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Polyethylene Reaction Analyses: Before, During and After

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Introduction

In recent years, the polyethylene (PE) manufacturing industry has faced strategic challenges including large-scale mergers, rising energy costs, regional oversupply and slower global economic growth. The impacts of these challenges have resulted in a more difficult operating environment for most polyethylene manufacturers. This environment requires that manufacturers consider productivity improvements that will enable the profitable supply of specialized and commodity PE products into the regional or global marketplace.

Improvements in reactor process control, response time, inventory control and the ability to better utilize plant staff resources are all key to profitable operational success.

This document outlines three areas where such opportunities exist for many PE manufacturers. The direct analysis of reaction performance including catalyst feeding, electrostatics monitoring and resin property analysis. Each offers significant proven advantages to PE manufacturers that are looking to improve efficiency and overall plant profitability.

Before Reaction

Even before the polyethylene (PE) reaction, manufacturers clearly need to be sure that high purity feedstocks are available and advanced catalyst systems are chosen to result in efficient chemical reactions. Equally important is the ability to monitor and control the feeding of these constituents to a degree that enables optimum reaction performance.

In particular, the direct determination of the catalyst mass flow as it is feed into the reactor is one of the most critical parameters of a PE reaction. Yet given this critical importance, it is surprising that many PE manufacturing plants still do not have any direct means of catalyst mass flow monitoring.

Poor control of a catalyst feed will significantly impact production capacity and product quality. As seen in Figure 1 below, it is clear to see the impact of the catalyst feed on the overall reaction rate. In addition, unexpected variations in catalyst feed can wreak havoc on process control and polymer properties. Given the difficult nature of feeding catalyst in a multi-phase flow (solid in liquid or solid in gas), it is no wonder that this is a common problem area in most PE reaction processes.

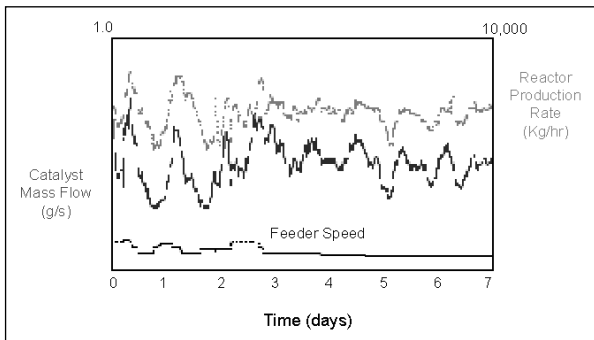


Figure 1: Production rate, feeder rate, catalyst and mass flow rate

progression's Correflow[®] Mass Flow Monitor (MFM) is designed specifically for the determination of catalyst flow monitoring in polyolefin processes. The MFM is well suited for implementation in-line in the catalyst feed system. With custom-built sensors, the MFM does not introduce any obstruction or

additional pressure drop in the catalyst feed line. In addition, the non-contact analysis uses no moving parts so it is a proven reliable technique for catalyst mass flow monitoring. Figure 2 shows where in a typical PE process the MFM sensor could be located.

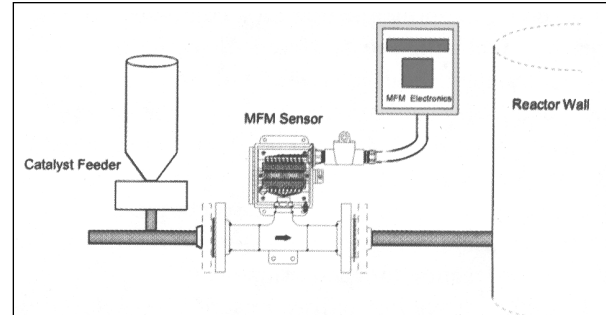


Figure 2: Correflow MFM for liquid and gas phase reactors

The graph in Figure 3 shows how a catalyst feeder system may occasionally operate with less efficiency than expected. This can be caused by a range of problems such as clogging, leaking, or valve sticking. The ideal slope 1 shows that in the best case, the catalyst feed rate is directly related to the catalyst mass flow. However, in most commercial scale plants, there is a lower efficiency resulting in slope 2 performance. The resulting "average performance" as shown will have adverse effects on productivity and create difficulty for operators trying to maintain tight PE quality specifications.

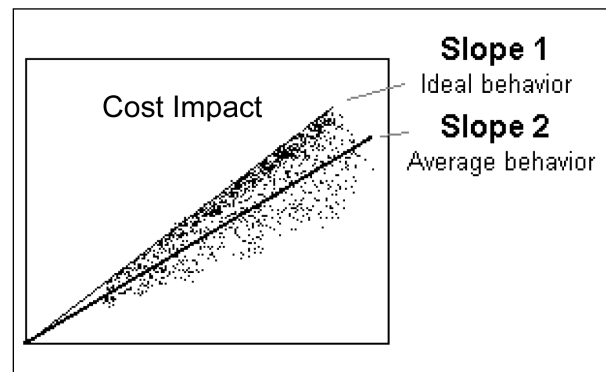


Figure 3: Catalyst mass flow versus feed rate

During Reaction

During the PE reaction process, manufacturers have a range of reaction conditions that are monitored. Parameters such as temperature, pressure, level and composition are commonplace on most plant DCS systems. In recent years, there has been an increased focus put on another basic reaction property: electrostatics. The development of newer high activity catalyst systems combined with advances in reaction technology such as condensed mode in gas phase reactors has created a growing need to monitor reactor electrostatic behavior.

In most PE reaction processes, the polymer resin or the carrier liquid will generate triboelectric charges as they move and come into contact with other materials. This activity results in the generation of electrostatic charges. Usually these charges will be generated and then dissipate via grounding paths in the reactor walls/pipes. However, under certain conditions, charge build up occurs in the reactor. This excess charging can cause a range of well-documented problems, such as fouling on the reactor walls, generation of agglomerations, lower reaction rates, quality problems due to inefficient exchanges. In extreme conditions, electrostatic problems will result in lengthy plant shutdown.

The ability to monitor real-time electrostatic behavior in PE reaction process is now possible in a range of configurations. **progression's** Correflow ElectroStatic Monitor (ESM) is the world's leading technology for the analysis of electrostatic behavior inside a polyolefin reactors.

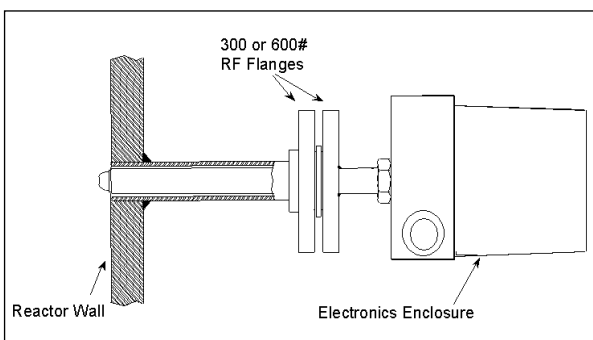


Figure 4: ESM reactor probe and reactor nozzle

Figure 4 shows how the ESM reactor probe would be inserted in a PE reactor. The Correflow

ESM system is designed to allow up to 8 electrostatic probes to be interfaced with one ESM transmitter. Figure 5 shows the corresponding data generated from two electrostatic reactor probes. It is clear that both probe 1 and 2 show an increase in electrostatic activity well before other indications such as temperature.

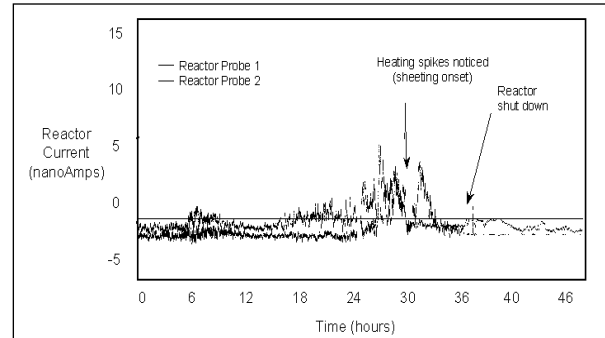


Figure 5: Static probe responses prior to sheeting event

Recent advances in ESM data processing, has allowed even more insight into the electrostatic phenomenon in polyethylene reactors. In Figure 6, raw electrostatic signals show an increase in activity, but this signal may be difficult for operators to fully interpret. Figure 7 shows the same the same ESM data after this signal is separated into AC and DC components.

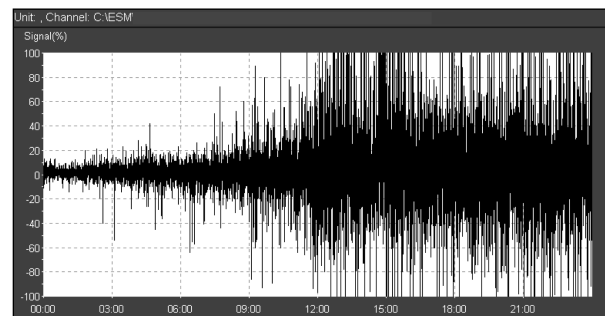


Figure 6: Real-time ESM Reactor probe data.

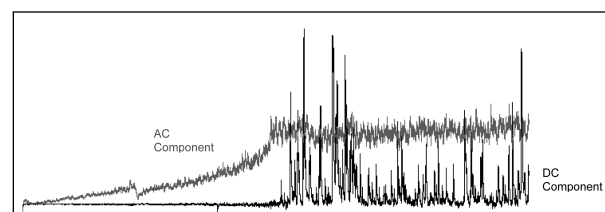


Figure 7: Real-time data de-convoluted

Note how the AC component of the signal changes significantly hours before the DC component varies at all. This same trend can be seen when reviewing data from other reactors.

After Reaction

In PE applications, the Magneflow® process NMR system is used to measure chemical and physical properties of the powder or pellets such as density, crystallinity and melt index.

In most applications, a small PE sample (<50 ml) is collected by a **progression** supplied sampling system from a transfer line after the reactor, purge tank or extruder. This sample is then pneumatically conveyed to the Magneflow analyser for measurement. After the analysis, the sample is pneumatically conveyed back to the process. The resin properties measured are directly reported to the DCS. The entire cycle is then repeated every 5–10 minutes. There is no wasted sample or consumable materials. The Magneflow is robust and designed for operation in hazardous locations.

Figure 8 below outlines where the process NMR unit and sampling system would typically be interfaced to a PE plant.

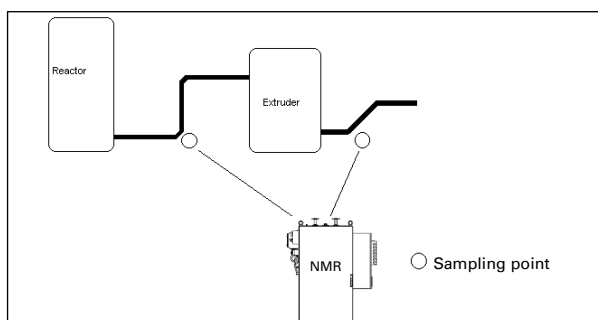


Figure 8: Magneflow sampling locations

Improving Polyethylene Consistency

Global and regional competition in the PE marketplace has increased significantly in recent years with the construction of several new world scale reactors. The ability to produce in-spec products consistently is now even more critical for producers to maintain key customers and grow market share.

The Magneflow process NMR system has repeatedly demonstrated the ability to measure in real-time PE resin consistency. The graph in Figure 9 below demonstrates how the on-line Magneflow density results provide a nearly continuous feed back to plant operators during this 24-hour steady state production run. The standard deviation as measured by the process NMR system is also slightly better than that of the more cumbersome lab density method.

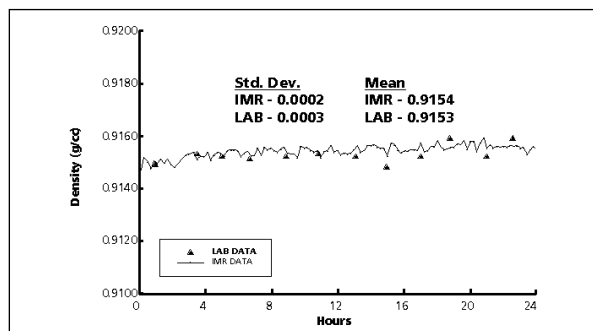


Figure 9: Steady state production results

With the use of process NMR, further consistency improvement can be achieved when a plant produces the same resin grade over and over again. Since the process NMR system is “seeing” the same grades in the production “wheel” every few weeks or few months, the system can determine exactly if the resin grades are the same from one production run to the next. Some **progression** customers have used this information to confirm batch to batch consistency for critical end user applications.

Transition Control

As a result of the trend toward larger PE reactors and higher production rates, it becomes particularly important to have better transition control and better information to determine the start and end point of a product transition. PE resin producers using on-line process NMR have achieved tremendous benefit from the ability to better “mark” transitions and switch to on-spec silos sooner. The graph in Figure 10 clearly shows how the process NMR system continuously reports the PE levels making it easy for an operator to decide the starting point and ending point of a grade transition. In addition, advanced users of **progression** process NMR solutions have utilized advanced process control techniques to shorten the transition times by up to 50% in some cases.

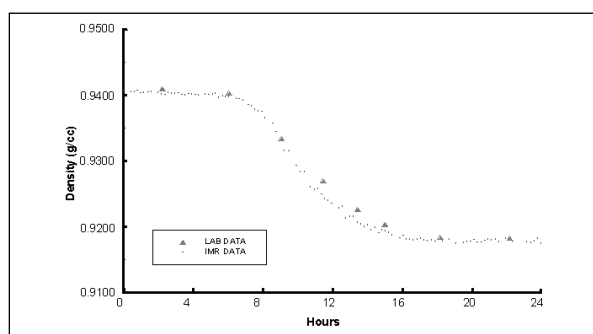


Figure 10

The Magneflow® Process NMR System

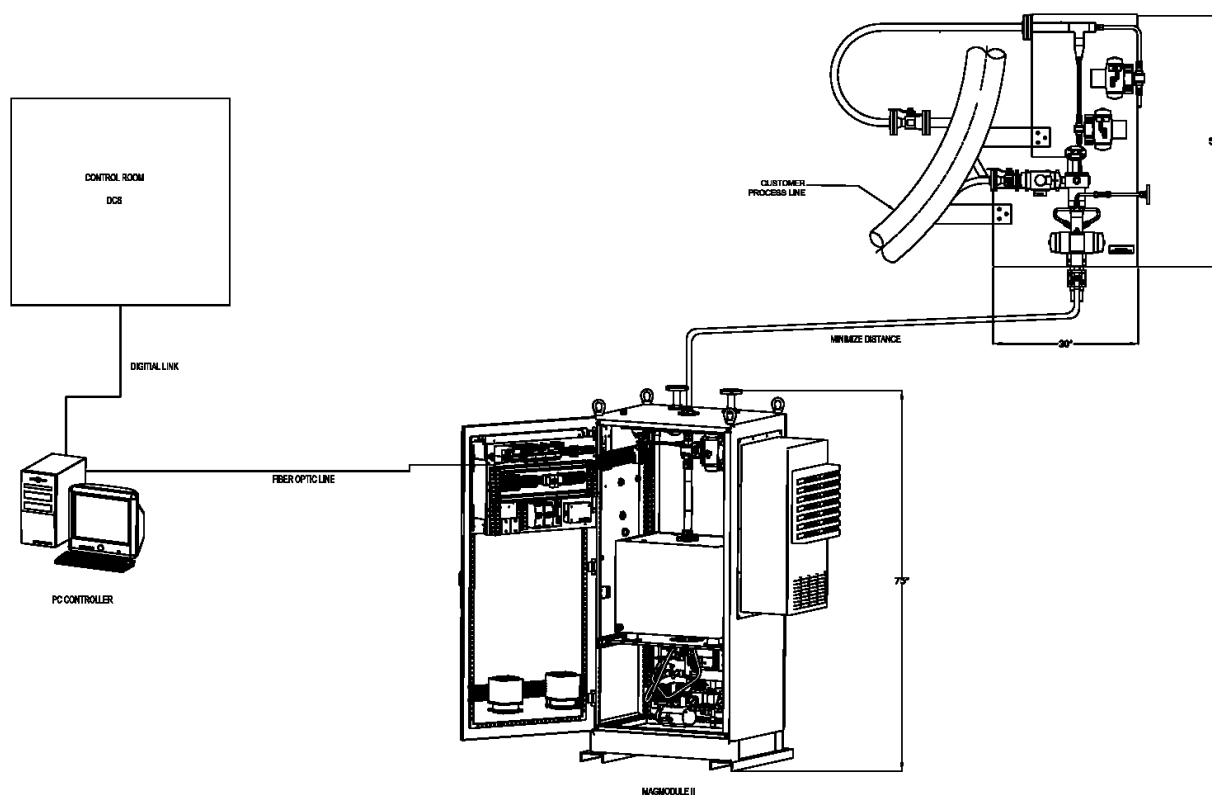
The Magneflow MagModule II system is the third generation on-line NMR technology. It represents significant advancement in the field of process NMR. The MagModule II system is 89% smaller than the previous MagModule systems. The system is fully approved for hazardous operation (ATEX) and is suited for nearly any climate. The MagModule II requires standard plant utilities (power, air, and N₂).

Please refer to the drawing below which indicates the layout of an on-line MagModule II system and a sample extraction system.

Summary

This paper has presented three improvement opportunities for polyethylene manufacturers in different areas of the PE reactor process. The direct analysis of catalyst feed mass flow rate, reactor electrostatic monitoring and polyethylene resin analysis by process NMR. Each of these advanced techniques is a proven tool for adding value to a PE manufacturing business. As polyethylene manufacturers continue to be a challenge by a dynamic business environment due to both technological and economic forces.

Plant and corporate management must recognize and implement technology advances that will help to ensure increased plant efficiency and profitability.



Appendix I MFM Theory of Operation

The Correflow MFM combines the technologies of two previously patented measurement techniques (velocity and concentration) in a single sensor designed to achieve a measurement of mass flow. The first measurement determines the two-phase slurry velocity and the second measurement determines the fraction of one of the phases of the mixture in relation to the other.

Velocity measurement

As a non-conductive liquid or solid flows in a pipe, small amounts of charge are generated due to frictional electrification (also known as the triboelectric effect). These charges, formed during frictional contact between dissimilar materials, are not allowed to dissipate i.e., if the pipe is not grounded. A section of the sensor pipe is fabricated out of an insulating material and two sensitive ring electrodes are placed around the outside of the pipe at some set distance apart. As the accumulated charges in the liquid or solid pass through the electrodes, a small but measurable current is induced due to capacitive coupling. This induced current is amplified by sensitive electronics and then digitized using high-speed analog to digital converters. The result is a digitized waveform from each sensor.

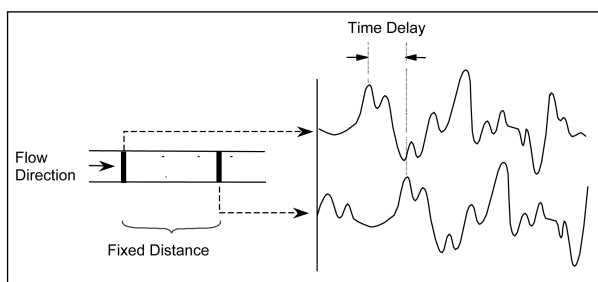


Figure 11: Correflow MFM velocity measurement

The measured waveforms at each sensor are similar in shape but shifted in time due to the time it takes a charged region to pass from the first to the second electrode. A time delay value can be determined mathematically in the microprocessor from these two signals. Thus, dividing the known ring sensor separation distance by the measured time delay yields the stream velocity. Please see Figure 11

Concentration measurement

The Correflow concentration measurement technique is based on the principle that each component of a two-phase system will have a different dielectric constant. In a mixture, the overall measured dielectric constant will fall somewhere between that of each of the pure phases through a known relationship. Thus measuring the dielectric constant of each phase (or by pre-calibrating the unit with known concentrations) enables the calculation of volume fraction for each component.

Correflow technology utilizes circumferential electrodes placed around the insulated pipe section (see Figure 12 below). The electric potential is driven from one electrode at a time and current is sensed at the opposite electrodes. The field is then electrically rotated to the next electrode through switching and the measurement is repeated. This process continues at high speed making several hundred equivalent revolutions per second. The entire pipe volume is effectively averaged resulting in an accurate overall dielectric constant measurement. The overall dielectric constant is then used to calculate the volume fraction of each component.

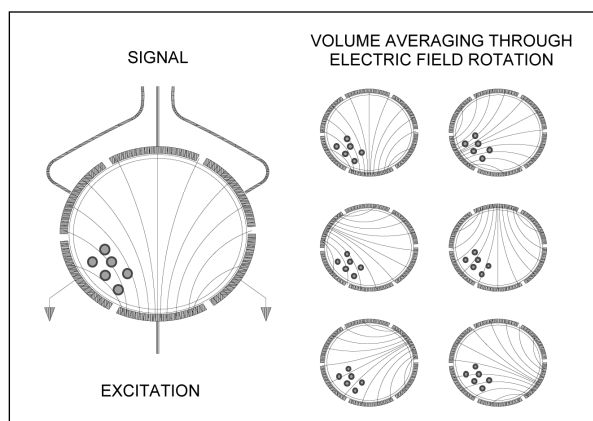


Figure 12: Correflow MFM solids measurement

The instantaneous mass flow can be integrated over many seconds or minutes to yield average mass flow. The average mass flow value has been quite useful in process control applications. As discussed previously, closed loop feedback control with the MFM has been extremely important for polymer reaction control.

The patented Correflow analyzer is ruggedized for the factory environment, fully automated and self-zeroing for unattended operation.

Appendix II ESM Theory of Operation

Triboelectric charging or frictional electrification, the transfer of charge as two materials contact or rub against each other, has long been known and has been characterized for many materials. The triboelectric phenomenon is complex and is a function of several mechanisms. Factors that contribute to the charge transfer between contacting materials include material work function, velocity, surface roughness, absorbed gasses (like moisture), particle concentration, size and pre-existing charge.

Electrostatic probes, first introduced many years ago were used to monitor particulate flows of all types in various industries and processes. The signal, which arises from the charge transferred to the probe by particulates impinging on the probe surface, is a function of several factors as indicated in the following equation:

$$i = \frac{kMv^n}{D} + QC \frac{M}{D^3}$$

Where:

i = triboelectric current

k = average constant unique to material

M = mass flow

D = average particle diameter

v = particle velocity

n = exponent unique to material (typically $n=2$)

Q = charge on contacting particles

C = unknown proportionality constant

Under many production conditions, such as in transfer lines, many of these factors are constant. Under such circumstances the signal will be proportional to concentration and may be used as a rough indication of flow. In applications like a fluidized bed reactor, the velocities are lower and thus discharge of pre-existing charge from particulate to the ESM probe surface will be the major contributor to the observed signal.

Sensitive measurements combined with an understanding of the mechanisms can yield important information as to how a PE process is performing and may be used to maintain proper reaction conditions and continuity.

Recent improvements in sensitivity, bandwidth, sensor construction and data processing now yield heretofore-unavailable information about the polyolefin PE polymerization process. This information is proving especially critical in new higher activity catalyst reactions.

The measured current is a function of the number of particulates contacting the probe per unit time and the charge per particle. If the dynamics of the reactor do not change significantly over time, then any change in monitored current can be assumed to be due to a change in the charge on the particles.

Since resistance from the ESM probe tip to ground is not critical, **progression's** probes are kept under 0.1 volts making it electrically similar to the grounded reactor wall as opposed to a high voltage foreign object in the reactor. This makes it safer for staff to work with as well. Secondly, the low voltage allows **progression** designed probes to have smaller and more robust insulator materials, which have proven to be more rugged for harsh reactor conditions.

Appendix III Magneflow Theory of Operation

The measurement of polymer properties is based on two fundamental properties of NMR:

- 1) The amplitude of the NMR signal is proportional to the quantity being measured.
- 2) The shape of the NMR signal is closely related to the morphology of the substance being measured.

The first property is the basis of most "benchtop" NMR systems, typically used in the food and agricultural industries (fat content measurements, oil in seeds, etc.) and the measurement of "spin finish" in the synthetic fiber industry.

The second property is of significance in the measurement of polyolefins, since polymer morphology is a fundamental important polymer property. Figure 13 shows the NMR signal of different polyethylene samples with different density values.

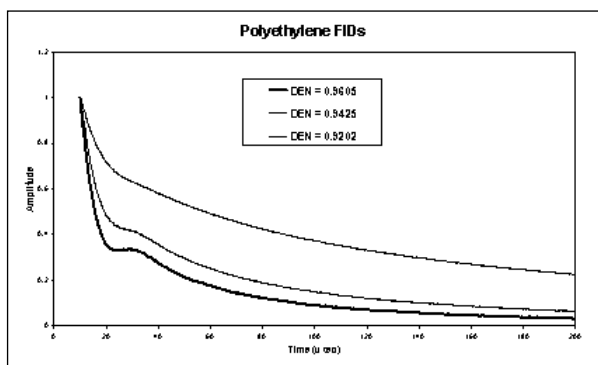


Figure 13

The shape of the NMR signal (known as a Free Induction Decay or FID), is very well understood in terms of how it reflects the morphology of the material. The NMR signals of crystalline material decay very fast, often in less than 20 microseconds. Amorphous material on the other hand, because of the more random and increased mobility of the molecules, decay much slower and in pure liquids can actually be several seconds long!

The analysis of low-resolution solid-state NMR signals is most efficiently performed using curve "deconvolution" or curvefitting techniques. NMR theorists have long known

that NMR signals of polyolefins can be resolved into three main components:

- 1) Fast Gaussian
- 2) Slow Gaussian
- 3) Exponential

These are shown below in Figure 14.

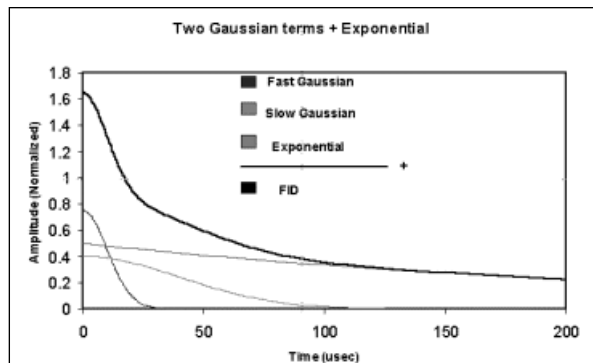


Figure 14: Typical polyethylene FID

The Fast Gaussian term represents the crystalline (isotactic) region of the polymer, whereas the exponential component reflects the amorphous (atactic) region. The slow Gaussian curve depicts what is commonly referred to as the "interfacial" region.

This mathematical technique thus converts the NMR signal "shape" into a set of numbers reflecting amplitudes and time constants which are then be used in calibration procedures.

Calibration Techniques

The most effective calibration technique to correlate the changes in the NMR signal shapes to standard laboratory measurement values is the use of multi-variate regression analysis. Of these, the technique of choice is that of chemometrics using the PLS (Partial Least Squares) method. It is essentially the use of advanced statistical analysis, in which all the input variables obtained from the NMR measurements, in this case the amplitudes and decay time constants of the individual curvefit components, are used in combinations so as to yield the most effective regression model, which is then used to predict resin properties of unknown samples.