Réjane Dastillung and Marc Loublier, Naphtachimie, France and B. Descales, J.R. Llinas, I. Cermelli and S. Destang, Ineos Technologies, France and D. Lambert, C. St Martin, M. Sanchez, B. Ribero and Z. Yu, Topnir Systems, France, explore steam cracker optimisation through online analysis and rigorous kinetic models.

Near infrared (NIR) spectroscopy is now a well established technology for the indirect measurement of hydrocarbon streams composition and properties. From the earlier works and patents in the late 1980s,[1-6] several industrial applications have been derived and implemented, mostly in the refining area but also in steam cracking plants. Here, it allowed the implementation of a full feed forward and predictive control of the furnaces using real time NIR analysers for the liquid feeds, whilst GC analysers did not provide such accurate and fast response time analysis. Recently, new works[12-15] showed the growing interest in this technology applied to olefins plants. Whilst Raman spectroscopy did not provide the same calibration performance,[14] mid infrared has also been used[13] and delivered good results at lab scale.

Another option to use online NIR analysis for real time optimisation of the furnaces was proposed by Timmermans and col.[11] NIR is used here to analyse the gaseous effluent from furnace coils outlet.

At Lavera, the steam cracker at Naphtachimie (a 50/50 subsidiary of Ineos Olefins and Total Petrochemicals) is the first in the world to be equipped with an online Topnir™ analysis of naphtha feedstock. The 26 furnaces of the plant produce more

than 740 000 tpy of ethylene. The naphtha represents between 70 and 95% of the whole feedstock of the plant.[1] Between 1991 and 2003, these furnaces were controlled by an in house online process control model, which was using 13 naphtha properties provided by Topnir online analyser to adjust in real time the furnaces' operating conditions.[7 - 10]

Since 2003, a new process control scheme, including SPYRO®[16] and a full online optimiser, has been installed and is also using the Topnir analysis results to control and optimise the whole plant.

Due to the high level of accuracy of Topnir analysis linked to SPYRO performances, the optimisation of steam cracker operations allows a substantial induced benefit in the range of US$ 1 - 2 million/y.

General principle

The system is composed of two parts. The first part is a sampling conditioning unit, which is devoted to prepare the sample for analysis in terms of filtration, water removal and temperature control. The second part includes the spectrometer and the measurement cell; these elements are linked together with optical fibres. The analyser scheme of this application is illustrated in Figure 1.

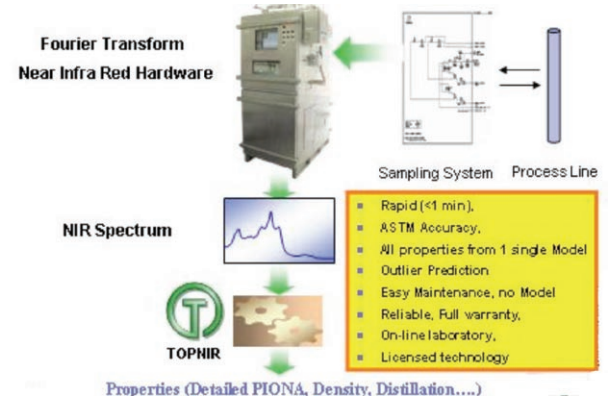

Figure 1. Topnir online analysis scheme.

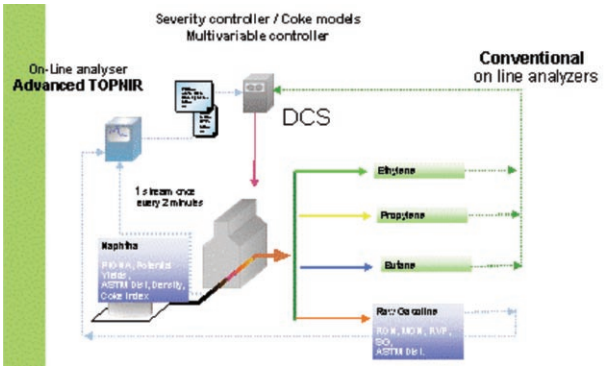

Figure 2. General scheme of Topnir application steam cracker.

In less than one minute this analyser displays approximately 75 key properties of naphtha including detailed hydrocarbon analysis (DHA) as required by SPYRO (more than 50 components ranging from C4 - C11).

The naphtha property vector is sent to the online process optimiser. This optimiser pushes the plant towards its identified constraints and adjusts in real time the operating conditions of all the furnaces according to the quality of the feeds as shown in Figure 2.

Moreover, the decoking scheduling of furnace radiation tubes and transfer line exchanger (TLE) is done through the coking index delivered by the Topnir analysis, which is specific of a given naphtha feedstock. This coking index is used to predict the coking rate of radiation tubes and TLE and therefore the skin temperature.

Online NIR analysis

The determination of product properties from the NIR spectra requires models to quantify the relationships between these spectra and the properties gathered in a databank.

These models are generally developed through regressional methods (multilinear regression, PLS, etc.) These methods, based on a least squares criteria, are easy to use to calibrate the property models, but contain some hidden numerical traps when the model has to be used in extrapolation for new samples. Moreover, they require developing and validating one model per property.

Concerning the treatment of unknown samples (outliers), the regressional techniques require a very heavy amount of work to maintain the models. It can rapidly become a bottleneck when the application involves a lot of properties, everyone requiring a specific calibration treatment. Indeed, it is mainly true in this naphtha feedstock application as more than 75 properties are required to be analysed every minute and therefore it would rapidly become a bottleneck to maintain approximately 75 calibration models.

Topnir delivers in less than one minute the full vector of properties from a single reference database (i.e. a single model) and takes into account immediately any outlier thanks to its extrapolation capabilities. Moreover, it does not require any update of the model due to its self learning character, and provides the full set of properties from a single model and results in very light maintenance.[6]

Users have the capability to update the model by adding new samples into the reference databank. As mentioned, this update is automatic after a new sample introduction in the calibration database. Indeed, model update is easy through the 'Add sample' facility to update the database.

As Topnir uses only a reference database to predict and calculate the properties of samples, the update of the application is easily done just by adding a new sample to the database, both with NIR Spectra and conventional analysis.

Topnir is really a self learning method with simple sample addition to the database avoiding the necessity of remodelling. As soon as the

Table 1. Comparision between GC and TOPNIR results accuracy

Properties	Standard deviation TOPNIR	Reproducibility TOPNIR 95% level confidence	Reproducibility GC	Standard deviation GC
CPC2	0.037	0.072	0.39	0.2
%LIN	0.2	0.39	0.88	0.45
%ISO	0.18	0.35	0.98	0.5
%NAPHT	0.13	0.25	1.57	0.8
%ARO	0.15	0.3	0.98	0.5
%BENZ	0.15	0.3	0.78	0.4
Density	0.0002	0.0004	0.0039	0.002

Table 2. Impach of DHA error of prediction on yield calculation

Naphtha names	NAB126		NAL129		ELS032		NAA223	
Analysis method	GC	NIR	GC	NIR	GC	NIR	GC	NIR
Detailed hydrocarbon analysis								
C4 Lin	0.62	0.4	0.8	0.84	1.2	1.22	0.2	0.24
C4 Iso	0	0	0.1	0.12	0.2	0.24	0	0.02
C4 Olef	0	0	0	0.05	0	0.01	0	0.04
C5 Lin	3.93	3.32	8.8	8.75	16.49	16.58	3.07	3.05
C6 Lin	5.69	5.53	7.2	7.26	8.77	8.82	4.13	4.12
C7 Lin	6	7.54	6	5.98	5.43	5.43	6.07	6.01
C8 Lin	5.38	5.83	5.3	5.29	3.68	3.65	6.22	6.22
C9 Lin	3.73	2.31	3.1	3.12	2.3	2.29	3.44	3.43
C10 Lin	0.83	0	2	2.04	0.96	0.99	0.16	0.18
C11 Lin	0	0	0.6	0.63	0.15	0.18	0	0.02
C5 Iso	3.52	2.31	5.6	5.59	11.28	11.22	1.9	1.93
C6 Iso	6	5.13	8	7.96	10.02	9.97	3.93	3.95
C7 Iso	5.9	8.54	6.2	6.15	6.17	6.14	5.88	5.87
C8 Iso	6.42	8.04	5.74	5.71	5	5.11	8.66	8.62
C9 Iso	5.9	6.43	4.01	4.02	3.09	3.09	6.65	6.60
C10 Iso	3.11	0.8	2.5	2.53	2.08	2.09	1.21	1.23
C11 Iso	0	0	0	0.06	0	0.01	0	0.06
C5 Nap	0.83	0.6	0.7	0.71	0.66	0.67	0.32	0.32
C6 Nap	6.63	6.43	4.2	4.16	2.98	2.92	4.09	4.08
C7 Nap	8.9	9.95	8.5	8.46	5.38	5.33	14.04	13.91
C8 Nap	7.66	9.15	4.81	4.81	3.65	3.67	11.72	11.60
C9 Nap	6.11	5.63	2.9	2.89	2.07	2.10	8.01	7.99
C10 Nap	1.45	0.3	2.04	2.03	1.29	1.34	0.93	0.96
C11 Nap	0	0	0	0.01	0	0.05	0	0.02
C6Aro	2.69	2.61	0.9	0.89	0.66	0.61	0.57	0.06
C7 Aro	3.31	3.92	2.6	2.57	1.71	1.68	2.86	2.88
C8 Aro	5.38	5.23	7.4	7.35	4.77	4.52	5.94	5.93
C9 Aro	0	0	0	0.06	0	0.04	0	0.05
C10 Aro	0	0	0	0.02	0	0.03	0	0.04
C11 Aro	0	0	0	0.06	0	0.05	0	0.06
C5 Olef	0	0	0	0	0	0	0	0
C6 Olef	0	0	0	0	0	0	0	0
C7 Olef	0	0	0	0	0	0	0	0
C8 Olef	0	0	0	0	0	0	0	0
C9 Olef	0	0	0	0	0	0	0	0
C10 Olef	0	0	0	0	0	0	0	0
C11 Olef	0	0	0	0	0	0	0	0
Operating condistions								
Feed rate te/hr/furnace	13.2	13.2	13.2	13.2	13.2	13.2	13.2	13.2
Feed rate te/hr/coil (4 coils/furnace)	3.3	3.3	3.3	3.3	3.3	3.3	3.3	3.3
Steam ratio	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3
CET (˚C)	804.8	804.8	805	805	805	805	805	805

sample is added, Topnir takes it into account. No specific end user expertise is required; model maintenance is very easy through simple sample addition to the database. No remodelling is required.

Concerning the naphtha quality determination, the following parameters are measured simultaneously with the online analyser: density, detailed hydrocarbon analysis (DHA) from C4 - C11, average molecular weight, potential yields in methane (CpC1), ethylene (CpC2), propylene (CpC3) and C4 unsaturated compounds (CpC4) and coking index. Those last properties, the potential contents and coking index, are in house specific parameters, which were defined at Lavera in the 1970s to better characterise the feeds.[2]

The potential yields represent the ability for naphtha to produce, for instance, ethylene under standard conditions. They were determined from the gas chromatography (GC) analysis combined with micro pyrolysis tests carried out on pure compounds.

The DHA gathers the percentage of linear, isoparaffinic, naphthenic, olefins and aromatic compounds by carbon number. The potential yields are not used more frequently by SPYRO but have been maintained to provide the operator with a single marker of naphtha quality. An in house coking model that is also interfaced with the online optimiser uses the coking index. All of these parameters are measured every minute and transferred to the process control computer.

The accuracy of property measurements is perfectly in line with the reference ASTM methods for classical properties having standardised measurements as shown in Table 1. For DHA analysis where there is no ASTM reference method, it has been proven that even the maximum deviation observed on DHA prediction does not impact significantly with SPYRO predictions on plant yields. This is highlighted in Table 2, where it was calculated cracking yield patterns by running SPYRO using both GC analysis and Topnir prediction for the naphtha (Reference Name NAB126) that exhibited the largest differences between GC and Topnir predictions.

Table 2 also shows the comparison with GC analysis of typical results obtained from Topnir predictions (reference names NAL129, ELS032 and NAA223). It can be seen that Topnir results are excellent in terms of minimising the difference between the GC conventional methods and therefore fits very well with the requirement of accuracy from process control.

Other sets of properties, for instance the ASTM distillation curve, can also be predicted on naphtha. This method is also valid for other types of feeds such as condensates or gas oils.

Process control scheme

The process control scheme involves several layers of optimisation involving a dynamic matrix controller (DMC) linked with the composite linear programme (CLP) and topped with an online optimiser.

The online real time optimiser (RTO), runs every two hours at steady periods to determine global optimised plant parameters such as severity, coil outlet temperature (COT), steam ratio, and so on.

Several DMCs control the different parts of the cracker plant through the targets calculated from the optimiser. There is also an intermediate optimisation layer, running permanently and checking that the constraints are fulfilled and able to take the corrective action in case some freedom is available. This intermediate optimiser, called composite LP, allows the feed throughput to be pushed at the optimum level for all the furnaces and makes sure that the plant is at maximum capacity.

Regarding the system arrangement, there are 36 DMC controllers for the furnaces and 6 DMCs for the cold separation section.

The online optimiser gathers 48 rigorous thermodynamic and mass balance sub models optimising 110 variables (e.g. furnaces flow rate and coil exit temperature, column reflux, reboiling, trays temperatures, recycling stream etc.) by using 4.000 DCS tags as well as 3.300 limits/constraints.

SPYRO yield prediction is used by the RTO tool. The second use of SPYRO is to act as a virtual severity analyser for the furnace control by the DMCs. Feedstock properties predictions from Topnir are used by SPYRO to give the associated yield patterns. The overall process control and optimisation scheme is displayed in Figure 3.

CE pressure (bar a)	1.6	1.6	1.6	1.6	1.6	1.6	1.6	1.6
Product yields (%) predictions								
Hydrogen	0.64	0.64	0.64	0.64	0.64	0.65	0.68	0.68
Methane	11.97	11.98	12.61	12.6	13.59	13.62	12.49	12.47
Ethane	4.6	4.56	4.75	4.74	5.28	5.29	4.33	4.32
Ethylene	19.33	19.23	29.87	29.85	21.92	21.96	19.39	19.37
Acetylene	0.12	0.12	0.14	0.14	0.15	0.15	0.14	0.14
Propane	0.6	0.6	0.61	0.61	0.68	0.68	0.57	0.57
Propylene	15.22	15.08	15.95	15.94	17.19	17.23	14.79	14.76
MAPD	0.29	0.29	0.33	0.33	0.36	0.36	0.31	0.31
nButane	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
iButane	0.24	0.17	0.05	0.05	0.06	0.06	0.05	0.05
nButenes	3.19	3.16	3.36	3.37	3.71	3.72	3.06	3.08
iButene	2.58	2.52	2.64	2.65	3.09	3.11	2.45	2.46
Butadiene	4.25	4.27	4.15	4.17	3.98	4.02	4.56	4.58
nPentane								
Benzene	6.54	6.62	4.84	4.86	4.09	4	5.92	5.95
Other gasoline	25.43	25.74	24.34	24.34	21.81	21.72	26.27	26.25
Fuel oil	4.98	5.02	4.7	4.7	3.42	3.41	5	4.99

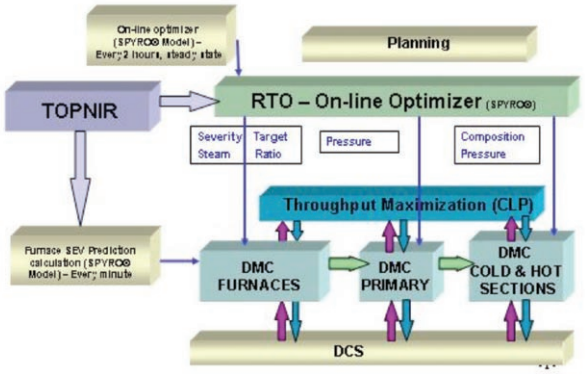

Figure 3. Naphtachimie overall process control and optimisation scheme.

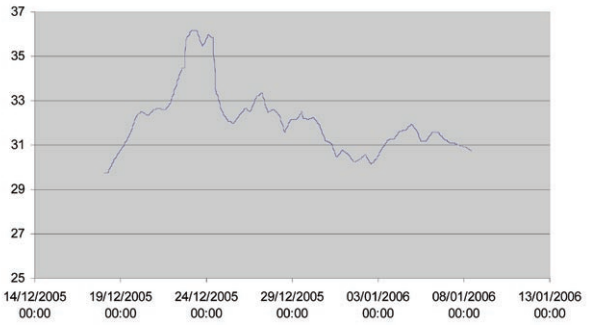

Figure 4. Naphtha feed transition in terms of percentage linear hydrocarbons.

Advantages and benefits

In the oil and gas industry, naphtha quality variations are common and depend on the spot market imports as well as on naphthas coming from an upstream refinery. Such rapid feed transitions, as shown in Figure 4, gather the quality variations of naphtha over several days. It can be observed day after day as a continuous evolution of naphtha quality, which would result in significant changes of yields without continuous adaptation of plant operating conditions, by the process control.

With a classical offline analysis, such changes could not be detected rapidly, which means a deoptimisation during the transition leading to a loss of production. The online Topnir analysis allows the user to react in real time and to adjust, through the optimisation loop, the furnace outlet temperatures and flow rates on the plant to take into consideration the new feed quality.

The order of magnitude of profit maximisation by severity optimisation is s € 1000/d per 0.01 severity point. This is the result of simulations and actual measurements. It varies with price structure, naphtha quality stability and so on.

A NIR analyser failure leads to approximately 0.03 - 0.04 severity points shift, which induces a loss of € 3000/d. Thus, the benefit, based on naphtha transition optimisation, is approximately US$ 1 - 2 million/y within a standard economical situation in terms of ethylene price. Such a benefit allows a very rapid pay back on the analyser investment. An additional and important benefit lies also in the stabilisation of distillation towers downstream of the furnaces as well as in the saturation of plant constraints.

Moreover, there is a great advantage in favour of a full characterisation of feeds allowing the full advantage of SPYRO rigorous kinetic model to be experienced16 beside those direct benefits on naphtha transition safety improvements in terms of plant operations while keeping maintenance cost at the minimum like a conventional standard analyser should be mentioned.

Online Topnir analysis has been running satisfactory for 14 years with in house process control models and four years with SPYRO and online optimiser with a reliability factor above 95%.

Conclusion

Online Topnir analysis of steam cracker feed quality allows the user to adjust, in real time, the Naphtachimie steam cracker plant operating conditions. It is of particular importance for the plant to have various sources of naphtha, monitoring of feed transitions and optimisation is of a major economical interest leading to an annual benefit of approximately US$ 1 - 2 million.

The non-linear and self learning models ensure both robustness and reliability of the analysis and are particularly suitable for industrial online applications. Indeed, the maintenance of the application is very light as there is no requirement for dozens of calibration models due to the Topology Topnir approach.

The association of online analysis with the online optimisation ensure maximum benefits from the data by adjusting in real time the set points of the steam cracker plant. Moreover, beyond every optimisation, the NIR online analyser is now a very useful tool for the operators to help with daily operations. This analyser is also considered as an essential 'watchdog' to detect any change in the cracker feedstock properties.

Notes

This application is the result of a collaborative work carried out for Naphtachimie by a team involving Naphtachimie, Ineos and Topnir™ Systems. The Lavera Steam Cracker Topnir technology application was implemented on the Lavera steam cracker unit in 1991. These NIR and Topnir technologies are patented worldwide[3 - 6] and are commercialised through Topnir Systems.

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