmitted in the fibre-optic probe, which needs to be as high as possible in order to maximize the signal-to-noise ratio. The IR beam intensity can be increased by using a fibre-optic bundle, using a more sensitive detector, using a more powerful IR source, optimizing the signal transmission at the probe tip and at the

FT-IR/fibre-optic probe interface (Harrick Fibremate™). More recent models of FT-IR also propose higher IR source intensity compared to the equipment used in the present study.

#### 4. Conclusions

A novel IR fibre optic probe was used to measure quantitatively and simultaneously solids volume fraction ( $1-\varepsilon$ ) and gaseous species composition ( $Y_i$ ) in a gas/solid fluidized bed. The fibre-optic probe was connected to a FT-IR to perform real-time and in-situ measurements of absorbance. The effect of solids volume fraction and gaseous chemical composition on the absorbance spectra were additive and could be independently calibrated. Experiments were conducted with methane/nitrogen and propane/nitrogen mixtures and FCC particles. Fuel mole fraction and solids volume fraction were varied between 1.8 - 10.1 mol% and 0 - 0.45, respectively. The fibre-optic probe was used in a fluidized bed to measure the molar fraction of a gas tracer inside the emulsion and bubble phases during gas tracer experiments. The measurement underestimated the methane volume fraction injected.

More measurements need to be performed in gas/solid systems at ambient and high temperatures to fully demonstrate the possibilities of this measurement method. High modulation frequencies from newer models of FT-IR should help resolve the problem of noise in the absorbance spectra caused by gas/solid movement. In theory, this method could also be used for liquid/solid, gas/liquid, liquid/liquid and gas/liquid/solid systems. However, work has to be performed in order to identify the limitations in these specific systems. It seems also that the accuracy of instantaneous fibre-optic probe measurements could be significantly improved by increasing the IR beam intensity. This could be achieved by using a fibre-optic bundle, using a more sensitive detector, using a more powerful IR source, optimizing the signal transmission at the probe tip and at the FT-IR/fibre-optic probe interface (Harrick Fibremate™). New FT-IR models also propose significantly higher IR signal intensity compared to the equipment used in the present study.

#### NOTATION

$A$	Absorbance
$d_p$	Average particle size ( $\mu\text{m}$ )
$f$	Modulation frequency (kHz)
$t$	Distance between probe tip and mirror (mm)
$Y_i$	Molar fraction of specie $i$ (vol%)
$(1-\varepsilon)$	Solids volume fraction
$\lambda$	Wavelength ( $\mu\text{m}$ )

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