Fourier transform near infrared application for advanced process control of an ethylene cracking plant

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Introduction

In the last 20 years, Fourier transform near infrared (FT-NIR) technology has been increasingly deployed for process and quality control applications. In particular, this technology is widely used for process control in the petrochemicals industry. The work described in this report, implementation of FT-NIR technology for the determination of virgin naphtha feed components, is part of a broader project in the area of Advanced Process Control (APC) for an ethylene cracker plant. To improve overall performance of the plant, APC requires the use of in-line analysers and the purpose of this work has been an evaluation of the use of an FT-NIR analyser. As a first step, this technique has been evaluated at-line in the control laboratory with the eventual goal of in-line implementation.

Ethylene is produced from virgin naphtha in steam cracking plants; the cracking furnaces are the most important process units within ethylene production plants. Thermal cracking reactions take place in the furnace and the valuable products produced are ethylene and propylene.

The pyrolysis, even though quite a complex phenomenon, can be defined as a dehydrogenation reaction involving simultaneous cleavage of carbon–carbon bonds of the organic radicals. These two basic reactions are endothermal so heat must be provided to facilitate the conversion. At high temperature, hydrocarbons became unstable and decompose into hydrogen, methane, olefins and aromatic compounds; side-products such as heavy aromatics and oils are also formed.

Given that the reactions are endothermic, pyrolysis is a process which consumes large amounts of energy. Process optimisation is therefore of fundamental importance in terms of achievable profit margins; advanced process control allows maximisation of the yield of ethylene and propylene at any given energy usage level.

The technology defined for the advanced process control system requires the use of the on-line SPYRO routine that needs, as input data, composition data for the feedstock (virgin naphtha). To obtain data on the 32 components required (Table 1), NIR technology was preferred over chromatographic analysis because it is faster and easier to implement in-line.

The layout of the APC (Figure 1) requires the use of SPYRO software. NIR-predicted composition is used as input data with a fixed tolerance (propylene : ethylene ratio). The most important output parameter of SPYRO is the Cracking Output Temperature (COT); once this is obtained, the APC is able to optimise the plant operating variables to keep the target set tolerance.

Figure 1. Operating diagram of the Advanced Process Control.

Instrumentation and methods

One hundred and seventy (170) samples of virgin naphtha were used to build the NIR models; 150 of these were used as a calibration set and 20 as a validation set. The PONA chromatographic method was used
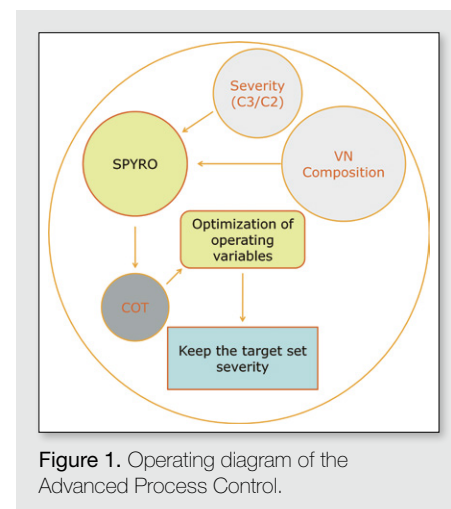
Table 1. Virgin naphtha components (n-32) to model by FT-NIR analysis

Component	Acronym	Component	Acronym
Benzene	BENZ	Naftenic pseudo compound 7	C7NAF
n-Pentane	NC5	Naftenic pseudo compound 8	C8NAF
i-Pentane	IC5	Naftenic pseudo compound 9	C9NAF
n-Hexane	NC6	i-Nonane	C9ISO
n-Heptane	NC7	i-Decane	C10ISO
n-Octane	NC8	Olefine C4–C7	OLE
Cyclohexane	CESAN	Xylenes	XYLO
i-Hexane	C6ISO	Ethylbenzene	EBENZ
i-Heptane	C7ISO	Alchyl aromatic pseudo compound 9	C9ARO
i-Octane	C8ISO	Naftenic pseudo compound 10	C10NAF
n-Butane	NBUTA	Alchyl aromatic pseudo compound 10	C10ARO
Toluene	TOLUO	i-Undecane	C11ISO
n-Nonane	NC9	Propane	C3H8
n-Decane	NC10	i-Butane	IBUTA
Cyclopentane	CPTAN	n-Undecane	NC11
Methyl cyclopentane	MCPTA	n-Dodecane	NC12

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Table 2. Calibration set (150 virgin naphta samples).

	P (w/w)	I (w/w)	O (w/w)	N (w/w)	A (w/w)
Max	48%	52%	5%	40%	15%
Min	12%	20%	0%	5%	1%

Table 3. Validation set (20 virgin naphta samples).

	P (w/w)	I (w/w)	O (w/w)	N (w/w)	A (w/w)
Max	36%	48%	4%	32%	15%
Min	18%	29%	0%	13%	5%

as the primary analytical method for all samples.

Tables 2 and 3 show the compositional range of the calibration and validation sets broken down into the relevant, different chemical families: **P**araffins, **I**so-paraffins, **N**aphthenes, **A**romatic compounds and **O**lefins.

For spectral acquisition, a Bruker Matrix-F instrument was used (Figure 2). This is a NIR spectrometer designed for use in an industrial setting and so does not contain a sample compartment but rather a multiplexer for six optical fibre connections. For sample analysis, the instrument was equipped with an external sample compartment connected to the spectrometer by a long (2 m) optical fibre.

Sample spectra were acquired in vials (8 mm of external diameter) with an optical path of 5 mm; every sample involved three replicate measurements, rotating the vial 120° before each acquisition, so as to minimise the effect of non-uniform vial diameter on the spectra. Spectra were collected at room temperature, at 8 cm^{-1} resolution over the spectral range between 4500 cm^{-1} and 12,000 cm^{-1}; 16 spectra

were developed using a PLS algorithm; different spectra pre-treatments and different spectral ranges were used for different measured parameters. For most of the calibration models, first derivative transformation followed by multiplicative scattering correction was used as a pre-treatment. For the paraffin models, spectral ranges between 9000 cm^{-1} and 8000 cm^{-1} (corresponding to the second overtone region of C–H stretching) and between 7500 cm^{-1} and 6500 cm^{-1} (second combination region) were mainly used (Figure 3).
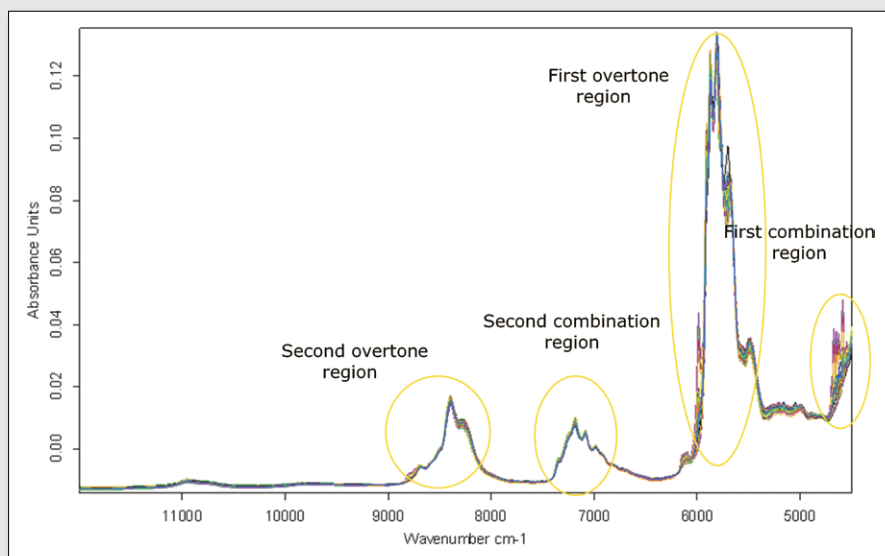

Figure 3. Virgin naphta spectra used for the calibrations.

Figure 2. (a) Bruker Matrix-F equipped with a 2 m optical fibre to connect (b) the external sample compartment.

were recorded and averaged before chemometric manipulation.

Results and discussion
Using the Bruker software (OPUS/QUANT), calibrations for each of the 32 components

To model aromatic components, the first overtone region (6200–5300 cm^{-1}) and the first combination region (5000–4500 cm^{-1}) were used instead.

Table 4 contains some details of Benzene and *i*-Heptane calibrations, i.e. the actual number of samples used (less than 150 on account of reference analysis difficulties for some samples), the number of factors in the model, the root mean square error in cross-validation (*RMSECV*) and the confidence limit at 95% calculated according to ASTM D1655-05 using the following formula:

$$\sigma = t \cdot RMSEE \cdot \sqrt{(1+D)}$$

where Student *t* defines the confidence level for different degrees of freedom in each system, *RMSEE* is the calibration error and *D* is the Mahalanobis distance for the calibration model.

For validation of the models, 20 new samples of virgin naphtha were used and
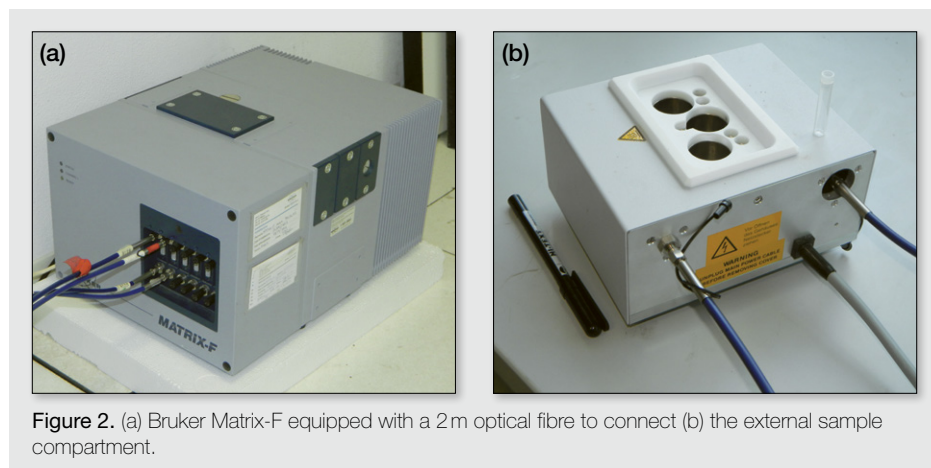
Table 4. Example of results obtained with the calibration set.

Component	Number of samples	Number of factors	*RMSECV* (%)	Confidence limit (95%)
BENZ	131	10	0.05	0.12
C7ISO	138	18	0.84	1.45

Table 5. Example of results obtained with the validation set.

Component	*RMSEP*	Confidence limit (95%)	% Error
BENZ	0.13	0.12	7.0%
C7ISO	1.71	1.45	28.1%

the root mean square error in validation has been compared to the confidence limit calculated from the calibration models.

For some models, such as C7ISO listed in Table 5, a high percentage error (calculated as the ratio between the *RMSEP* and the average value of the component in the validation set) was found, but for this kind of application the classical way for the validation of chemometric models is not the most appropriate. To compare NIR models with the chromatographic primary method, NIR-predicted values and chromatographic values are used as input data for the SPYRO software and then the differences of the SPYRO output data are evaluated. In this way, it may be observed that SPYRO provides output data very similar to those when NIR or chromatographic values are used as input data, in spite of the high percentage error of some models.

Concentration values of the 32 components for the 20 virgin naphtha samples in the validation set are provided as input data to SPYRO and then the root mean square

error for the output components of the simulation software (propylene, ethylene, FOK etc.) are evaluated.

Conclusion

The NIR-PLS calibration models for the 32 components of virgin naphtha can be considered as excellent for the application addressed in this report, i.e. using the NIR prediction values as input data for the kinetic simulation software of a virgin naphtha pyrolysis. In Figure 4, it is clear that the ethylene and propylene yields calculated by SPYRO with NIR and GC input data separately are perfectly comparable.
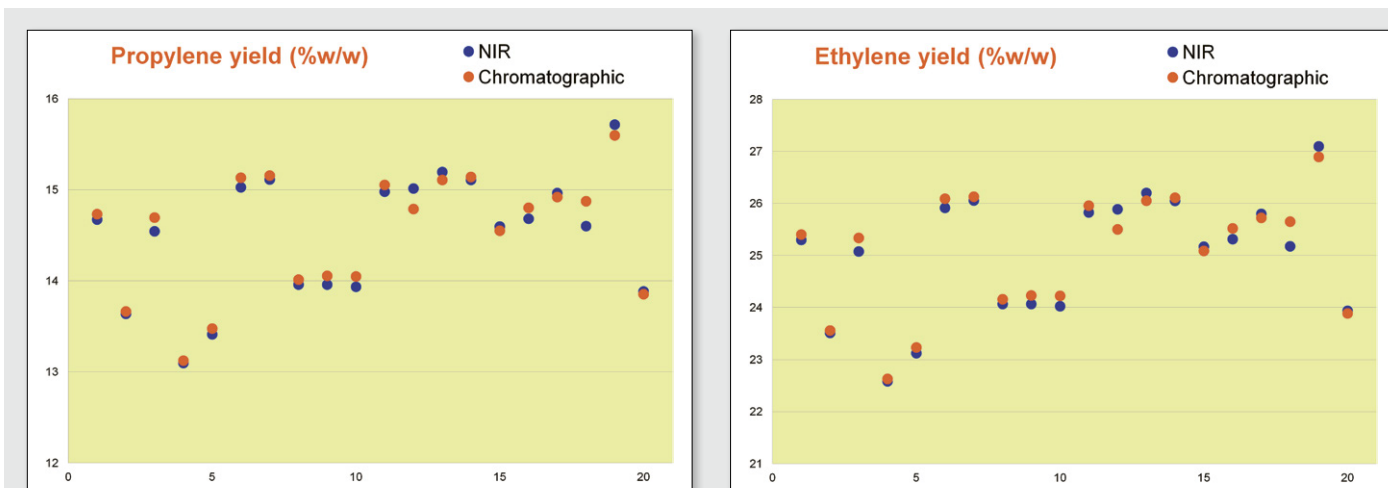
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Table 6. Root mean square error for the SPYRO output components using the NIR and GC analytical values of the 20 virgin naphtha validation set samples as input data.

Component	RMSEP (NIR/GC)
COT (°C)	0.86
Hydrogen	0.01
Methane	0.15
Acetylene	0.01
Ethylene	0.19
Ethane	0.05
C_3H_4	0.01
Propylene	0.11
Propane	0.03
Butadiene	0.03
Buteni+Butani	0.08
Others mix C4	0.00
Sum C5 s	0.07
Benzene	0.09
Toluene	0.11
ETB XIL ST	0.09
BCP	0.15
FOK	0.15
LOSSES	0.00

Figure 4. Propylene and ethylene yield comparisons using NIR and GC analytical data as SPYRO input data.