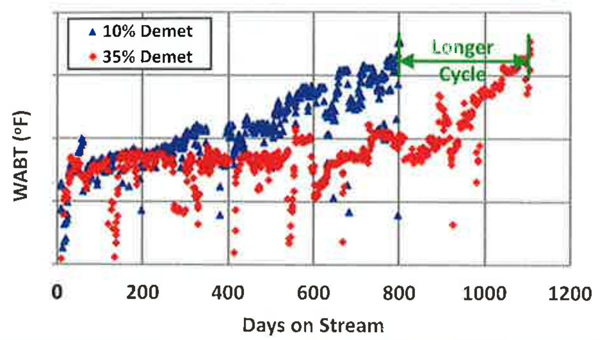


Figure 11. Increased demet leads to greater stability.

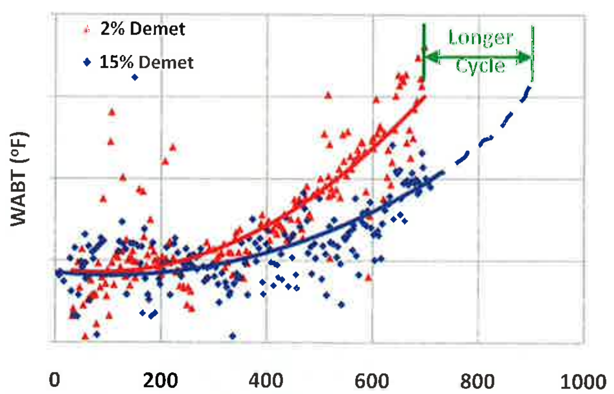


Figure 12. Longer cycle with increased demet.

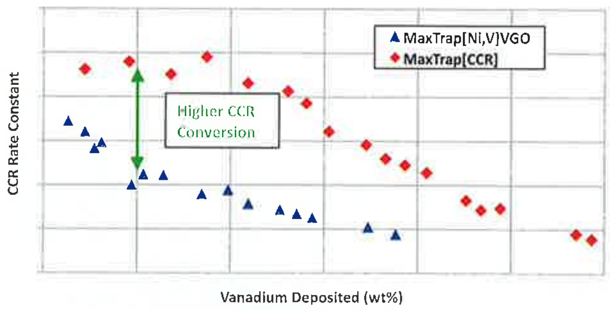


Figure 13. Higher CCR activity of MaxTrap[CCR].

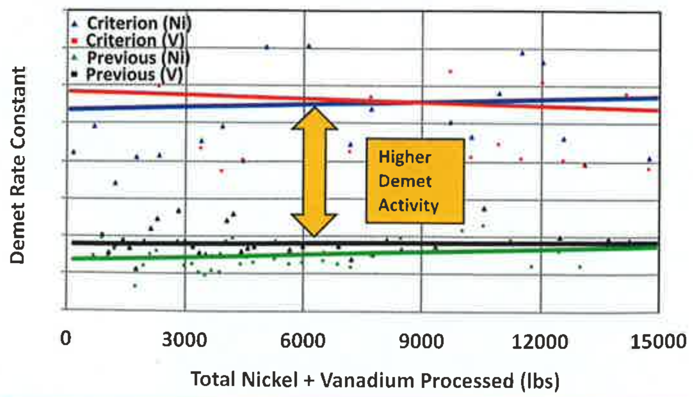


Figure 14. Higher demet activity of Criterion's system.

HVGO and HKGO with 8 ppm feed metals also benefitted from an increase in demet volume from 2 vol% to 15 vol%. Changes in crude quality and source resulted in an increase in feed metals compared to the historical average. Both cycles had similar SOR activity and were stable for the first year, at which point the cycle with 2% demet started to show signs of metals deactivation. The cycle with 15% demet was stable for 500 days before WABT had to be increased. The second cycle was terminated after 700 days for turnaround optimisation but, as the dashed line in Figure 12 indicates, it could have run for 900 days, which is a 30% increase in run length over the previous cycle.

Criterion also offers MaxTrap[CCR], a NiMo catalyst designed for maximum CCR conversion. Testing has shown that its demet and HDCCR activity is more than twice that of MaxTrap[Ni,V] VGO at similar metals on catalyst (Figure 13).

Example 3

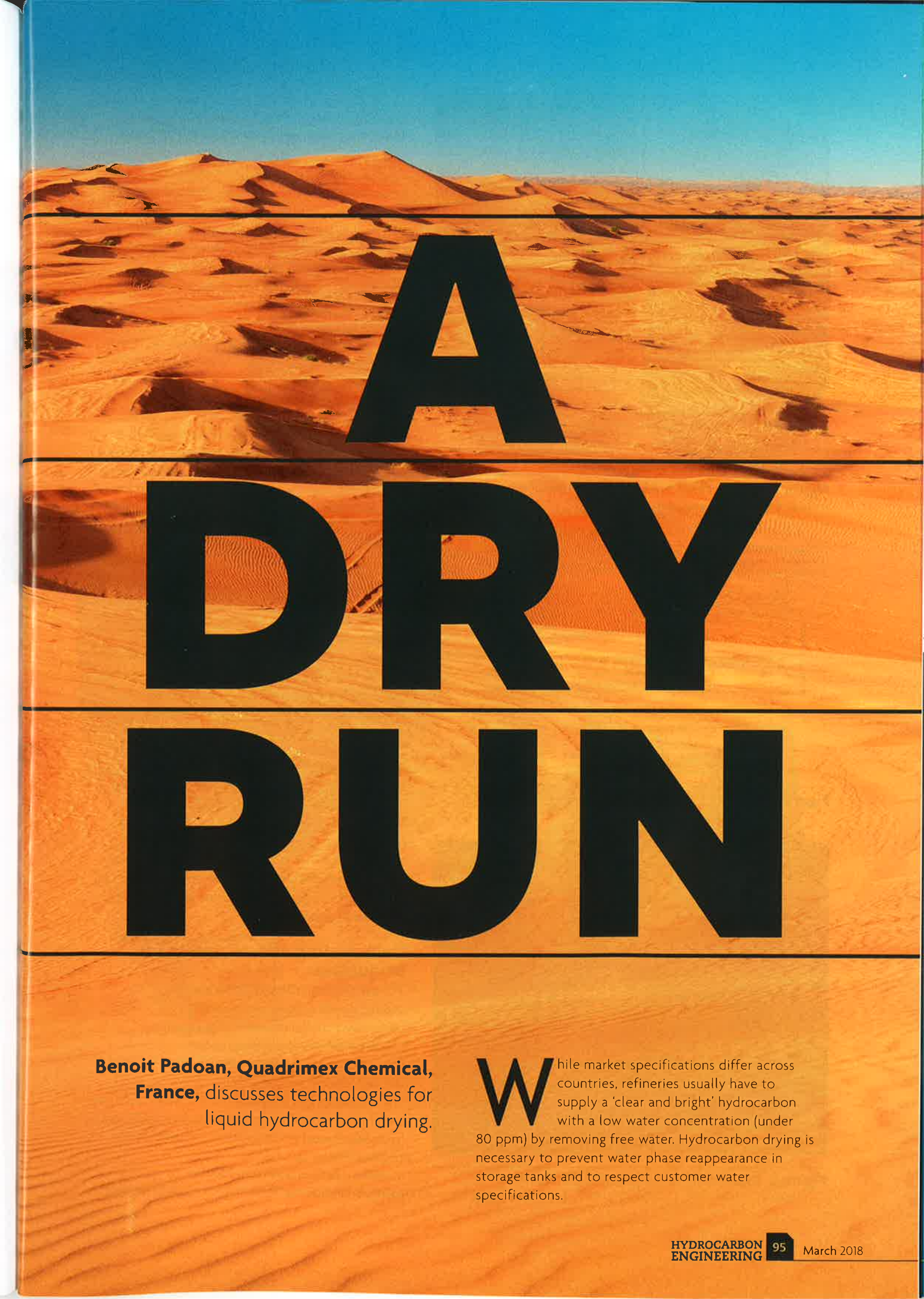
A FCCPT unit recently switched to a MaxTrap[Ni,V] and MaxTrap[CCR], and observed significant improvement in demet activity and stability. Figure 14 shows the demet rate constant for nickel and vanadium removal as a function of total nickel and vanadium processed. The demet activity of the Criterion load is higher at SOR and the activity advantage is maintained through the cycle. CCR removal in the first reactor has remained stable through nine months of operation even with high feed metals. During this period, the average metals removal was 95% with a CCR conversion of 72%, and feed nickel and vanadium content was 8.4 ppm.

Conclusion

In summary, increases in feed contaminants due to crude changes or problems in upstream units can lead to premature catalyst deactivation; an unplanned shutdown to replace catalyst has severe financial consequences. Catalyst system design has to balance demet and main catalyst volume, while also accounting for unique requirements, such as heat integration and bed delta T limit, which vary from unit to unit. The primary purpose of demet catalysts is to protect the main catalyst from feed contaminants. They play a critical role in initiating easy reactions and generating delta T for the lower beds. Main catalysts need to be robust and have the ability to withstand contamination from feed poisons without significant decline in activity. Employing a fit-for-purpose demet catalyst in the right quantity along with a high activity and stable main catalyst is critical for achieving unit objectives, maintaining robust hydroprocessing operations, and maximising refinery profitability.

Note

This article was previously presented at the AFPM Annual Meeting, San Antonio, Texas, US, (19 – 21 March 2017).



A DRY RUN

Benoit Padoan, Quadrimex Chemical, France, discusses technologies for liquid hydrocarbon drying.

While market specifications differ across countries, refineries usually have to supply a 'clear and bright' hydrocarbon with a low water concentration (under 80 ppm) by removing free water. Hydrocarbon drying is necessary to prevent water phase reappearance in storage tanks and to respect customer water specifications.

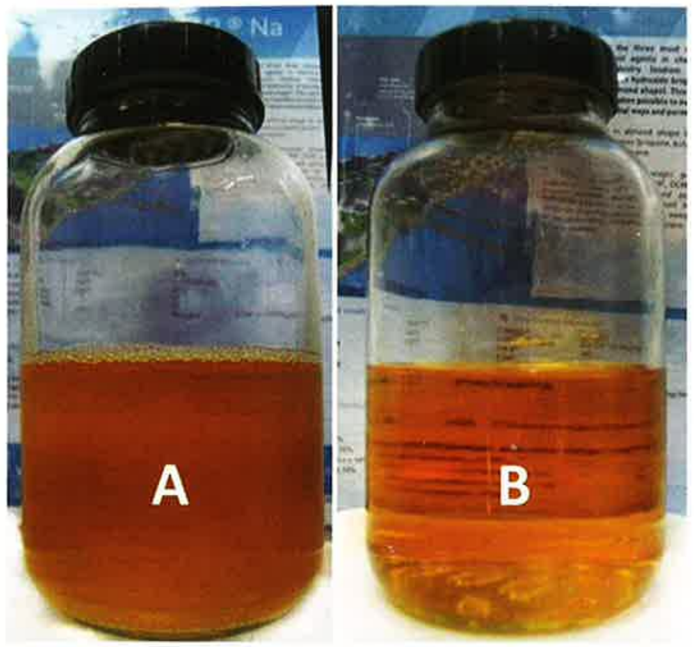


Figure 1. A visual comparison of a hazy hydrocarbon (A) and a clear and bright hydrocarbon (B).

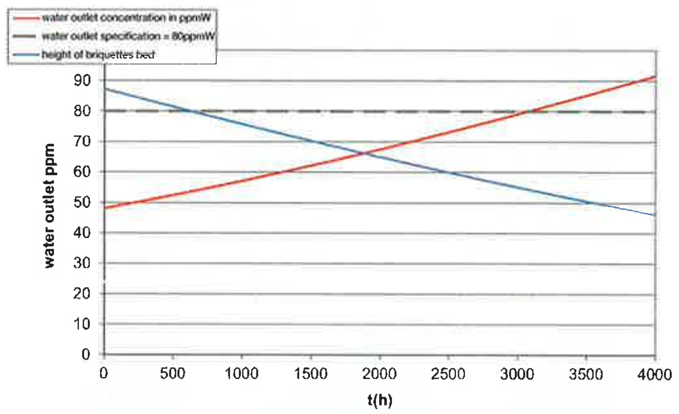


Figure 2. Example extract from the software.

Figure 3. Solid drying in the petroleum industry.

In partnership with IFP (French Petroleum Institute), Quadrimex Chemical has been working to develop a hydrocarbon drying technology for the dehydration of satured hydrocarbons. The technology can be used for different types of hydrocarbons in refineries (for LPG, kerosene and diesel) and in petrochemical facilities (for butadiene, xylene, vinyl chloride monomer and acetylene). The Newton's® technology is based on two main stages: first, the design of the dryer with the associated software, and second, the supply of dehydrating and deliquescent briquettes that are adapted to the specific dryer.

Figure 1 provides a visual comparison between haze hydrocarbons before the company's dryer (A in Figure 1) and 'clear and bright' hydrocarbons after the dryer (B in Figure 1).

Dryer and software

It is advantageous to develop a dryer alongside a predictive drying software. The company's technology is based on the capacity of desiccant and deliquescent briquettes to trap free and soluble water from the inlet hydrocarbons.

The dryers look like vertical reactors and are made of several parts including: a boot to collect the brine, a dispenser to homogenously distribute hydrocarbon, a ceramic balls layer for pre-drying, and a bed of briquettes for hydrocarbon dehydration. While they are dedicated to removing soluble water, the dryers can also remove free water and acid traces. Deliquescent briquettes offer a good compromise between robustness, flexibility, low investment and drying efficiency.

The software, which was created with the help of IFP, underwent several pilot tests in a laboratory. According to data related to the inlet hydrocarbon and the specifications of the customers, the software provides an indication of the final size of the dryer (including its diameter, height, the quantity of briquettes needed and the time required between reloading).

After each case study, it is also possible for the process engineers to simulate and predict dryers' real technical performance by using the results of the software (Figure 2).

Dehydrating and deliquescent briquettes

The use of consumable desiccant solids to dry organic liquids is common in chemistry processes that involve moderate water concentrations (<1000 ppmW). A current application of desiccant solids in the refining and petrochemicals industry is the dehydration and sweetening of hydrocarbons. The briquettes can be used in hydrotreaters, kerosene sweetening units, fluid catalytic cracking (FCC) units, hydrofluoric acid (HF) alkylation units, and steam crackers (Figure 3).

There are four types of briquettes containing: calcium chloride ($CaCl_2$), sodium hydroxide (NaOH),

Figure 4. NaOH briquettes, weighing 29 g each.

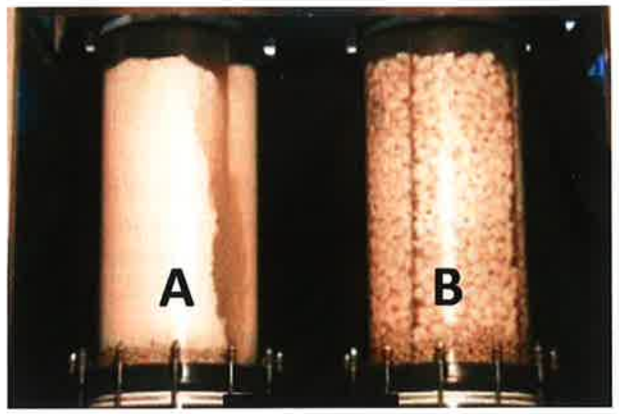


Figure 5. A comparison between prills (A) and briquettes bed (B).

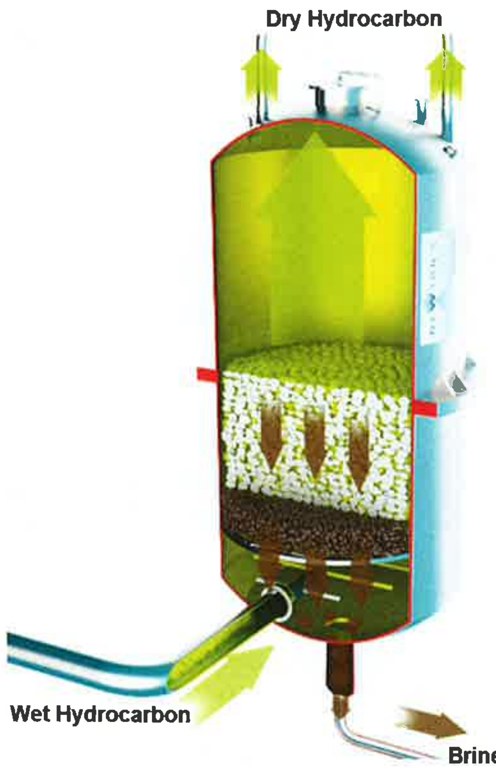


Figure 6. A dryer using briquettes (in operation).

potassium hydroxide (KOH) and lithiuchloride (LiCl). Their use depends on each customer's problem and the results of preliminary studies.

When hydrocarbons contain water, two kinds of water can be identified:

- Soluble water, which is invisible and non-coalescable. When hydrocarbons are saturated with soluble water, free/insoluble water appears. This is also dependent on the temperature of the hydrocarbon.
- Free/insoluble water, which is visible (water droplets).

Compared with many other drying products (such as rock salt; NaCl), briquettes can remove not only free water, but also soluble water that is contained in wet hydrocarbons (Figure 4).

Solid briquettes are also able to withdraw acid traces.

Advantages of the shape of briquettes

Briquettes have a higher contact area between the solid and liquid compared with pearls for the same volume. This results in a specific area gain of approximately 20%, with a similar pressure drop.

Other shapes and sizes are available (such as small prills or flakes), but these shapes cause the pressure drop through the bed to be higher, and chimneys or preferential paths can be formed during operation (Figure 5, bed A). With prills, even if the residual volume is theoretically able to treat the hydrocarbon, the refinery will have to regularly renew the consumable product.

This could have many consequences on the unit, such as more frequent shutdowns, higher consumption of solid products and, therefore, increased outlay on pellets or flakes.

The briquettes are usually restored every three to four months, by adding 20 t of briquettes to reach the technical performances required. This is initially determined for each customer, using the results/findings of the preliminary case study.

Operating principles for dryers using briquettes

The liquid phase flows through the fixed bed of the vessel in an upward flow direction. The inlet hydrocarbon that contains free and soluble water enters at the bottom, through the dispenser's holes. The fluid then emerges toward the inert balls layer (pre-dehydration) and the briquettes bed (dehydration), where brine is generated (the brine is the result of the reaction between the briquettes and water).

The dried hydrocarbon leaves the dryer at the top, while the brine goes down and enhances the solvent dehydration by further extraction in counter-current flow. The bed of briquettes is progressively consumed during the dryer operation and further reloads are needed to restore initial performances (Figure 6).

Case study

In Singapore, one of Quadrimex Chemical's customers was facing two major challenges: increasing flow rate of the diesel unit to 200 m^3/hr and maintaining the 'clear and bright' quality of the final product.

To help overcome these challenges, the engineering division designed a new $CaCl_2$ diesel drying unit especially for the customer. The dryer was implemented between the existing vacuum dryer and the diesel storage tank, allowing the refinery to increase the flow rate by 20% and reach the 80 ppm water specification on the hydrocarbon at the end of the process.

The initial load was 110 t of specific $CaCl_2$ briquettes, manufactured in France. According to the company's forecast, the dehydrating bed should be replaced every four months. Figure 7 shows monitoring data for a period of two months, indicating high quality results, despite unpredictable inlet hydrocarbon water content. The graph presents the water quantities contained in the wet hydrocarbons before (green points) and after drying (purple points) week by week, between two briquettes reloading.

Conclusion

Advances in dryer technology offer refineries a good compromise between OPEX and CAPEX. Requirements for meeting water specifications evolve a lot and customers are increasingly demanding for final product quality. The simple technology requires low investment and has been exported in many countries worldwide for the last few years.

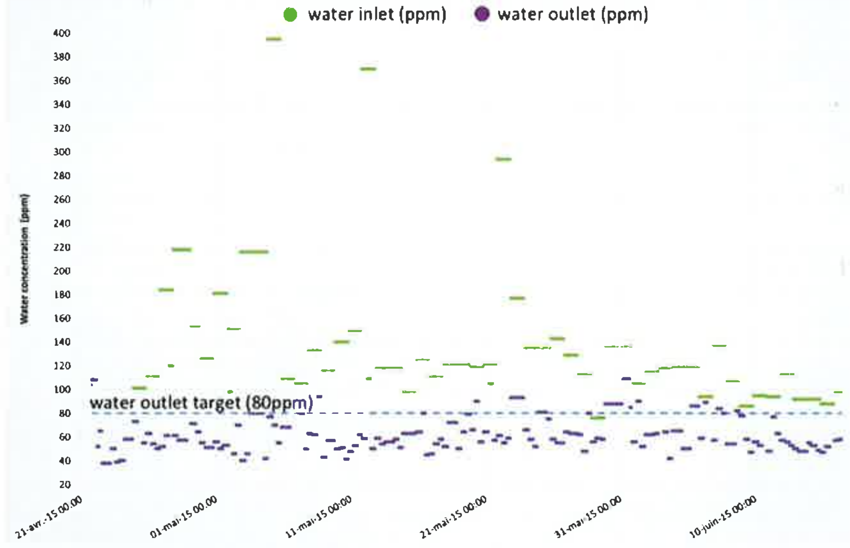


Figure 7. Monitoring data of the diesel dryer using briquettes. Water inlet concentration (green) vs water outlet concentration (purple).