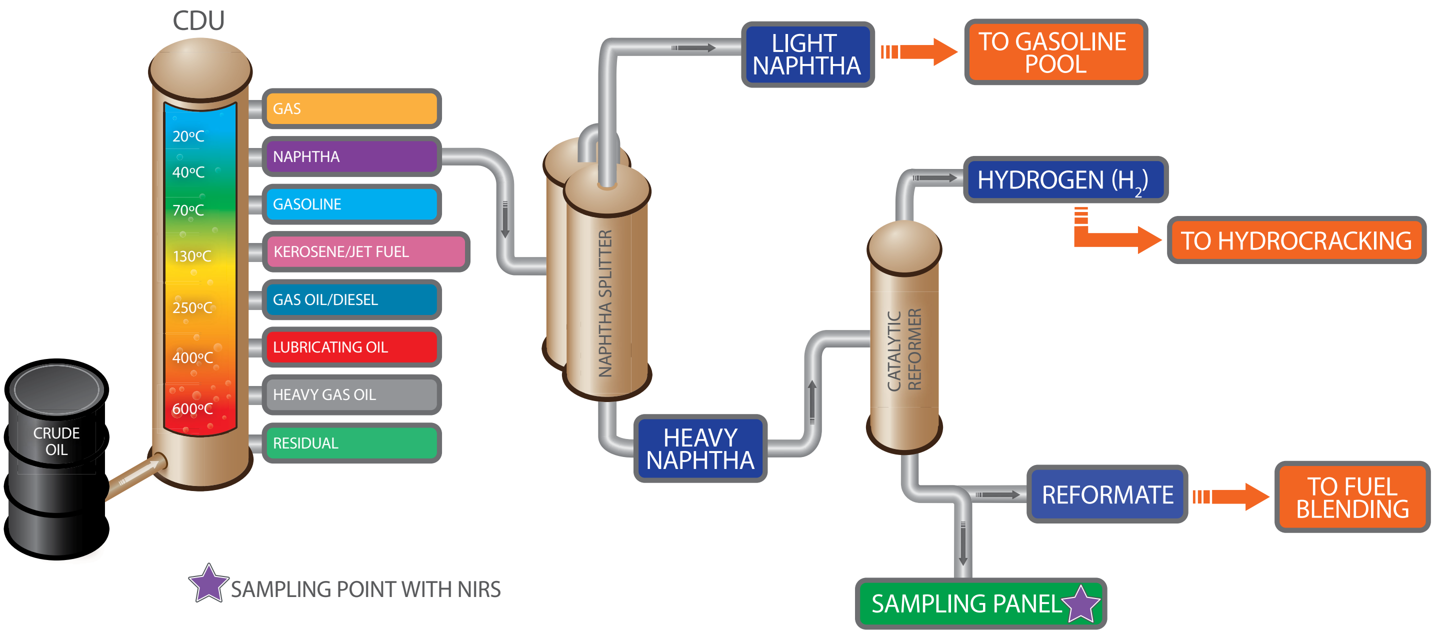
Online process monitoring of octane number during catalytic reforming by NIRS following ASTM D2699 and ASTM D2700

The octane number is a key parameter measured in the petrochemical refining process which indicates the performance of commercial fuels (*e.g.* gasoline and jet fuels). It determines the tendency of the fuel to resist auto-igniting in the engine during combustion (knock resistance). The octane number is measured based on the knocking resistance of two reference fuels, iso-octane (C_8H_{18}) and n-heptane (C_7H_{16}). Iso-octane has a high resistance to knocking under harsh conditions, and is therefore assigned an octane number of 100. Conversely, n-heptane has a low resistance to auto-igniting, thus it is assigned an octane number of 0. Since the knocking resistance varies based on the operating conditions, there are two main types of octane numbers: the Research Octane Number (RON) and the Motor Octane Number (MON). The RON is measured under lower temperatures and speeds, and the MON is measured under high temperatures and speeds.



Detail of the catalytic reforming process of naphtha with stars noting suggested online near-infrared spectroscopy (NIRS) measuring point.

In refineries, high octane products are desired since they are used to produce premium gasoline. The refining process which produces high octane products is called catalytic reforming. Catalytic reforming converts heavy naphtha (paraffin mixture with low octane rating) into a high octane liquid product called «reformate» (a mixture of aromatics and iso-paraffins C_7 to C_{10}). Therefore, catalytic reforming has a significant impact on the refinery profitability.

The octane numbers of the produced reformate must be constantly monitored to ensure high throughput along the refining process. Traditionally, the RON values can be measured by two different methodologies: Inferred Octane Models (IOM) and laboratory octane engine analysis. However, these methodologies do not provide «real-time» results and require constant maintenance and human intervention to adapt to current operation conditions. Furthermore, calibration of the octane engine for RON > 100 (a common value for reformate) requires specific blends. These calibrations are not always available. Indeed, in refineries, octane engines are mostly used to analyze and qualify final blended products (gasoline), with RON between 92–98.

Keywords: RON, MON, petrochemicals, NIR, spectroscopy, XDS, ATEX, ASTM E1655, ASTM D6122, ASTM D6299, ASTM D2699, ASTM D2700

Metrohm Process Analytics

«Real-time» analysis of the octane number in fuels can be performed online via near-infrared spectroscopy (NIRS) technology, which fits well within the international standards (ASTM). However, the reformate samples contain solid particles in the stream which interfere with the measurements. Therefore, for reproducible and accurate measurements, a preconditioning panel is necessary to filter the samples and maintain a constant temperature to avoid fluctuations. Additionally, another advantage of using a preconditioning panel is that a sample take-off point can be implemented as well as a port for validation samples.

Our NIRS Process Analyzers enable comparison of «real-time» spectral data from the process to a primary method (Cooperative Fuel Research «CFR» testing) to create a simple, yet indispensable model for your process needs. Gain more control over your production with a Metrohm Process Analytics NIRS XDS system configured for applications in **ATEX** zones, capable of monitoring **up to 9 process points** with the multiplexer option.

Compliance with ASTM:

Method Development	Method Validation	Instrument Validation
ASTM E1655	**ASTM D6122**	**ASTM D6299**

Different steps for the successful development of quantitative methods according to international standards

Application: After samples are preconditioned, NIR measurements are performed in a flow-through cell. The instruments used in refineries are ATEX or Class 1 Div 1/2 certified. They are either mounted in the plant where they will require positive air pressure or in a pressurized shelter. The distance between the instrument or shelter and the sample points can be hundreds of meters apart. Every 30 seconds, RON and MON values are transmitted to the programmable logic controller (PLC) or distributed control system (DCS) depending on the communication protocol used.

Key Parameters and ranges:

Parameter	SECV (Accuracy)	Precision	Range	Reference ASTM	ASTM Accuracy
RON	0.27	0.01	90–107	D2699	± 0.9 (RON 103)
MON	0.15	0.01	80–100	D2700	± 1.2 (MON 96)

Benefits for NIR spectroscopy in process:

- Optimize product quality (seasonal effects, crude swing...) and increase profit
- Greater and faster return on investment
- Improved product quality and manufacturing efficiency
- Detect process upsets via automated analysis

International Standards (petrochemicals):

- **Standard-compliant fuel analysis**
- **Standard-compliant biofuel analysis**

Related Application Notes:

- **AN-NIR-025** Real-time inline predictions of jet fuel properties by NIRS
- **AN-NIR-022** Analysis of petroleum products (e.g. cetane index, TAN, aromatic hydrocarbons and sulfur)
- **AN-PAN-1047** Inline monitoring of water content in naphtha fractions by NIRS

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