Product Consistency and Manufacturing Flexibility Using Process NMR

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Introduction

In recent years, the polypropylene(PP) 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 PP manufacturers. This environment requires that PP manufacturers make efficiency improvements that will enable the profitable supply of specialized and commodity PP resins into the marketplace.

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

This presentation outlines the use of process NMR for the real-time direct analysis of multiple key PP resin properties. The use of process NMR is one opportunity for PP manufacturers that has demonstrated significant technical and commercial benefits to many production facilities.

The Application of Process NMR

Nuclear Magnetic Resonance (NMR) is a widely accepted technique as a powerful analytical tool in chemistry and the biological sciences and as a preferred imaging technique in medicine. It has also played an increasingly important role as a routine measurement technique in polyolefin process and quality control. The industrial use of low resolution NMR or Industrial Magnetic Resonance (IMR) for polyolefins was pioneered in 1989. Presently NMR is used for quality control in over 90% of the North American PP sites and close to 70% of the European PP plants. The more advanced PP manufacturers have taken this powerful and proven method beyond the QC lab and have applied the same NMR measurements to on-line process control. On-line process NMR systems provide critical process and product information in a reliable and timely manner. This emerging application of on-line process NMR is providing immense value to resin manufacturers and allowing significant efficiency improvements. Currently, 38% of all PP resins produced in North America are made using on-line process NMR. In Europe, over 20% of PP reactors will use on-line NMR by the end of this year. Newer markets such as in China, South America and the Middle East are also prime opportunities for this improved methodology.

The **progression, inc.** process NMR technology, Magneflow® has been applied to virtually all PP manufacturing process technologies. The analysis is fully automatic, non-destructive and can be performed on powders or pellets.

In PP applications, the Magneflow® system is used to measure chemical and physical properties such as solubles (xylene, decalin, heptane), ethylene content, rubber content, melt flow rate, flexmodulus and crystallinity.

In most applications, a small PP 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 1 below outlines where the Magneflow and sampling system would typically be interfaced to a PP plant.

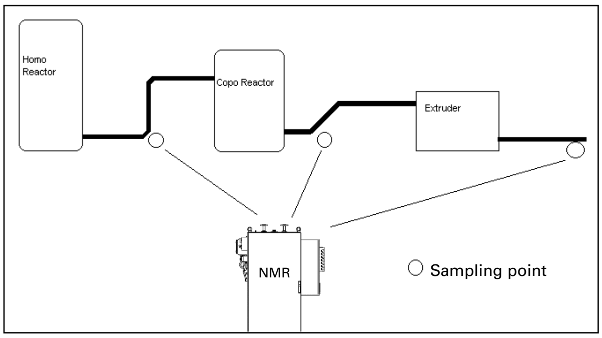


Figure 1

Improving Polypropylene Consistency

Global and regional competition in the polypropylene (PP) 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 PP resin consistency. Many customers have documented CpK improvements as a result of having on-line NMR analysis of resin properties. One example of such improvement in product consistency is shown below in Figure 2. The top trend shows the plant performance when using the wet chemistry XS analysis in the lab and SPC control. The bottom trend shows the plant's improved product consistency when using a Magneflow NMR system. The data were generated at the same facility with the same operators making the same resin grades.

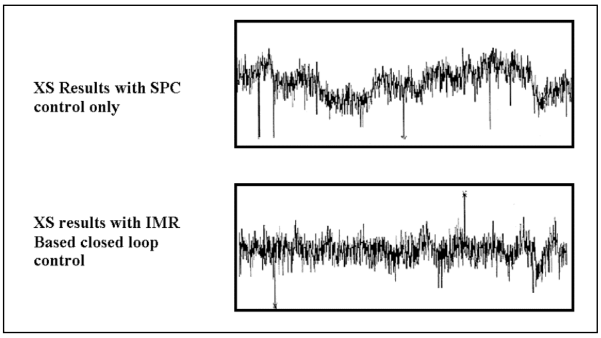


Figure 2

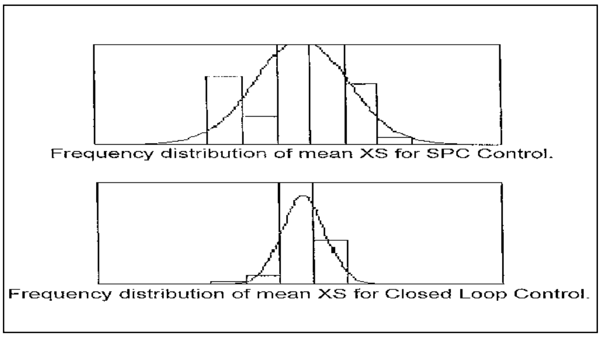


Figure 3

In Figure 3 one can see the significant reductions in XS variations from the use of closed loop process NMR. In this example, the NMR distribution is about 3 times better than the lab XS and SPC.

The NMR results shown in Figures 4 and 5 were collected from **progression** process NMR systems installed at commercial PP plants. The two sites are both producing similar PP products in the range of 3 – 4% XS.

The difference in the quality of the laboratory data between the plot in Figure 4 and the plot in Figure 5 is obvious. Since the Magneflow® system is calibrated using the laboratory data, it is important to use the best data possible during the Magneflow calibration process to insure that the on-line NMR performance is optimum.

What is most important is that in each case the on-line Magneflow data is a faster and a more reliable measurement of the PP xylene solubles. As a result, plant operators are able to make more consistent product during steady state conditions and respond instantly to any process variations.

Using the Magneflow on-line system further consistency improvement can be achieved when a plant produces the same resin grade over and over again. Since the Magneflow 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 Magneflow customers have used this information to confirm batch to batch consistency for critical end user applications.

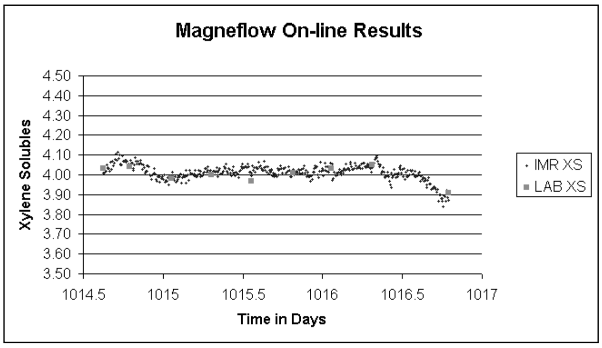


Figure 4

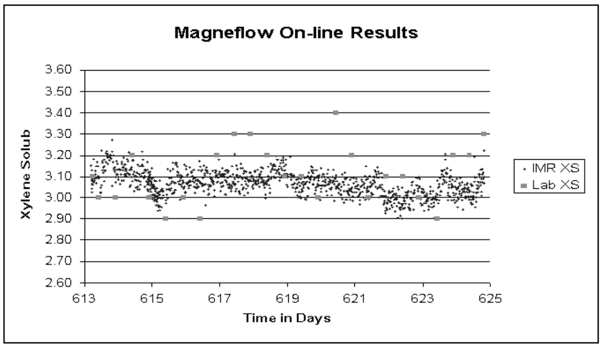


Figure 5

The data in in the following table demonstrates that the calibrated on-line Magneflow system provides better xylene solubles precision than the lab-wet chemistry. This is not surprising, given the difficulty of the wet chemistry tests and the operator dependence of the method. The faster feedback and the improved standard deviation are an ideal combination for better overall control of key resin quality parameters such as XS.

	Standard Deviation	
	Lab	**Magneflow**
Figure 4	0.10	0.040
Figure 5	0.14	0.058

Transition Control

With the move towards larger PP 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. PP 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 below clearly shows how clearly the process NMR system continuously reports the XS 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.

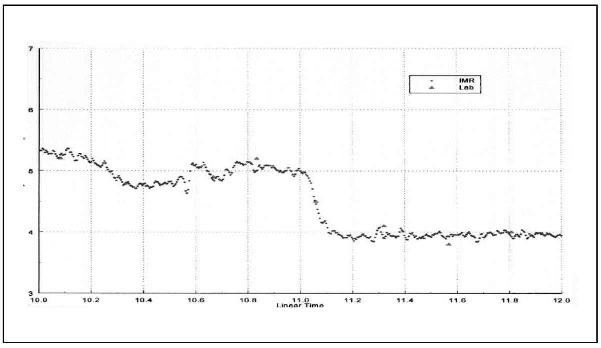


Figure 6

Simultaneous and Independent Analysis of Multiple Properties

One benefit of using on-line process NMR is that multiple resin properties can be determined from the same sample. An example of this is shown in the graphs below supplied by Basell Polyolefins from a copolymer plant with on-line process NMR analysis from **progression**.

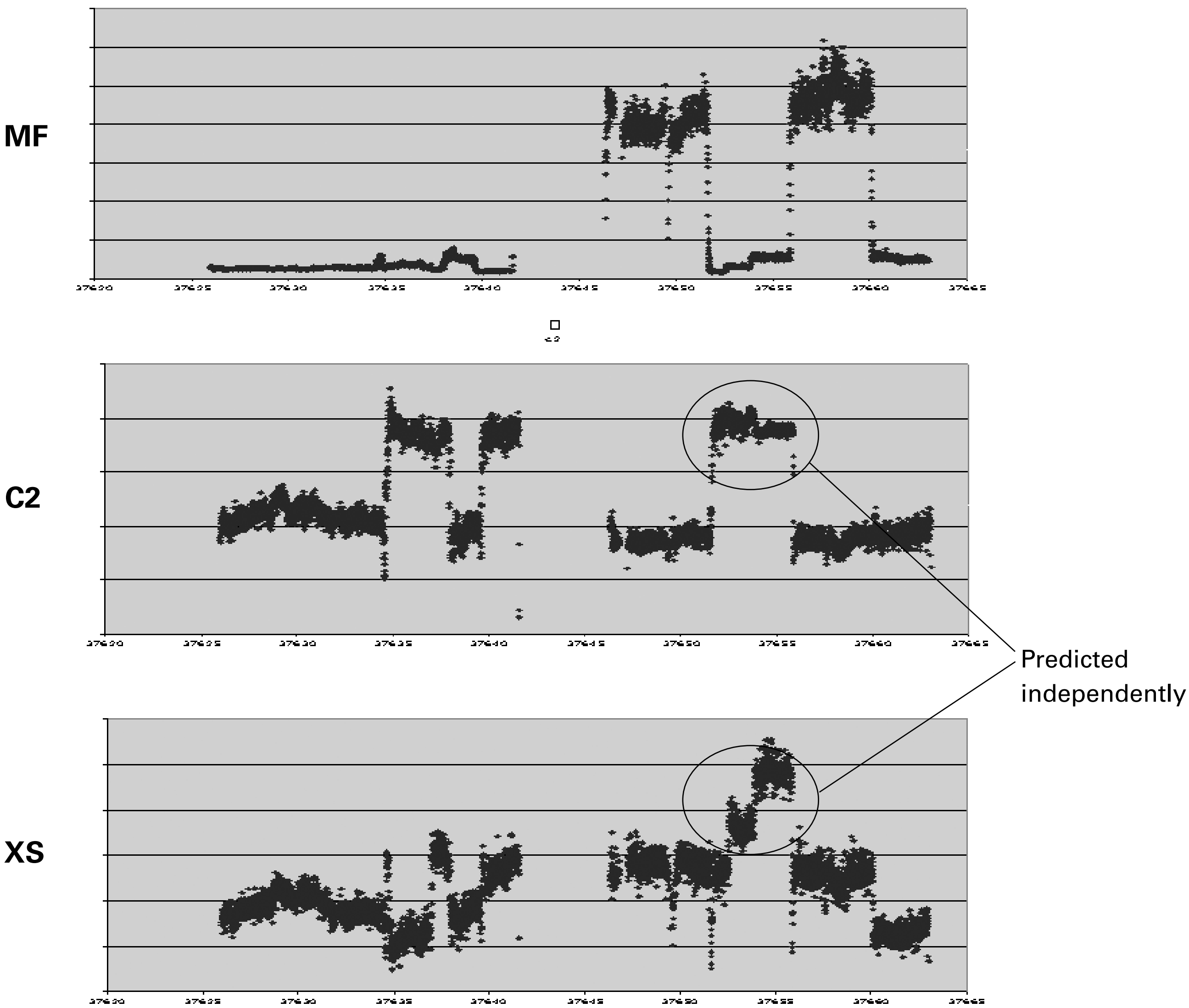
Independent predictions are performed for each parameter. Note the independent C2 and XS results as measured by the Magneflow® on-line NMR system. The financial benefit is multiplied in the cases when multiple parameters are measured with one single on-line process NMR system.

On-line NMR Benefits at Basell

- Provides XS, C2, and MFR every 10 minutes providing operators a clear view of the process
- “Invaluable” for detection of controller anomalies and upsets
- Reduced wet testing*
- Reduced solvent consumption (impacts HSE and cost)
- Reduced transition times
- Reduced off spec material
- Increased customer confidence in Basell

*shared benefit with at-line approach

basell
Polyolefins



The Magneflow® Process NMR System

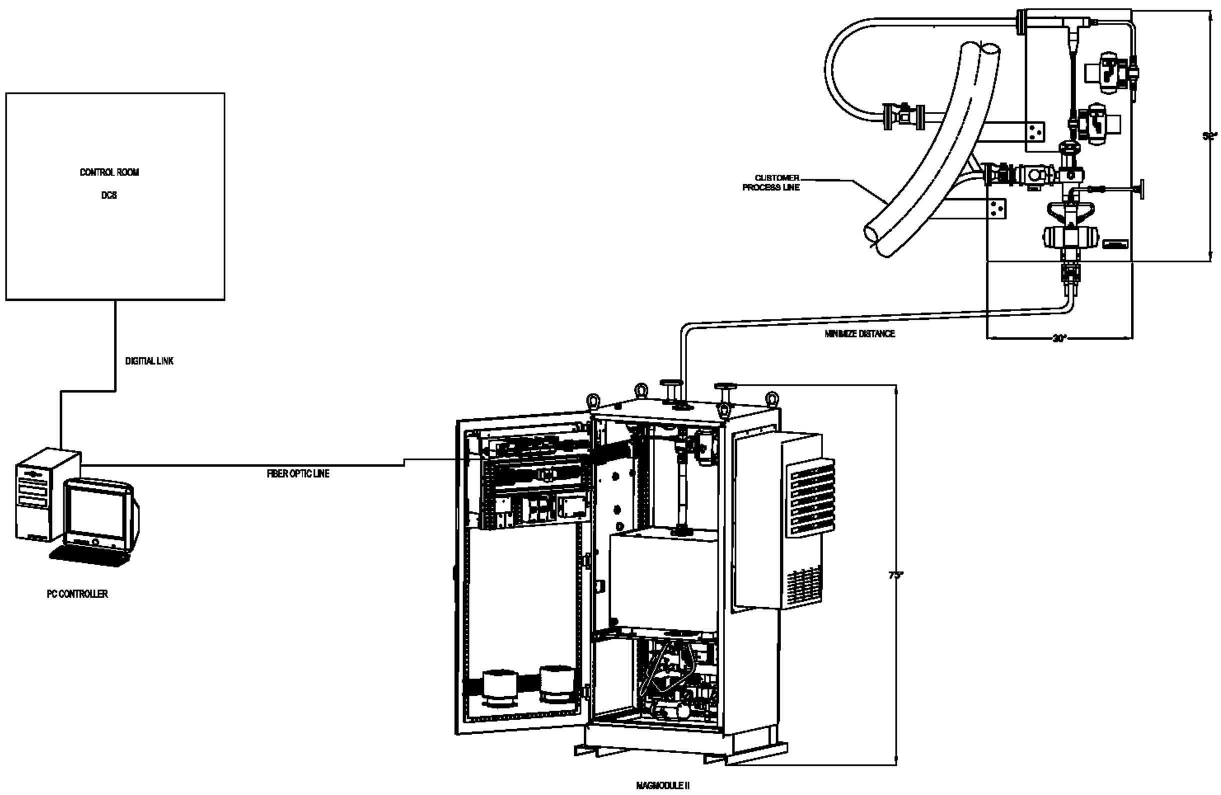
The Magneflow MagModule II system is the third generation on-line NMR technology. It represents significant advancement in the field of process NMR. The MagModule II system is 89% smaller than the previous MagModule systems. The system is fully approved for hazardous operation (ATEX) and is suited for nearly any climate. The MagModule II requires standard plant utilities (power, air, and N_2). Plant wire connections have been minimized by the use of fiber optics (two per system). The on-site installation and commissioning time can be completed in only five days. All Magneflow systems also offer a full remote service access via modem for optimum service, support coverage and flexibility.

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

Summary

Process NMR technology has provided tremendous benefits to PP manufacturing companies. The Magneflow NMR products from **progression** have a proven record of on-line and off-line analysis of key PP resin properties. The global use of process NMR continues to grow in PP manufacturing. The faster feedback provided by process NMR gives PP manufacturers added flexibility in transition control and inventory planning. With on-line determination of key resin properties, reduction of lab testing also results allowing better use of valuable plant staff.

The newly released Magneflow MagModule II from **progression** is an advanced process NMR system that provides cost-effective efficiency improvements to PP manufacturers.



APPENDIX I

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 A shows the NMR signal of different polypropylene samples with different XS (tacticity values).

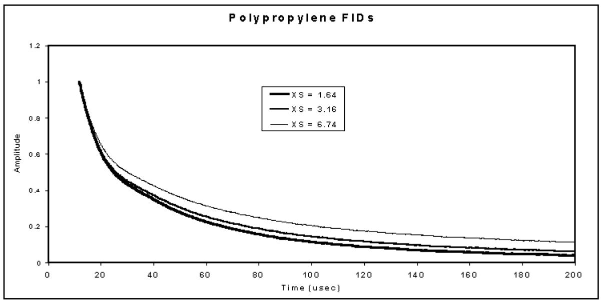


Figure A

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 then 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 B.

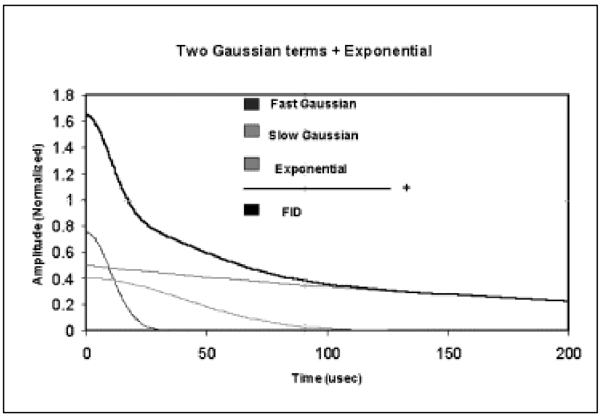


Figure B

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.