Advanced solutions for efficient crude blending

The use of nuclear magnetic resonance-based process analysers supports the production of blends at lowest cost

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n the past, refineries were constructed to distill conventional light crude oils. Current economics, variations in the price of crude oils and shifting demand for distillates have forced refineries to reduce the cost of their distillation feedstock. Commonly, this is achieved by blending high-value light crude oils with heavy (unconventional) crude oils of inferior quality, or by buying ready-made blends. Low quality crudes include heavy crudes from known locations, as well as opportunity crudes that are brought on the market by traders worldwide. These crudes, of lower quality, can be purchased at low cost. Blending of these with costly crudes is inevitable to produce crude blends that bear optimal properties to be processed, and at minimum cost.

Refineries worldwide are constructed from an engineering point of view and from materials that enable the distillation of well-defined types of crude oils. These refineries were built based on the availability of certain types of crude oils in their neighbourhoods, the cost of certain crude oils on the market, and demand for predominantly light distillates for gasoline production.

Distillation of crude oil was mainly targeted to produce gasoline components, such as light and middle distillate. More recently and especially in the US and in Europe, demand for fuels has shifted from gasoline towards diesel fuels. This means that while in the past predominately light crudes were distilled, today refineries must be able to distil heavier crude oils to increase the amount of middle and heavier distillates. Refining margin for many refineries which were not able to adapt to the changing situations decreased. Technological limitations caused many refineries to buy expensive light crudes that do not produce specifically those distillates that are most needed in the market. For many refineries, the losses were too large. Many closed or changed their activities from distilling toward blending.

Nowadays, crude blending is

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performed either by blenders or by refineries themselves which buy various types of low cost crude oils. They upgrade their chemical and physical properties to produce a synthetic crude oil at lowest cost, which can be processed in refinery equipment and will yield high value distillate.

Characteristics of crude oils

Quality properties determine the market value of each type of crude. The most important quality characteristics are the density, the total acid number (TAN) and the sulphur content. The API ranges from light crudes (high API, low density) to heavy crude oils (low API, high density). Sulphur is present in crude oils as hydrogen sulphide and as polysulphides. These sulphur containing molecules will partially decompose during distillation, while hydrogen sulphide evolves. The sulphur content and other acidic components in crude oil, such as naphthenic acids, are highly corrosive, and responsible for crude oil to be of a sour or sweet character. These characteristics mostly lead the price paid for different types of crude oils.

Refinery equipment

High TAN crude oils are characterised by fewer light components, high density and viscosity, low solidification point, high nitrogen content, high gel-asphalt content, high salts and high heavy metals contents and a low yield of light oil distillates. Oil separation in the desalter is more difficult than in conventional crudes. These properties also cause these crudes to give low quality products and they are very corrosive. Commonly, high TAN crude oils are called 'opportunity crude oils'. The price is about 80% that of conventional crude oil. The additional cost of processing high TAN crude is within the range \$1.15–10.73/bbl, but the savings compared to conventional crude processing are \$43.54-62.7/bbl. Utilising these crude oils in any way possible is therefore very attractive to refiners.¹

In the past, most refineries were designed and constructed from materials according to the crude oil

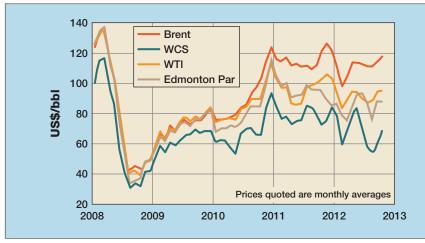


Figure 1 World oil price according to benchmarks

available and its ease of purchase. This limits the versatility of many refineries to purchase other crude oils of different qualities. Many of those refineries that are constructed to distil light and low sulphur crude oils are restricted as regards processing heavy fuels.

Critical differences in their physical and chemical properties make heavier crudes oils more difficult to distil than light crudes. Heavy crude oils are sour and more corrosive than light crudes. Higher viscosities, fouling tendencies and different flow streams make it more difficult to maintain stable crude charge rates, which are required for stable product yields, quality and reliability. Differences in boiling points between light and heavy crudes require different process temperature requirements such as pre-heating, different distillation temperatures, overheads and so on. Heavy fuels are rich in asphaltenes and metals and other contaminants which cause poorer desalting performance.

Product shifting

Demand for certain distillates and refinery products is shifting. It is expected that middle distillates will comprise some 45% of global demand per barrel by 2015, which is a rise of 10% compared to 2005. It can be expected that production of diesel gas oil in developing nations will increase by 10 million b/d from 2009 to 2030.²

The US is the largest consumer of crude oil. While US demand remains stable, today China is in

second place with an annual 4% increase in demand for crude oil. New refineries, built nowadays, are already designed as such that they are not limited to a small range of crude oils.

The major operational cost of the refinery is contributed by the price of the crude oil, an estimated by 80-90% of cash flow. Reducing the cost of the crude feedstock, without changing the range and volumes of high valued distillates, increases the refining margin. Refinery profits are a direct outcome of the strategy applied by the refinery to purchase low cost crudes and to produce distillates with a high market value. To increase refining margin and remain competitive, refineries are obliged to minimise the cost of their crude feed, without affecting their capacity to produce high value distillates. As heavier crudes are more difficult to process, and with the increase of consumption of diesel oil as compared to gasoline, light sweet crude oils are marketed at a higher price than heavy crudes. Reducing the cost of the crude input, without changing the range and volumes of high valued distillates increases the refining margin.

Potential crude blenders

Two broad types of organisation deal with the business of crude blending, refineries and blend producers/trading companies. Crude blending is applied directly by refineries to prepare low-cost and compatible blends for internal consumption or for trading in the market. Efficient crude blending opens opportunities for oil blenders, oil trading companies and terminals to bring low cost blends onto the market. These blends can be sold to refineries with a high market value and quality.

Crude mixing can be applied throughout the entire supply chain of crude oil, from its well enabling transportation, through terminal blending to the refineries. The final crude supply to the distillation unit may be a combination of these activities.

The strategy of crude oil blending includes several parameters. Each of them contributes to the overall final cost of crude oil entering the crude distillation unit as well as the refining margin:

• The engineering limitations of crude distillation units to refine any type of crude oil

• Cost differences of crude oils according to their location of origin, and their chemical and physical properties. An increased ability to process unconventional crudes leads to improved refinery margin

• Product shifting in the market from gasoline towards diesel fuels. Increased demand for diesel fuels in the European market caused refineries to increase diesel yield over naphtha yield

• High viscosity, especially in heavier crude oils, affects the flow properties of crude during transportation. Blending these types of crude oils with diluents or conventional crudes may be required to reduce viscosity and to improve flow properties.

Crude oil economics

Previously, refineries distilled crude oil from single locations, but nowadays refinery profits are a direct result of the ability to create blends that include lesser quantities of high value crude oils and higher quantities of unconventional crudes, such as heavy and extra heavy crudes, sour crudes and bitumen extracted from oil sands. However, these blends should still have those physical and chemical properties that are required to enable smooth and continuous operation of the distillation unit at the lowest possible cost.

Basically, crude oils can be divided into four major groups:

• Light low sulphur (API 30-40°, S ≤0.5% mass)

• Light, moderate sulphur (API 30-40°, S=0.5-1.5% mass)

• Heavy, high sulphur (API 1-30°, S 1.5-3.1% mass)

• Extra heavy high sulphur (API = 15° , S $\geq 3\%$ mass).

The ratio of a component in a blend is actually limited by the physical properties required for production of the highest valued distillates to the largest extent, and by the construction of equipment to process the blend.

Current values based on the benchmark of light Brent crudes and the somewhat heavier WTI crudes show differences in price of around \$10/bbl a barrel (see **Figure 1**).⁴

Opportunity crudes are of course much cheaper. Various crude oils, such as some Venezuelan and Canadian crudes, are very heavy and are attractive for bitumen production. Their processing is limited by their very low API gravity. To produce other distillates from these crude oils, they must be upgraded by dilution with light crudes or kerosene.

The high viscosity of many of these heavy crudes is another drawback. Blending with light crude oils, kerosene or other diluents is also required to give them flow properties that enable their transport through pipelines without heating.

It is the aim of each refinery to maximise the consumption of opportunity crudes.

Heavy oils are hydrogen deficient and have high levels of contaminants such as sulphur, nitrogen, organic acids, vanadium, nickel, silica and asphaltenes. The method for upgrading heavy oils at relatively low cost is to dilute them with hydrogen rich, higher quality light crude oils or by using hydrogen rich diluents to increase the H/C ratio.

Blending processes

Crude oil blending can be performed by two technologies.

In-tank blending (batch blending) Specific volumes of different kinds of crude oils stored in separate tanks are loaded into a blending tank where they are mixed until a homogenous composition is achieved. The tanks are mechanically stirred. Samples must be withdrawn to determine whether the blend is homogeneous and whether it conforms to its predetermined specification. In the event of discrepancy, correction of the blend must be conducted. The entire procedure of in-tank blending is very time consuming and expensive.

In-line blending

In contrast to tank blending, in-line blending is performed by simultaneously transferring different crude oils through an on-line static mixing device to the final blend

To operate the blending process efficiently and without error, on-line process analysers are required

tank. The predetermined flow ratio between the different crudes will provide a blend of the required quality. In-line blending enables on-line correction of the quality of the blend, by changing the ratio between feeds. The blend is produced instantaneously and no stirred 'blending tanks' are required.

To operate the blending process efficiently and without error, on-line process analysers are required to instantaneously measure the blend downstream and to feed the blending operators with the required quality details of the blend in production. This enables real-time and on-line correction during the blending process, providing the blend of predetermined properties. This reduces corrective re-blending of an entire tank, as well as unnecessary giveaways.

Determination of blending recipes

Simulation software, such as linear programming (LP) modelling, is widely used to predict the ratio between individual components to prepare a blend. Based on the composition data of crudes used, and using the proper algorithm, this software is commonly applied to calculate and predict the physical properties of blends.

The software calculates the ratio of different crudes, resulting in a crude blend with the appropriate properties, leading to the desired distillates at optimal vields. Incorporation of a large database which covers a broad range of crude oils is required to predict accurately a blend of predetermined physical properties and with the potential to maximise production of high-value distillates. Adequate blending simulation models should include not only the chemistry of crude oil distillation but also its economics. It must be able to calculate the composition of different crudes to provide the best economic blend at the lowest cost. Such blends contain maximised volumes of those crude oils of lowest cost, but still bear the most attractive refining properties. This strategy will minimise variable costs and maximise profit.5

LP is based on the assay of different crudes oils to be blended. Any changes in the assay will affect the LP's predicted blend.

Fundamentally, effective crude blending simulation software should include the following features:⁶

• Calculation of the blend components and their ratios

• Ratio limits

• Predicted fraction temperatures

• Constraints in the properties of the blend

Properties of the fractions

• Constraint limits.

Next to the chemico-physical properties of the blend, the software should also focus on the potential profit derived from the blend. This requires software also to relate to:

• Cost of various crude oils and crude oil blends

• Prices of final distillates and other refinery products.

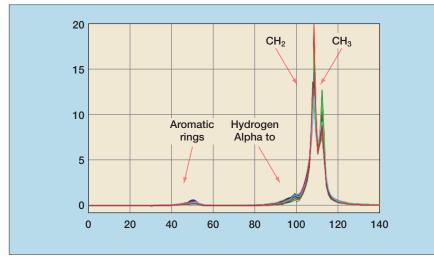


Figure 2 Typical NMR spectra of crude oils

• Volumes of final distillates required by the market

Time consuming and costly laboratory analyses are required to verify the 'real' physical properties of the blend. Re-blending is required if these properties are not achieved.

Efficient blending requires on-line monitoring of the blend properties

throughout its entire production. Chemical compositions differ from crude to crude. Notwithstanding whether the crude oil is pure, or a blend of crude oils, on-line corrections are continuously conducted to maintain stable product quality. This requires real time collection and validation of physical properties from the blend through-

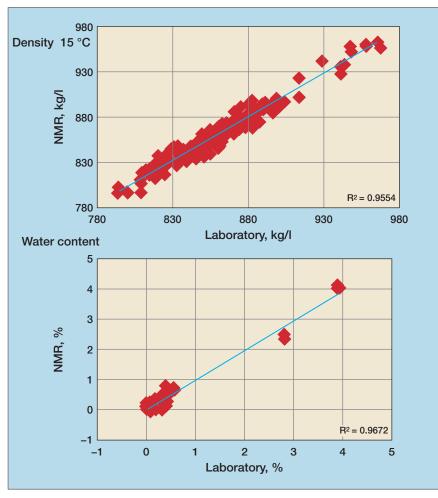


Figure 3 Correlation between NMR predicted results and laboratory measurements

out its entire production process. Among all of the analysers available in the market, nuclear magnetic resonance (NMR) process analysers are the most suitable for that purpose.

The first NMR process analysers were launched in the late 1990s. In hydrogen nuclei in a NMR. magnetic field absorb and re-emit electromagnetic (EM) energy at a specific resonance frequency. The basics of NMR process analysers are the alignment of nuclei in a magnetic field. An external radio frequency (RF) pulse is applied; this distorts the alignment of the nuclei in the magnetic field. The resonance frequency depends mainly on the strength of the magnetic field. When the RF pulse ends, the protons relax and align back to their initial equilibrium position, which generates a decay signal, the free induction decay signal (FID).

Crude oil is a mixture of organic chemical compounds, mainly carbon and hydrogen-based molecules. Neighbouring atoms, such as carbon, oxygen and sulphur, and neighbouring chemical bonds, influence the strength of energy absorption and emission by hydrogen nuclei in a magnetic field. Accordingly, the signal of each hydrogen atom shifts differently in the NMR spectrum. These welldefined chemical shifts represent the chemical structure of molecular species. Linear correlation between the intensity of the signal and the hydrogen concentration makes it possible to quantify the different hydrogen nuclei.

Physical properties in crude oils and in distillates correlate with their chemical compositions. This allows chemometric methods to correlate between the measured spectral data and the physico-chemical properties of crude oil or other distillates. In contrast to other chemometricbased spectral technologies, such as Raman and NIR spectrometry, which are based on fingerprints, due to its molecular specificity and its linear quantitative correlation NMR technology requires far fewer reference samples to establish a chemometric model.

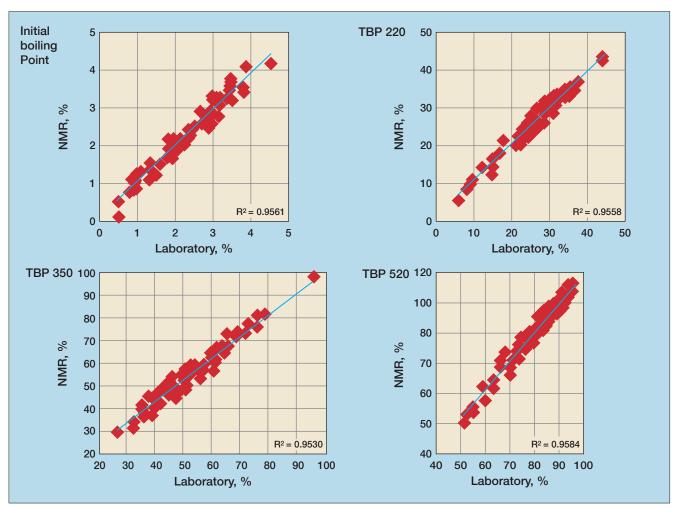


Figure 4 Correlation between NMR predicted boiling points and laboratory measured boiling points

NMR-based on-line spectrometers are not limited to transparent fluids, but can be applied to transparent and opaque liquids alike. Crude oils contain water heteroatom molecules, which are easily distinguished by NMR spectrometry.

NMR on-line spectrometry with appropriate chemometrics has the ability to determine the following properties in crude oil:

- Specific gravity
- True boiling point yield
- Aromatic content, %
- Olefin content, %
- Pour point
- Water, %
- Sulphur, %.

Following these parameters is most important during crude blending. Their on-line measurement makes it possible to blend synthetic crude to deliver predefined properties, either from a physico-chemical point of view or from an economic point of view.

On-line monitoring of the blending process prevents the production of blends that do not comply with the requirements of the refinery. Blending errors and giveaways can be prevented which can lead to annual savings of millions of dollars.

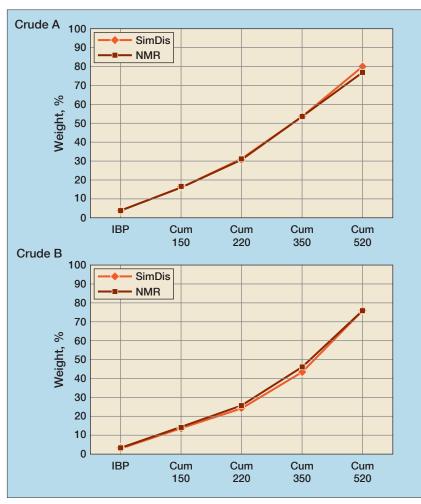
Precision of NMR process analytics

High accuracy in the correlation between a NMR process analyser's results and laboratory results characterises the new generation of NMR process analysers. NMR magnets are sensitive to temperature differences. Earlier generations of NMR process analysers were especially sensitive to temperature differences due to the accumulation of heat produced by their electronics and heat-conducting measuring probes. In the new generation of NMR process analysers, the overall design excludes any accumulation of heat in the magnet or in its surroundings by uncontrollable fluctuations in temperature. This increased analysers' stability to heat fluctuation from ±2°C to $\pm 10^{\circ}$ C. This means that any heating

of crude oil required prior to blending, or after the desalter, is possible without affecting the analytical results, as long as a temperature deviation of $\pm 10^{\circ}$ C is maintained.

Figures 3 to **5** show the correlation between an NMR analyser's predicted results and laboratory analyses of different crude oils.

The figures demonstrate the high accuracy in correlation between NMR predicted results and laboratory measurements. Partially these measurements relate to chemical matter such as water and sulphur, and partially to physical properties such as the distillation curve, and an excellent overlap between simudistillation lated and NMR results. analytical Taking into account the time required for laboratory analyses, the cost to perform crude oil assays, or purchase and maintenance costs justifies the use of NMR process analysers in crude blending processes, especially in cases of in-line blending. NMR makes it possible to monitor



Figures 5 Overlapping NMR and simulated distillation curves

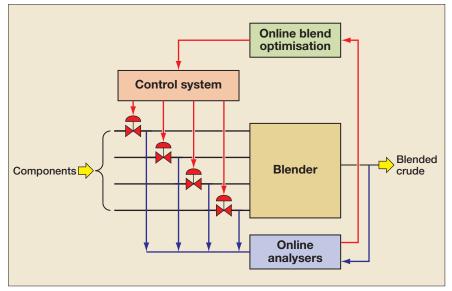


Figure 6 Set-up of a crude blending station with incorporated NMR process analyser, simulation modelling and blending control. (Components can be high and low quality crude oils, diluents and/or gasses (NLG)

precisely the quality of the blend in production and, if required, to change the ratio between different crude oil feeds to establish and maintain the quality of the final blend.

Optimised crude oil blending station

A crude blending station consists of a blending skid to receive liquid or gas streams, optimisation software and analytical equipment. Analytical equipment should be able to provide online measured data of component and product streams involved in a blending operation. This data is transferred to optimisation software whose target is to support production of a blended product with minimum product cost, minimal quality giveaway, and minimal deviation from individual raw material properties. To achieve this objective, the optimisation system continuously receives quality feedback of the finished product using on-line analysers.

Using the inputs from on-line analysers, the optimisation system performs either feed-forward or feedback control of raw materials based on the quality of product samples obtained from the blend header.

Both LP simulation and NMR process analysis can operate 'standalone'. However, for best optimisation of the crude blending process, it is essential to integrate the two technologies.

Efficient blending optimisation is a dynamic process involving mixing, continuous blend analysis, simulation model adjustment and process control. All of these elements should be taken into account (see **Figure 7**). Any missing link in this chain of operations will impact the efficiency of the entire process and reduce its revenue.

Alternative applications of on-line NMR process analytic

Other uses of NMR on-line process analytics are of interest, in addition to the application of NMR process analysers for blending different crude oils.

Crude oil compatibility during blending

Blending different crudes, especially when unconventional crudes are involved, may cause precipitation of asphaltenes, which causes fouling in the pipes and process units. Asphaltenes are soluble in polar aromatics, such as toluene, but insoluble in paraffinic nonpolar solvents. On-line analyses of the SARA content (saturates, resins, aromatics and asphaltenes) can be a potential tool for on-line determination of quantitative ratio between different crudes to be blended, or between crude oils and polar solvents, without causing asphaltenes to precipitate.

Natural gas liquids in crude oil blending

Natural gas liquids (NGL) are produced by refrigeration and distillation processes in gas plants and refineries and are considered byproducts in the oil and gas industry. Gas plants extract NGLs for profit and/or to ensure production of pipeline quality natural gas.

NGL prices are relatively low. They and other off-spec materials from natural gas production are used by refineries and blending companies to upgrade heavy crude oils. Another application is lowering the viscosity of heavy crudes to make them flow more easily through pipelines. Implementation of on-line NMR process analysers provides an effective tool for efficient blending of NGLs and crude oil to deliver the required physical properties at lowest cost.

Conclusions

Different blending options exist to upgrade unconventional crude oil into synthetic crudes of higher values. An automatic crude blending station integrates LP with on-line NMR process analytics. It can be used either by traders who offer blending services, or directly by refiners. Cost, market value, availability and choice of technology are the main factors to be considered in planning a configuration to be used for upgrading unconventional crude oil.

Two principal technologies are required for optimised crude blending:

• On-line process analytics monitors crude oil and blend quality at any time and at any stage

• Dynamic simulation modelling (blending simulation models) are commonly used to determine the required blend composition. Highest blending optimisation can be achieved only by updating the simulation program with real time analytical data for crude oil and blend quality.

NMR-based process analysers can

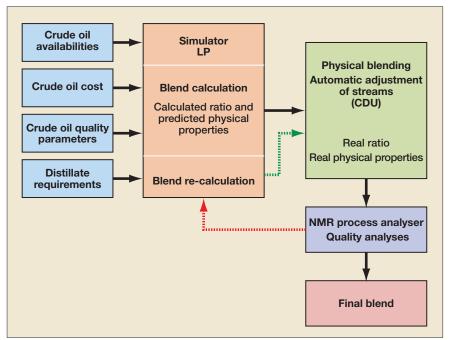


Figure 7 Dynamic process of mixing, continuous blend analyses, simulation model adjustment and process control

be used to determine chemical composition and physical properties in dark and opaque streams. The benefit of NMR spectrometry lies in its linear correlation between the hydrogen atoms of the molecules present in crude oil and the chemical nature of its components. Chemometrics transforms spectrometric measurements into the

Implementation of on-line NMR process analysers provides an effective tool for efficient blending of NGLs and crude oil

characteristic physical properties of crude oils and blends.

This technology provides real time data and information about the physical and chemical properties of the blend in process. On-line adjustments and changes between blend components can be performed accordingly until the required physical properties are achieved.

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