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# Optical fiber extrinsic refractometer to measure RI of samples in a high pressure and temperature systems: Application to wax and asphaltene precipitation measurements

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**Abstract**

An optical fiber extrinsic sensor for measurement of changes in the refractive index of liquids confined in chambers for high pressure and temperature experiments is described. One head sensor composed by two fibers is fixed in front of a high pressure and temperature cell filled with the sample. The operation principle is based in the reflectivity dependence in the refractive index of the glass–liquid interface. Excellent results and a sensitivity of $10^{-5}$ RI were obtained for pure liquids. The applicability of the sensor is demonstrated following the changes in the refractive index for pure liquids at different pressure and temperatures and by measuring the asphaltenes and wax precipitation in crude oils under pressure. The extrinsic probe designed for refractive index measurement proves to be a reliable tool for measuring heavy organics deposition in crude oils under high pressures and temperatures where the sample to be measured is not very accessible.


*Keywords:* Refractometer; Flocculation; Asphaltene

## 1. Introduction

Refractive index measurements are of great interest in different fields of the industry for chemical analysis as well as for phase behaviour and light scattering in diffraction experiment. Most of the instruments used for refractive index (RI) determination are based in the accurate determination of the critical angle of total internal reflection. However, direct measurements of RI are in some cases unattainable either due to sample opacity, or to technical difficulties. Different systems have been developed to measure RI for various samples, and the variations of Abbe refractometer have been widely used [1,2]. Implementation of total internal reflection and prism coupling [3,4] are frequently used but experimental set-up are complex and sensitive to external perturbation. Some devices based in the detection of the change in the optical path of the light through a sample [5,6] have a great accuracy when is used with samples of low absorption coefficient. In the last few years different fiber optics sensors (FOS) have been developed for the measurement of refractive index in complex systems, most of them being intrinsic sensors. Several authors [7,8] have propose an intrinsic optical fiber reflection refractometer, which uses two fibers, and a mirror as reflector. Here, the system is immersed in the sample and the measurement principle is based on reflective intensity modulation. In 2003, Frot Didier [9] patented an optical

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fiber refractometer based in the short angle reflection of the light at the interface. Because miniature size and easefulness in use, this device is ideal for the application in numerous in-line chemical, food, beverage or medical analysis. The system can be used to measure directly the refractive index of samples in small containers. Interferometric refractometers [10] are the most popular systems used to measure the refractive index of liquids. Although these intrinsic devices perform with high accuracy in favourable cases, their applicability to viscous and low optical density materials, such as opaque asphaltic and/or waxy oils is very limited. Samples with a high density (crude oils, asphaltene solutions, etc.) or viscosity tend to stick on the surface, thus leading to low accuracy and poor reproducibility in the results.

In this work, we have engineered and build an extrinsic fiber optic sensor where the refractive index measurement are based on the reflectivity intensity modulation at a wide angle configuration. Our principal interest is to follow changes in the refractive index of mixtures at high pressure and temperature; that is to say at experimental conditions at which typical sensors cannot be used. In our set-up a high pressure cell with a sapphire window is filled with the sample for which refractive index is measured. Depending of the reflectivity of a laser beam emitted by one fiber at the sapphire–liquid interface, the light intensity in the collection fiber will vary. Variations in the reflected intensity are related by the Fresnel reflectance coefficient with the refractive index of the sample. One of the key features of this new apparatus is that the calibration can be carried out at atmospheric pressure because the optical device, placed outside the cell, is not affected by the pressure or the temperature of the experiment as described below. This system allows the measurement of the refractive index of high absorption coefficient samples in experiments at HP and HT conditions. Thus it has all the characteristics required to measure indirectly the phase transition in opaque fluid. In particular this technique can be used to detect the formation of solid phase in crude oils under pressure. To demonstrate these capacities, the apparatus was used in this work to detect both the onset of asphaltene flocculation and wax precipitation in two different oil samples.

## 2. Measurement principle

The extrinsic FOS described in this work uses two optical fibers (see Fig. 1). Light from a He–Ne laser of 632.8 nm wavelength is carried to the measurement cell by a 1 mm fiber and the reflected signal is carried out to a detector by a second fiber. The inset in Fig. 1 shows a schematic view of the sensor head. The incident light in the form of cone of emittance from the illuminating fiber gets reflected back in the form of expanding cone of light towards the receiving fiber. The cone of emittance only depends on the characteristics of the fiber and on the width of the sapphire window of the cell. At the glass window–liquid interface part of the emitted radiation is reflected with an angle of reflectance $\theta r(n) = \sin^{-1}$ (NA/$n$) where NA is the numerical aperture of the fiber, and $n$ the refractive index of the transmittance

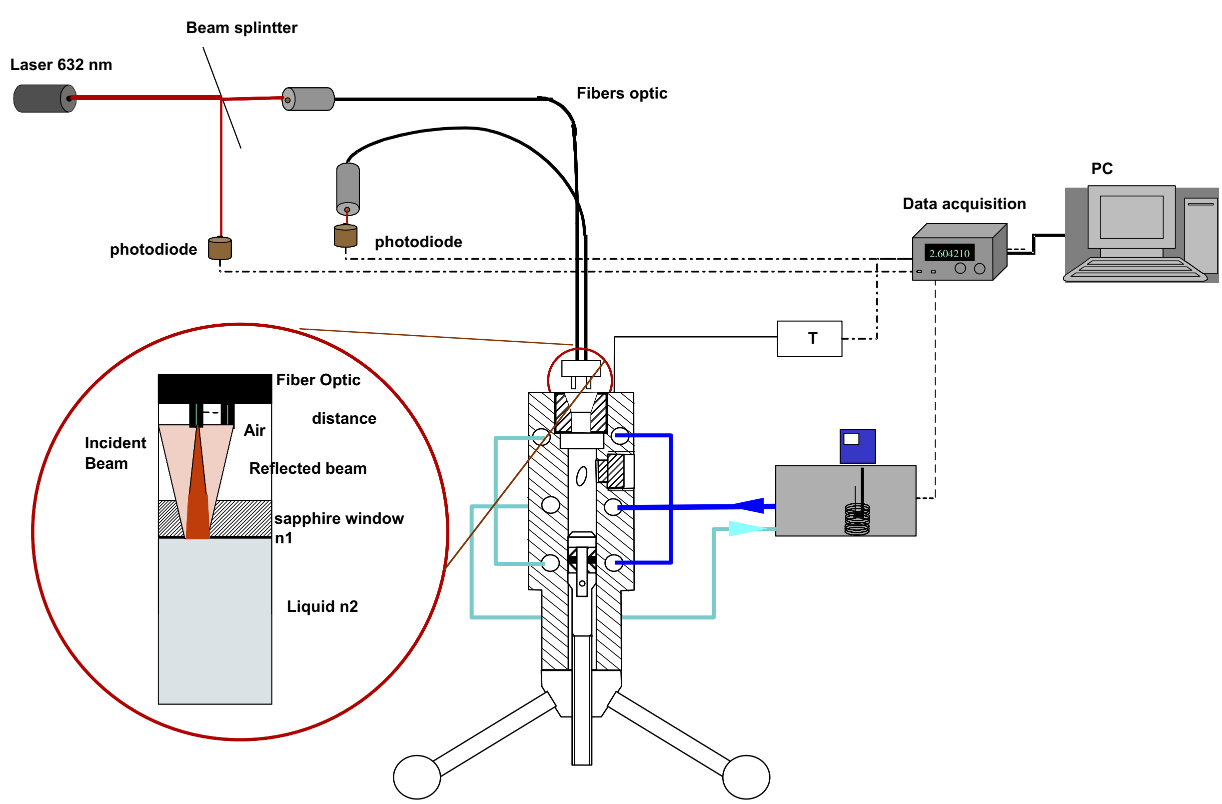


Fig. 1. Schematic diagram of the experimental set-up. The expanded circle is the detail of the sensor head.