# ADVANCES IN DIRECT AND INFERENTIAL ANALYSIS FOR ONLINE PROCESS CONTROL AND OPTIMISATION IN THE PETROCHEMICAL INDUSTRY – A PERSPECTIVE

The petrochemicals industry makes and sells products with defined chemical composition. To assure the quality of these products and the processes used to create them, high resolution chemical analysis techniques are required. Within the domain of process analytics, this has been achieved through extensive deployment of chromatographic analysers, with other devices based on spectroscopies of different sorts growing in importance. Few techniques based on alternative measurement principles provide the sensitive and highly resolved on-line or in-line chemical analysis that is required for process control.

Advances that have or can be achieved in petrochemicals process analysis are primarily due to innovations in GC and spectrometry instrument design, or the application of sophisticated data analysis procedures, or the development of powerful modelling methods that allow inferential monitoring of processes.

### Innovations in analyser design and operation

Chromatography has been the mainstay of on-line process analysis in petrochemical plants for decades and has served the industry well. Although the fundamental use of gas chromatography has not changed, there have been useful advances in column technology and thermal conductivity detectors, miniaturisation of equipment, and the development of integrated and intelligent sampling and analysis systems.

It might be argued, however, that advances in spectroscopy instrumentation offer more interesting opportunities for process analysis. For example, developments in micro electromechanical systems have enabled construction of smaller and potentially lower cost instruments. Laser developments are helping advance process applications of mid-infrared (MIR) and Raman spectroscopies, and the range of wavelengths covered by tunable lasers has increased. Applications of Raman spectroscopy are also benefiting from instrument design innovations to improve the sensitivity of measurements whilst maintaining high spectral resolution. Mass spectrometry is also growing in importance in petrochemicals.

Two examples of advances in photonic based devices are single photon avalanche diodes (SPAD) detectors and quantum cascade lasers. The big advantage of SPAD detectors is that they provide time correlated single photon counting, which is good for stand-off imaging and low photon intensity applications. QML Technology Ltd, a spin-out company from Bristol University, has recently reported the monitoring of methane emissions using their single photon LIDAR imager [1]. The analyser combines tunable diode laser absorption spectroscopy in a light detection and ranging format, with time-correlated single photon counting to enable detection and ranging of methane concentrations at a relatively low laser power. It seems that methane leak rates of less than 0.1 gram per second can be detected at a range of up to 90 m.

The characteristics of SPAD detectors are also ideally suited to remote sensing by Raman spectroscopy, as illustrated by the Fraunhofer Centre for Applied Photonics (F-CAP) based at the Strathclyde university campus [2]. The growing interest in hydrogen as an alternative fuel means that sensitive detection of hydrogen leaks from tanks, pipelines and other infrastructure is important. The use of a time correlated SPAD device to detect Raman scattered photons gives information on the position of the molecules, their composition and their concentration (Figure 1). The analyser built at F-CAP allows simultaneous detection of hydrogen and two other molecules in air, water and nitrogen [2]. It has been shown that hydrogen concentrations below 0.1% can be detected at up to 35 meters, although it is believed that detection up to 100 metres is possible.

Returning to hydrocarbon analysis, the development of quantum cascade lasers has opened opportunities to replace chromatography with laser absorption spectrometry for some measurements. Two potential applications in ethylene production are the detection of acetylene breakthrough when cracking ethane, and compositional analysis at the fractionation tower to quantify low concentrations of impurity molecules in ethylene such as methane, C2 molecules, and carbon monoxide and dioxide [3]. Both these applications need fast analysis with low limits of detection, which quantum cascade laser absorption spectrometry can provide.

Another exciting application of quantum cascade lasers is in mid-infrared dual comb spectroscopy, which offers a number of potentially attractive features for process analysis. The spectrometer produced by IRsweep [4] uses two frequency comb QCLs which emit at many discrete wavelengths. The two combs have very slightly different line spacings, which allow heterodyne detection to be used to produce MIR absorbance measurements. The technique has a number of attributes; from the perspective of process analysis, it is the high power output of the source that is attractive, which means longer lengths of MIR optical fibre (e.g. 10 m to and from the process) can be used between the spectrometer and the in-line measurement probe [4]. The light sources in conventional MIR instruments normally only allow a couple of meters of fibre between the probe and spectrometer.

### Advances in multivariate data processing and modelling

Applications of near infrared hyperspectral imaging (HSI) are growing in importance. Although more widely applied in food analysis, interest in recycling plastics back to virgin monomer means that hyperspectral imaging is an option for high speed sorting of plastics. In HSI, material is scanned and image cubes comprising multiple spectra are produced. The challenges of high through-put process measurements are that a lot of images are generated, which require some pre-processing prior to analysis and the spectral information has to be combined with spatial data to produce comprehensive process models. These were the challenges that Puneet Mishra and Alison Nordon of the University of Strathclyde addressed through an EU Marie Curie funded project. They devised data analysis methods to de-noise spectra using Shearlet-based methods, optimised compression of the data, and combined spectral and visual information to improve modelling [5]. And they were able to automate these features for high through-put operations.

The perennial problem of calibration model transfer in quantitative process analysis is another area of data processing where recent advances can have a positive impact in the petrochemicals industry. Building effective multivariate calibration models for analysis of multi-component mixtures is time consuming and expensive. If a probe or analyser has to be replaced, the

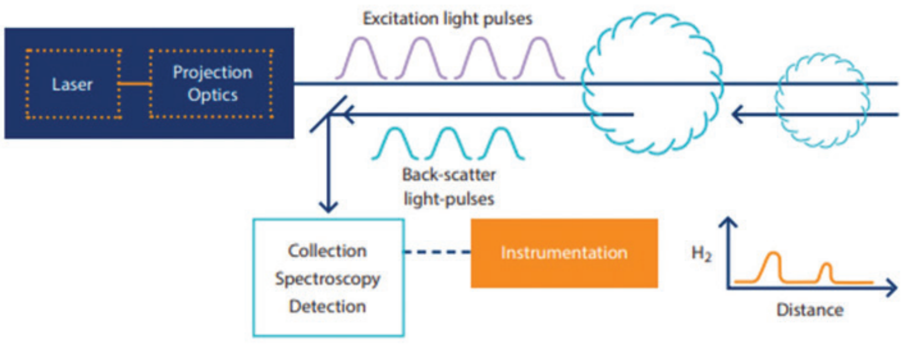


*Figure 1: Schematic representation of measurement of hydrogen concentration in air by time correlated Raman spectrometry (Fraunhofer Centre for Applied Photonics).*

*Table 1: Root mean square error (RMSE) for prediction of concentrations of mixed solvents using MIR ATR probes*

| | Reference Model built with 3 mm diameter MIR ATR probe | | |
|---|---|---|---|
| Test data obtained with | Acetone | Ethanol | Ethyl acetate |
| 3 mm probe | 3.7 | 3.0 | 1.1 |
| 12 mm probe | 78.4 | 103.0 | 45.5 |
| 12 mm probe using SST model transfer with scaling | 1.6 | 1.5 | 0.9 |

performance of the model may be affected requiring re-calibration, which is not desirable. In this situation mathematical approaches which compensate for instrumental changes are desirable. Research in CPACT led by Professor Zengping Chen at Hunan University has led to the development of improved methods for transfer of multivariate calibration models without the need for full re-calibration. One such method, Spectral Space Transformation (SST), eliminates spectral differences in the measured signals caused by a change in the instrumental set-up [6]. An example is transfer of a calibration model for analysis of a mixture of solvents when a change was required in the diameter of the mid-Infrared fibre optic probe used for in situ analysis. This is a problem that can be encountered when moving from a small to a large vessel such as from lab scale to pilot plant scale or to full scale manufacturing. The MIR probes use an attenuated total reflection (ATR) crystal to obtain a spectrum of the process mixture. When the diameter of the crystal is altered the spectrum changes, because the optical pathlength changes. This means that a multivariate calibration model built at small scale using a 3 mm diameter ATR probe cannot be use directly when making measurements in a larger vessel with a 12 mm diameter probe, as shown in Table 1 by the root mean square error (RMSE) values for the prediction of the solvent concentrations. SST solved this problem and was simpler and faster to apply than Piecewise Direct Standardisation, which requires additional iterative optimisation of the data window size to achieve optimal results.

## Soft-sensor inferential analysis

Why is this area of research important in process analysis? One of the main drivers is the difficulty of making direct real-time measurements of key attributes that affect product quality in many aspects of manufacturing in the process industries. Especially when off-line laboratory based analysis is too slow to provide adequate control of these processes.

If, however, the status of the processes can be inferred by modelling combinations of variables that can be measured, better control can often be achieved, avoiding the manufacture of off-specification products. More specifically, by modelling the relationship between a primary output and secondary outputs and inputs, estimates of a difficult to measure primary output can be generated at the frequency at which the easily measured variables are measured. If sufficiently accurate, the inferred states of primary outputs can then be used for automatic control and optimisation of the process.

Bootstrap aggregated models have proved useful for inferential analysis, but early successes have often been overlooked. One example from previous CPACT research involves the use of aggregated neural networks and partial least squares (PLS) models for inferential estimation of kerosene dry point under conditions when the feed crude oil changes [7]. In this situation, estimation of product quality by soft sensors becomes difficult because the relationship between process variables and product quality variables change when the crude changes. This required a two-step solution – to build an inferential model for each type of feed oil and use an on-line feed oil classifier to determine which model to apply. The on-line feed oil classifier was built using bootstrap aggregated neural networks, and bootstrap aggregated PLS regression models were developed for each feed oil. Sixteen measured process variables were used as inputs for the inferential estimation model. When tested on simulated and industrial data, it was

*Table 2: RMSE of industrial unseen validation data for single and bootstrap aggregated partial least squares models for different crude oils*

| | single | aggregated |
|---|---|---|
| Oil I | 1.08 | 1.02 |
| Oil II | 1.39 | 1.22 |
| Oil III | 1.08 | 0.95 |
| Oil IV | 1.56 | 1.14 |

shown that the procedure significantly improved the inferential estimation of the kerosene dry point. Table 2 shows that the root mean square error (RMSE) of industrial unseen validation data was lower for bootstrap aggregated PLS models for each specific oil type compared to the data for single PLS models. If estimations were made using a model built for a different crude oil, the RMSE values were 2-5 times higher than those in Table 2.

Another approach for quantitative parameter estimation is to combine mechanistic models based on physical and chemical knowledge of a process with data-based statistical models to create so-called hybrid models (Figure 2). CPACT researchers at Newcastle University did pioneering research in this area. An example concerns control of an industrial reactive distillation column used in the production of epichlorohydrin (EPI), which involves reaction of a mixture of alkaline agents and dichloropropanol isomers, with separation of the product through steam distillation [8]. The problem with this process is that there is an unwanted side reaction which should be minimised to improve the yield of the product. It was known that the amount of dissolved organic carbon (DOC) in the column bottom effluent was related to the side reaction, so the control strategy was to reduce production of DOC. Direct measure of DOC was difficult, but its level in the effluent was correlated with alkalinity. Maintaining the alkalinity at the optimum level was a way to achieve optimal production of EPI. The solution developed started with a simple mechanistic model (based on knowledge of material balances and the kinetics of the process), and then a recurrent neural network model was used to capture residuals from the mechanistic model's predictions of conversion of the reactants to the product. The hybrid model gave tighter control around the alkalinity set point which improved production of EPI; the standard deviation of the spread of alkalinity around the set point was reduced four-fold [8].

## Future trends and challenges

The traditional approach in petrochemicals process analysis is to locate chromatographic and other analysers in an analyser house or shed and pipe gases to the shelter. There are clearly advantages in moving some analyses to the process, but how viable and acceptable is a transition from on-line to in-line measurement within the industry? How well will innovations in photonics, for example, allow adoption of in–process measurements in an intrinsically safe manner? Such a transition from on-line to in-line analysis may be helped by the drive to build small, lower-cost and potentially faster analysers, but will they be capable of the chemical differentiation required for real-time control? Will deployment of multiple miniature analysers be necessary at the same location to provide collectively the required monitoring efficacy?

Then there is the challenge of making better use of the process data and the extent to which modelling data adds to process knowledge for better control. In particular, is there scope for wider use of soft sensors to augment chemical measurements or even replace some process analytics?

A big area are the heart of industrial digitisation is the trust that can be put on data, and quantifying the effects of the propagation of measurement uncertainties through a multi-step process. In this area, there is a need for universally applied digitisation standards and frameworks that ensure best practice is followed. So, is there consensus on what is required and if so, which organisation will produce the standards and framework?

And finally, there is the issue of maintaining the appropriate level of knowledge and expertise within the workforce. How do we make sure that those with the required subject knowledge are attracted into the industry; and that there is sufficient opportunity and commitment to upskill the existing workforce?

## Final comments

It is undeniable that timely provision of high quality analytical data is essential for safe and efficient operation of petrochemical and related processes.

However, there can be no doubt that energy and climate issues will increasingly dictate operational changes in the petrochemicals and related industries, which will bring new monitoring and control challenges.

Working in isolation is not an option in this respect and it will be important to encourage learning across industrial sectors, because many of the measurement and modelling challenges are similar. So cooperation is both sensible and probably essential.

This means that there is an ongoing need for communities of practice such as CPACT where analytical scientists and process engineers can be supported and where technical innovations can be devised and assessed.

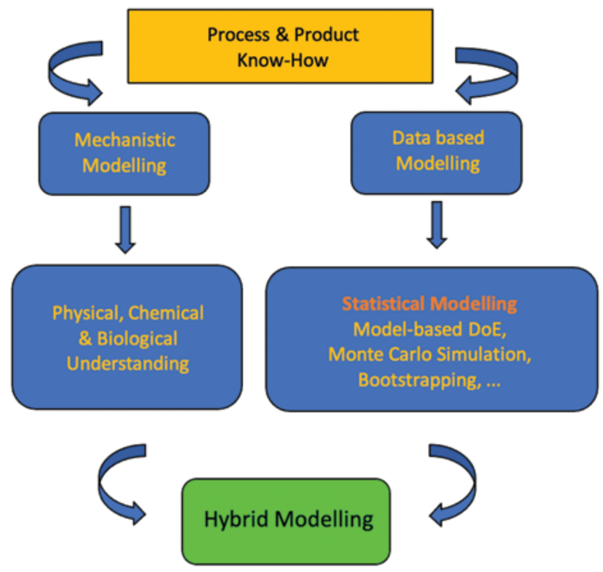


*Figure 2: Production of hybrid models by combining outputs from mechanistic and data based modelling*

## About CPACT

The Centre for Process Analytics and Control Technology (www.cpact.com) is the leading network for companies seeking advice and research on all areas of process performance monitoring and control. It was established in 1997 as an inter-disciplinary industry-university "community of practice" to promote the development and use of advanced process monitoring and control techniques.

The mission of CPACT is to enable the application of intelligent measurement and control technologies in the process industries through research, knowledge exchange and training. It supports scientists and engineers working in process analysis, chemometrics and statistics, and process modelling and control, through unique cross-sector cooperation. The current membership of 48 organisations worldwide includes: academic and research institutes, manufacturers in the petrochemical, chemical, pharmaceutical, biochemical, food and materials processing industries; analytical vendor companies; and control system solution providers.

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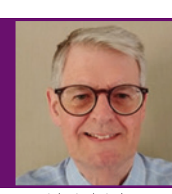
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