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Process Raman spectroscopy for the monitoring of distillations

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Introduction

Among the thermal separation processes, distillation has the longest tradition and has already been used to separate spirits (alcohols) from fermented food. Thanks to its driving force, the differences in vapour pressure of the components in question, adding thermal energy is already sufficient to achieve separation.

However, industrial distillations aim at maximising efficiency, throughput and yield, which in the past led to column designs that optimised the required phase contact between liquid trickling down and gas rising up the column. Packed columns have turned from Raschig rings into structured packings like the Sulzer MellapakPlus™, and trays have turned from sieve plates into designs with specific valves like Sulzer MVG™ (Figure 1).

Inline monitoring of distillations

Vibrational spectroscopies like infrared and Raman are well-established techniques for the analysis of mixtures. The comparably simple correlation between signal intensities and component concentrations gives access to mixture composition through a variety of chemometric analysis methods.

Typical fibre-optic immersion probes can easily be introduced even onto the trays of a column. Commonly, offline GC monitoring is used for distillation analysis. However, the required sampling is detrimental for the process equilibrium in these stages of the column.

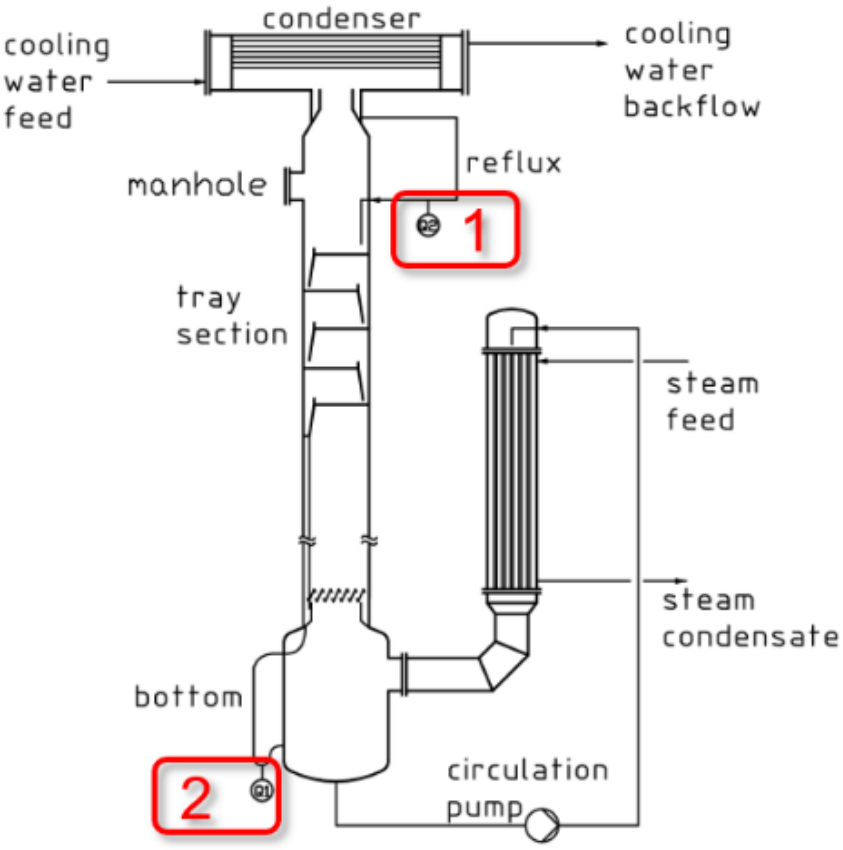

Fig. 2: Schematic drawing of the total reflux distillation with Raman probes at condenser (1) and boiler (2).

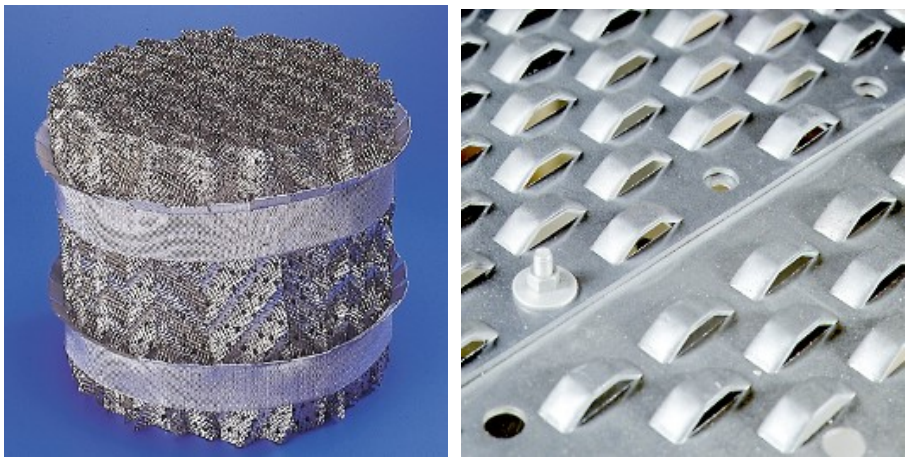

Fig. 1: Typical column packings and trays.

Spectroscopic measurements are fast compared to chromatography (seconds instead of minutes), which allows monitoring of dynamic operation phases in a column at a reasonable data resolution, e.g. start-up, shut-down, feed changes, and fraction changes.

In this contribution, we present two types of distillation processes that have been monitored with Raman spectroscopy:

a) the performance control of continuously operated columns in a process development and plant design stage and
b) the process monitoring of a batch distillation used for product purification.

Application 1:
Column performance monitoring

A continuously operated column that is operated at full reflux is a typical stage on distillation process design, since it can be operated in full thermodynamic equilibrium. Hence, it gives an indication of how good the thermal separation of a mixture can be under nearly ideal conditions.

Analyzer Installation

Two Raman probes for liquid measurements (WetHead™, ½" OD) were installed through packing gland connectors (Conax Technologies) into the reflux line from the condenser, and in the reflux from the lowest packing to the boiler. Both probes were connected to an ATEX-certified Raman Rxn 2™ analyser placed outside the hazardous area. As the analyser can operate up to four probes, two additional measurement points could be set up in other stages of the column.

For characterization of mass transfer equipment like packing or trays, some standard test mixtures are accepted and used worldwide. Sulzer's test columns are operated with chlorobenzene (CB) / ethylbenzene (EB) or cis-/trans-decaline. These components can be excellently distinguished by their Raman signature (Figure 3).

Spectra were recorded at 35 mW laser output power (ATEX conformity) with a total exposure time of 60 sec (12 x 5 sec) and a sampling frequency of 4 minutes.

Analysis

The spectra resulting from the inline measurements show the dynamic and stationary phases during the operation of the column (Figure 4).

Because of the distinct peaks of the components, a chemometric model based on Peak Integration (PI) and trained with few mixture samples measured at ambient temperature resulted in an accuracy of the prediction (RMSEP) around 0.5 %.

Process monitoring

The chemometric model was directly embedded into the data acquisition setup in Kaiser's HoloPro™ software by means of the PEAXACT Application Server. Thus, every Raman spectrum acquired was immediately transformed into concentration values for CB and EB. Concentration profiles from a typical load change experiment are displayed in Figure 5.

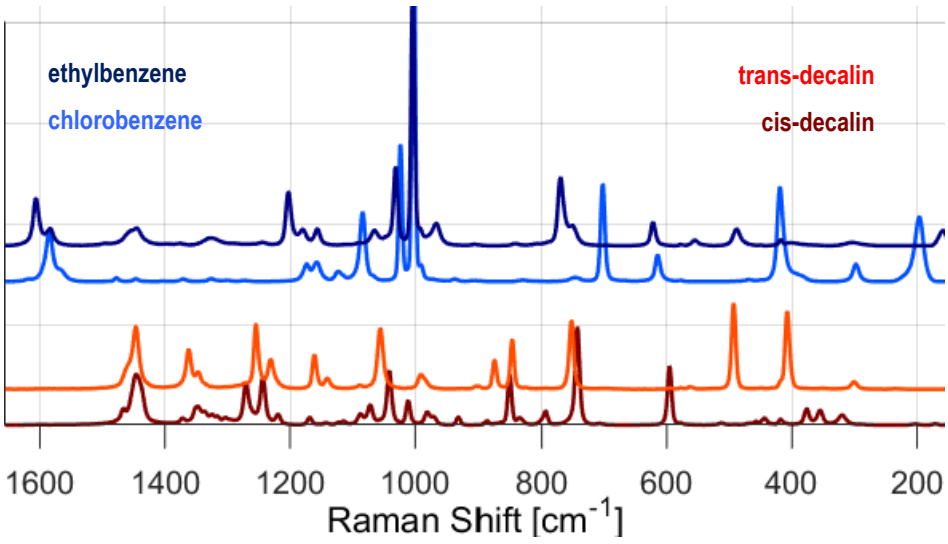

Fig. 3: Raman spectra of binary mixtures for characterising high-performance columns.

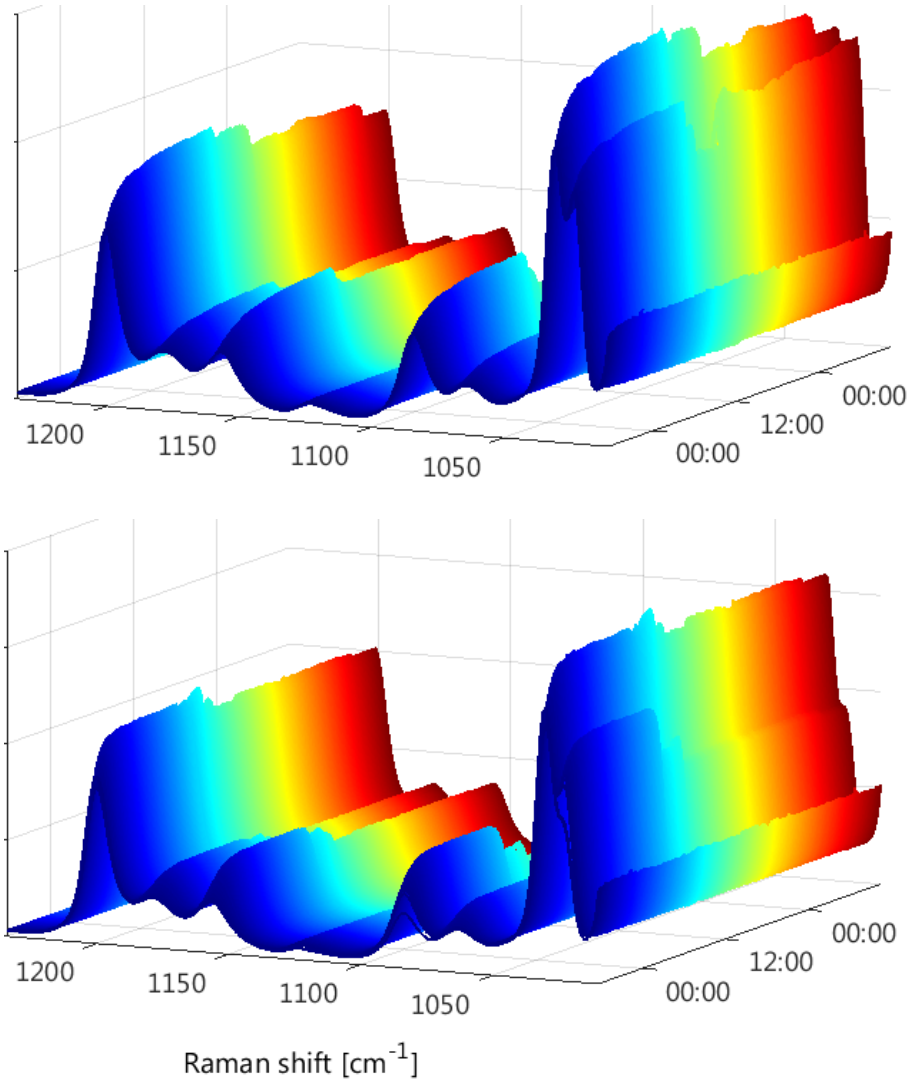

Fig. 4: Time profiles of Raman spectra in condenser (top) and boiler (bottom), operated with CB+EB mixtures.

The prediction in the steady operation states of the column is extremely robust and reproducible, helping to specify precisely the performance of the column and packing. The high resolution of the dynamic phases is remarkable and allows the prediction of start-up or load change behaviour, which are crucial

inputs for design and layout of the column. Both its precision and time resolution make process Raman spectroscopy a universal design tool for separation columns.

Application 2: Purification of a high-melting product in a batch distillation

AlzChem is a producer of high-melting highly functionalised organics which are often typically derived from pre-functionalised materials. Typical synthesis steps include the formation of CN, NH_2 or related moieties, inducing melting and boiling point increase in the product, but also favouring the formation of high-melting by-products from consecutive reactions.

Distillation under reduced pressure is therefore one of the key purification steps when it comes to removal of unreacted substrate and cleanup of the target product. Offline sampling from the hot condensate stream is challenging due to the elevated melting point, so an inline composition measurement is of interest.

The highest benefit is expected from the rapid detection of product change in the condensate, allowing an optimisation of the switching point between fractions without product losses or contamination.

Analyzer installation and configuration

The Raman analyzer installation is equivalent to the one described above. Two ½" WetHead™ probes are immersed into the process streams through packing gland connectors that are welded or screwed into standard process flanges. Measurement points are located in the external heating of the boiler and in the product transfer line behind the condenser (Figure 6).

In order to benefit from the excellent time resolution that is achievable with optical measurements, an exposure time of 10x 1 sec was used, so that for each measurement location a spectrum was recorded in a 30 seconds interval.

Process monitoring

From the spectra recorded in the condenser line an identification of the transfer points between the fractions is already visible without further chemometric analysis (Figure 7).

However, in order to define thresholds for the fraction changes, a quantitative analysis model is easily calculated based on peak integration of the characteristic product signal and one of the substrate signals available in the fingerprint region of the Raman spectrum.

A typical prediction of the fraction change phase shows that the critical phase of the transition takes less than 5 minutes, resolved in 10 predicted values (Figure 8).

The definition of a typical threshold concentration jump of 0.5 % allows an identification of the optimum fraction change with a precision of better than 1 minute. This minimises the contamination of the product with the side fractions and the need for further downstream purification.

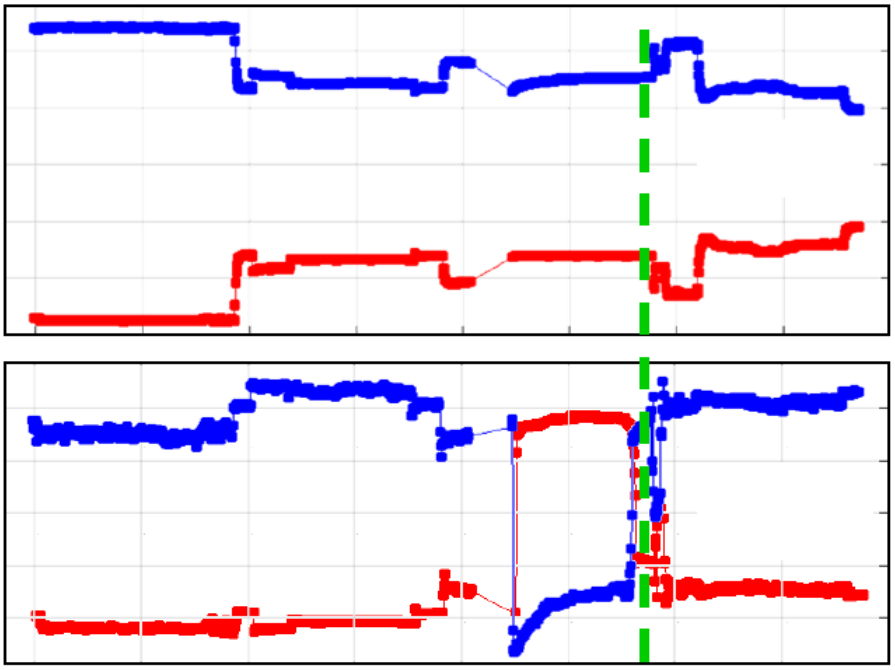

Fig. 5: Predicted EB (•) and CB (•) concentration profiles in condenser (top) and reflux to the boiler (bottom). The green line indicates a reduction of column pressure.

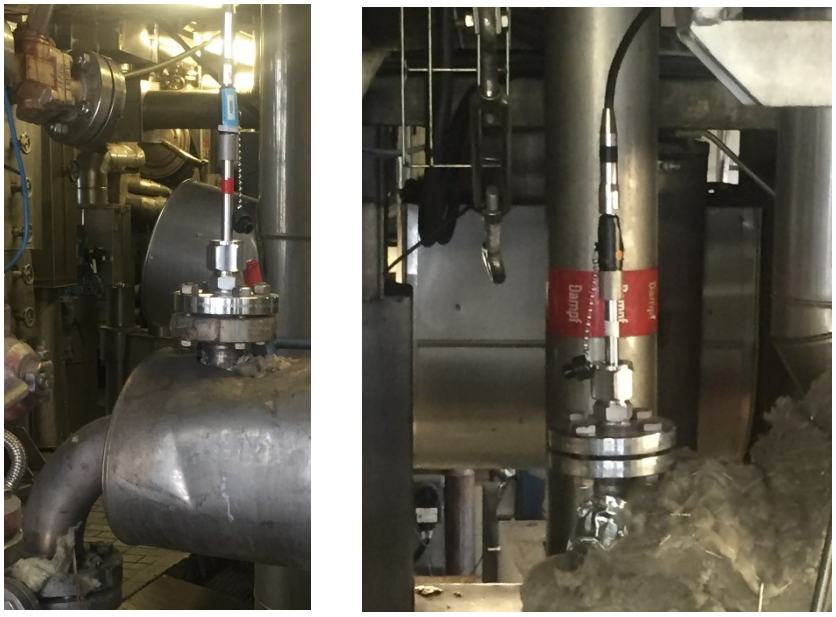

Fig. 6: Installation of the probes into transfer lines of the boiler and condenser of a batch distillation plant.

Summary

Process Raman spectroscopy has demonstrated its value in both continuous and batch distillations. Users of Process Raman spectroscopy profit from reduced energy input thanks to optimised column design and improved real-time operation control. Additionally, throughput can be increased, and higher purity is achieved in the target products. The high flexibility of a spectroscopic method combined with the achieved precision of predictions and the excellent time resolution are beneficial both for dynamic and steady-state operation of distillation columns.

Acknowledgments

Application 1 was developed at the Sulzer Chemtech pilot facilities in Winterthur (CH) for the team of I. Ausner, F. Kehrer and P. Schaeffer.

Application 2 was developed with the nitriles production team at AlzChem AG, Trostberg (DE). We thank A. Garnreiter and S. Putz for approval to publication.

S-PACT and Kaiser Optical Systems Inc., world's leader in Process Raman Analyzers and a 100% affiliate of Endress+Hauser, recently announced an alliance to serve customers with custom Raman Process Analyzers and Global Solutions for dedicated markets. By aligning the resources of S-PACT with Kaiser, new customers in new territories and industries can benefit from new process analytical solutions.

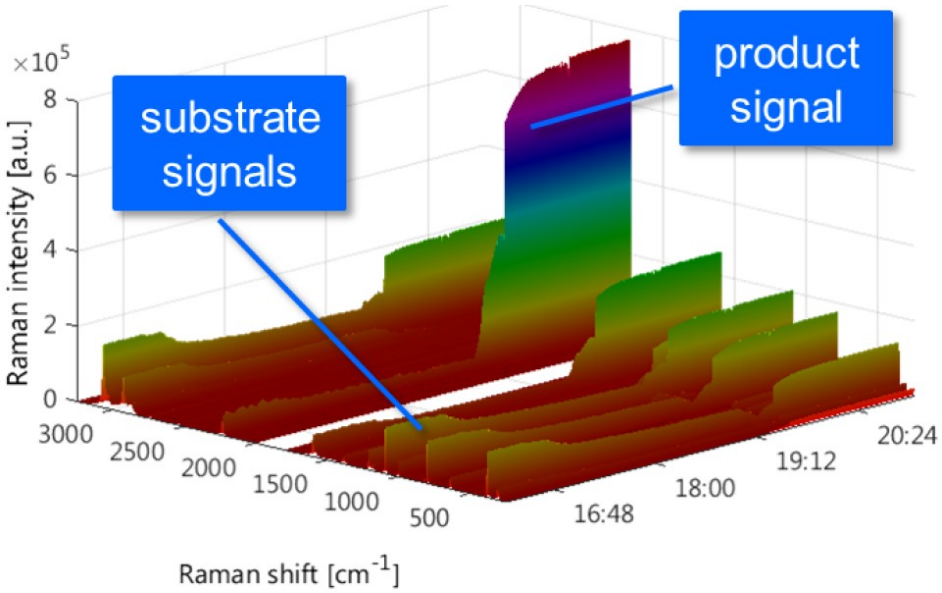

Fig. 7: Time profile of condenser spectra.

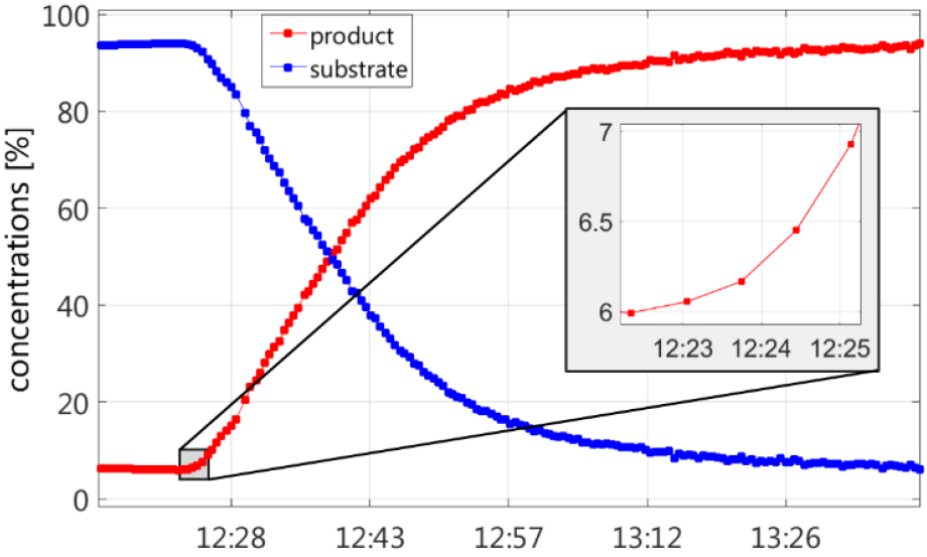

Fig. 8: Typical prediction profile for a fraction change in a batch distillation process.

Fig. 9: Raman analyser Kaiser Optical Systems, Inc.