Process analytics in the refining sector: a role for FT-IR

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It is perhaps not widely acknowledged, how very different the process analytical context and culture is in the refining industry, as compared, for example, with speciality chemicals. Almost all refineries have been extensive users of on-line process analytics since very early in their history—and the analytical platforms used have therefore been well-adapted to the refinery environment. The applications tend to be concentrated in on-line gas chromatographs (GCs) and on-line physical property analysers, such as density meters, distillation analysers, cloud and flash point analysers etc. For this reason, when approaching the potential possibility for an on-line spectroscopy-based process analytical solution, the context and direction is likely to be from an on-line analyser, process engineering and unit optimisation perspective, as opposed to, for example, a laboratory, R&D led approach. These expectations, in terms of analyser packaging, demonstrable short-term return-on-investment, analyser uptime percentages in the high nineties, and validated accuracies fully compliant with ASTM or similar requirements, are translated directly into the specifications for process FT-IR in the refinery.

Process analytical FT-IR applications in refineries cover a wide range of different processes, including distillation units, conversion units and final product blend optimisation. However, in an economic climate where despite rising crude oil costs, refining margins have improved significantly, and look set to be maintained, driven by increased global light fuel demand, then the most advantageous applications of process FT-IR in refining will tend to focus on high bbl/day (barrels per calendar day) units.

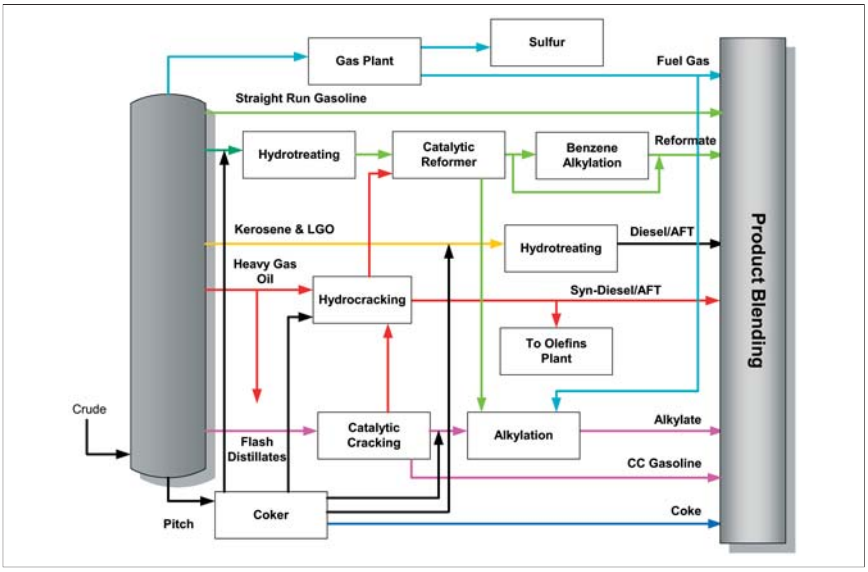

Figure 1. Refinery process stream schematic.

Traditionally this has emphasised the role of process FT-IR in high-value final product optimisation applications, gasoline and gasoil product blending. However, the highest volume units on most refineries are those for crude distillation, and on petrochemical plants for naphtha cracking. This range of analytical applications implies quite a wide variety of packaged analyser solutions—there is no "one-size-fits-all" technology solution in refinery process FT-IR. There needs to be a flexible adaption to the demands both of the site, the application and (perhaps most significantly) the potential ROI for a given process unit.

It may be helpful to start by considering some of the characteristics of refinery process streams:

- Refinery streams, unit feeds, unit rundowns and blended product are remarkably complex hydrocarbon mixtures, but they are (at least in the medium term) at equilibrium. The goals of refinery process analytics are rapid unit feed and rundown characterisation to achieve unit optimisation. There is rarely or never a need for in-reactor analysis. It is clear (given the range of boiling points for refinery streams) that there may be a need for analysis at temperatures ranging from ambient to well over 100°C, but this is purely to achieve correct sample flow characteristics.
- Samples from refinery streams are normally very regularly captured for laboratory analysis using well-established methodologies. These laboratory methods may be slow, they may have questionable repeatability, but they are the *de facto* criterion for product release. As such they form the basis for on-line process analyser validation, and also provide, fortuitously, a rich background of analyti-

cal information for chemometric model development.

- In marked contrast to the chemicals sector, the key product quality criteria for most refinery process streams are not straightforward chemical component concentrations. Indeed for some applications, the traditional GC-based methodology is weak, precisely because it is a separation-based technique, better suited to discrete component measurements. For even a relatively simple refinery unit feed stream such as naphtha, there are at least 50 to 60 discrete components present at above trace levels. Collective and bulk properties, such as octane, boiling point, viscosity or cold-filter plugging point, although obscure, are of far greater significance in unit optimisation than n-C12 vol%.

Refinery process streams, whether feeds or rundowns, are normally flowing in pipes from which sample take-offs can easily be arranged, and to which samples can normally be returned into a pump suction. Thus (and this is also emphasised by the GC analyser history) extractive sampling into a fastloop sample conditioning system is the accepted norm in the refinery context, and for good reason. It allows for appropriate sample flow control, filtration to remove particulates and water if hydrophobic self-cleaning filter membranes are used, and finally exact temperature control of the sample is very easily achieved. However, this does not imply only one fixed analyser configuration. Indeed there are roles in FT-IR-based refinery process analytics for a range of analyser formats including integrated units located in a full specification analyser shelter, field-mounted units located close to sample take-offs to limit fastloop run lengths, and also fibre-optic based units allowing for discrete sample flow cells per stream where the application requires a variety of sample temperatures for different streams.

The choice of appropriate process FT-IR analyser format will be governed by a number of factors, which will include:

- The sample temperature required for good sample flow. If this is significantly higher than ambient, then long fastloop runs are undesirable, and either field-mounted or fibre-optic based analyser formats are preferred.
- If the application involves final product blend characterisation, then it is very likely that an analyser shelter will in any case be present or required for additional, non-FT-IR analysers. Moreover, the blender is a high bbl/day unit with significant added value, so the added burden of a shelter will not significantly effect ROI. For other process streams, particularly conversion unit rundowns, then the FT-IR analyser may be a unique opportunity to provide rapid data for on-line optimisation, and a field-mounted unit without an analyser shelter allows faster ROI.
- Where the application involves streams with very different densities (for example CDU rundown streams ranging from light naphtha to heavy gasoil), stream switching between streams over a wide density range is better avoided, and fibre-optic extractive systems with discrete cells per stream allow this option.
- Some process streams, for example the HF acid recycle stream in an HF alkylation unit, require to be treated in a particular way for safety reasons. Here specialised metallurgy, complex safety interlocks and remote fibre-optic sample cell formats are necessary.
- In other cases, for example crude blend assay and CDU feed analysis, specialised extractive fastloop sample systems are required with multi-stage temperature control and backflush filtration, to achieve a sample in optimum condition for FT-IR analysis.

When all of these various aspects are properly considered, process analytical FT-IR for refineries offers very specific advantages. It is a multi-stream, multi-property, rapid, low-maintenance on-line analytical technique, providing exactly the type of fast analytical response required for on-line process unit optimisation schemes. If correctly implemented, validated and monitored, it has been shown capable when installed on high added value refinery processes to yield multi-million dollar ROI year on year.

Table 1. Example Analyser Applications

Process unit	Stream	Analyser format	Properties
Crude distillation	Feed	Fieldmount, extractive	TBP, TAN, density
Crude distillation	Rundowns	Shelter, F-optic, Extractive (local)	ASTM D86, PINA, CP, FP, Aro%
Naphtha cracker	Feed	Fieldmount, extractive	PINA, C-number, ASTM D86
Reformer unit	Feed & rundown	Fieldmount, extractive	PINA, RON, Aro%, Bnz%
Alkylation unit	HF acid recycle	Shelter, F-optic, Extractive (remote)	HF%, water%, ASO%
Alkylation unit	iC4 recycle etc.	Shelter, F-optic, Extractive (remote)	iC4%, nC4/C3 ratio
Gasoil hydrotreating unit	Rundown	Fieldmount, extractive	Cetane, Aro%, ASTM D86
FCC gasoline hydrotreating unit	Rundown	Fieldmount, extractive	RON, ASTM D86
Gasoil blender	Feed & rundown	Shelter, extractive	Cetane, Aro%, ASTM D86, CP, PP etc.
Gasoline blender	Feed & rundown	Shelter, extractive	RON, MON, ASTM D86, Bnz% etc.