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Innovation in Fischer-Tropsch: A Sustainable Approach to Fuels Production

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Abstract

A sustained global effort is required over the next few decades to reduce greenhouse gas emissions, in order to address global warming as society seeks to deliver the Paris Agreement temperature goals. The increasing availability of renewable electricity will reduce our reliance on fossil fuels. However, some applications, such as long-haul aviation, are particularly challenging to de-carbonise. The conversion of waste, biomass or existing CO₂ emissions into sustainable fuels via FT synthesis offers one solution to this problem. This paper describes some of the challenges associated with this route to these alternative fuels and how Johnson Matthey and bp have solved them.

Introduction

Global energy demands are increasing and so too is the need for more renewable and sustainable sources of energy to help transition us to a post-fossil-fuel-powered world. The EU has recently increased its renewable energy target to 32% for 2030¹, with many countries planning to ban internal-combustion-engine-powered cars by 2040 or sooner. However, the transportation industry is one of the most challenging sectors to adapt to using low-carbon fuels. Transportation modes such as aircraft, heavy-duty and marine vehicles demand high power and energy capacity that are currently unmet by renewable technologies. In the interim, we need clean, sustainable methods, continuous improvement and new innovations in renewable fuels to meet EU and other similar worldwide targets.

Johnson Matthey and bp have been collaborating for the past two decades² to develop an efficient reactor system and catalyst for the Fischer-Tropsch (FT) process. This offers a cost-effective method of converting any carbon source into high-quality liquid hydrocarbon fuels.

Creating Syngas from Waste

Today the world consumes more than 55 million barrels per day of transportation fuels³, the vast majority of which originates from crude oil. In addition to being a finite resource, each barrel of crude-oil-derived fuel typically contributes about 475kg of CO₂⁴ into the atmosphere over its life cycle (based on a 2010 European average). At the same time, hundreds of millions of tonnes of municipal solid waste are incinerated or sent to landfill each year, whilst similar quantities of woody biomass decompose to CO₂ and methane (a more potent greenhouse gas than CO₂)⁵. Industrial processes release more than 8 billion ⁶tonnes of direct CO₂ emissions, and flaring of natural gas releases a further 275 million tonnes⁷ of CO₂ equivalent per year.

These wastes and emissions are rich in carbon which can be extracted through gasification, reforming or capture of CO₂ (which can then be converted to syngas via Reverse Water Gas Shift). Converting this carbon to useful syngas rather than allowing it to be emitted to the
atmosphere as CO₂ creates an opportunity to significantly reduce fuel life-cycle emissions and its impact on global-warming. The carbon intensity of the resulting fuel can typically be reduced by more than 70% (relative to conventional fuel), with reductions of more than 100% possible as grid electricity becomes increasingly renewable and/or CO₂ sequestration is added to the technology mix.

Gasification of biomass is not new technology. However, it has typically been used to produce syngas for the generation of electricity, rather than chemical synthesis. Effective FT synthesis requires a specific ratio of H₂ and CO, and the catalyst used for this reaction is particularly susceptible to poisoning by impurities that may be present. Gasification of waste introduces the potential for a wide range of contaminants that need to be removed. The range of potential poisons, and the low levels necessary to ensure continued high-level performance for the FT synthesis catalyst make syngas purification a critical step of the process. Effective removal of these impurities also ensures that FT products are ultra-clean and high purity.⁸

As a world leader in purification and pre- and post-treatment of syngas gas for downstream applications, Johnson Matthey has a range of solutions to condition the syngas (irrespective of its original source) ready for conversion into sustainable fuel.

The FT Process

The FT process was originally developed by Franz Fischer and Hans Tropsch in 1925. It is a way of converting any carbon source into liquid hydrocarbon via syngas, effectively creating synthetic fuel (see equation 1).

\[
[2\text{H}_2 + \text{CO}]_n + \text{H}_2 \rightarrow \text{CH}_3(\text{CH}_2)_n\text{CH}_3 + n\text{H}_2\text{O} \quad (1)
\]

Syngas can be generated from various carbon sources, including coal, natural gas, municipal solid waste and biomass. The process mainly produces linear, long-chain paraffins that require further upgrading to produce liquid fuels, such as diesel and kerosene. The upgrading step comprises catalytic hydrocracking to both isomerise and crack the long-chain paraffins into smaller-chain paraffins with the correct properties for fuel applications. The various stages in the process are shown in Figure 1, below. In the quest for sustainable fuel solutions, FT-derived synthetic fuels provide a cleaner way to power cars, heavy-duty vehicles and aeroplanes. The latest developments in FT technology mean that the production of fuel from sustainable carbon sources is now closer to being commercially viable at all industrial scales.
Figure 1 - typical FT commercial processes utilise a syngas feed from bio or fossil fuels and convert to FT product.

Catalysts are required for the FT process to increase the rate of reaction and make the process industrially viable. There are broadly two options for FT synthesis, using cobalt or iron catalysts\(^9\). While cobalt is more expensive than iron, it mainly produces normal paraffins. Iron catalysed FT synthesis also incorporates the water-gas-shift reaction for CO\(_2\) products and makes a mixture of olefins & paraffins.

The most commonly used catalyst is cobalt, due to its high activity, selectivity to liquid hydrocarbons, and stability. Commercial synthesis of hydrocarbons occurs at moderate temperatures of 200-240°C and pressures of 20-40 bar. During the process, H\(_2\) and CO are converted into long-chain paraffins or waxes over the supported catalyst (see Figure 1). Pore diffusion and mass-transfer effects therefore play a key role in FT catalyst performance due to the need for H\(_2\) and CO to move into and along the catalyst pores against the movement of product molecules going the other way.

The FT synthesis reactions are all highly exothermic, making efficient removal of heat essential for any reactor design. There are a number of benefits of using conventional fixed-bed tubular reactors\(^10,11\) which is why Johnson Matthey & bp have favoured this design. They are a proven technology with many manufacturers able to fabricate reactors at large scale. They work by holding the catalyst in place via a static bed, which has the advantage of preventing catalyst loss, which could lead to product contamination as can occur in slurry reactors. The reactors have a modular design, which makes increasing capacity as simple as adding tubes; however, conventional fixed-bed tubular reactors are limited by the need to balance tube diameter and catalyst pellet size to achieve effective temperature control without excessive pressure drop. These reactors generally contain tens of thousands of tubes of around 1 inch (25 mm) diameter, resulting in high construction costs with catalyst
pellets in the range of 1-2 mm (0.04-0.08 inch) diameter, which reduces catalyst productivity and selectivity to hydrocarbon liquids.

An alternative synthesis route is through slurry reactors. This type of reactor is more efficient at heat removal and uses catalyst powder of the order of tens of microns diameter to minimise pore diffusion resistance. However, slurry reactors can suffer from catalyst attrition, which leads to catalyst loss and product purity issues, and are also less straightforward to scale up compared to fixed-bed alternatives.

The Johnson Matthey and bp collaboration

Since 1996, Johnson Matthey and bp have been collaborating to bring FT synthesis to the industrial scale. The first major joint venture in 2002 was to build the Nikiski demonstration plant in Alaska (Figure 2), based on the ‘first generation’ (Gen1) FT catalyst contained within conventional tubular reactor technology. The Nikiski plant produced a nominal 300 barrels per day of synthetic crude product from pipeline natural-gas feedstock; and by the time it was decommissioned in 2009, the plant had exceeded all its performance goals related to catalyst productivity, hydrocarbon selectivity, carbon monoxide conversion, methane selectivity, and catalyst lifetime. A single charge of catalyst ran for just over 7000 hours enabling Johnson Matthey to predict an expected three-year lifetime without any regeneration.

The integrated plant combined three processes for testing FT technology: a novel compact reformer for syngas generation; a fixed-bed FT reactor; and mild hydrocracking of FT waxes to produce synthetic crude. The original fixed-bed tubular reactor technology was developed as a method of monetising stranded natural gas in remote locations. However, it was only competitive at large scale, above 30,000 bbl/d (~3850 mtpd), in areas with low natural gas prices and high oil prices.
Figure 2 - the Nikiski demonstration plant [courtesy bp Plc]

**Novel catalyst carrier devices for FT synthesis**

More recent interest in FT technology is in small-scale applications to produce renewable fuel from municipal solid waste or cellulosic biomass. This involved developing technology that lowered costs whilst improving efficiency. In 2009, Johnson Matthey designed a novel catalyst carrier device to fit inside a tubular reactor that allows for the use of smaller catalyst particles. At the same time, bp developed an improved second-generation (Gen2) catalyst formulation\textsuperscript{13}. Both organisations then worked to combine both the new catalyst and the novel catalyst carrier device, which produced a step change in commercial FT performance (see Figure 3). The **CANS\textsuperscript{TM}** catalyst carrier technology received global recognition, winning both the Research Project Award and the Oil and Gas Award at the IChemE Global Awards in 2017, and the Rushlight Clean Energy Award and Rushlight Bioenergy Award in January 2020. These accolades demonstrate how advanced FT technology will dramatically impact the chemical engineering industry, with many real-world applications.
Figure 3 - step change in performance provided by novel reactor technology and Gen2 catalyst

The novel catalyst carrier reactor design\(^\text{14}\) combines the advantages of the fixed-bed tubular reactors and the slurry-phase systems. Its modular design enables low-risk scale-up and simple operation, while the smaller catalyst particles offer high productivity and selectivity. The stacked catalyst carriers have a unique design that aids their ability to perform FT synthesis as shown in Figure 4. Syngas arrives from the catalyst carrier above and travels down a porous central channel (A), flowing radially through the catalyst bed where the FT reaction occurs and heat is evolved (B). The gas exits via a porous outer wall, flowing towards the top inner side of the catalyst carrier body (C). Cooling occurs as the gas flows down the narrow annulus between the body and the inside wall of the tube, through the transfer of heat to boiling water on the shell side (D). A seal prevents gas bypassing the next catalyst carrier and the gas then enters the catalyst carrier below, where the process repeats itself (E).
A reactor tube contains 60-80 of the CANS™ catalyst carriers and effectively creates a series of mini adiabatic radial-flow reactors with interbed cooling. Radial flow through each CANS™ catalyst carrier means that, although the reactor tubes are 10-15 m (33-49 ft) long, the effective catalyst bed thickness is only around 15% of the overall tube length. This enables the use of sub-millimetre catalyst particles, which improves selectivity and activity whilst limiting the reactor pressure drop to that of a conventional fixed-bed tubular reactor. Wide-diameter tubes of 3-4 inches (75-100 mm) are used in the novel reactor, which has the effect of reducing the heat-transfer surface per unit volume of catalyst. However, this is compensated by a larger temperature difference at the wall, where reactants are hottest (as opposed to the centre of the tube in conventional fixed-bed tubular reactors). Combining this structure with a high gas velocity through the narrow annulus between the CANS™ catalyst carrier body and tube wall results in excellent heat transfer. By separating heat removal from the catalyst bed, good control of the reaction temperature is also achieved without the risk of quenching the reaction. The advanced reactor technology also enables operation with >50% inerts in the reacting gas, allowing a single-stage FT reactor to be used in a recycle loop to maximise overall conversion of CO to >90% (Figure 5).
Compared to conventional fixed-bed tubular reactors, the new CANS™ catalyst carrier and optimised catalyst reduces the number of reactor tubes by 95%, significantly simplifying the design and fabrication of the reactor, resulting in a reduction of capital expenditure costs of around 50% for the FT unit. There is also a three-fold increase in production for the same size reactor as the catalyst performance is closer to that of a powder, with excellent heat and mass transfer to, from and within catalyst particles. The increased productivity at least halves the catalyst volumes usually required for the same production rate. Additionally, containing the catalyst inside the CANS™ catalyst carrier removes the requirement to filter the catalyst from the wax product. Instead the catalyst is easily replaced by removing the entire catalyst carrier, meaning there is no interaction with the hazardous cobalt catalyst material. Fundamentally, this makes FT applications possible at both small and large scales, with around 6,000 bbl/d (770 mtpd) achievable in a single reactor of around 900 mt. For areas with tighter transport restrictions, 2000 bbl/d can be delivered in a single reactor of around 4 m diameter and 250 mt in weight.

**Proving the concept**

One of the main challenges to overcome was proving that the concept worked at commercial scale, and so Johnson Matthey has invested in extensive testing to develop the
engineering science necessary to implement the novel reactor concept. This involved building customised rigs to validate heat-transfer performance, hydraulics, and accurately measure reaction kinetics on high-throughput micro-reactors. Significant engineering effort has been required to develop models capable of accurately predicting the performance of commercial-scale reactors. The initial proof of concept work was carried out using CANS™ catalyst carriers manufactured by an experienced prototyper.

Fischer-Tropsch catalysis is strongly influenced by cobalt crystallite size, support properties and catalyst treatments. Selection of the cobalt crystallite size is critical to obtaining the required performance. Larger cobalt crystallites result in a less active catalyst due to the lower surface area to volume ratio, and thereby require higher temperatures to achieve a target conversion. Alternatively, if cobalt crystallites become too small the chemistry favours chain termination (methane formation) over chain growth (C-C coupling). While the desirable cobalt crystallite size is in the narrow range of 8 to 10 nm for FT synthesis, the activity of a good catalyst can be significantly reduced by sub-optimal treatments, such as the reduction stage of the cobalt oxide to the active metallic phase. Cobalt based FT catalysts are normally made by impregnating the support with a cobalt salt, calcination to give cobalt oxide (Co3O4) and subsequent reduction under hydrogen in the plant to give the active cobalt metal phase. The catalyst reduction process is defined in equation 2, which highlights the significant levels of water that are produced throughout the catalyst bed, and this in turn can sinter, re-oxidise or damage the catalyst significantly if not fully catered for under process conditions. Catalyst bed profile effects are also significant as the bottom sections of the bed are exposed to the water produced at the top of the bed, while higher pressures required commercially also lead to higher water partial pressures in the catalyst pores.

Co3O4 + 4H2 → 3Co + 4H2O (2)

bp originally developed the Gen2 catalyst formulation as a drop-in for conventional fixed-bed tubular reactors and this formulation has been adapted to the CANS™ technology by Johnson Matthey to produce sub-millimetre size catalyst particles at scale. Developing the new formulation to achieve improved activity, selectivity and stability, while optimising the catalyst activation has required thousands of hours of testing at laboratory scale in high throughput and pilot plant test units. This has been supported by a state-of-the-art FT unit, with exceptional online analytics for all products up to C18 and analytical capabilities such as in situ X-ray diffraction and temperature programmed reductions which enable catalyst evaluation under process conditions.

Whilst the hydrocarbons and oxygenates that were identified are known compounds formed during the low temperature, Co catalysed, FT process the combination of the multiple analysis techniques used has allowed a level of detail to be gained on the FT product composition that is seldom reported. Typically, the long-chain 1-alcohols and carboxylic acids were found to be present at levels of 1/10th and 1/1000th that of hydrocarbons of equivalent carbon chain length respectively. Additionally, H-NMR and C-NMR analyses were used to quantify the average class compounds concentration of 1-olefin, cis- and trans-2-olefins, 1-alcohol and aldehyde as appropriate for the technique used. The 1-olefin:n-paraffin ratio in the hydrocarbon liquid and wax products was found to
decrease significantly with increasing carbon chain length in both phases and much more so than those of the 2-olefin or 1-alcohol.

Catalyst activity and selectivity is only part of the process however, with stability, robustness to process events and life duration also playing a vital role in a commercial catalyst. Johnson Matthey Davy and bp built on their extensive experiences of the first-generation catalyst in the Nikiski demonstration plant to optimise this further for the second-generation catalyst. This included several catalyst life tests which operated for many thousands of hours at steady FT process conditions. This included the catalyst formulation used in CANS™ catalyst carriers operating with exceptional performance over an 18,000 hour life test. The gradual drop in catalyst activity over this period was compensated by an increase in operating temperature within the reasonable limits of a commercial reactor. Despite frequent shut-downs and other challenges associated with laboratory-scale operation, the catalyst was still showing good activity and selectivity at the end of this test. This is a result of the process having been designed to be robust and operate in chemically stable conditions.

The CANS™ catalyst carrier concept has been successfully demonstrated at commercial scale on a pilot plant at Johnson Matthey’s R&D facilities in Stockton-on-Tees. It is not practical to test a full-length commercial reactor tube at these facilities, due to limitations on gas supply and product storage capacity, so a creative approach was required. Flexible design of the pilot plant enabled testing of multiple commercial-size CANS™ catalyst carriers in a much shorter tube; by recycling gas, liquid products and produced water to simulate the full range of conditions and flowrates present in a commercial reactor tube. This, coupled with raising steam in the reactor cooling jacket, has enabled full demonstration of the catalyst, CANS™ catalyst carriers, hydraulics and heat transfer at commercial conditions, flows and tube diameters.

Over 20,000 hours of testing under commercial flowsheet conditions has demonstrated the performance of the CANS™ catalyst carrier and the Gen2 catalyst with a confirmed product slate and stable catalyst life. A C5+ selectivity of around 90% and C5+ productivities in excess of 300 g/l/hr have been demonstrated on the pilot plant. The crude FT product consists of a wax stream which is liquid at reaction conditions and solid at ambient temperature and a light hydrocarbon condensate stream which is liquid at ambient temperature. Figure 6 below shows both these products are high quality, clean and catalyst-free (Figure 6).
Scaling up to support the industry

The International Energy Agency has measured the share of global energy-related carbon dioxide emission from transport at 23%, with aviation contributing 2–3% of worldwide anthropogenic carbon emissions\(^\text{18}\). There is great potential for this figure to be reduced by using synthetic fuels from sustainable feedstocks, and this makes fuels produced via the FT process an attractive alternative to current aviation fuels. Synthetic fuels also burn cleaner, due to the absence of sulphur and aromatics, while also producing fewer particulates\(^\text{19}\). As a result, FT fuels lead to increased combustion and turbine life, while the enhanced thermal stability reduces deposits on engine components and fuel lines. This results in a dual advantage for the aviation industry, in terms of both improved fuel economy and less maintenance of aviation equipment.

The scale of the market is substantial, with air transportation alone expected to consume at least 500m tonnes per year (11 million barrels per day) of fuel by 2050\(^\text{20}\). Practical limitations on the supply of waste feedstocks or local, low-cost renewable power for hydrogen production typically limit the scale of each project to less than 5,000 barrels per day. With tens of thousands of filled CANSTM catalyst carriers required for each project, the ability to consistently and efficiently produce both the CANSTM catalyst carriers and the FT catalyst which they contain is crucial for successful commercial deployment of the technology.

To address this, Johnson Matthey have collaborated closely with a company skilled in delivering sustainable engineered solutions for vehicle exhaust aftertreatment systems, to develop a mechanical design for the CANSTM catalyst carriers that is economical to make, can be easily filled with catalyst, and meets the functional specifications developed by Johnson Matthey. This has been confirmed by testing of commercial prototypes.

A production line has been constructed and commissioned for mass manufacture and catalyst filling of the CANSTM catalyst carriers, and the first charge has now been produced for the first commercial project. The production line is fully automated to allow the safe
filling of the cobalt-containing catalyst and contains state of the art equipment and in-line quality control to assure the CANS™ catalyst carriers meet the required functional specifications. The functional specifications were established during the development of the CANS™ catalyst carriers from concept to prototype with testing performed on in-house built rigs at the Johnson Matthey Technology Centre in Teesside. Identifying these upfront allowed Johnson Matthey and the manufacturer to work together to ensure the resulting production line would safely, efficiently and consistently produce high-quality units.

A collaborative team of engineers from Johnson Matthey and the manufacturer worked closely during initial commissioning of the line to work through the various challenges associated with scale-up to mass manufacture of a novel process. This knowledge will be invaluable as further improvements and optimisations are implemented.

In order to achieve high-quality performance, challenging activity and selectivity targets were set for the FT catalyst. Scale-up of the chosen formulation took place at Billingham in the UK. Catalyst preparation was initially at laboratory scale with short-term and long-term testing of development samples conducted using both micro-reactors and CANS™ catalyst carriers, facilitating accurate modelling of the performance of a full-scale FT reactor.

As scale up continued, preparation of the FT catalyst moved into the Manufacturing Science Centre (MSC) where appropriate technologies were identified for each of the steps involved in catalyst production. The technical risk of scale-up was minimized by using down-scaled versions of full-scale production equipment.

A fully developed catalyst manufacturing process was transferred from the MSC to a dedicated production asset located at Clitheroe in the UK. Careful attention was paid to the specification of the raw materials used. To ensure a proper understanding of the impact of trace impurities on long term FT catalyst performance, a series of experiments were conducted in which the FT catalyst was doped with different FT poisons.

Every production batch of FT catalyst has been tested against an agreed quality assurance specification. Conforming product was loaded into CANS™ catalyst carriers as it was manufactured, thus minimizing the overall production timeline.
Commercial Application

The Johnson Matthey Davy/bp FT technology incorporating CANS™ catalyst carriers offers benefits to both small- and large-scale operations with good economics, opening up the prospect of exciting future applications.

Fulcrum BioEnergy is the first to licence the Johnson Matthey Davy/bp FT technology in its Sierra BioFuels Plant, located near Reno, Nevada. The Sierra plant will be the first in the USA to produce a renewable low-carbon transportation fuel from municipal solid waste or household garbage. The plant will first sort the waste to recover recyclables and remove material not suitable for processing, so is not in competition with recycling processes. The remaining material will be processed into a feedstock before being fed into a gasification system to produce a synthesis gas. This is then converted into hydrocarbons by the FT technology for the production of renewable fuels. The Sierra plant construction is approaching completion and when operational will convert approximately 175,000 mt of Municipal Solid Waste (MSW) into approximately 11 million US gallons (42 million litres) of renewable FT product each year.

Multiple projects are being developed in the United States and Europe, which can make a significant contribution to meeting the demand for renewable transportation fuels in the next decade.
Conclusion

In order to meet greenhouse gas emissions reduction targets, especially for aviation\textsuperscript{21}, production of sustainable fuels will have to substantially increase. There are a range of sustainable fuels potentially available, but limitations on sustainable feedstocks and viable technology routes mean that diesel and jet fuel production via FT synthesis will need to form a key part of this industry.

Producing fuels via FT synthesis is not new. However, cost of production was always a barrier, with existing large-scale producers of FT fuels unable to economically scale down to match the size of the waste facilities that feed them.

The CANS\textsuperscript{TM} technology addresses this problem, offering an economic and efficient solution at the scales required by the industry.

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