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Abbreviated title: **Densitometry in Primary Upgrading Processes**

by

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ABSTRACT

Gamma-ray densitometry has been applied in developing processes for upgrading heavy oils, refinery residua, tar sand bitumen and coal into synthetic crudes. These processes normally operate at high temperatures and pressures thus non-invasive monitors are highly desirable. Examples of applications at CANMET are given for the following three areas: gas-liquid and gas-liquid-solid multiphase flow hydrodynamic studies, monitoring of ash concentration and measurement of thermal expansion coefficient of liquids.

INTRODUCTION

CANMET is the technological research centre of the Department of Energy, Mines and Resources Canada. Established in 1907 as the federal Mines Branch, the name was changed in 1974 to the Canada Centre for Mineral and Energy Technology, to reflect more accurately the growing range of activities in two areas - mineral and energy technologies.

The development of techniques to produce synthetic fuels is important because the depletion of conventional crudes cannot be prevented. One of the major programs in CANMET is the development of processes to convert heavy oil, refinery residues, bitumen and coal to synthetic fuels [Pruden 1987,Lunin 1981]. The objective of these processes is to produce lighter, low boiling point hydrocarbons with a higher hydrogen to carbon ratio (H/C) from heavier high boiling hydrocarbons with a lower H/C ratio containing mainly pitch with a boiling point $>524°C$. The process unit is usually integrated into an existing refinery, e.g., the 5000 b/d CANMET hydrocracking demonstration plant has been built in Petro-Canada's Montreal refinery. Its products are then blended in various streams for secondary upgrading such as hydrotreating to remove sulphur and nitrogen.

In order to increase the H/C ratio in the products, two primary upgrading approaches can be taken. One is thermal cracking where the H/C ratio of a portion of products is enhanced at the expense of the remaining portion which has a very low H/C ratio. The other is to increase the H/C ratio by adding hydrogen, e.g., hydrocracking and coal liquefaction.

Our research has been focused on the hydrogen addition

approach.   Because heavy crudes are used and enhancement of
hydrogen transfer from gas phase into the reactive liquid phase
is required, multiphase flow reactors operating at high
temperatures and pressures are used.   Much of the development
involves continuous pilot operation.   On-line monitoring of
operating parameters such as voidage or of ash concentration in
process streams is required, but adequate instruments are often
unavailable.   The use of probes commonly used for monitoring
liquid-solid multiphase flows is impractical at high pressures
and temperatures.   It should be noted that in multiphase flow
chemical reactors, the volume occupied by the individual phases
and the mixing of materials are vital factors which affect
conversion efficiency and reactor performance.   Therefore,
techniques which do not involve the penetration of instruments
through the reactor wall thus reducing reactor volume and
disturbing the flow are highly desirable.   The demand for non-
invasive "probes" for hydrodynamic studies and instruments for
rapid ash measurements prompted a study of the application of
radiation methods.

     This paper describes examples of applications which
have been made in the last few years.   The instruments which were
used to generate information for this paper were designed,
constructed and assembled by the Atomic Energy of Canada Limited
- Chalk River Nuclear Laboratories (AECL-CRNL).

MULTIPHASE FLOW REACTOR HYDRODYNAMIC STUDIES

SCANNING DENSITOMETRY

A Cs-135 scanning densitometer equipped with a NaI(Tl) detector was used (Fig. 1). A Canberra multichannel analyzer (MCA) was used to record the counting rates as a function of time by using its multichannel scale recurring (MCSR) mode. The combination of a rate meter with an MCA allows the probability density distributions (PDD) to be directly measured by using its sampling voltage analysis (SVA) mode.

Although the scanner has been used for fundamental studies in which transparent columns were employed, it has been used mainly for on-line pilot plant reactor measurements using thick-wall steel vessels. In the latter case, the gamma-ray scanner can be positioned at one of four fixed locations using a movable platform. The scanner itself has a vertical scan range of 1 m. Combining this with the four platform positions, almost the entire 3.9 m long reactor can be scanned.

The scanner allows a narrow-beam gamma ray to be positioned precisely in a vertical and horizontal two-dimensional (2D) space for stationary measurements as well as for scanning in both directions. Scan speeds can be adjusted continuously.

The precise 2D positioning of the gamma ray is needed because of thermal expansion of the reactor and the associated pipes.

PILOT PLANT

On-line measurements were made in the hydrocracking pilot plant, a brief description of which is presented here. Figure 2 shows a schematic of the pilot plant. Feed is kept in a stirred tank at a convenient temperature. The feed is pumped into the system by a piston pump. The liquid combines with a recycled gas stream before passing through a series of preheaters operating at selected elevated temperatures. The gas/liquid mixture is then injected into the reactor bottom. The reactor temperature is maintained at a desired value by electric heaters (Fig. 3). The product flows through a cross-over line at the top into a series of two separators where the heavy and light oils are separated and discharged. The gas continues to flow through a water scrubber and then an oil scrubber which control the hydrogen purity. Fresh hydrogen is introduced into the system to make up the amount consumed in the reaction and the losses along with discharged streams. The gas is recirculated by a compressor. This gas stream is then preheated to the inlet feed temperature before merging with the liquid feed to enter the preheater. Flowrates of various streams are monitored continuously.

POSITIONING OF GAMMA RAY

The reactor hydrodynamics were studied by using a scanning gamma-ray densitometer. A view of the densitometer and a portion of the reactor without insulation is shown in Fig. 3. The top of the reactor is fixed. The reactor has an internal

diameter of 3.8 cm and has 1.9 cm walls. The thermal expansion of the reactor and the inlet line at the bottom cause the reactor position to vary with changes in temperature. Once the scanner is moved to a selected position, the MCSR spectra can be recorded for constant speed scans.

The gamma ray can be located readily at a desired vertical reactor position because the top of the reactor is fixed and each section of the vertical scan MCSR spectrum has a characteristic pattern (Fig. 4) caused by the attenuation of heaters and flanges.

To locate the gamma ray across the axis of the reactor, a constant horizontal scan is made across the reactor and its MCSR spectrum is recorded. The minimum count rate occurs when the gamma-ray beam just grazes the inside of the reactor wall. Figure 5 shows an MCSR spectrum for the scan from one side of the reactor wall to the other and back to the centre. The time for a scan across an inner diameter of the reactor is the duration between the first two minima of the MCSR spectrum (Fig. 5). It is equal to the product of the dwell time, i.e., the time required for one channel measurement, multiplied by the channel number between these two minima. Half of this time is used to move the gamma ray from one side to the centre of the reactor.

HYDRODYNAMIC MEASUREMENTS

Information on holdups and flow regimes is important for control and scale up of multiphase flow reactors [Shah 1978]. Hydrodynamic phenomena can be different from one location to another in both commercial and pilot-scale reactors.

Therefore, measurements were made at 12 points along the reactor. The techniques involve the measurements of MCSR spectra and probability density distribution (PDD) functions. The flow regimes can usually be identified from the MCSR spectrum according to its features, for instance, a peak appears whenever a large bubble passes through the gamma ray (Fig. 6), a relative flat low count rate spectrum may result from a homogeneous bubble flow and a flat high count-rate spectrum may be obtained from an annular, dense fine bubble or foaming flow. Ambiguity in the determination of the flow regime by MCSR spectrum alone could occur. It is therefore necessary to examined carefully the PDD spectrum, which will provide unambiguous information [Lipsett 1986, Liu 1985].

The spatial local voidage $\epsilon(z)$ was determined by the spectrum analysis methods described [Lipsett 1986]. Figure 7 shows the results of local voidage measurements along the reactor carried out at 380°C and 13.9 MPa for a hydrogen/vacuum tower bottoms (VTB) system at low and high superficial velocities (quotient of volumetric rate/cross-sectional area). A pronounced change in voidage was observed at about the 1/4 length of the reactor from the bottom when a high superficial gas velocity was used.

The temporal-spatial mean void fraction $<\epsilon_{ts}>$ was determined by:

$$<\epsilon_{ts}> = (1/L)\int_0^L \epsilon(z).dz \qquad (1)$$

where

    L   is the length of the reactor

    z   is the distance from the reactor bottom

For multiphase flows operating at ambient conditions, the mean void fraction is commonly determined by the pressure drop across the length of the reactor if the density of fluid is known or by measuring the volume occupied by liquid when the gas flow is stopped. The latter approach can be conveniently carried out by the gamma-ray scanner. Figure 4 shows a vertical scan to find the liquid level when the gas flow bypasses the reactor. The discontinuity in the count rate at the liquid level is sharp thus the location of the interface between liquid and gas can be easily determined.

The liquid level search method should, in principle, result in the same values as those derived from Eq. 1. Figure 8 shows a comparison of measurements carried out at 13.8 MPa and various high temperatures. The overall voidage obtained from local measurements are considered to be highly accurate. One reason for the small difference between results of the two methods could be vaporization of liquid during the scan to find the liquid level.

These experiments show the advantages of using scanning densitometry to measure hydrodynamic phenomena in continuous processes at high temperatures and pressures. Accurate measurements can be made without perturbing the system.

ASH MEASUREMENT

FUNDAMENTALS

Ash concentration, [Ash], is measured by burning a sample according to the standard method given by the American Society for Testing and Materials [ASTM 1980]. Although this parameter is only a qualitative measure because the elemental composition is not considered, it is often used as a quantitative control parameter in the petroleum and coal industry.

An ASTM ash assay requires more than 8 h. As ash measurements are often required for process control, a much quicker method is desirable. A narrow-beam dual-energy gamma-ray densitometer was therefore developed in collaboration with AECL-CRNL. The principle of dual-energy gamma-ray densitometry for analyzing samples containing two elements has been described previously [Taylor 1985]. The theory is extended for ash measurement below.

Defining the attenuation ratio, R, for two energies E_1 and E_2 as:

$$R = \ln(I_1/I_{1o})/\ln(I_2/I_{2o}) \tag{2}$$

where

$\quad I_i \quad$ is the intensity of the attenuated beam

$\quad I_{io} \quad$ is the intensity of the unattenuated beam

The atomic ratio for an absorber (sample) consisting of two elements (AB) can be determined by [Taylor 1985]:

$$N_A/N_B = (\sigma_{1B} - R\sigma_{2B})/(R\sigma_{2A} - \sigma_{1A}) \qquad (3)$$

where

N_j is the number of atoms of the jth element per unit volume of the absorber (j = A or B).

σ_{ij} is the attenuation cross-section per atom of the jth element (A or B) of the absorber for the energy E_i

Equation 3 shows that the atomic ratio is independent of the absorber thickness. This is a great asset for industrial applications.

Assuming that the process samples consist of two components, i.e., metal for j = A and hydrocarbons for j = B, and $N_B \gg N_A$, we can approximate the ash concentration as:

$$[Ash] \sim N_A/(N_A + N_B)$$

$$= (\sigma_{1B} - R\sigma_{2B})/[R(\sigma_{2A} - \sigma_{2B}) - (\sigma_{1A} - \sigma_{1B})] \qquad (4)$$

where $\sim$ is defined as approximately proportional to.

By selecting E_1 in the photoelectric domain and E_2 in the Compton domain, i.e., $(\sigma_{1A} - \sigma_{1B}) \gg (\sigma_{2A} - \sigma_{2B})$, Eq. 4 can be simplified to:

$$[Ash] \sim (R\sigma_{2B} - \sigma_{1B}) / (\sigma_{1A} - \sigma_{1B}) \qquad (5)$$

A linear relationship between [Ash] and R is therefore expected

for low ash concentration samples.

DUAL-ENERGY DENSITOMETER AND TESTS

A Cd-109 densitometer was designed and constructed by AECL-CRNL under contract to EMR. The system consists of a source, a compartment to house the metal sample cans and a NaI(Tl) detector. The Cd-109 radiates two energies at ~22.6 keV (E_1) and 88 keV (E_2).

Two series of pilot plant runs were carried out using a refinery VTB with a small amount of additive. The additive concentration in the feed for the series B was twice that in the feed for the series A. The experiments were conducted at 13.9 MPa and selected high temperatures. Samples were withdrawn from the reactor at the bottom, middle, upper quarter and top positions and directly discharged into their own metal cans.

Count rates for the metal sampling cans without and with samples were measured separately by a Canberra MCA in peak height analysis (PHA) mode for 100 s and 600 s, respectively. Areas under the peaks were integrated to provide I_{io} and I_i from which R was derived according to Eq. 2. Following the gamma densitometry measurements, the ash concentration was determined by the ASTM method. Results are shown in Fig. 9. They indicate that, as expected according to Eq. 5, the correlation of [Ash] with R is close to linear. The correlation is very reproducible for the same type of additive used and is independent of the initial amount of additive. The large deviation from the trend shown in Fig. 9 was due to the deviation in ASTM ashing caused by difficulties in the sample preparation.

Applications in monitoring ash in samples with a wide range of concentration, a non-linear correlation may be necessary. This is because the assumption for Eq. 4 that [Ash] is proportional to $N_A/(N_A + N_B)$ may not be true when the ash concentration is high. In this case, a polynomial correlation can be easily derived for practical applications.

This method is quick as long as the correlation between R and ash concentration has been predetermined. Clearly, the correlation can easily be obtained by measuring selected samples over the range of interest using both methods. The tedious and sometimes troublesome sample preparation procedure for ASTM ashing has been eliminated for routine monitoring.

LIQUID THERMAL EXPANSION COEFFICIENT

The thermal expansion coefficient (or volume expansivity) is defined as [McCabe 1976]:

$$\beta = (1/V)(\partial V/\partial T)_P \tag{6}$$

where P, T and V are pressure, temperature and volume, respectively.

Considering a mass m of a liquid in a volume V, the temperature derivative of its density, ρ, at constant pressure is:

$$E = d\rho/dT = d(m/V)/dT = -(m/V^2)dV/dT$$

$$= -(m/V)\beta = -\rho\beta \tag{7}$$

This equation shows that by measuring the density of liquid as a function of temperature in a sealed constant pressure vessel, the thermal expansion coefficient can be determined.

Gamma-ray densitometry is an ideal technique for this application. In a series of tests, a sealed stainless steel container of 0.0368 m ID welded to a bellows, designed and constructed by AECL-CRNL, was used as the sample container. This vessel was suspended within a pressure vessel which was heated to various temperatures up to 300°C. The pressure vessel was connected to a high pressure tank of nitrogen to maintain 13.8 MPa. The gamma-ray attenuations were then measured at various temperatures. The measurements were repeated when the sample vessel was full of light Arabian VTB. The measurements provide information on the density of a liquid as a function of temperature. From this function, the temperature derivatives (Eq. 7) were obtained to determine the thermal expansion coefficients.

It was found that a precise alignment of gamma ray with respect to the vessel is not necessary. Details of theory and experimental have been described by Liu et al [Liu 1988].

CONCLUSIONS

Gamma-ray densitometry has been extensively applied in our laboratory to develop primary upgrading processes for producing synthetic fuels.

Gamma-ray gauges can be used to measure hydrodynamic parameters in thick-wall reactors at high temperatures and pressures. The long assay time required using ASTM-482 method to measure ash concentration in hydrocarbon samples can be shortened dramatically, and the expansion coefficient of liquid at high temperatures and pressures can be easily measured.

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FIGURES

1. CANMET gamma-ray densitometry scanner
2. Schematic of CANMET hydrocracking pilot plant
3. Narrow gamma-ray densitometer and the pilot plant reactor without insulation
4. MCSR spectrum of a vertical scan along a portion of the reactor
5. MCSR spectrum of a horizontal scan across the reactor
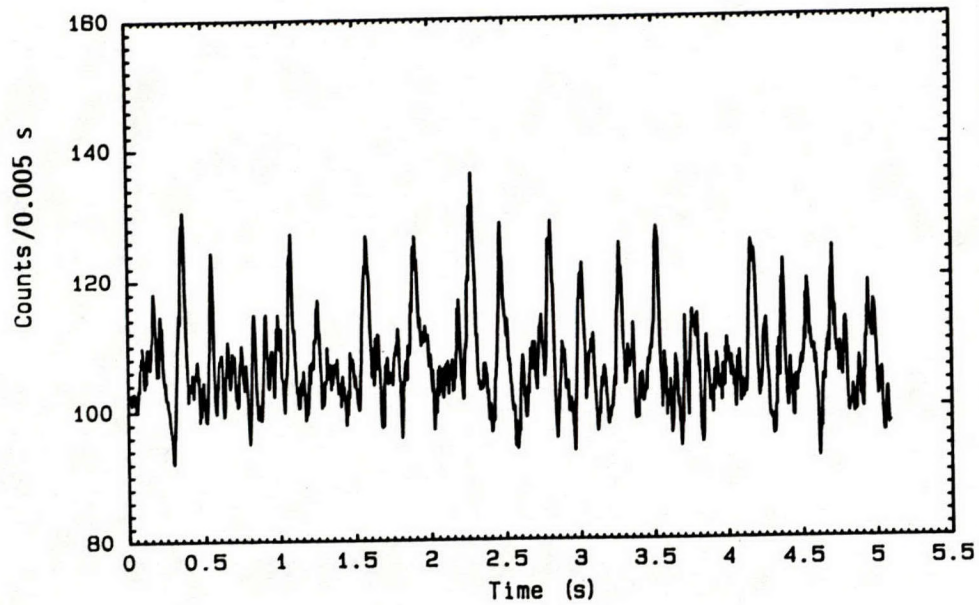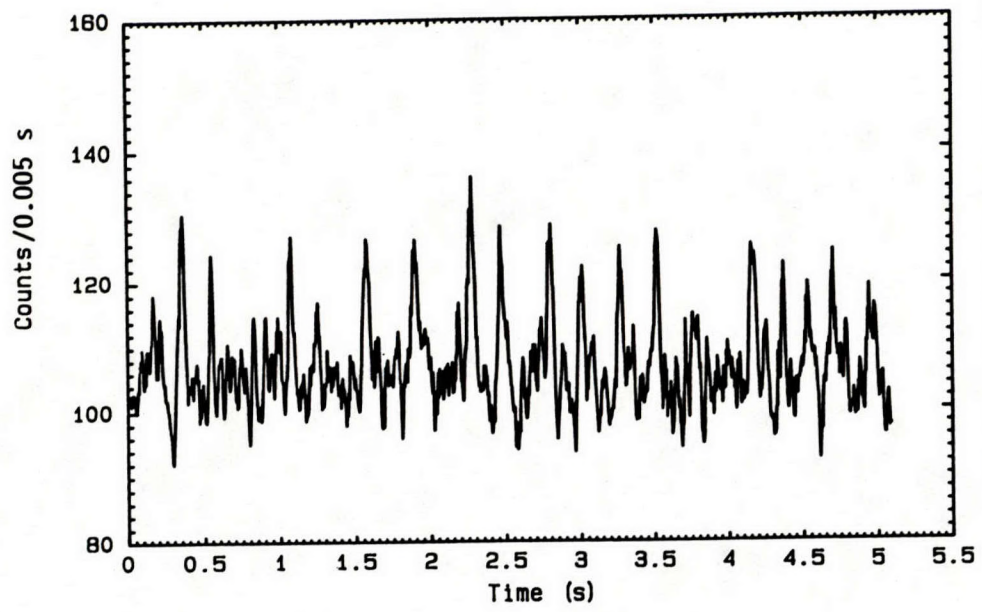6. MCSR spectrum of a gas-liquid two phase flow
7. Local void fraction $\epsilon(z)$ as a function of the reactor coordinates z
8. Comparison of the total void fraction measured by the PDD method versus those measured by liquid level searching technique
9. Ash concentration as a function or attenuation ratio
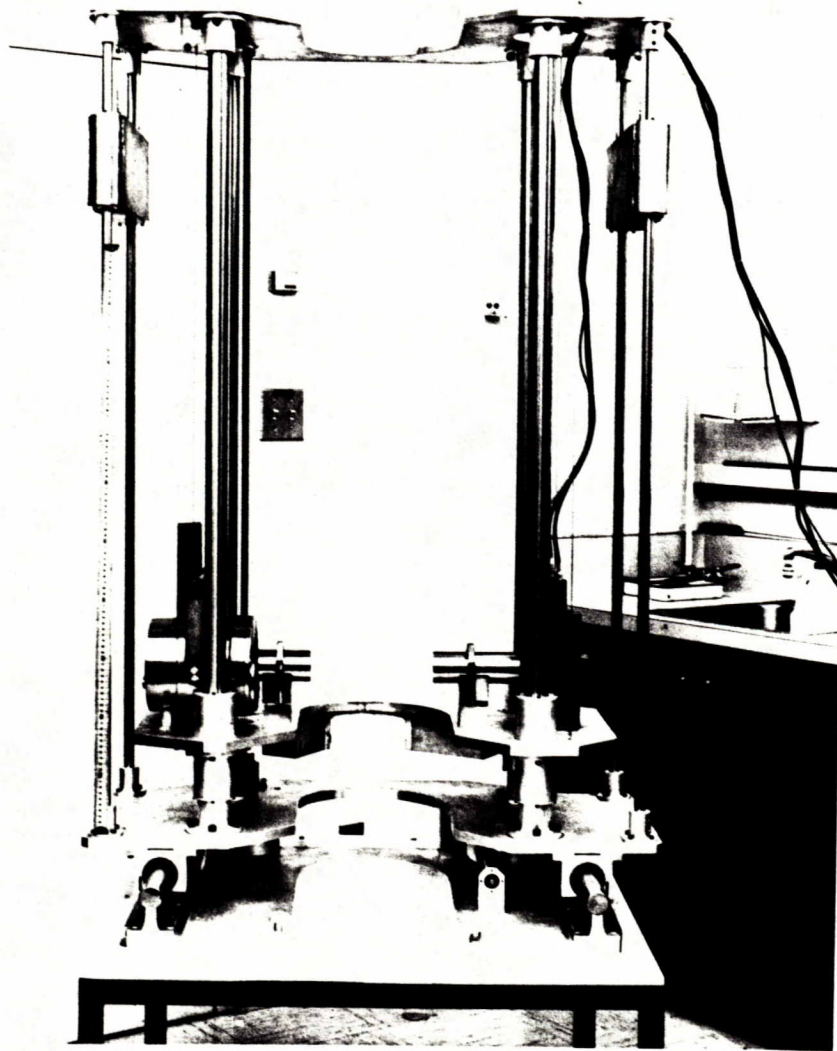
Fig. 1.   CANMET gamma-ray densitometry scanner
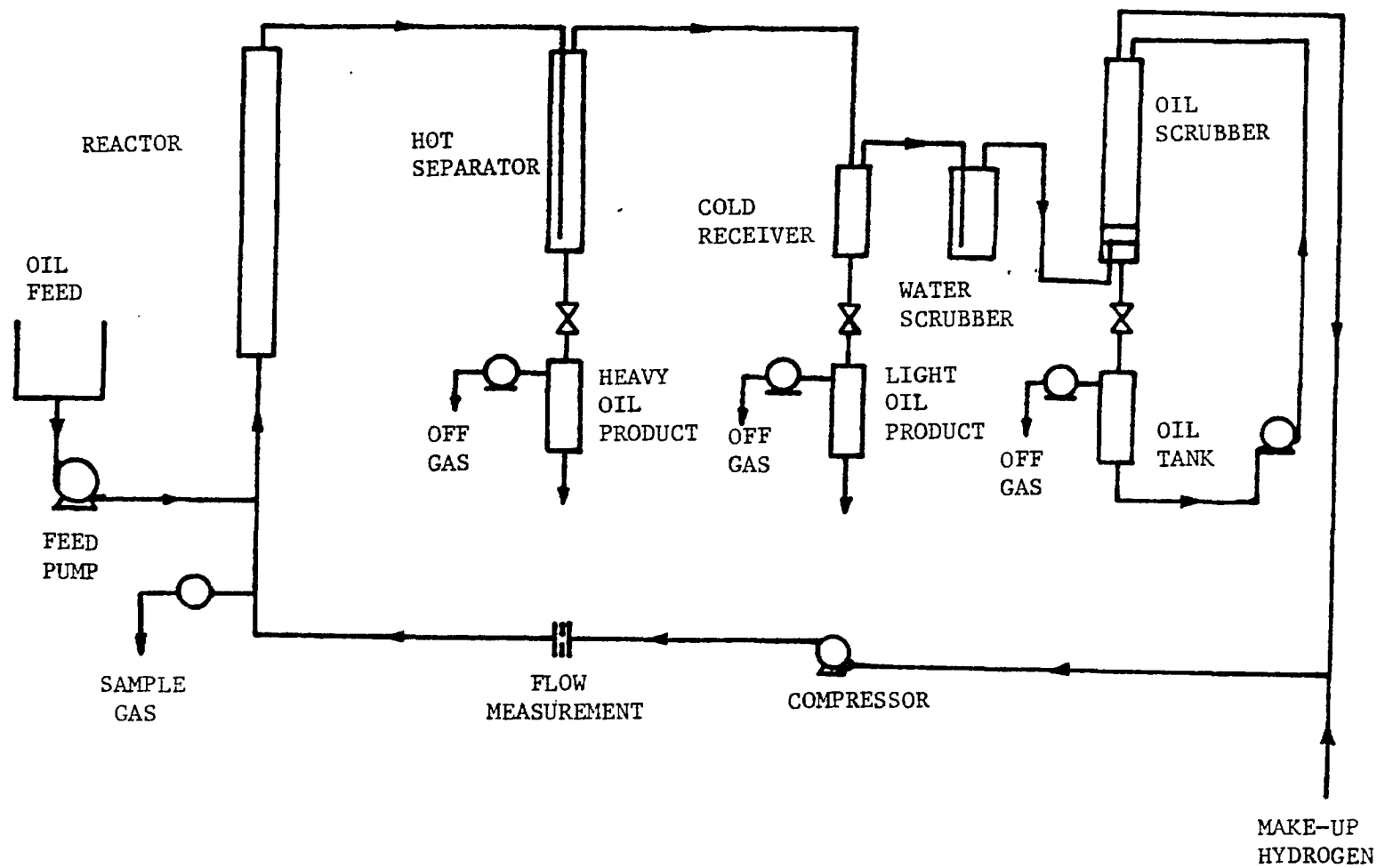
Fig. 2.   Schematic of hydrocracking pilot plant
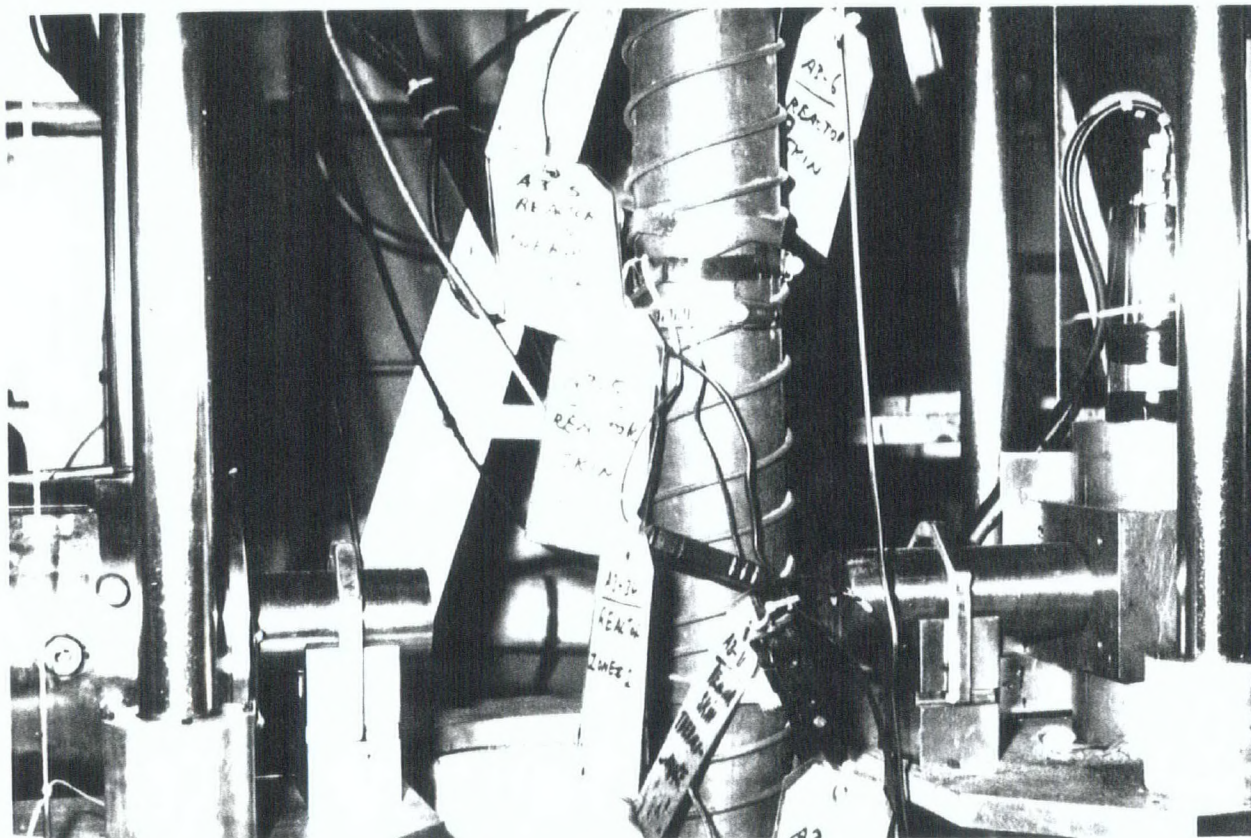
Fig. 3. Narrow gamma-ray densitometer and the pilot plant reactor without insulation
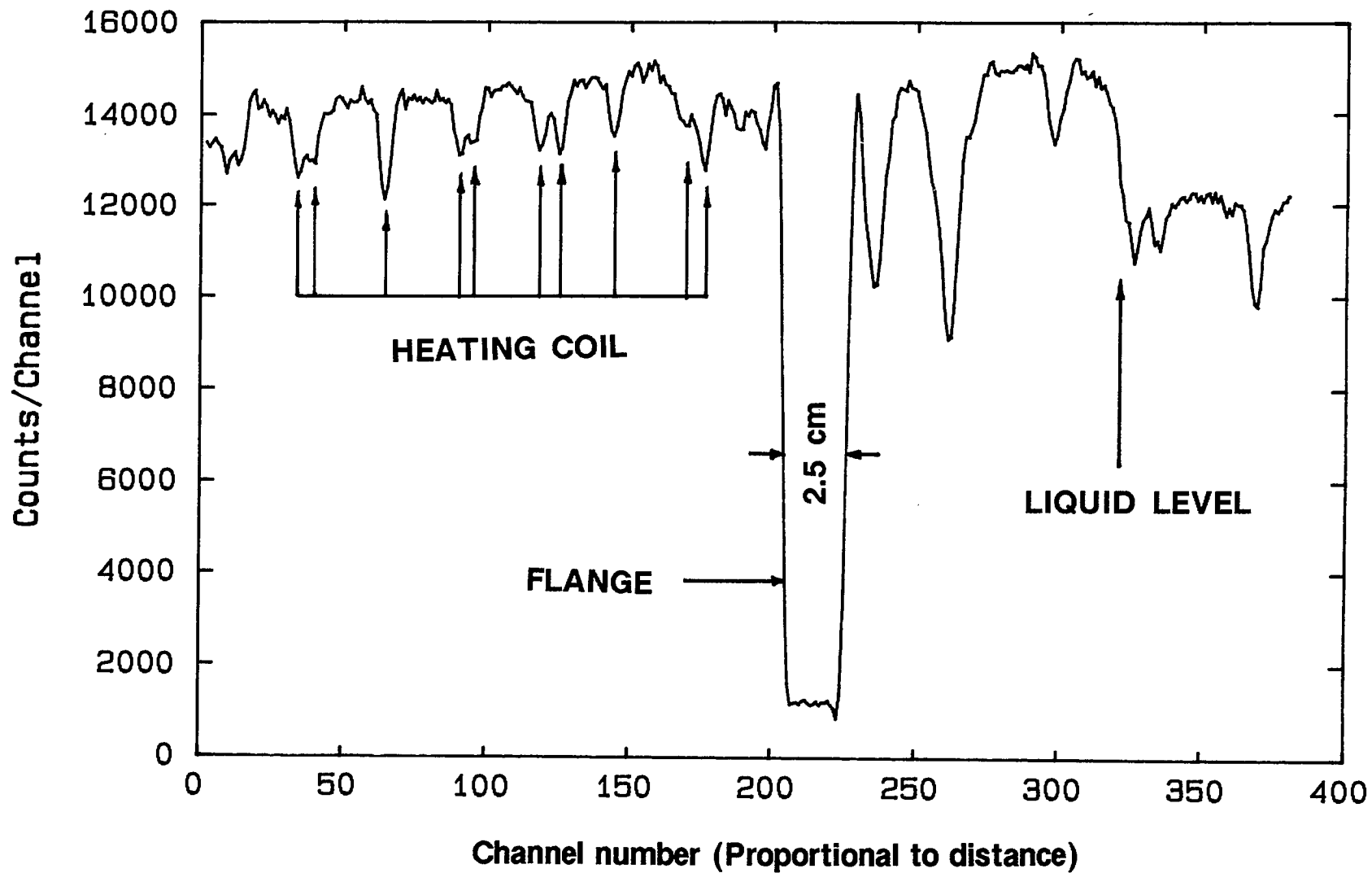
Fig. 4. MCSR spectrum of a vertical scan along a portion of the reactor
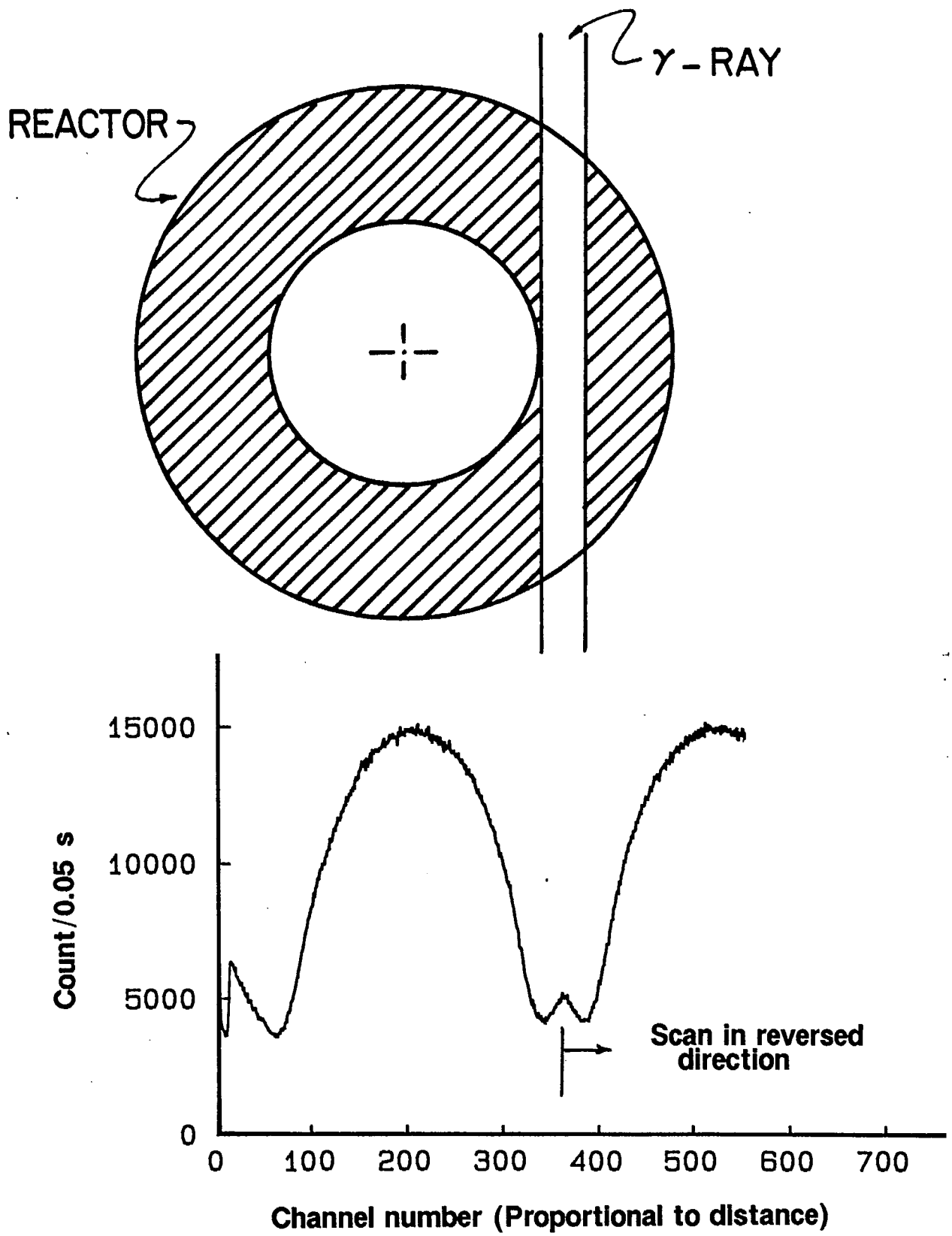
Fig. 5. MCSR spectrum of a horizontal scan across the reactor

Fig. 6.   MCSR spectrum of a gas-liquid two phase flow

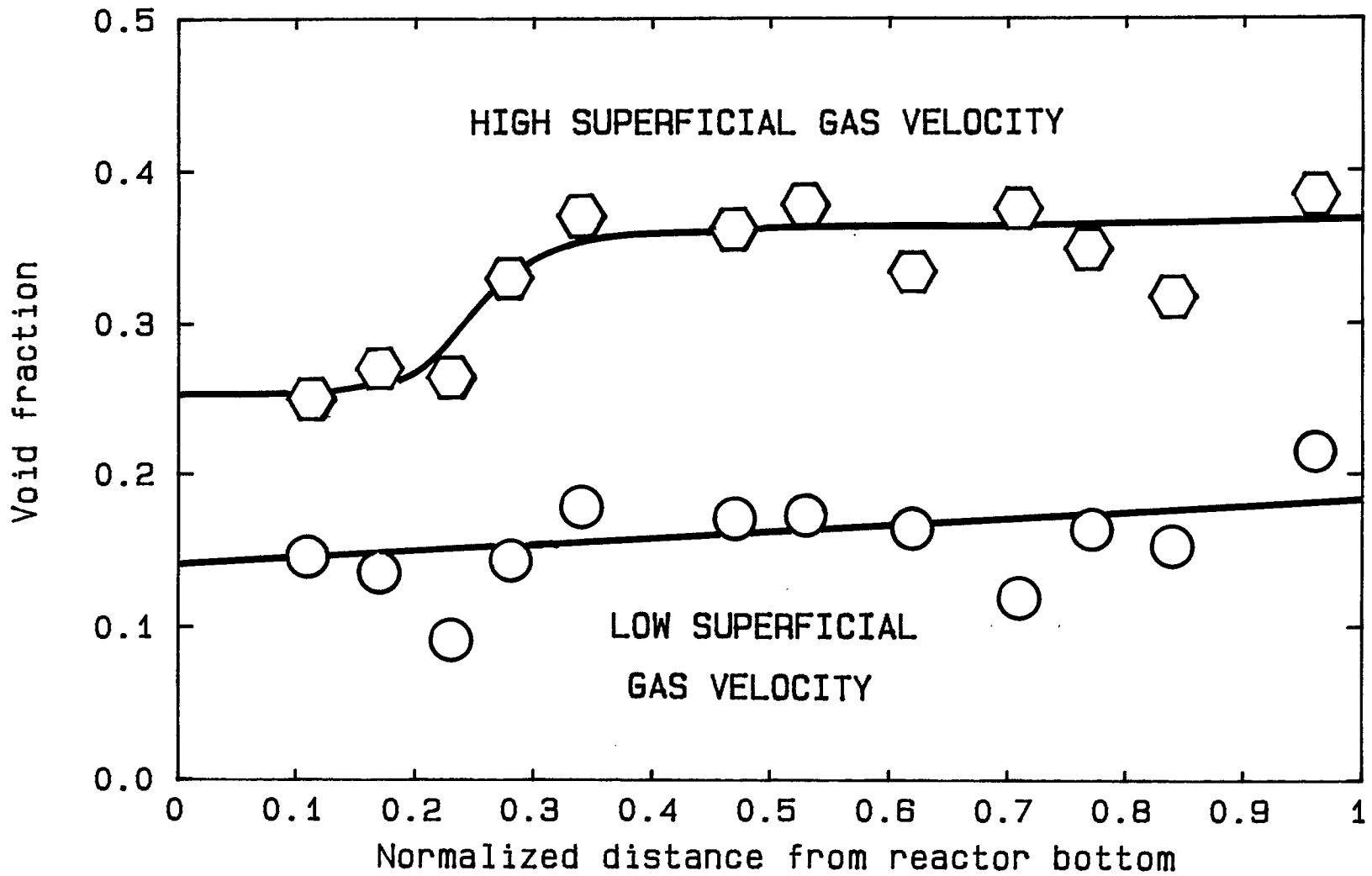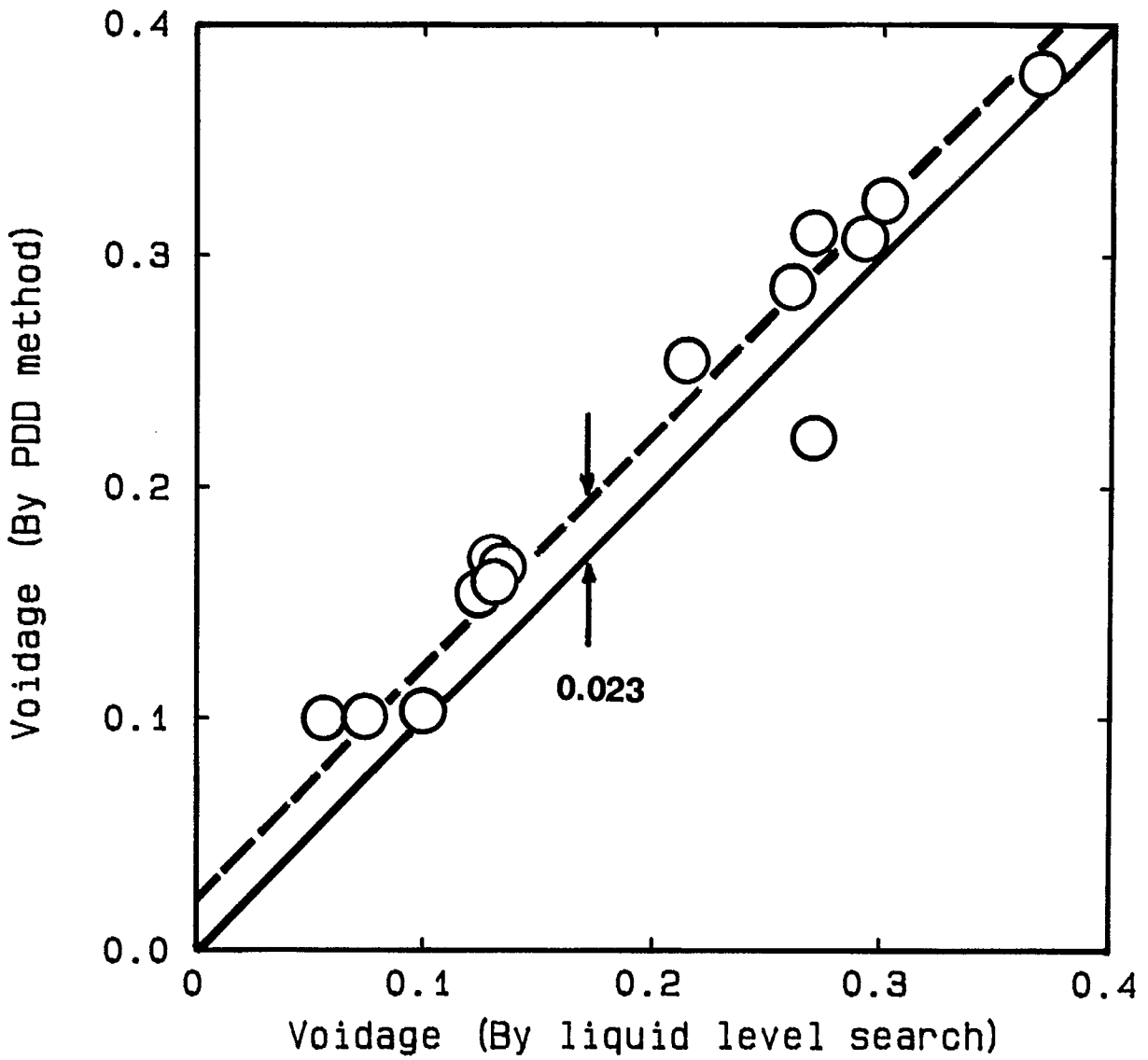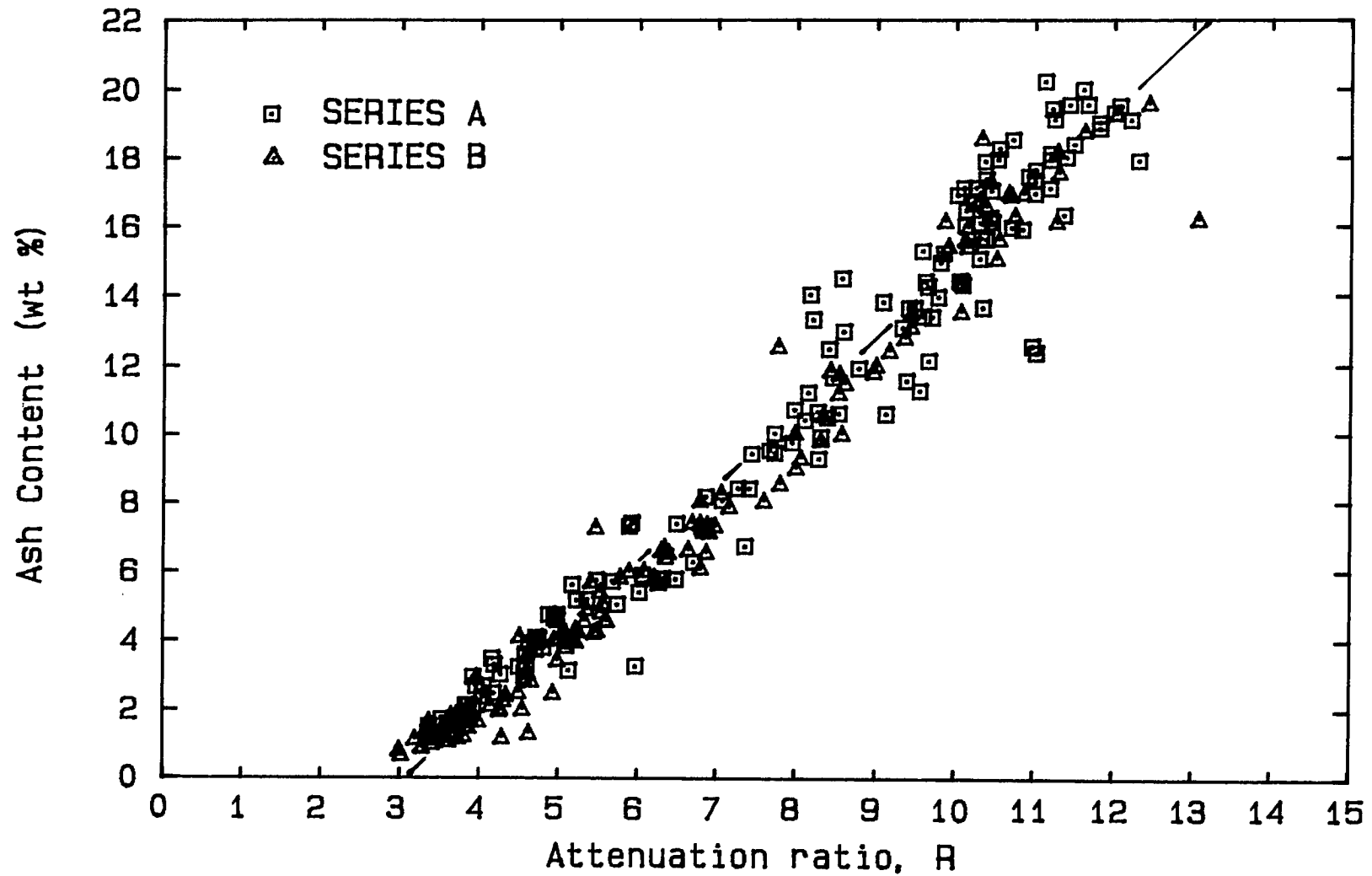Fig. 6.   MCSR spectrum of a gas-liquid two phase flow

Fig. 7. Local void fraction $\varepsilon(z)$ as a function of the reactor coordinates z

Fig. 8. Comparison of the total void fraction measured by the PDD method versus those measured by liquid level searching technique

Fig. 9.   Ash concentration as a function or attenuation ratio

FIGURES