As one of the largest contributors to anthropogenic greenhouse gas emissions, the transportation sector faces significant challenges in order to meet rising global demand while simultaneously achieving increasingly ambitious targets for sustainable and renewable sources of energy. Although passenger vehicle technology is transitioning to electrification, with many EU countries planning to ban fossil fuel powered cars by 2040, other modes of transportation such as aviation and marine vehicles are more challenging to decarbonise.

One means of reducing the carbon footprint of these types of fuels is by using Fischer-Tropsch synthesis (FTS); by this process a bio-derived synthesis gas can be converted into ‘synthetic’ long-chain hydrocarbons. In addition to the sustainability of the feedstock, these synthetic fuels also burn cleaner, due to the absence of contaminants such as sulfur and aromatics, and produce fewer particulates.

BP and Johnson Matthey have been jointly developing their Fischer-Tropsch (FT) technology for many years, with the latest generation of reactor and catalyst technology...
(FT CANS™ technology) capable of achieving 90% selectivity to C5+ and a productivity in excess of 300 kg/(m²cat hr). This development makes the production of synthetic fuels from sustainable carbon sources a more commercially viable proposition, revitalising FT technology as a contributor to a sustainable and circular economy, not as world-scale plants but as regional and delocalised facilities. For example, the Fulcrum BioEnergy plant under construction in Sierra, Nevada, US, is expected to process 175 000 tpy of household waste into approximately 50 million l/yr of transportation fuel.

Low temperature, cobalt-based FTS products are predominantly linear paraffins. As such, if they are to be used as fuels, a degree of processing is required to introduce branching in order to improve their cold flow properties and meet the relevant fuels specifications. Figure 1 shows a typical boiling point curve and gas chromatography (GC) traces for the FTS product stream. It can be seen that n-paraffins comprise 90% of the syncrude and carbon numbers up to at least 90 are detected; carbon numbers higher than this are challenging to speciate.

A typical process scheme for upgrading FTS products is illustrated in Figure 2. The FTS product stream is fed to the dewaxing reactor together with hydrogen. The dewaxing reactor contains a bi-functional catalyst comprising active metal sites for (de)hydrogenation reactions as well as acid sites for isomerisation and cracking reactions. Mild hydrocracking converts the high molecular weight paraffins into middle distillate product range material, and isomerisation introduces branching into the hydrocarbons. The dewaxing products are separated in the fractionation section and unconverted heavy wax is recycled to the reactor inlet section.

The R&D work on FTS wax upgrading comprises many different aspects: kinetic studies to support process modelling, identifying the optimal upgrading catalyst system, optimising operating conditions for maximising the target product yield, avoiding over-cracking to less valuable lighter products, avoiding local hot spots and thermal runaways, and mapping the impact of different feedstock compositions and qualities on catalyst performance and necessary processing conditions. In the study presented in this article, an overview of the challenges in conducting and analysing the performance of the dewaxing reaction will be given, and the way in which the high throughput test equipment has been used to support industrially relevant catalyst and process R&D will be illustrated.

When performing laboratory testing of FTS wax upgrading, in high throughput mode in particular, a few challenges must be dealt with:

- For all laboratory testing, heavy FTS wax requires high temperatures (> 100°C) to ensure it remains as a stable, homogeneous liquid throughout the test equipment for weeks and months on stream. Any cold spots can cause plugging. Hence, proper heat tracing and insulation is essential.
- When mapping a wide operating window by utilising a high throughput unit with as many as 16 reactors in parallel, the test unit must be capable of handling the whole feed and product range, from heavy waxes to very light ends, simultaneously.
- A comprehensive analysis of the dewaxing feed and product requires detailed measurements to elucidate the complex composition of the hydrocarbon mixtures. For high throughput test equipment, this
challenge is amplified by the need for rapid analysis, due to the large amount of data that is generated within a short time and over the whole test campaign.

hTe has developed a robust workflow, starting with handling the challenging FTS feedstock through to processing it in a high throughput unit and analysing feed and product samples. For managing the data produced by such a test campaign, an integrated software workflow and automated data evaluation in a comprehensive database is key to success. Figure 3 illustrates the principle of such a software workflow solution. Dewaxing of FTS wax results in light ends that are typically analysed by online GC in the gas phase, as well as heavier hydrocarbons that are liquid or even solid at ambient temperature that are typically analysed by offline GC methods (among others). High throughput testing results in evaluation of up to 300 complex chromatograms a week. In order to obtain a fast and robust data evaluation, all online and offline data are uploaded into a database where the GC chromatograms undergo an automated peak identification process, converting peak areas into absolute concentrations. Online and offline data are then automatically merged and can be further interrogated based on pre-defined calculation scripts to finally obtain the required performance metrics (e.g. conversion, selectivity). All these steps are realised with myhTe™, hTe's powerful software database customised for efficient handling of large amounts of complex data. With these techniques, mass balances (typically in the range of 100 ± 2%) can be presented with high precision in yields and selectivity.

The basic reaction mechanism behind catalytic dewaxing can be described as follows: the long-chain n-paraffins first undergo dehydrogenation at the metal sites to form olefins, which are subsequently protonated over the acid sites to form carbenium ions. These carbenium ions then undergo either cracking and/or isomerisation reactions. The relative rates of cracking and isomerisation reactions dictate the position of a maximum in the iso-paraffin yield as a function of conversion (defined here as conversion of material with boiling point greater than 360 °C). Further conversion beyond this optimum leads to over-cracking, yielding less desirable light hydrocarbon products.

Figure 4 shows a typical yield pattern as a function of hydrocracking conversion. In this example, the kerosene fraction is the desirable product. It can be seen that there is an optimum conversion level for producing kerosene. Increasing conversion beyond this point results in an increase in the production of lighter fractions at the expense of kerosene, a classical indication of over-cracking. Generally, dewaxing systems display maxima in yields that occur at higher conversions for lighter product fractions, with the yield of the C₄⁺ fraction increasing monotonically with conversion. Similarly, considering selectivity as a function of conversion (plot not shown) the selectivity of the target kerosene fraction rises with increasing conversion, until an optimum is reached, and subsequently drops. Concomitantly,
the gas selectivity decreases with conversion to a minimum before rising again at conversions above 60%.

Figure 5 shows typical carbon number distributions for the dewaxing feed, and products acquired at two different conversion levels obtained by operating at two different reaction temperatures. It clearly illustrates the shift towards lighter products with increasing conversion. In the dewaxing case, another key parameter to be analysed is the ratio of n- to iso-paraffins, since this ratio determines the cold flow properties of the synthetic fuel. Iso-paraffins have weaker van der Waals interactions than n-paraffins due to the lower contact area of the molecules. Consequently, crystallisation occurs at a lower temperature for iso-paraffins than n-paraffins of the same carbon number, which in turn affects bulk fluid cold flow properties such as cloud point, pour point and freeze point. Also illustrated in Figure 5 are the proportions of iso- and n-paraffins in the feed and dewaxing product as a function of the carbon number. It can be seen that with increasing conversion the proportion of iso-paraffins increases.

The task of the R&D work is to find catalyst systems and operating conditions that give the maximal yield to fuel product fractions containing the optimal proportions of iso-paraffins to ensure that cold flow properties meet specification. The fast and comprehensive data evaluation provided by myhte, as given in Figures 4 and 5, provides a deeper understanding of the product composition as a function of conversion, which in turn allows correlations to be drawn between catalyst characteristics, operating conditions, and bulk product properties such as cloud point and freeze point. Understanding these relationships is the foundation for developing tailor-made catalyst systems.

In conclusion, while FTS is a mature technology, development efforts continue to optimise the production of synthetic fuels, especially from sustainable carbon sources. Research has not only to focus on FTS technology, but also on downstream wax upgrading in order to obtain the target products, such as sustainable aviation fuel, in the highest possible yield with best product characteristics, such as cold flow properties. Doing so will ensure FTS technology finds its place in a more sustainable world.

References