A TYPICAL RADIOTRACER TEST DESIGN: APPLICATION TO A FLUID CATALYTIC CRACKING UNIT

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ABSTRACT

The concept of residence time distribution (RTD) is an important tool for performance assessment of industrial units and reactors. This paper discusses the residence time distribution concept, how to obtain the residence time distribution curve of a process reactor using radioactive tracers (radiotracers) and its importance in process performance assessment. Focussing on the fluid catalytic cracking unit (FCCU) of a petroleum refinery, radiotracer tests to determine catalyst and vapour traffic velocities and slip through the riser and its implications for efficient cracking, and the flow distribution through the riser and regenerator are discussed.

Key words: Radiotracer, Residence time distribution, fluid catalytic cracking, flow distribution, riser and regenerator

1. INTRODUCTION

The residence time distribution (RTD) of a chemical reactor is a probability distribution function that describes the amount of time a fluid element could spend inside the reactor (Fogler, 2005). Chemical engineers use the RTD to characterize the mixing and flow within reactors and to compare the behaviour of real reactors to their ideal models. This is useful, not only for troubleshooting existing reactors, but in estimating the yield of a given reaction and designing future reactors. The RTD can be determined through numerical methods and experimental means. In the experimental determination of the RTD, tracers which are chemical substances with measurable properties like absorbance, fluorescence, pH and salt conductivity are employed (Wittrup, 2007, IAEA, 1990). However, the applications of radiotracers are methods of choice for obtaining the distribution in industrial process vessels (Dagadu et al, 2012, Lelinski et al. 2002). The Radiotracer RTD method has been extensively used in industry to optimize processes, solve problems, improve product quality, save energy and reduce pollution (Mumuni et al., 2011; Pant et al., 2009, 2001; Pant &Yelgoankar, 2002; Yelgoankar et al., 2009). Though the RTD technology is applicable across a broad industrial spectrum, the petroleum and petrochemical industries, mineral processing and wastewater treatment sectors are identified as the most appropriate target beneficiaries (IAEA, 2008). This paper discusses the RTD concept, how to obtain the residence time distribution curve of a process unit and its importance in process performance assessment. Focussing on the FCCU of a petroleum refinery, radiotracer tests to determine catalyst and vapour traffic velocities and slip through the riser, flow distribution through the reactor and the regenerator are discussed.

2. THEORY

2.1 Tracers

A tracer is any substance whose atomic or nuclear, physical, chemical, or biological properties provide for the identification, observation and following of the behaviour of various physical, chemical or biological processes (dispersion, mixing, kinetics and dynamics), which occur either instantaneously or in a given lapse of time. There are many kinds of tracers. Radioactive tracers are mostly used for online diagnosis of industrial reactors because they have high detection sensitivity for extremely small concentrations (Charlton, 1986; IAEA, 2008; Pant, 2001). For instance, some radionuclides may be detected in quantities as small as 10-17 grams. Moreover, the amount of radiotracer used is virtually insignificant. For example, 1 Ci of ^{131}I- weighs 8 μg, while 1 Ci of ^{82}Br- weighs only 0.9 μg. That's why, when injected, they do not disturb the dynamics of the system under investigation as well as offering possibility of "*in-situ*" measurements, providing information in the shortest possible time (IAEA, 2008). Two major producers of artificial radioisotopes are nuclear reactors and accelerators. Radionuclide generators are chemical/physical/mechanical devises, based on mother-daughter nuclear genetic relationship and allows for the separation and extraction (elution) of the short-lived daughter from the longer-lived stationary mother are also radioisotope sources (Lowenthal and Airey, 2001; Leiser, 2001). For reliable and meaningful results, an industrial radiotracer must meet the basic requirements such as suitable half-life and energy of radiation, physical and chemical stability, easy and unambiguous detection (Charlton, 1986). It is often difficult to meet all the requirements of an ideal tracer and certain compromises have to be made. For reliable and meaningful results, an industrial radiotracer must meet the basic requirements such as suitable half-life and energy of radiation, physical and chemical stability and easy and unambiguous detection. It is often difficult to meet all the requirements of an ideal tracer and therefore certain compromises have to be made where necessary (IAEA, 2008).

2.2 Residence Time Distribution Concept and Measurement

The theory of RTD generally begins with three assumptions: the reactor is at steady-state, transports at the inlet and the outlet takes place only by advection, and the fluid is incompressible (Wittrup, 2007). The principle of the RTD consists in a common impulse-response method: injection of a tracer at the inlet of a system and recording the concentration-time curve C (t) at the outlet as shown in figure.2. A sharp pulse of radioactive tracer is injected upstream of the vessel and a detector located at the inlet marks time-zero. A second detector, located at the outlet, records the passage of the tracer from the vessel. The response of this detector is the residence time distribution, E (t) of the vessel (IAEA, 2008).

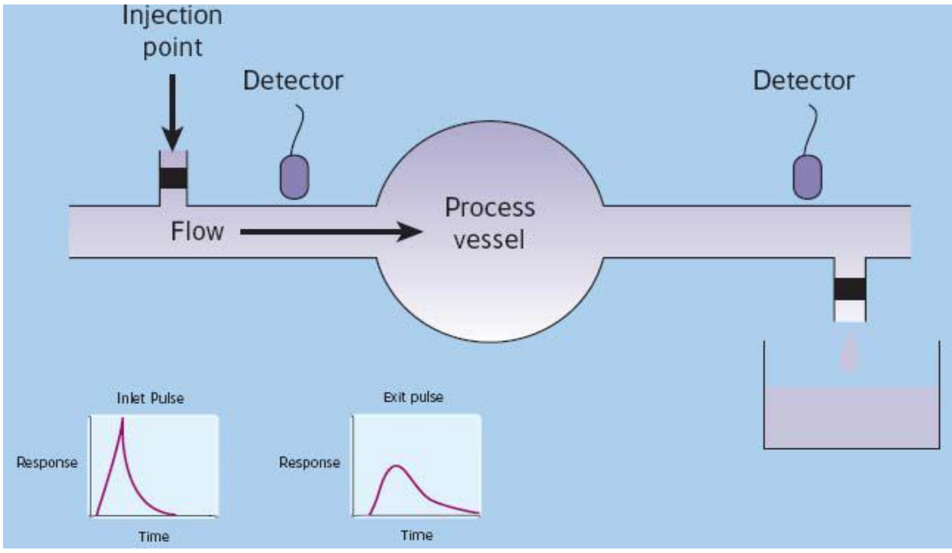

Figure 2: Principle of RTD

The RTD function E (t), is represented by the equation:

$$E(t) = \frac{C(t)}{\int_0^{\infty} C(t)dt}$$

Where C (t) is the tracer concentration with respect to time at the outlet of the system. The experimental RTD is calculated from the count rate distribution at the outlet of the system in count per seconds (cpm) or counts per minutes (cpm).

2.3 Planning and Executing a Radiotracer RTD Experiment

Injecting a compatible radiotracer into an appropriate inlet upstream of a vessel and monitoring its passage through the vessel allows the RTD of the fluid to be measured. Sensitive radiation detectors are placed at strategic elevations or locations on the vessel. The detectors are relatively small and easy to mount at each position. Each one is connected by a cable to a central data logging device that records the radiotracer concentration versus time information. Scintillation detectors, sodium iodide (NaI) are commonly used for industrial tracer applications because of their high efficiency for gamma ray detection. When the radiotracer passes each detector, a response is registered and recorded. Prior to the test, each detector is assessed and its response normalized such that each detector responds identically to a given unit of radiotracer. The experimental RTD curve can be obtained either by online measurement of the radioactivity, or by sampling and subsequent measurement in laboratory (IAEA, 2008; Dagadu et al, 2012).

The amount and activity of radiotracer required for a RTD test depends on the expected accuracy, efficiency of the radiation detection system, expected level of dilution/dispersion, the half life of radiotracer used and the background radiation level. The lower limit of the amount of tracer is estimated according to measurement sensitivity, desired accuracy, dilution between injection and detection points and background radiation level. However, the upper limit is set by radiological safety considerations (IAEA, 2008; Charlton, 1986).

To be able to implement an RTD test, there is the need for a complete understanding of the system under investigation and the process. This should include the properties of the process material such as phase, density and viscosity as well as process parameters such as flow rate, volume, pressure, temperature, expected mean residence time (MRT) etc.) and the expected degree of mixing. The feasibility of carrying out the experiment should be assessed by a planned visit, and a discussion with plant engineers. During the visit, suitable injection and detection points of the tracer should be identified. Radiation waste disposal should also be considered (IAEA, 2008).

Other factors to consider include the calibration of the detection system, the preparation of, dilution, dispensing, labeling and packing of the radiotracer and its transportation to the experiment site. At the site, the installation of the injection system, collimators and detectors at suitably selected locations is done; background radiation levels measurement, injection of tracer and its measurement are carried out whiles radiation surveillance is provided by the radiation safety officer (IAEA, 2008).

2.4 RTD Formulation

The analysis of the measured RTD depends upon the specific aim for which the experiment is carried out. Some of the common applications are discussed here.

Normally the RTD experimental data contain statistical fluctuations and other parasite influences. Figure 3 shows a typical experimental response in a form of discrete points (IAEA, 2008).

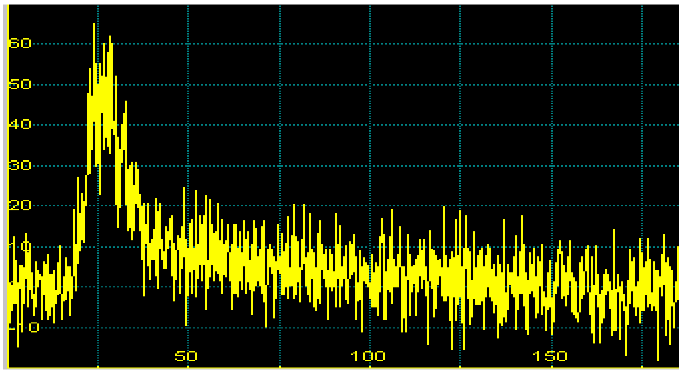

Figure 3: Radiotracer cloud on the screen of the data acquisition system

The main treatments (or corrections) of the experimental response curve to obtain the corrected RTD curve are the following:

2.4.1 Background correction

Prior to the injection of the radiotracer into a system, it is necessary to measure the background radiation level, which is subtracted from the experimental data. An example is shown in Fig. 4.

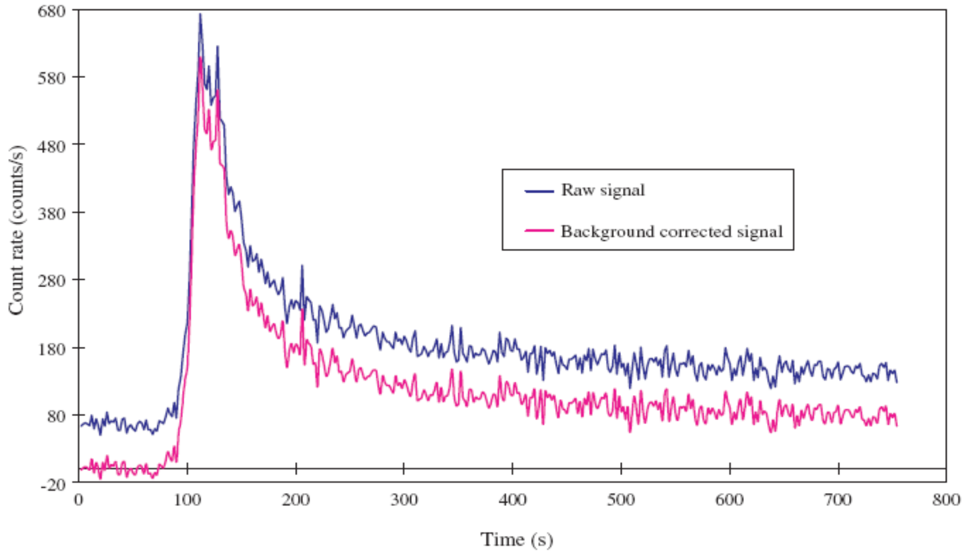

Figure 4: Raw signal and background corrected signal

2.4.2 Radioactive decay correction

Since radioisotope tracers decay exponentially with time, it is necessary to apply decay correction to the measured data (otherwise, more weight would unduly be given to early measurements)(IAEA,2008). The decay corrected count rate $n_c(t)$ is given as:

$$n_c(t) = n_{bg}(t)exp(\lambda t) = n_{bg}(t)exp\left(\frac{0.693t}{T^1/_2}\right)$$

Where: n_{bg} is the background corrected count rate, λ is the decay constant, t is the time and T½ is the half-life of the radioisotope tracer.

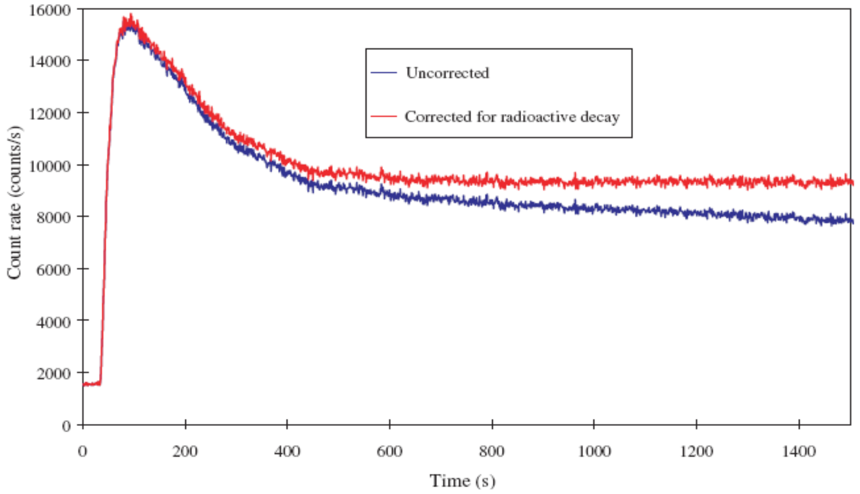

Figure 5: Effect of correction for the radioactive decay of Indium-131

2.4.3 Filtering (or smoothing)

The aim of filtering is to eliminate, or at least decrease, fluctuations due to counting statistics or electronic noise as shown in Fig.6. Several methods for smoothing a signal are available. The Fourier transform is very effective as many high frequencies can be filtered without altering the general shape of the experimental RTD curve. The Fourier method requires that the data be sampled at equidistant (regular) intervals. Cumulating or re-sampling counts is a simpler technique for smoothing fluctuations. Counts are cumulated by groups of 5, 25 and 100 (IAEA, 2008).

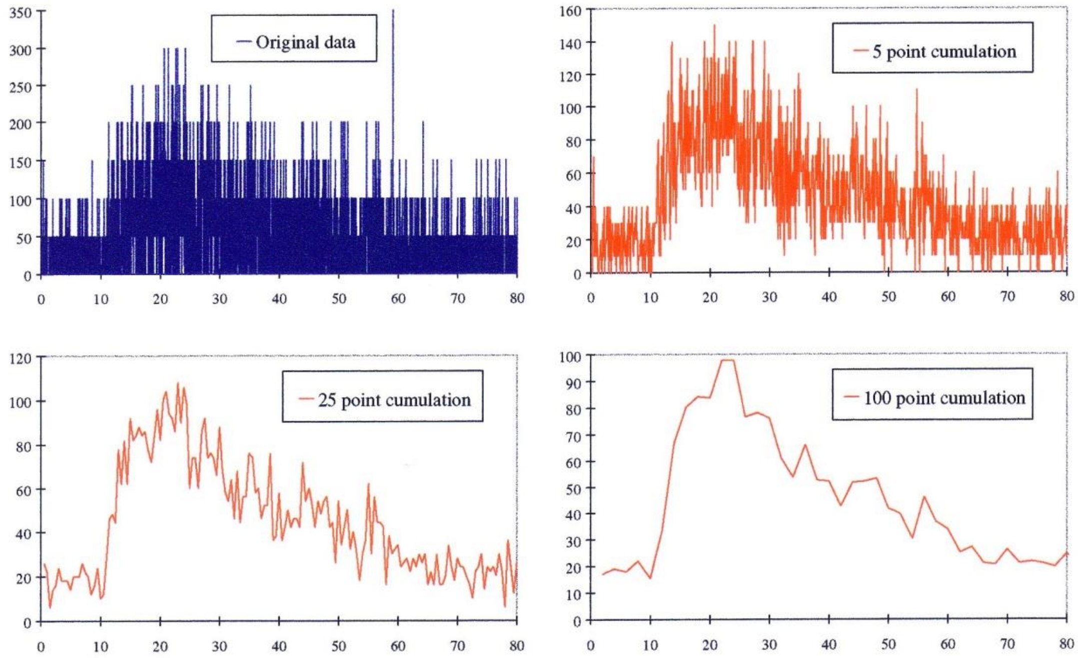

Figure 6: Filtering of fluctuations in an experimental RTD curve.

A typical curve obtained after the corrections is shown in fig. 7

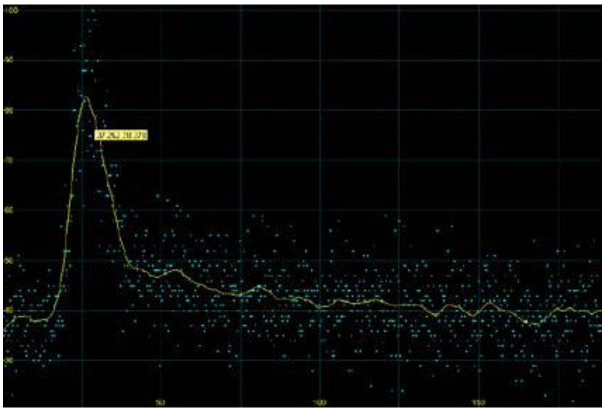

Figure 7: A typical experimental curve obtained after corrections

2.4.4 Data Extrapolation

Data extrapolation is needed when the end of the measured tracer curve is missed for different reasons. This could be due to a large RTD, a long tail and/or data acquisition system problems. Regular tracer test assumes that the count rates go back to zero after the end of the data acquisition sequence, as illustrated in Fig. 32. Mostly, extrapolation is performed mathematically using exponential decay function (IAEA, 2008).

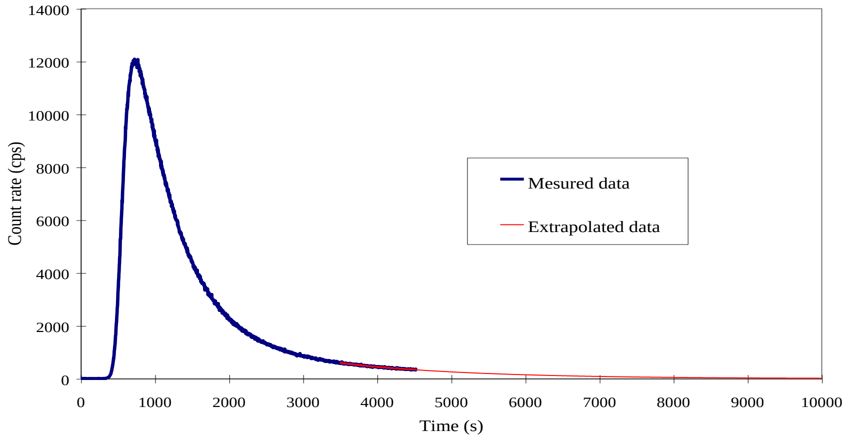

Figure 8: Incomplete experimental curve from tracer test and its extrapolation

The aim of data extrapolation is to extend the tracer curve in some plausible way. The most common procedure is to check that count rates decrease exponentially at the end of the experiment. This is easily done by plotting the logarithm of count rates versus time, which should exhibit a linear behaviour towards the end. A decaying exponential function should then be adjusted on that part of the curve, and the data extended with this function until count rates are negligibly small (IAEA, 2008).

2.4.5 Normalization of the area of experimental tracer curve

Area normalization is compulsory when modeling the RTD data using suitable software. The tracer concentration curve is normalized by dividing each data point by the area under the curve (i.e. the total count number):

$$E(t) = \frac{n_c(t)}{\int_0^\infty n_c(t)\,dt}$$

Where $n_c(t)$ is the corrected count rate (i.e. the result of all the previous operations)
E (t) is the normalized function.

2.5 Analysis of RTD curve for troubleshooting

Analysis of the tracer distribution curve is done by relating the moments of the distribution curve to the possible flow models in the reactor. The first moment of a distribution is the mean of distribution i.e. mean residence time of material in the reactor. The second moment represents the variance which can be related to the Pecklet number, a dimensionless number giving a ratio of convective to dispersive forces and the third moment the skewness. From these moments, flow conditions varying from plug flow to fully mixed flow can be described inside a reactor (Sharma, 2005).

RTD technique using radiotracers has been routinely used to diagnose imperfect mixing (de Andrade, 2005, Lelinske, 2002). Deviations from ideal flow patterns are most often determined by examining the shape of the E (t) since this function is readily obtainable from impulse tracer responses (Dudukovic and Feldar, 1983). The shape of the E (t) curves may indicate malfunctions such as the existence of stagnant zones or dead zones, bypassing or channeling and internal recirculation. Some commonly occurring E (t) curves are shown in Fig.9.

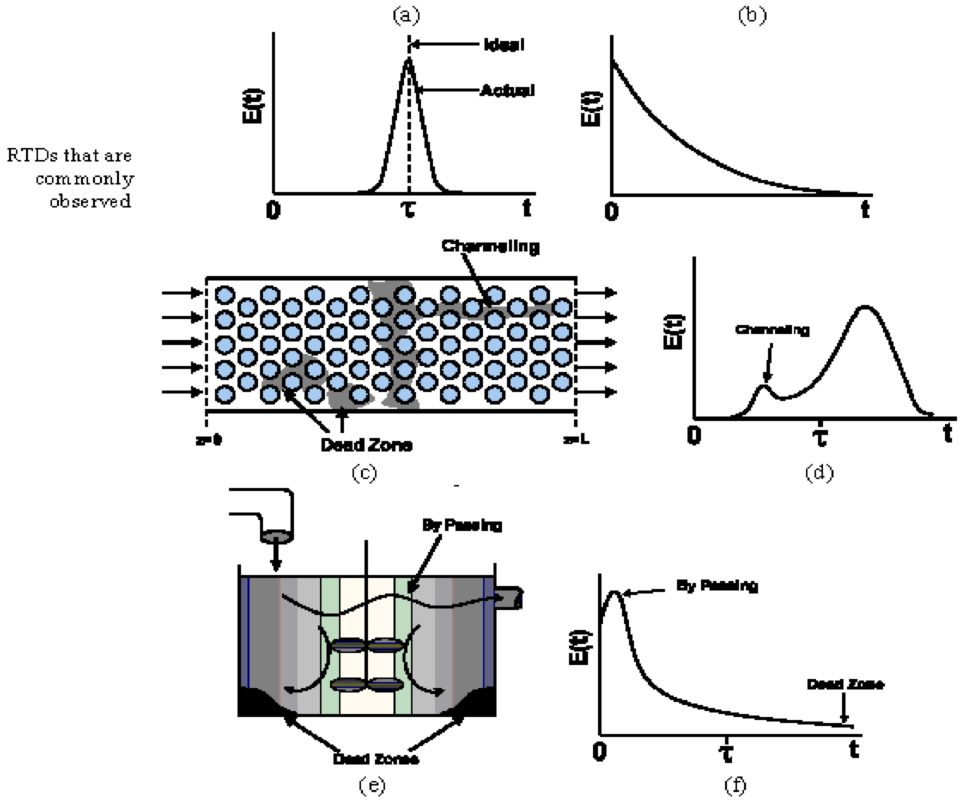

Figure 9:(a)RTD for near plug flow reactor (b)RTD for a nearly perfectly mixed stirred reactor; (c)packed bed reactor with dead zones and channeling; (d)RTD for packed bed in (c);(e)reactor with short-circuiting flow(bypass);(f)RTD for a reactor with channeling (by-pass or short circuiting) and dead zone

2.5.1 A Radiotracer test in a FCCU

Fluid catalytic cracking (FCC) is one of the most important and complex processes in petroleum refining which is used to upgrade heavy petroleum gas oils into gasoline and other valuable products. The FCC process comprises mainly 2 parts: (1) a riser reactor where high molecular weight hydrocarbons come into contact with a catalyst and crack to lower molecular weight products with the simultaneous deposition of coke on the catalyst surface and (2) a regenerator where the coke on the catalyst is burnt with air and the catalyst is returned to the riser for the next run of cracking (Moharri, 1984). A schematic diagram is shown in Fig.10.

Technically, it is also the most complex unit, involving as it does the interaction of multiple phases: solid catalyst, vaporized feedstock steam and air. Because of the construction and extreme operating conditions of FCCUs, the only effective way to diagnose their anomalies in their behaviour is through the application of radiotracers.

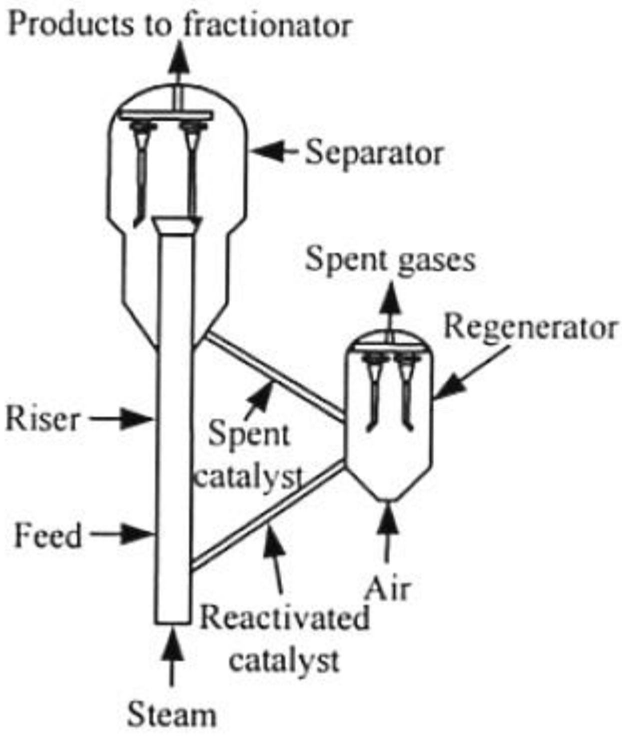

Figure 10: A schematic diagram of an FCCU

Radiotracer investigations in FCCU are performed by injecting compatible radiotracers for catalyst and steam phases into the riser, and regenerator, and monitoring the passage of the tracer through various sub-systems by means of externally mounted detectors (IAEA, 2008).
Detectors are mounted at strategic locations throughout the unit. The detector responses are recorded and analyzed using suitable software. From the detector responses and analysis, velocities, residence times, and flow distribution characteristics of the vapour and catalyst in various sub-systems of the unit are measured. The results of the investigation can help to improve the design, increase product yield and quality. Table 1 shows the experimental details of some typical radiotracer investigations performed in an FCCU.

Table 1: Experimental details of some typical radiotracer investigations performed in an FCCU.

FCCU component Phase	Phase	Tracer	Activity used mCi	Number of detection points
Riser	Catalyst	^{140}La	60	15
Riser	Gas	^{79}Kr	215	15
Stripper-North side	Gas	^{79}Kr	190	13
Stripper-south side	Gas	^{79}Kr	190	13
Stripper-North side	Catalyst	^{140}La	40	13
Stripper-South side	catalyst	^{140}La	40	13
Regenerator	Gas	^{79}Kr	115	10
Regenerator	Catalyst	^{140}La	20	10

(Source: IAEA, 2008, La = Lanthanum, Kr = Krypton, mCi = millicurie)

2.5.1.1 Determination of Slip Velocity in the Riser

One common application to the FCCU is the measurement of stream velocity. Ideally, the fine catalyst and the gas oil vapour should be in plug flow condition to eliminate back-mixing, which can produce undesirable secondary reactions during the cracking. However, because of its greater density, the catalysts always flow up the riser at a slower rate than the oil vapour. This phenomenon is known as “catalyst slip”. An ideal plug flow riser should have a slip factor of 1.0 (IAEA, 2008). Deviations from this ideal factor or design expectation are often used as a measure of the fluidization performance.

The slip factor can be determined by measuring the velocities of the oil vapour and catalyst employing radiotracers. The velocities are calculated by dividing the distance between two detectors by the elapsed time between their responses. If this is done for the vapour and catalyst traffic, the vapour/catalyst slip ratio can be calculated. Fig. 11 shows the results of the vapour and catalyst velocity in the riser. Mean residence times of the vapour and catalyst phase were found to be 1.4 and 2.3 s, respectively. Thus, the vapour and catalyst velocities were calculated as 10.5 m/s and 7.0 m/s, respectively. The slip factor then is 1.5 implying the need for adjusting some operational parameters to bring the slip close to 1.

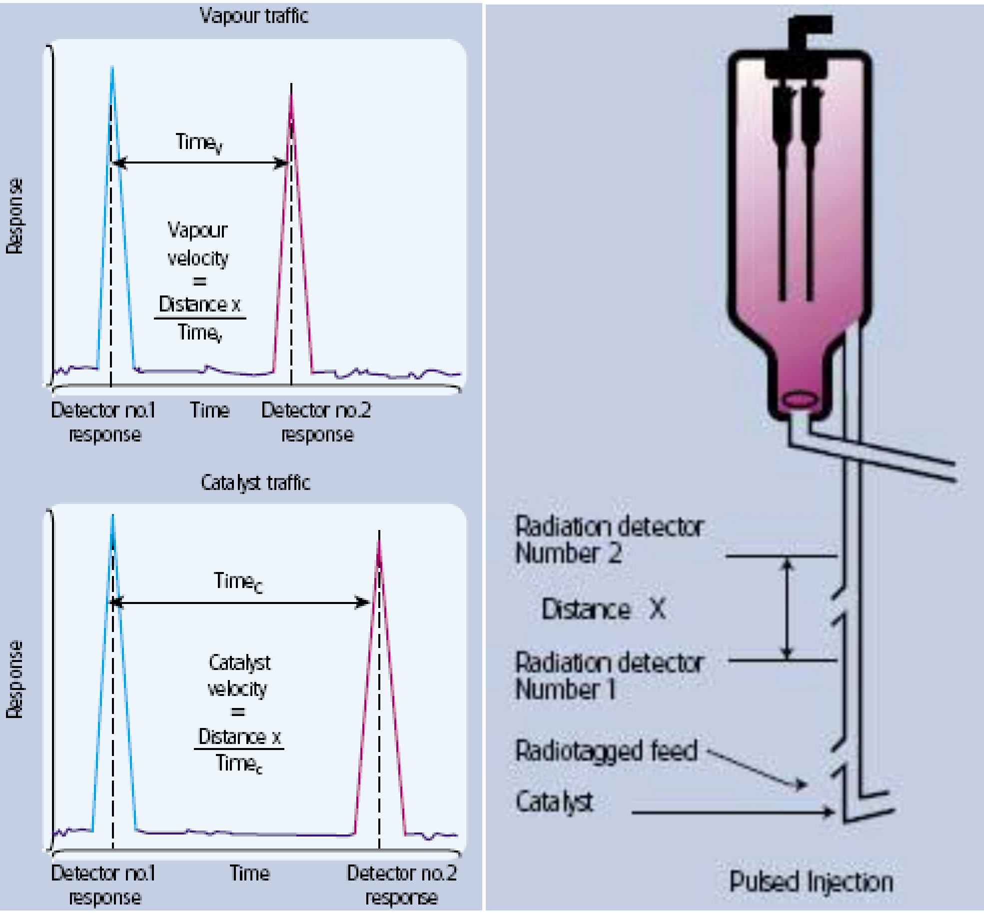

Fig 11: Riser traffic velocity and slip measurements

2.5.1.2 Riser flow Distribution

In the measurement of flow distribution through the riser, instead of placing only one detector at each elevation, four detectors are located around the circumference of the riser at ninety degree intervals (Figure 12). Prior to the testing, each of these detectors is calibrated such that they yield an identical response to a given intensity of tracer (IAEA, 2008).

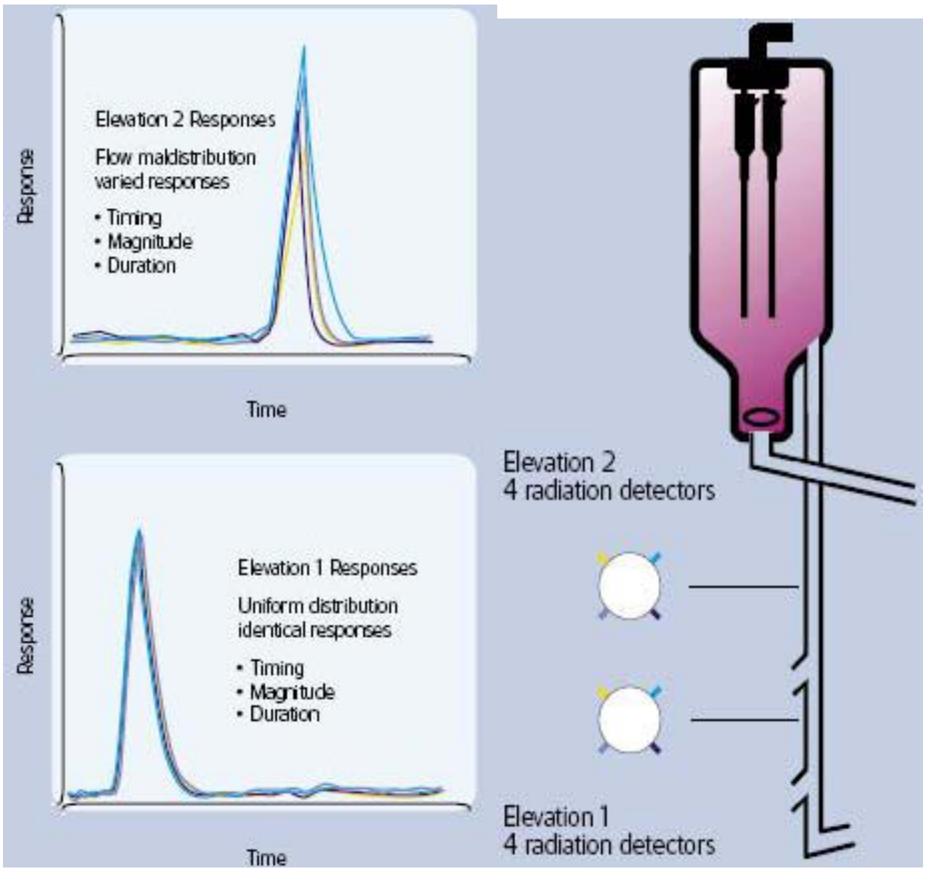

Figure 12: Radial distribution of gas phase flow in the riser

As the tagged process stream flows past the measurement elevation, all four detectors respond to it. If the tagged process stream is uniformly distributed, all four detectors will show identical responses. A flow maldistribution will be represented by varying detector responses, with more traffic causing a larger response and less traffic causing a reduced response (IAEA, 2008).

From the figure 12, it can be seen that no radial misdistributions of gas phase exist at the bottom part (elevation 1) of the riser. This is because the detector responses are of similar magnitude, duration and event timing. However, in the upper part (elevation 2), the distribution is slightly deteriorated probably from abnormal regime of temperature distribution. In this case, the greatest amount of gas flow passes through the quadrant monitored by the blue detector, whilst the yellow detector measures the least amount of flow (IAEA, 2008). This also signals the presence of a large degree of back mixing in the case of solid flow with the flow of gas phase being plug.

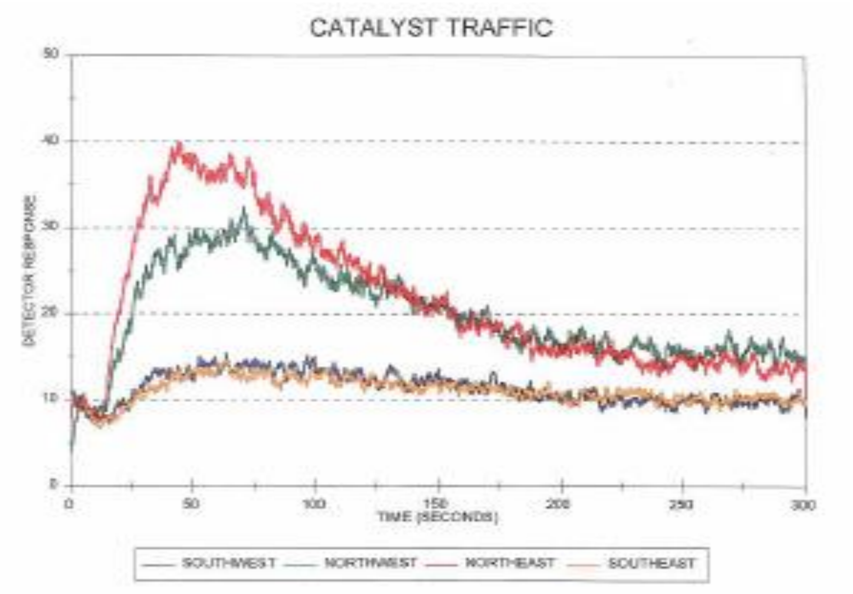

Figure 13: Riser radial distribution of catalyst flow

2.5.1.3 Regenerator Flow Distribution

Detector responses of a radiotracer RTD test in the regenerator of an FCCU are shown in Fig. 14. The radial distribution of the catalyst is poor. As expected, the non uniformity of flow distribution is more evident in catalyst phase than in gas phase. This clearly has implications for efficient combustion of the coke on the deactivated catalyst.

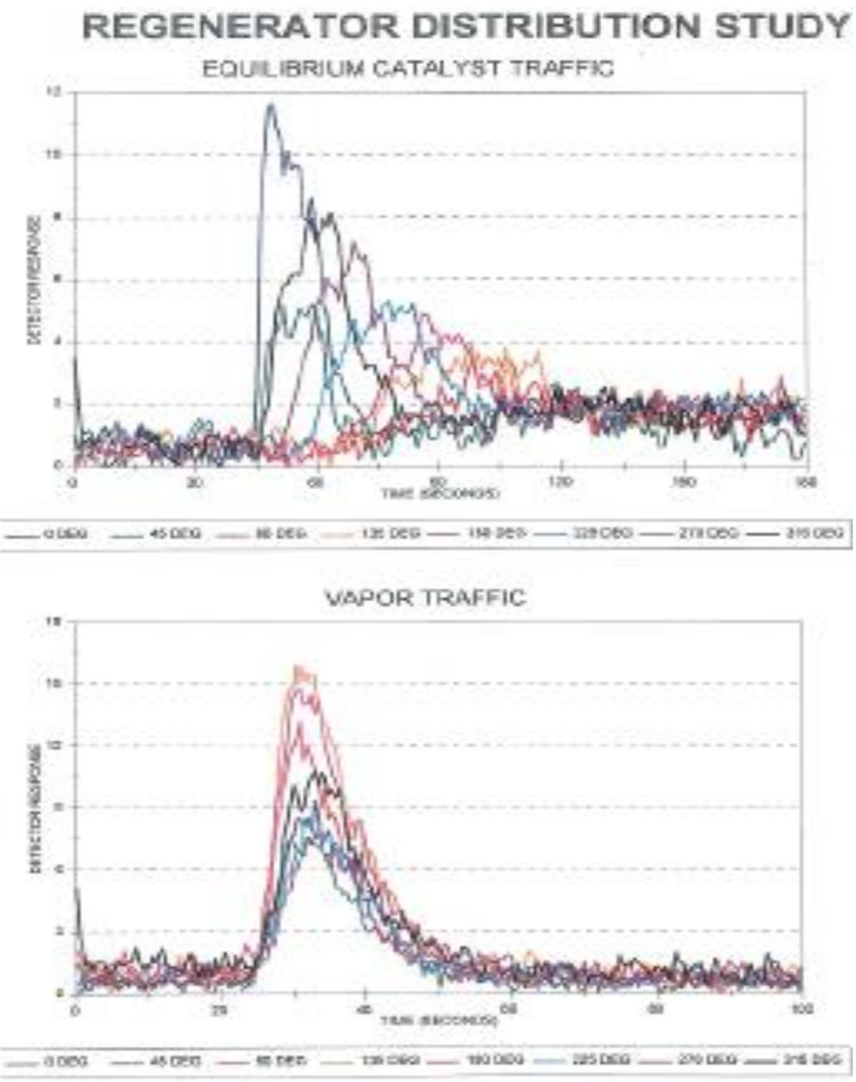

Figure 14: Regenerator radial distribution of vapour and catalyst flow

3. CONCLUSION

Radiotracers are playing more and more important roles in industry.Radiotracer RTD technique is a quick, useful and effective method of identifying misbehaving chemical units. Once the anomalies are detected, relevant operating parameters can be adjusted to achieve the desired results. It is also worthy of note that the test can be performed while the plant is on-stream, hence avoiding losses in production time through shut down and restart- up. Although computational fluid dynamics provides an alternative to acquiring the E (t) curve numerically, these models must always be validated with experimental data which can be provided by radiotracer RTD experiments. Despite its potential, radiotracer techniques are not patronised heavily by stakeholders partly because of its perceived high cost and the lack of expertise in the field. It is hoped that this article and many of its kind will go a long way to increase interests in and renewed commitments to the use of radiotracer RTD techniques in industries.

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