Quantitative carbon distribution analysis of hydrocarbons, alcohols and carboxylic acids in a Fischer-Tropsch product from a Co/TiO$_2$ catalyst during gas phase pilot plant operation

Roy Partington[1*] , Jay Clarkson[2], James Paterson[1], Kay Sullivan[3] and Jon Wilson[3]

Abstract

Comprehensive two-dimensional gas chromatography (GCxGC) analysis for 1-alcohols and gas chromatography–mass spectrometry (GC-MS) analysis for carboxylic acids, derivatised as their methyl esters, have been applied to liquid and wax Fischer-Tropsch (FT) hydrocarbon products. These methods in combination with conventional one-dimensional gas chromatography (GC) analysis of the aqueous, gaseous, liquid hydrocarbon and wax products plus conventional high-performance liquid chromatography (HPLC) analysis of the aqueous phase has allowed a quantitative distribution analysis of FT hydrocarbon and oxygenated products to be demonstrated for a Co/TiO$_2$ catalyst operating in a fixed bed gas phase pilot plant utilising CANS[TM] catalyst carrier devices. The GC-MS method used is, to the best of our knowledge, the first application of this derivatisation route for the quantification of individual carboxylic acids in FT hydrocarbon product streams.

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 product composition that is seldom reported.

Additionally, ^{1}H nuclear magnetic resonance spectroscopy (NMR) and ^{13}C NMR analyses were used to quantify the average concentration of 1-olefin, *cis*- and *trans*-2-olefins, 1-alcohol and aldehyde as appropriate for the technique used. Comparison of GCxGC versus ^{1}H NMR and GC-MS versus a KOH titration confirmed the applicability of the chromatographic methods for the quantitative analysis of FT oxygenated compounds. Long-chain 1-alcohols and carboxylic acids, $\geq C_3$, were found to be present at levels of 1/10th and 1/1000th that of hydrocarbons of equivalent carbon chain length respectively. The 1-olefin:*n*-paraffin ratio in the hydrocarbon liquid and wax products was found to decrease significantly with increasing carbon chain length and much more so than those of the 2-olefin or 1-alcohol.

Keywords: Fischer-Tropsch products, Comprehensive two-dimensional gas chromatography, Gas chromatography–mass spectrometry, 1-alcohol, Olefin, Carboxylic acid, ^{1}H NMR, ^{13}C NMR

* Correspondence: roy.partington@uk.bp.com
[1]BP Group Research, BP International, Saltend Chemicals Park, Hull HU12 8DS, UK
Full list of author information is available at the end of the article

Introduction

Fischer-Tropsch (FT) synthesis is a well-known and much studied catalytic process for converting synthesis gas to hydrocarbon and oxygenate products having linear carbon chains ranging from C_1 to over C_{100} (Day 2002; Khodakov et al. 2007). However, improvements to process design, catalyst efficiency and analytical methods for the detailed analysis of products are continuously being made.

BP and Johnson Matthey (JM) have been collaborating over many years to commercialise a propriety FT synthesis technology (Coe and Paterson 2019; Peacock et al. 2020). A tubular reactor demonstration plant was commissioned in Alaska in 2002 (Collins et al. 2006) using a Co/ZnO catalyst. This facility is the largest FT plant built in the US, producing 300 bbl/day of synthetic crude product from pipeline natural gas feedstock. When the plant was decommissioned, in 2009, it had exceeded all its performance goals related to catalyst productivity, hydrocarbon selectivity, carbon monoxide conversion, methane selectivity and catalyst lifetime. The original fixed bed tubular reactor technology was developed as a method of monetising stranded natural gas in remote locations but was typically only competitive at large scale (> 30,000 bbl/day) in areas with low natural gas prices and high oil prices.

Recent innovations in the BP/JM FT technology offers both small- and large-scale operations with good economics. In 2009, JM designed a novel catalyst carrier device (CANS™ carrier) inside a tubular reactor (Gamblin 2014), shown in Fig. 1, that allows for the use of small catalyst particles and, at the same time, BP developed a new second-generation catalyst. The combination of an improved catalyst and CANS™ reactor design produced a step change in FT performance achieving the advantages of both fixed-bed tubular reactors and slurry phase systems (Coe and Paterson 2019; Peacock et al. 2020). This step improvement in FT technology gives three times the catalyst productivity and halves the capital expenditure when compared with conventional multi-tubular fixed bed FT reactors. This simple to operate and cost advantaged technology can be utilised to economically convert synthesis gas, generated from sources such as municipal solid waste (MSW) and other renewable biomass, into long-chain hydrocarbons suitable to produce base oils, speciality waxes, diesel, and jet fuels. Fulcrum BioEnergy will use the technology in their new Sierra BioFuels Plant located in Storey County, Nevada. The Sierra plant will be the first commercial scale plant in the US to convert MSW feedstock, or household garbage that would otherwise be landfilled, into a low carbon, renewable transportation fuel (JM press release 2018).

Catalysts are required for the FT process to increase the rate of reaction and make the process industrially
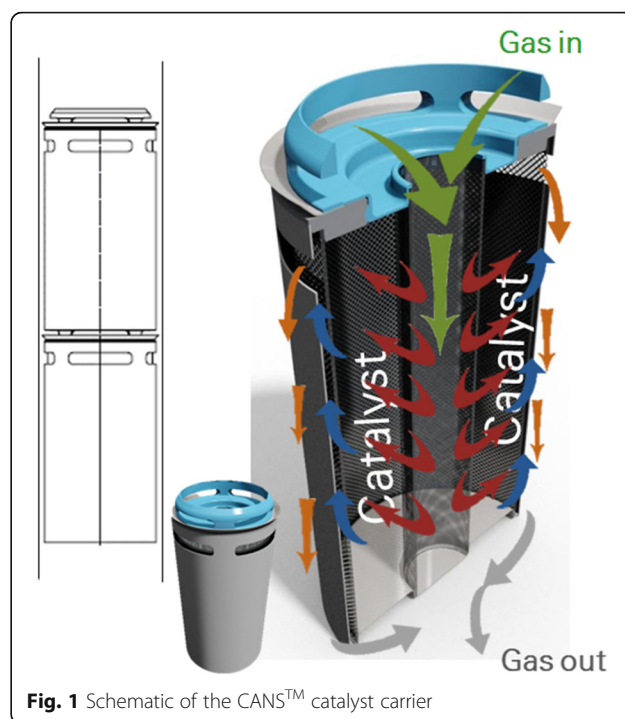

Fig. 1 Schematic of the CANS™ catalyst carrier

viable. The catalysts usually employed are based on Co or Fe, usually with modifiers added to optimise performance, and in the case of Co can be supported on oxides such as SiO_2, Al_2O_3, TiO_2 or on carbonaceous material (see review articles and references within by; Oukaci et al. 1999; Fu and Li, 2015; Gholami et al. 2020). Typically, Co catalysts operate at temperatures between 200 and 240 °C and pressures between 2 and 4 MPa, whereas Fe-based processes often use temperatures in excess of 300 °C and utilise the water-gas-shift reaction to control the syngas feed composition.

The products of the FT reaction are complex (Shafer et al. 2019), more so from Fe-based catalysts, with paraffinic, olefinic, alcohol and carboxylic compounds being observed. Additionally, aldehydes, ketones and ester can also be formed. There are numerous papers describing methods for analysis of the gas phase (Bertoncini et al. 2009; Grobler et al. 2009; Seomoon et al. 2013; Pei et al. 2015), aqueous phase (Anderson and White, 1994; Grobler et al. 2009; Pei et al. 2015; Ma et al. 2019), liquid hydrocarbons and wax products (Bertoncini et al. 2009; Grobler et al. 2009; van der Westhuizen et al. 2010; Silva et al. 2011; Fernandes et al. 2015; Pei et al. 2015; Shafer et al. 2019) but in general the quantitative distribution analysis of alcohols and carboxylic acids versus carbon chain length is difficult to achieve when these compounds are present at the low levels normally expected in a cobalt-catalysed FT product. This can be due to (i) the sensitivity of analytical methods at low oxygenate

concentrations, (ii) the challenge of keeping high boiling point compounds in the vapour phase and then chromatographically separating a complex mixture of components when using on-line gas chromatography (GC) and (iii) the difficulty in obtaining an acceptable mass balance of all product phases when combining on-line and off-line analyses (Xiao et al. 2017; Yang et al. 2017). Some success in quantifying C_1 to C_{18} alcohols, formed over a silica-promoted Co catalyst designed to produce a high level of FT oxygenates, has been shown by combining data from gaseous, aqueous and liquid hydrocarbon samples when using simple on-line and off-line GC analyses, but no attempt was made to identify or quantify any carboxylic acids that might also have been present (Pei etc. 2015).

Furthermore, for a truly representative analysis across the full carbon range, the sampling of the FT products needs to be conducted only once the catalyst has been operating in a stable manner for a suitably long period of time and allowance has been made for effective purging of product traps and analysis lines. Achieving truly stable FT catalyst performance can take hundreds of hours before representative product samples are available. These requirements can be easily accommodated during pilot plant operation, such as described in our work, but may not be possible for many academic and small-scale micro-reactor studies.

Comprehensive two-dimensional chromatography (GCxGC) coupled with time-of-flight mass spectrometry has been used in many cases for the identification of trace components in FT products and sometimes quantification has also been given. Such examples show (i) the analysis of products from Co/Al_2O_3 operated under slurry conditions demonstrating an Anderson-Schulz-Flory (ASF) plot of carbon distribution over the C_1 to C_{20} range for paraffins, olefins and oxygenates (Bertoncini et al. 2009); (ii) the quantification of 1-alcohols in liquid hydrocarbon from a Co/Al_2O_3 catalyst (Silva et al. 2011); (iii) the quantification of paraffins, olefins, aromatics and oxygenates in samples of oil made during high-temperature FT experiments (van der Westhuizen et al. 2010); (iv) the quantification of paraffins, olefins, alcohols, aldehydes and carboxylic acids up to C_{15} produced from a precipitated Fe catalyst in slurry operation (Grobler et al. 2009); and (v) the simultaneous identification and quantification of alcohols and carboxylic acids, as their trimethylsilyl derivatives, in FT syn-crude and distilled products (Fernandes et al. 2015). The use of supercritical fluid chromatography coupled with two-dimensional gas chromatography–mass spectrometry for the separation and identification of saturated, unsaturated, aromatic and oxygenate species in hydrocarbon samples derived from a high-temperature FT reaction has also been demonstrated (Potgieter et al. 2013),

clearly indicating the diversity of class and number of organic compounds present in such products.

In this paper, we show the application of comprehensive two-dimensional gas chromatography (GCxGC) for the quantification of alcohols and gas chromatography-mass spectrometry (GC-MS) for the quantification of carboxylic acids, derivatised as their methyl esters, in liquid and wax hydrocarbon FT products. The latter method is, to the best of our knowledge, the first demonstrated application of this derivatisation method for the analysis and quantification of individual carboxylic acids in FT hydrocarbon product streams. GC-MS analysis, without the derivatisation step, has been reported for the identification of strongly adsorbed carboxylic acids present on a used Co/Al_2O_3 catalyst after FT operation (Peña et al. 2014). In that study, the used catalyst was first cleaned of paraffinic wax by a Soxhlet procedure and then the carboxylic acids, and other strongly adsorbed species, were extracted into a $CH_2Cl_2:CH_3OH$ solvent mixture for subsequent identification.

In our study, GCxGC and GC-MS methods in combination with conventional one-dimensional gas chromatography (1D-GC) analysis of the aqueous, gas, liquid hydrocarbon and wax products plus conventional high-performance liquid chromatography (HPLC) analysis of the aqueous phase has allowed a quantitative product distribution, from C_1 to C_{100}, to be demonstrated for a Co/TiO_2 catalyst operating in a fixed bed gas phase pilot plant utilising the novel CANS^{TM} carrier and reactor. 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 product composition that is seldom reported.

Additionally, ^1H NMR analysis was used to quantify the average concentration of 1-olefin, internal olefin, 1-alcohol and aldehyde compounds in the liquid hydrocarbon and wax products whilst ^{13}C NMR and ^{13}C distortionless enhancement by polarisation transfer (DEPT135) NMR were used to confirm the location of unsaturation of the internal olefins, and the ratio of *cis* and *trans* isomers. Comparison of GCxGC versus ^1H NMR and GC-MS versus a KOH titration was also conducted in order to confirm the applicability of the chromatographic methods for quantitative analysis of FT oxygenated compounds.

Materials and methods
Production of Fischer-Tropsch products
A cobalt-based FT catalyst, supplied by Johnson Matthey PLC, with the active phase supported on TiO_2 was loaded to several CANS^{TM} carriers placed in series in a CANS^{TM} reactor pilot plant. A schematic diagram of the

pilot plant is shown in Fig. 2. After reduction using H_2, syngas was added to the reactor and the temperature was ramped to achieve target CO conversion. Wax, light hydrocarbon liquid and aqueous phases were collected post-reactor under appropriate conditions for subsequent off-line analysis. The exit gas containing unreacted syngas and C_1 to C_6 hydrocarbons were recycled over the catalyst bed allowing any volatile olefins present the opportunity to further react to alkanes and oxygenates. A purge stream prevented inert compounds from building up in the recycle.

For a period of 5 h, at 1630 h on stream, the mass flow of the liquid and solid phases collected per unit time and the flow rate of the product gas were recorded to allow the analytical data from the gas, aqueous, liquid hydrocarbon and wax hydrocarbon phases to be combined to give a detailed view of the FT product distribution. The aqueous, liquid hydrocarbon and solid wax samples collected during this time are referenced as Aq1, LHcL1 and Wax1. The catalyst had good stability and at this time on stream the CH_4 selectivity was 7.9% and C_{5+} selectivity was 85.0%.

Gas phase analysis of hydrocarbons

The gas phase was analysed by on-line gas chromatography using a PGC5000 GC consisting of 12 packed columns, one single-measurement thermal conductivity detector (TCD), one dual-measurement TCD, 6 air actuated solenoid valves to switch between columns and 4 carrier gas streams—one nitrogen, three hydrogen operating with an isothermal oven temperature of 100 °C.

This allowed the complete analysis of CO, H_2, N_2, CO_2 and C_1 to C_8 hydrocarbons.

Aqueous phase—analysis of 1-alcohols

The aqueous sample (Aq1) was analysed for C_1–C_{10} linear alcohols by gas chromatography using a flame ionisation detector (FID). A model 7890A GC and G4513A automatic liquid sampler from Agilent Technologies was employed. The analysis was achieved using a CP-Wax52CB capillary column 60 m in length with an internal diameter of 0.25 mm and a stationary phase thickness of 0.25 μm supplied by Agilent Technologies. It was operated with an initial temperature of 40 °C held for 6 min then increased at 10 °C/min to 200 °C. Helium carrier gas at a flow of 1.5 mL/min was used. A sample volume of 0.2 μL was injected into a split injector at 200 °C with a split ratio of 30:1. Detection was by flame ionisation detector at 250 °C. Calibration was performed with standards prepared volumetrically using linear alcohols with purity > 98% supplied by Sigma-Aldrich. Dilutions were made with laboratory 18 MΩ water. An internal standard of propan-2-ol was added for quantification.

Aqueous phase—analysis of carboxylic acids

The aqueous sample (Aq1) was analysed for C_1–C_4 linear carboxylic acids by liquid chromatography using an ultraviolet (UV) detector. A model 1100 quaternary LC from Agilent Technologies was employed. Separation was achieved using a 300 mm Aminex 87H column with a diameter of 7.8 mm supplied by Bio-Rad Laboratories. The column was operated under isocratic conditions at
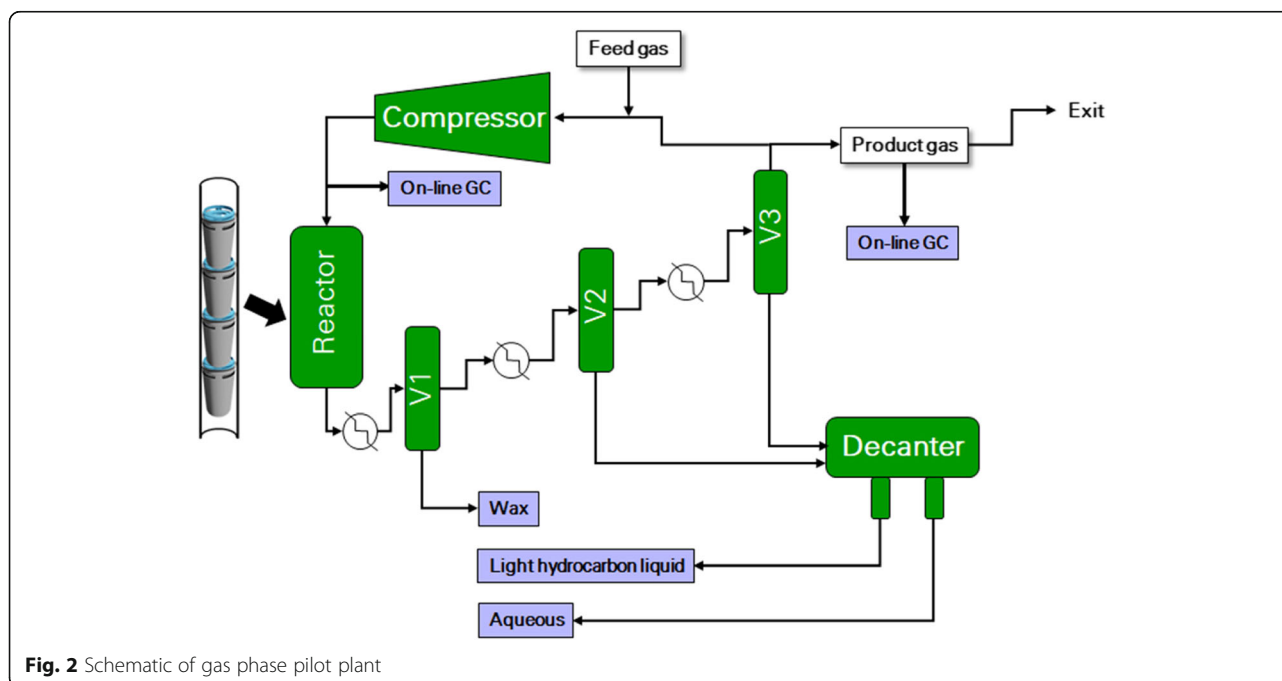

Fig. 2 Schematic of gas phase pilot plant

ambient temperature with an aqueous mobile phase of 0.005 M sulfuric acid at a flow rate of 0.6 mL/min. A 25 µL injection volume was used together with UV detection at 210 nm and a bandwidth of 8 nm. Quantification was by external standard with response factors determined by calibration using standards prepared volumetrically in laboratory quality 18 MΩ water. Carboxylic acids were supplied by Sigma-Aldrich.

Light hydrocarbon liquid—analysis of hydrocarbons

The light hydrocarbon liquid sample (LHcL1) was analysed for a carbon distribution in the range $C_5–C_{50}$ by gas chromatography with flame ionisation detection. A model 6890 GC from Agilent Technologies was employed. The analysis was achieved using a VF-5HT metal capillary column 30 m in length with an internal diameter of 0.25 mm and a stationary phase thickness of 0.1 µm supplied by Agilent Technologies. It was operated with an initial temperature of 50 °C held for 4 min then increased at 10 °C/min to 430 °C and held for 20 min. Helium carrier gas at a flow of 2.3 mL/min was used. A sample volume of 0.1 µL was injected into a PTV injector at 400 °C with a split ratio of 120:1. Detection was by flame ionisation detector at 400 °C. Quantification was by an area normalisation method assuming an equivalent mass response for all components. Identifications were established by analysing Agilent Technologies reference mixtures GC Boiling Point Calibration Standard for SimDis #2 (5080-8678) and Boiling Point Calibration Standard #1 for simulated distillation (5080-8716).

Light hydrocarbon liquid—analysis of 1-alcohols

The light hydrocarbon liquid sample (LHcL1) was analysed for 1-alcohol distribution in the range $C_3–C_{17}$ by comprehensive two-dimensional gas chromatography (GCxGC) with flame ionisation detection. A model 7890A GC from Agilent Technologies equipped with an Agilent capillary flow technology flow modulator was employed. The analysis was achieved using a 30-m-long HP-5 capillary column in the first dimension (^{1}D) with a stationary phase film thickness of 0.25 µm; the second dimension (^{2}D) column was a 5-m-long HP-Innowax column with a phase thickness of 0.15 µm; both columns had an internal diameter of 0.25 mm and supplied by Agilent Technologies. The columns were operated with an initial temperature of 50 °C and increased at 5 °C/min to a final temperature of 240 °C where they were held for 20 min. Helium was used as the carrier gas with the first dimension and second dimension column flows set to 0.6 mL/min and 26.0 mL/min respectively. A modulation period and sampling time of 1.58 s and 1.45 s respectively was used. A sample volume of 0.3 µL was injected into a split injector at 240 °C with a split ratio

of 50:1. The flame ionisation detector was operated at 250 °C. Calibration was performed with standards prepared volumetrically in cyclohexane using linear alcohols with purity > 98% supplied by Sigma-Aldrich. An internal standard of 2-methylbutan-1-ol was added for quantification.

Light hydrocarbon liquid and wax—analysis of carboxylic acids

The method used was based on the esterification of the organic acids to the methyl ester and measurement by GC or GC-MS (Martínez et al. 2012). Approximately 0.1 g of homogenised sample was accurately weighed (3 decimal places) in the bottom of a suitable culture tube and then 200 µL of an internal standard solution containing 9.3 µg/mL of 2-methylpentanoic acid in toluene was added as internal standard. This was followed by the methylating reagent (1 mL), prepared daily by carefully adding 2 mL of concentrated sulfuric acid to 18 mL of cooled, dry methanol. The culture tube was capped and heated to 80 °C for 60 min. After cooling to room temperature, 600 µL of heptane followed by 1.0 mL of 1 M aqueous sodium chloride solution was added. The tubes were capped and vortexed for 2 × 6 s periods. After standing to allow the layers to separate 200 µL of the top organic layer was removed, and further diluted with heptane if required. All reagents were supplied by Sigma-Aldrich. The prepared sample was analysed on a 7890A GC from Agilent Technologies with an Almsco BenchToF time of flight mass spectrometer supplied by Markes International. The analysis was achieved using an HP-5 capillary column 30 m in length with an internal diameter of 0.25 mm and a stationary phase with a thickness of 0.25 µm supplied by Agilent Technologies. It was operated with an initial temperature of 50 °C increasing at 8 °C/min to 320 °C and held for 10 min. Helium carrier gas at a flow of 1.5 mL/min was used. A sample volume of 1.0 µL was injected into a multi-mode inlet (MMI) injector at 200 °C with a split ratio of 30:1. Detection was by mass spectrometry with the electron ionisation source operated at 200 °C and an applied energy of − 70 eV. The transfer line temperature was 250 °C. Data was acquired at 8 spectra/s between m/z 34 to m/z 400. The methyl esters were quantified against the internal standard using the extracted ion chromatograms of m/z 74 and m/z 88 respectively. GC-MS response for the methyl esters was established by dilution in cyclohexane of a certified 1000 µg/mL C_4 to C_{24} fatty acid methyl ester (FAME) standard and addition of methyl 2-methylpentanoate as internal standard. All materials were supplied by Sigma-Aldrich. The relative standard deviation (RSD) established for analyte response at a concentration of 10.0 µg/mL over 10 analyses was determined for the methyl esters of $C_6–C_{24}$ carboxylic acids

(Additional file 1: Table S1). Finally, the linear response of selected FAMEs under the conditions used in the GC-MS analysis were validated with methyl 2-methylpentanoate, methyl hexanoate, methyl octadecanoate and methyl tetracosanoate being used for this purpose (Additional file 1: Figure S1).

Wax—analysis of hydrocarbons

The wax product (Wax1) was analysed for a carbon distribution in the range C_8–C_{96} by gas chromatography with flame ionisation detection. A model 6890 GC from Agilent Technologies was employed. The analysis was achieved using an MXT-1HT metal capillary column, 5 m in length with an internal diameter of 0.53 mm and a stationary phase thickness of 0.2 μm supplied by Restek. It was operated with an initial temperature of 40 °C then increased at 10 °C/min to 420 °C. Helium carrier gas at a flow of 10 mL/min was used. A sample volume of 0.5 μL was injected into an on-column injector at 3 °C above the column oven temperature. Detection was by flame ionisation detector at 400 °C. Sample preparation involved taking approximately 0.01 g of homogenised sample and dissolving in 10 mL of cyclohexane by sonication and then heating gently in warm water. Data was interpreted after subtracting a thermal cycle blank run from the raw sample data to remove baseline drift caused by column bleed. Quantification was by an area normalisation method assuming an equivalent mass response for all components. Identifications were established by analysing Agilent Technologies reference mixtures GC Boiling Point Calibration Standard for SimDis #2 (5080-8678) and Boiling Point Calibration Standard #1 for simulated distillation (5080-8716).

Wax—analysis of 1-alcohols

The wax product (Wax1) was analysed for 1-alcohol distribution in the range C_9–C_{17} by comprehensive two-dimensional gas chromatography (GCxGC) with flame ionisation detection. A model 7890A GC from Agilent Technologies equipped with an Agilent capillary flow technology flow modulator was employed. The analysis was achieved using a 30-m-long HP-5 capillary column in the first dimension (^{1}D) with a stationary phase film thickness of 0.25 μm; the second dimension (^{2}D) column was a 5-m-long HP-Innowax column with a phase thickness of 0.15 μm; both columns had an internal diameter of 0.25 mm and supplied by Agilent Technologies. The columns were operated with an initial temperature of 50 °C and increased at 5 °C/min to a final temperature of 240 °C where they were held for 20 min. Helium was used as the carrier gas with the first dimension and second dimension column flows set to 0.6 mL/min and 26.0 mL/min respectively. A modulation period and sampling time of 1.58 s and 1.45 s respectively was used.

A sample volume of 0.3 μL was injected into a split injector at 240 °C with a split ratio of 50:1. The flame ionisation detector was operated at 250 °C. Calibration was performed with standards prepared volumetrically in cyclohexane using linear alcohols with purity > 98% supplied by Sigma-Aldrich. An internal standard of 2-methylbutan-1-ol was added for quantification.

Light hydrocarbon liquid—analysis of acidity by KOH titration

The method used was based on ASTM D664, Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. The light hydrocarbon liquid (LHcL1) sample was miscible with the titration solvent of toluene and propan-2-ol at the sample volume (approximately 20 g) recommended in the ASTM method for low total acid number (TAN) values. This sample was titrated potentiometrically using 0.1 N alcoholic KOH with a Metrohm 848 Titrino autotitrator.

^{1}H NMR—analysis of light hydrocarbon liquid

All NMR data was collected using a Bruker Avance 300 MHz instrument with Bruker Topspin acquisition software. Data processing was completed using Spectrus from ACD Labs. All reagents and consumables were supplied by Sigma-Aldrich. The ^{1}H NMR spectra of a 10% v/v solution of light hydrocarbon liquid (LHcL1) in deuterated chloroform (CDCl$_3$) was collected using a 2-s relaxation delay and 1000 scans.

^{1}H NMR—analysis of wax

The ^{1}H NMR spectra of a 0.1% w/w solution of wax (Wax1) in CDCl$_3$ was collected using a 2-s relaxation delay and 1000 scans.

^{13}C NMR—analysis of light hydrocarbon liquid

Quantitative ^{13}C NMR of the light hydrocarbon liquid (LHcL1) was performed in a similar manner to that detailed by others (Burger et al. 2015). A 50% v/v solution of the hydrocarbon liquid in CDCl$_3$ containing 60 mmol chromium (III) acetylacetonate was prepared and 2000 scans were collected using an inverse gated sequence with a relaxation delay of > 10 s.

^{13}C DEPT 135 NMR—analysis of light hydrocarbon liquid

^{13}C DEPT135 NMR (distortionless enhancement by polarisation transfer) shows signals due to **C**H$_3$ and **C**H group as positive signals and those due to **C**H$_2$ as negative signals. Quaternary carbons do not show any signal. The technique was useful in confirming the origin of signals present in the ^{13}C NMR spectra. The ^{13}C DEPT 135 analysis of the light hydrocarbon liquid (LHcL1) was performed using a 50% v/v solution of the sample in

CDCl$_3$. Further, 1000 scans were collected using relaxation delay of 2 s.

Results and discussion
Aqueous phase composition
The main product in the aqueous phase were the 1-alcohols from C$_1$ to C$_{10}$ with trace levels of methyl acetate, 2-methylpropan-1-ol and ethanoic acid also being observed in the GC chromatogram (Additional file 1: Figure S2). Quantification of the 1-alcohols is given in Table 1.

The chromatogram obtained from the analysis of carboxylic acids by HPLC (Additional file 1: Figure S3) shows the major acids to be methanoic and ethanoic acid with much lower levels of propanoic acid and butanoic acid. Quantifying any carboxylic acids with carbon numbers >C$_4$ was not possible due to the sensitivity of the method and co-elution of other compounds at the longer retention times. The quantification of the acids is shown in Table 2.

Gas phase analysis
The relative concentration of the C$_1$ to C$_6$ gas phase organic hydrocarbon compounds relative to the methane are given in Table 3. Only the data recorded from the FID are shown since the other compounds present in the gas phase do not contribute to the hydrocarbon distribution analysis. The mass flow of each hydrocarbon was calculated from the absolute concentration in the gas phase and the volumetric flow of the gas and these data were used for input to the calculation of overall hydrocarbon product distribution.

Carbon distribution of light hydrocarbon liquid and wax phases
The GC chromatogram of the light hydrocarbon liquid (LHcL1) is shown in Fig. 3 and the insert gives an expanded view of the C$_{11}$ region of the chromatogram. This shows the order of elution was iso-paraffins, 1-

Table 2 HPLC analysis of aqueous phase, Aq1

Oxygenate	Concentration (ppmw)
Methanoic acid	230
Ethanoic acid	265
Propionic acid	12
Butanoic acid	13

alcohol, 1-olefin, *n*-paraffin and *trans*-2-olefin and lastly *cis*-2-olefin. However, the carbon chain length of the 1-alcohol was not the same as the hydrocarbons in this region but was the C$_{n-2}$ alcohol. Achieving acceptable resolution of these species in the analysis of the wax sample (Wax1) was not possible (Additional file 1: Figure S4). The peak capacity of a chromatography separation is finite and co-elution of the 1-alcohol with the iso-paraffins became increasingly evident as carbon chain length increased and the number of potential isomers also increased.

Where it was possible to differentiate the *n*-paraffin, 1-olefin, 2-olefins and 1-alcohol peaks in the LHcL1 chromatogram, in the C$_7$ to C$_{14}$ range, a detailed integration of these peaks allowed their ratio to the corresponding *n*-paraffin to be quantified. Since the alcohol that eluted just before the *n*-paraffin had two carbons less, then this feature was accounted for when conducting the ratio analysis. The result shows that the 1-olefin decreased relative to the *n*-paraffin as the carbon number increased (Fig. 4a). This has been found in other studies of FT products (Bertoncini et al. 2009) and is attributed to the increasing likelihood of the 1-olefin being reabsorbed on the catalyst surface where it can lead to initiation of a new propagating alkyl chain before it can diffuse through the wax filled pores of the catalyst particle. This mechanism is not open to *n*-paraffins since they cannot undergo surface reattachment and participate in chain initiation due to unfavourable thermodynamics (Iglesia 1997). So, paraffins become an end-product of the chain growth process. Further secondary reactions of alcohols

Table 1 GC analysis of aqueous phase, Aq1

Oxygenate	Concentration (wt%)
Methanol	0.448
Ethanol	0.287
1-Propanol	0.070
1-Butanol	0.061
1-Pentanol	0.034
1-Hexanol	0.012
1-Heptanol	0.004
1-Octanol	0.001
1-Nonanol	<0.005
1-Decanol	<0.005

Table 3 On-line GC analysis of gas phase hydrocarbons

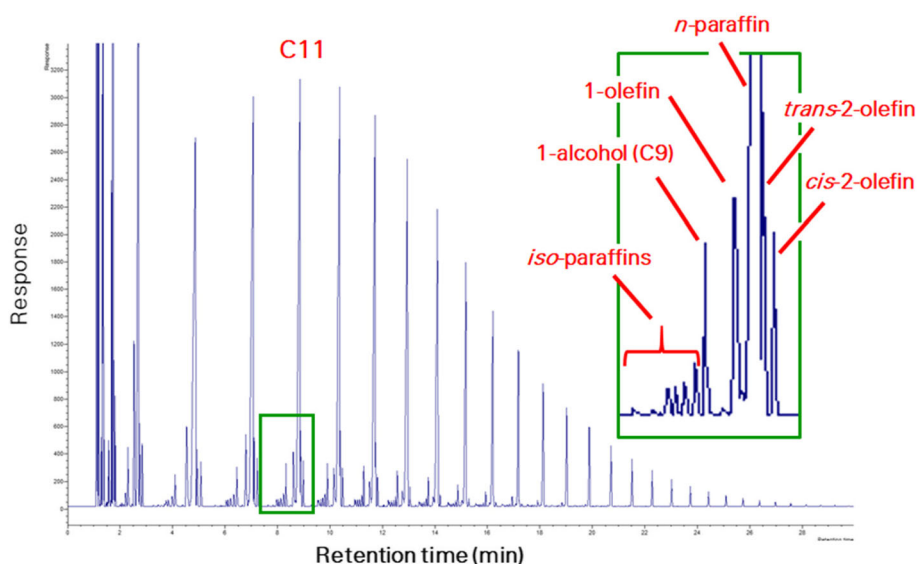| Component	Molar concentration relative to methane
Methane	1.00000
Ethane	0.06022
Ethylene	0.00040
Propane	0.08947
Propylene	0.01000
Total butanes	0.06227
Total butenes	0.00900
Total pentanes	0.03700
Total pentenes	0.00627
Total C6s	0.01778

Fig. 3 1D GC analysis of light hydrocarbon, LHcL1

and carboxylic acids may be possible (de Klerk 2011) but their participation in any further chain re-initiation chemistry is less clear. Indeed, a ^{14}C-labelled alcohol tracer study using ethanol and 1-propanol co-feeds suggests that the C–O bond of these alcohols is mostly stable on the cobalt surface under FT reaction conditions (Gnanamani et al. 2015). Certainly, in our analyses, the relationships of the 1-alcohol and 2-olefins to the *n*-paraffin were not the same as for the 1-olefin and these must either have a lower propensity to re-initiate new chains or be more difficult to re-adsorb on the active site than the 1-olefins. The same type of analysis was also conducted for the wax sample but using an analysis method suited for the separation of the light hydrocarbons in the C_9 to C_{15} range, allowing the 1-olefins to be resolved from the *n*-paraffins. The 1-olefin:*n*-paraffin ratio in the wax was also found to decrease as the carbon number increased as shown in Fig. 4b.

1-alcohol content of light hydrocarbon liquid and wax phases

The analysis of the light hydrocarbon liquid (LHcL1) and wax (Wax1) materials by comprehensive two-dimensional GC (GCxGC) allowed an effective separation of the 1-alcohols from the hydrocarbon species. The GCxGC chromatogram of LHcL1 is shown in Fig. 5. This resulted in a more accurate quantification of the alcohols across a wider carbon range than could be achieved by the conventional GC method previously described. It was also apparent that the major products were *n*-paraffins, 1-olefins, 2-olefins and 1-alcohols with trace amounts of iso-paraffins. There were no other products detected in the two-dimensional GC analysis.

A comparison of the 1-alcohol quantified for C_7–C_{14} carbon numbers in the LHcL1 sample by the conventional GC and comprehensive two-dimensional GC analyses showed that within this range, similar data were obtained (Additional file 1: Figure S5). However, the two-dimensional GC method generally gave slightly higher values. The one-dimensional GC method takes no account of the different detector mass response for oxygenated components which would lead to an under recovery for these components, in addition the quantification in the one-dimensional method could be further complicated by the possibility of coelution with iso-paraffins and difficulty in accurately integrating non-baseline resolved peaks.

The range of alcohols analysed by comprehensive two-dimensional chromatography could be extended to higher carbon numbers with an alternative column set capable of higher temperature operation (e.g. HP-5/BPX-50) than we used along with the suitable temperatures, gas flows and modulation conditions required. A severe limitation to the range of chromatography conditions that can be employed in GCxGC is introduced with the use of simple flow modulation, in particular the column dimensions and flow rates used in the second dimension and the modulation period. Cryogenic modulation, whilst usually more capital intensive and often requiring additional services such as liquid cryogens, allows optimisation closer to ideal chromatographic conditions.

Carboxylic acid content of light hydrocarbon liquid and wax phases

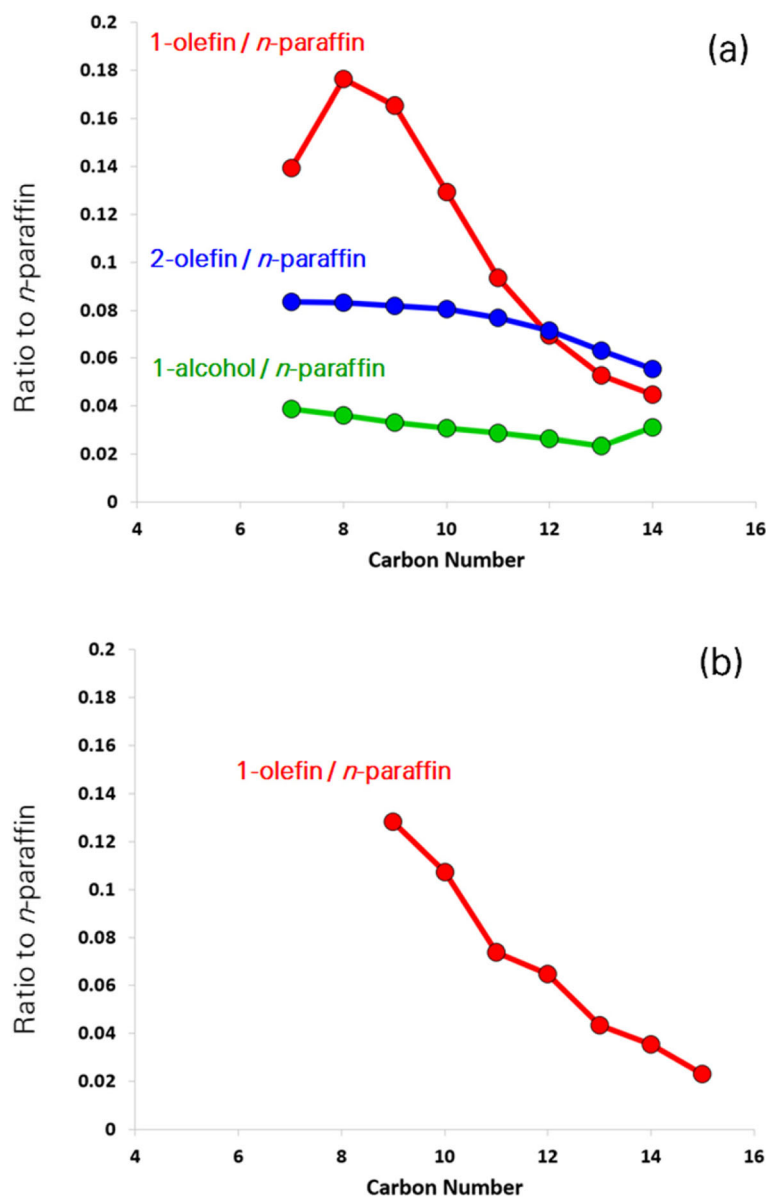The concentration of organic acids in the Fischer-Tropsch hydrocarbon liquids and wax materials studied

Fig. 4 Molar ratio of olefin and 1-alcohol to *n*-paraffin. **a** Molar ratio of olefins and 1-alcohol to *n*-paraffin in LHcL1 for C_7–C_{14}. **b** Molar ratio of 1-olefin to *n*-paraffin in Wax1 for C_9–C_{15}

were typically two orders of magnitude lower than that of the primary alcohols. These would therefore have been present below the limit of quantification for the GCxGC approach used for the analysis of alcohols. Whilst extraction methods could be used to concentrate the acid analytes, a derivatisation method was chosen to provide the additional benefit of improved chromatography for the separation of methyl esters over that which could be achieved for carboxylic acids.

The method applied to the analysis of carboxylic acids was based on that used successfully for the quantification of organic acids in milk (Martinez et al. 2012). Methylation of the carboxylic acids was quantitatively

achieved using H_2SO_4/methanol with subsequent concentration and recovery of the product methyl esters by addition of a small quantity of heptane. GC-MS analysis of the heptane phase allowed for low levels of the methyl esters to be accurately quantified and therefore giving the concentration of the carboxylic acids in the parent samples for both the light hydrocarbon liquid and wax materials.

Methyl esters of linear carboxylic acids characteristically give an intense peak in the electron impact ionisation spectra corresponding to m/z = 74 due to the McLafferty rearrangement ion (Takayama 1995; rearrangement reaction is shown in Additional file 1:
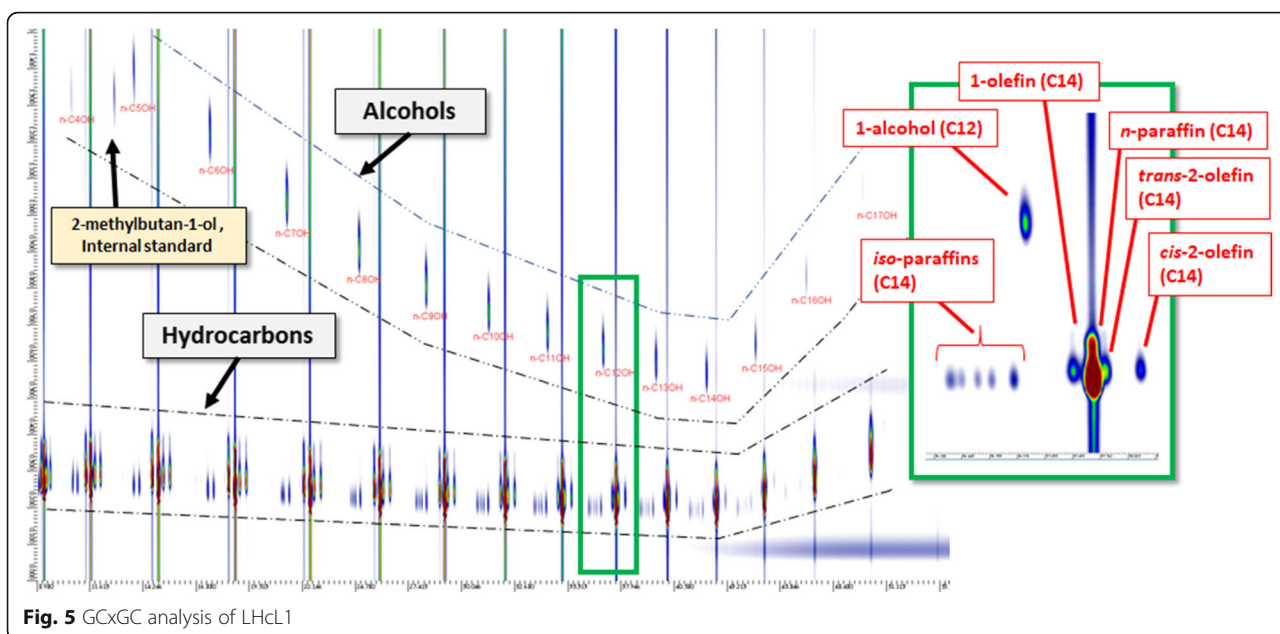
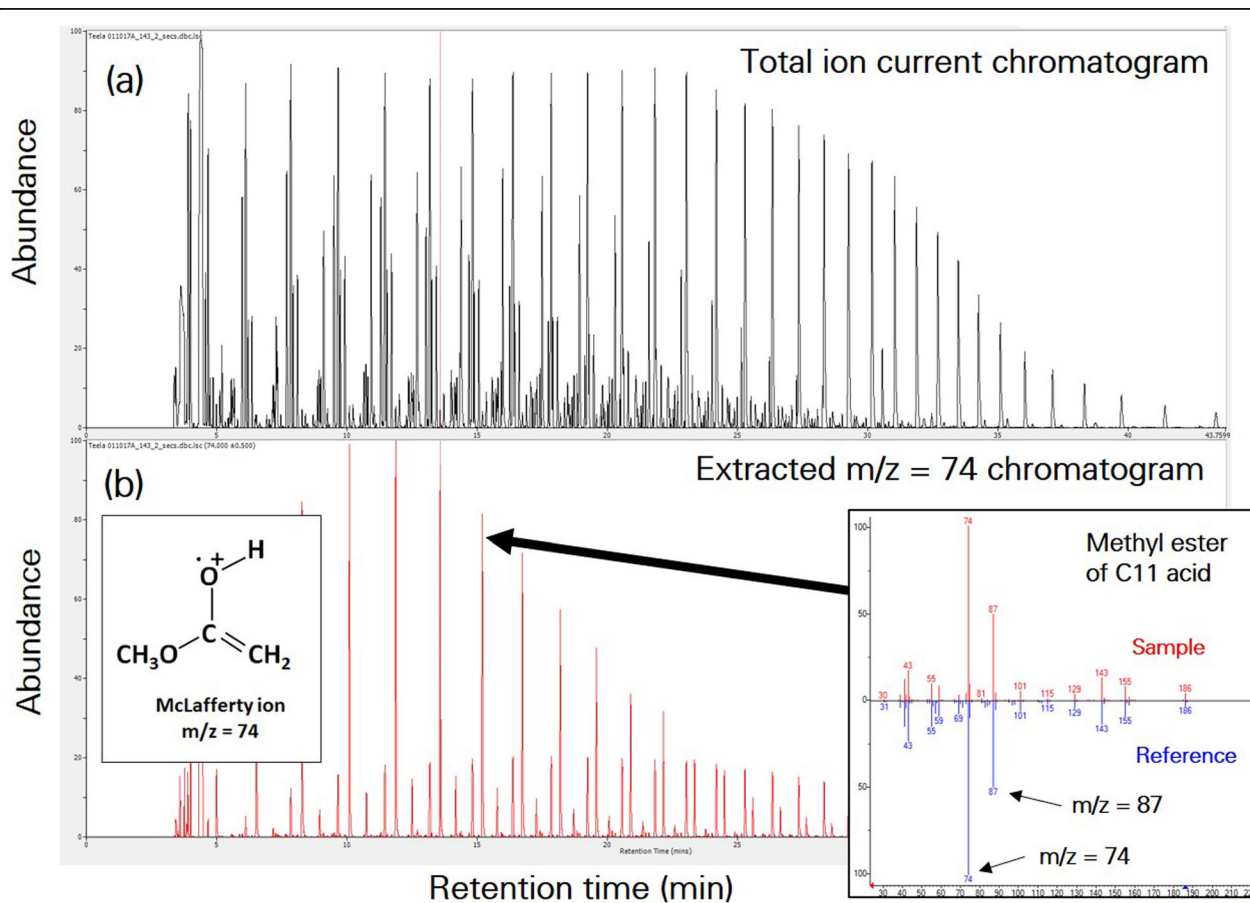**Fig. 5** GCxGC analysis of LHcL1

Fig. 6 GC-MS chromatogram of methyl esters of carboxylic acids

Figure S6). In addition to the McLafferty ion, there are a series of related ions formed having the general formula $[(CH_2)_nCOOCH_3]^+$ where $n = 2$ gives the next most abundant peak at m/z = 87.

The GC-MS chromatogram of a heptane extract showing the total ion current, background subtracted, is given in Fig. 6. This also shows the mass spectra obtained from the C_{11} methyl ester against that of the reference spectra. The peaks at m/z = 74 and m/z = 87 are clearly visible and were the most intense peaks present. Analysing the chromatogram using the McLafferty rearrangement ion, m/z = 74, allows for a significant increase in the signal/noise improving the detection limit and thereby the quantification of the ester.

The GC-MS method was demonstrated to give a satisfactory analysis of carboxylic acids in FT liquid hydrocarbon and wax products by (i) measuring the linearity of response of selected FAMEs, including that of the internal standard, under the conditions used in the GC-MS analysis; (ii) quantifying the relative standard deviation (RSD) for the methyl esters of C_6–C_{24} carboxylic acids over 10 analyses; (iii) estimating the recovery of hexanoic acid, decanoic acid and octadecanoic acid standards during the derivatization reaction; and (iv) conducting duplicate sample preparations for analysis. The results of these investigations (Additional file 1: Figure S1 and Tables S1, S2 and S3) showed that the method was reproducible, had a linear response to methyl esters of carboxylic acids spanning the C_6 to C_{24} range, showed close to 100% recovery for C_6, C_{10} and C_{18} carboxylic acids in the derivatization reaction and also gave reproducible analysis for a real FT liquid hydrocarbon product.
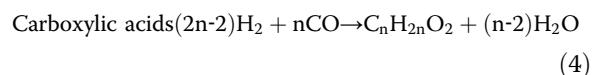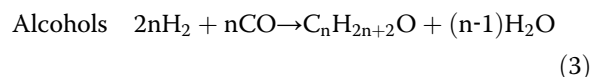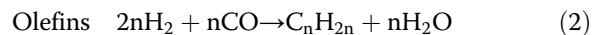
Summary of chromatographic analyses of light hydrocarbon liquid and wax samples

The concentration of the hydrocarbons (*n*-paraffins, iso-paraffins, olefins), 1-alcohols and carboxylic acids in the light hydrocarbon liquid (LHcL1) and wax (Wax1) products are summarised in Tables 4 and 5, along with the analysis method used. The combined concentration of the paraffin and olefin for each carbon number plus the individual concentrations of the 1-olefin and 2-olefin, where chromatographic separation from the *n*-paraffin and iso-paraffins was possible, are also given. Hydrocarbons with carbon numbers > 30 have been combined, although these were reported separately up to C_{96}.

Full Fischer-Tropsch hydrocarbon and oxygenate product distributions

The products of the FT synthesis reaction are hydrocarbons and oxygenate products having linear carbon chains ranging from C_1 to over C_{100}. The balanced

equations for the paraffinic, olefinic, alcoholic and carboxylic acid products of the FT process are given in Eqs. 1 to 4.

$$\text{Paraffins} \quad (2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O \quad (1)$$

$$\text{Olefins} \quad 2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O \quad (2)$$

$$\text{Alcohols} \quad 2nH_2 + nCO \rightarrow C_nH_{2n+2}O + (n\text{-}1)H_2O \quad (3)$$

$$\text{Carboxylic acids} (2n\text{-}2)H_2 + nCO \rightarrow C_nH_{2n}O_2 + (n\text{-}2)H_2O \quad (4)$$

Many mechanisms have been proposed for the FT reaction and this remains an active area for research and debate (Krylova 2014). A simplified reaction network based on an oxygenate mechanism can be used to show the potential routes to forming all the class of compounds that are found in gas, liquid and wax FT products (de Klerk 2011). This type of mechanism is illustrated in Fig. 7 and shows the initiation by hydrogenation of adsorbed CO to form a surface methylene group, the stepwise growth in the carbon chain length by CO insertion, hydrogenation of intermediate oxygenates to remove oxygen as water and then further CO insertion. Finally, products are liberated from the active site either by desorption (aldehydes and olefins), by addition of water (carboxylic acids) or by addition of hydrogen (alcohols and paraffins). The reactions can, however, be kinetically described by the step-growth polymerisation of C_1 surface species where the product distributions can be explained by the ASF growth probability factor, α, (van de Laan and Beenackers, 1999; de Klerk 2011). Usually, this growth probability factor is calculated from the analysis of hydrocarbons and oxygenates with $\geq C_3$ carbon atoms, since the C_1 and C_2 products do not adhere to the same growth kinetics. The value of α is obtained as the gradient of a plot of Log (mol. fraction of compound with Cn) versus Cn where Cn is the carbon number of the compound.

The analysis of the gas phase, aqueous phase, light hydrocarbon liquid and wax phases (Tables 1, 2, 3, 4 and 5) along with the volumetric or mass flows per unit time of these phases allows the compilation of the detailed and quantitative ASF distribution for hydrocarbons, 1-alcohols and carboxylic acids. This is shown in Fig. 8 for carbon numbers up to C_{40}. The overall ASF α number for the hydrocarbons between C_{10} to C_{40} was 0.92 and there was some loss in recovery of C_4 in the gas phase, and some loss of C_7 fraction was evident in the light hydrocarbon fraction.

Parallel lines with slopes having the same gradient as the ASF fit for the hydrocarbons have been overlaid on the 1-alcohol and carboxylic acid distributions with

Table 4 Summary of 1D-GC, GCxGC and GC-MS analyses, LHcL1

Carbon number	Paraffin + Olefin (wt%)	1-olefin (wt%)	2-olefin (wt%)	1-alcohol (wt%)	1-alcohol (wt%)	Carboxylic acid (wt%)
	1D-GC				GCxGC	GC-MS
1						0.00015
2						0.00130
3					0.02	0.00017
4					0.06	0.00086
5	4.31				0.14	0.00202
6	6.02				0.24	0.00335
7	7.80	0.92	0.55	0.26	0.29	0.00455
8	9.04	1.25	0.59	0.26	0.29	0.00494
9	9.36	1.22	0.60	0.24	0.28	0.00565
10	9.27	0.96	0.60	0.23	0.26	0.00600
11	8.89	0.68	0.56	0.21	0.24	0.00627
12	8.30	0.48	0.50	0.18	0.20	0.00607
13	7.50	0.34	0.40	0.15	0.18	0.00501
14	6.48	0.25	0.31	0.17	0.15	0.00370
15	5.30				0.10	0.00235
16	4.10				0.06	0.00162
17	3.02				0.03	0.00088
18	2.16					0.00061
19	1.54					0.00035
20	1.14					0.00025
21	0.82					0.00016
22	0.62					
23	0.46					
24	0.35					
25	0.26					
26	0.19					
27	0.14					
28	0.10					
29	0.08					
30	0.06					
C_{31}–C_{50}	0.15					

these being allowed to fit to their C_3 carbon values. This indicates that the probability of chain propagation for 1-alcohols was similar to that of the hydrocarbons for C_{3+} alcohols and that this was also possibly the case for the carboxylic acids, at least in the C_3 to C_{17} range, although there was a poor recovery of acids between C_5 and C_{10}. Since the GC-MS method had already been shown to give close to 100% recovery for hexanoic and decanoic acids in a liquid hydrocarbon phase analysis, then this poor overall carboxylic acid recovery in the C_5 to C_{10} range was suspected to be due to the non-quantification of these acids in the aqueous phase HPLC analysis. This

could have been due to the low sensitivity of the HPLC method coupled with the very low concentration of the acids expected in aqueous phase. To confirm this hypothesis, an estimation was made of the concentrations of the C_5 to C_{10} acids that would have been required in the aqueous phase to allow a fit to the expected acid ASF distribution. These data are compared in Table 6 to reference data for the measured solubility of linear carboxylic acids in aqueous media at ambient temperature (Bell 1973). This confirmed that the acids should have had the required solubility in the aqueous phase and that the poor recovery was likely due to the low sensitivity of

Table 5 Summary of 1D-GC, GCxGC and GC-MS analyses, Wax1

Carbon number	Paraffin + Olefin (wt%)	1-Olefin (wt%)	1-Alcohol (wt%)	Carboxylic acid (wt%)
	1D-GC		GCxGC	GC-MS
1				0.00015
2				0.00057
3				0.00017
4				0.00016
5				0.00006
6				0.00008
7				0.00013
8	0.12			0.00023
9	0.16	0.02	0.02	0.00049
10	0.27	0.02	0.05	0.00064
11	0.45	0.03	0.04	0.00100
12	0.68	0.04	0.15	0.00152
13	1.03	0.04	0.14	0.00214
14	1.39	0.05	0.24	0.00264
15	1.92	0.04	0.19	0.00279
16	2.42		0.13	0.00262
17	2.96		0.13	0.00246
18	3.43			0.00215
19	3.62			0.00183
20	3.84			0.00159
21	3.78			0.00136
22	3.68			0.00136
23	3.55			0.00119
24	3.42			0.00104
25	3.31			0.00089
26	3.17			0.00076
27	3.05			0.00061
28	2.94			0.00049
29	2.77			
30	2.64			
31 to 96	41.71			

the HPLC analysis. Whilst not pursued in our work, a method that could be investigated for improving the quantification of high molecular weight carboxylic acids at very low concentrations in the aqueous phase would be to conduct a neutralisation step using NaOH followed by low-temperature evaporation of the aqueous phase, acidification and then extraction into an organic phase possibly as the methyl ester as described here for the carboxylic acid determination in FT wax and light hydrocarbon materials.

The FT product distribution had a higher level of methane than would be expected from an extrapolation of the hydrocarbon C_{3+} ASF distribution, as usually observed in Co-based FT catalysis (de Klerk 2011). There were also significant levels of methanol, ethanol, formic acid and ethanoic acid which were above the extrapolation of the C_{3+} ASF distribution for the 1-alcohols and carboxylic acids. These observations were replicated in micro-reactor tests, using the same catalyst type, where aqueous and wax products were collected post-reactor for off-line analysis using the same analytical methods. It is expected that C_1 and C_2 products may not fit the ASF distribution since they are either independent of the polymerisation kinetics or are heavily influenced by the
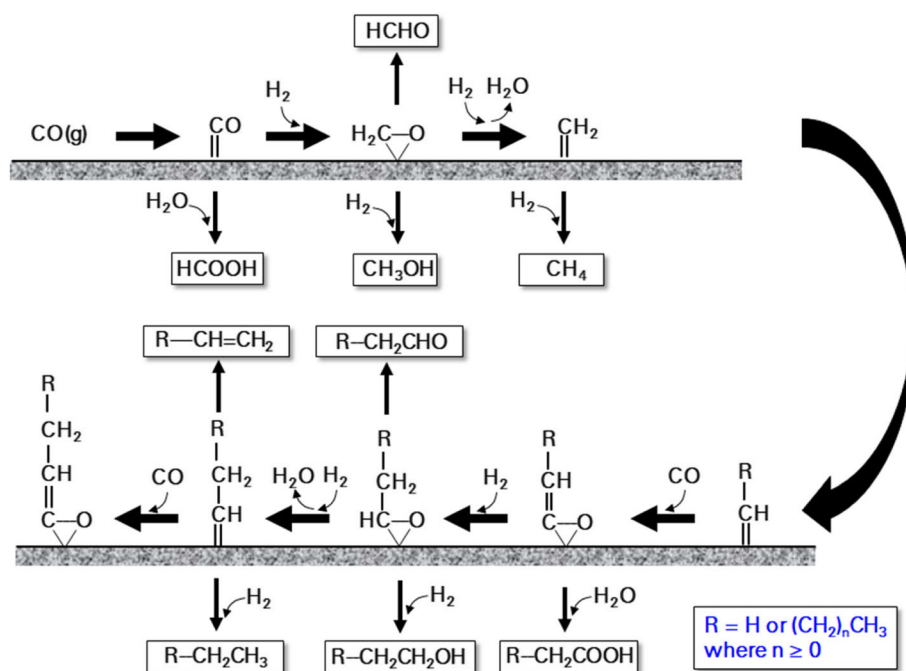
Fig. 7 Simplified Fischer-Tropsch reaction network based on an oxygenate mechanism

re-adsorption and subsequent reactions of ethylene (van de Laan and Beenackers 1999).

The recycling of the gas phase product led to some re-incorporation and hydrogenation of the light olefins over the catalyst giving a disconnect to the expected distribution of the olefins compared with the LHcL1 and Wax1 products, which were not recycled. The paraffin and olefin distributions for the combined products are shown in Fig. 9 and clearly show a disconnect between the absolute values of olefins of the light hydrocarbons
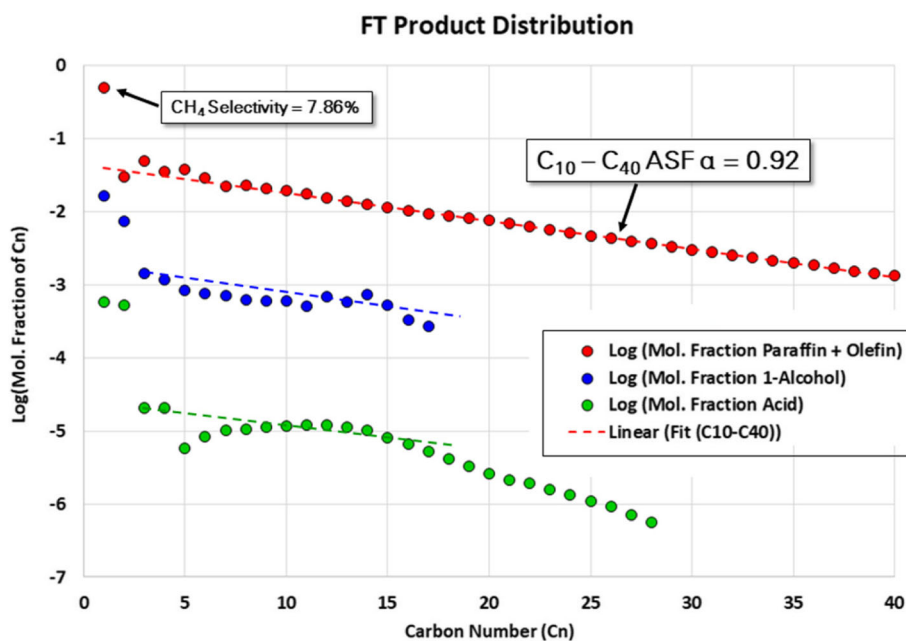
Fig. 8 Anderson-Schultz-Flory distribution for hydrocarbons, 1-alcohols and carboxylic acids

Table 6 Solubility of carboxylic acids required in aqueous media for fit to ASF distribution

Linear carboxylic acid	Required solubility to fit ASF distribution (ppmw)	Solubility of acid (ppmw) (Grobler et al. 2009)
5	15.6	24960 at 30 °C
6	13.5	8024 at 25 °C
7	11.2	1716 at 25 °C
8	8.5	321 at 30 °C
9	7.4	120 at 30 °C
10	5.1	–

(C_3–C_5) and those of the hydrocarbon liquid and wax (C_7–C_{14}).

^{1}H NMR, ^{13}C NMR and ^{13}C DEPT NMR analysis of light hydrocarbon liquid and wax

Previous work (Speight et al. 2011) demonstrated ^{1}H NMR for FT wax speciation whilst both ^{13}C NMR and ^{1}H NMR have been used for the analysis of FT liquid hydrocarbon products (Cookson and Smith 1989). We applied similar methods of analysis to our light hydrocarbon liquid and wax samples. The potential of ^{1}H NMR for quantification of alcohol and olefin class compounds and average carbon number for long-chain hydrocarbons was confirmed by analysis of the C_{14} standards, tetradecane, 1-tetradecene and 1-tetradecanol in CDCl$_3$ solvent. All standards returned average carbon numbers of between 13.5 and 14.1 and with a class compound group value of 0.98 per carbon chain for both 1-tetradecene and 1-tetradecanol, these being close to the

expected value of 1.00 (Additional file 1: Figure S7 and Table S4). There was no evidence for alcohols or olefins in the analysis of the tetradecane standard. The reproducibility of the ^{1}H NMR analysis for FT products was demonstrated by preparing three solutions of a wax sample with each of these being prepared and analysed on separate days. The ^{1}H NMR spectra and concentration of each class groups present in each of the three samples are given in Additional file 1: Figure S8 and Table S5.

The solution ^{1}H NMR analysis of the LHcL1 and Wax1 samples confirmed that the major classes of compounds present were 1-alcohol, 1-olefin and internal olefin (Fig. 10). The ^{1}H NMR analysis could not distinguish the position of the internal double bond, i.e. whether this was in the 2-position or located further into the hydrocarbon chains, but the ^{13}C NMR and ^{13}C DEPT 135 NMR were able to confirm that the internal olefins were the *cis*- and *trans*-2-olefins, in approximately equal amounts, as shown in Fig. 11. The peaks labelled 1 and
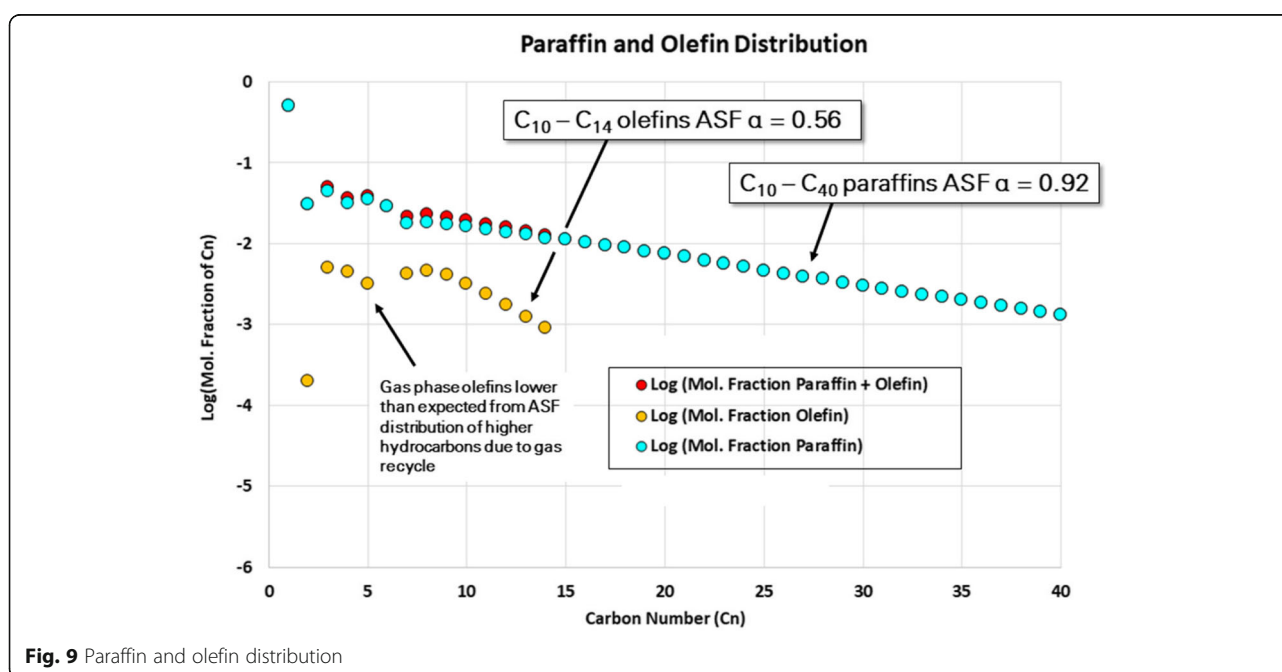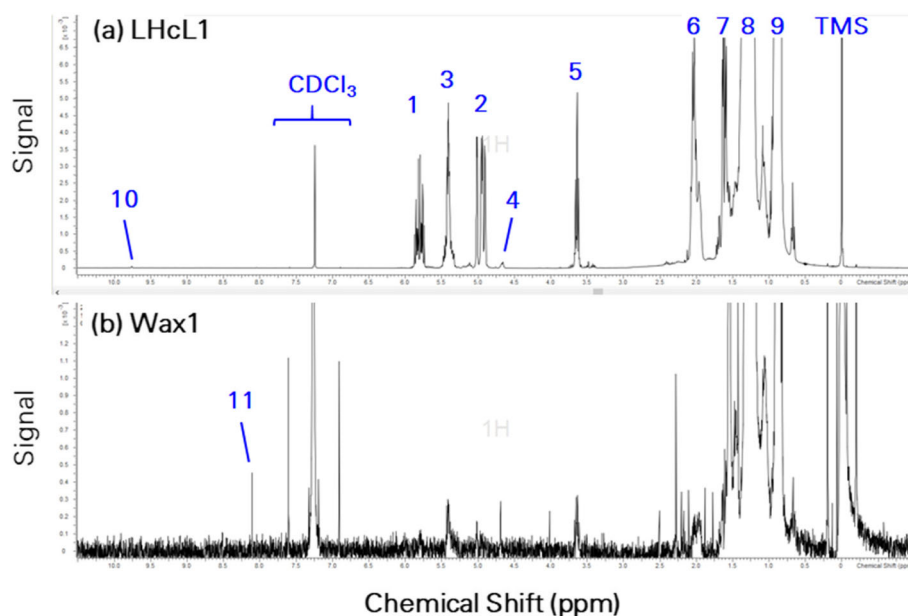

Fig. 9 Paraffin and olefin distribution

Fig. 10 ^{1}H NMR analysis of LHcL1 and Wax1. **a** ^{1}H NMR of LHcL1, − 1 to 10.5 ppm range. **b** ^{1}H NMR of Wax1, − 1 to 10.5 ppm range

2 are due to the 1-olefins, those labelled 3 and 4 are from the *trans*-2-olefins and those labelled 5 and 6 are from the *cis*-2-olefins. The peak labelled 8 was due to the terminal methyl group associated with the 2-olefins. The complete assignments of the ^{1}H NMR and ^{13}C NMR peaks are given in Tables 7 and 8 along with their input into the calculations used to give average carbon number and average concentration of the class groups, as described in Additional file 1.

Comparison of class group concentrations by NMR and chromatographic methods

A summary of the class group concentrations in the LHcL1 and Wax1 samples are given in Tables 9 and 10.
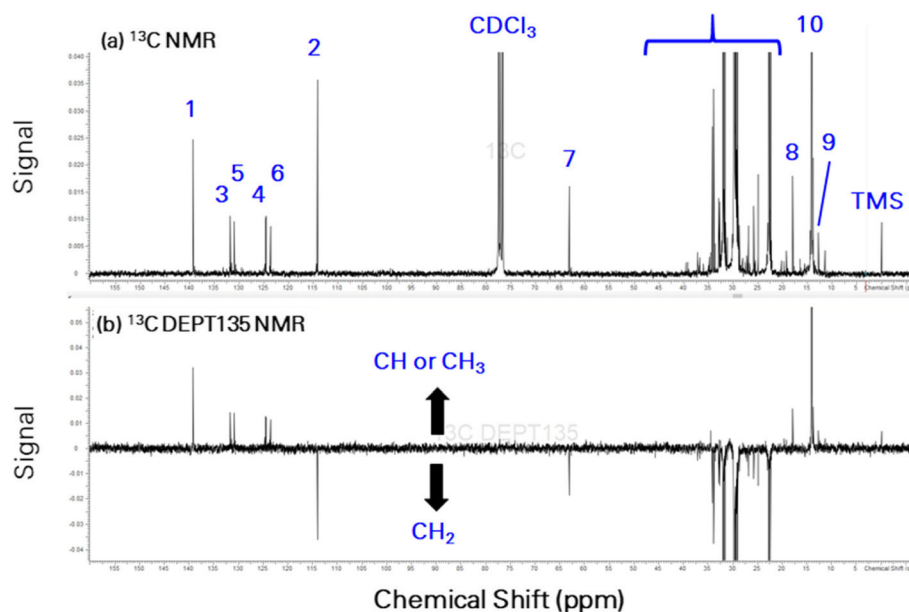

Fig. 11 ^{13}C NMR and ^{13}C DEPT 135 NMR analysis of LHcL1. **a** ^{13}C NMR, 0 to 160ppm range. **b** ^{13}C DEPT 135 NMR, 0 to 160ppm range

Table 7 ^{1}H NMR Peak assignments in CDCl₃ solvent

Peak ID	^{1}H NMR Peak (ppm)	Assignment	Input to calculations given in Additional file 1[1]
1	5.80	R-C**H**=CH2	A
2	4.95	R-CH=C**H2**	B
3	5.40	R-C**H**=C**H**-CH3	C
4	4.70	R-C(CH3)=C**H2**	Not included
5	3.65	R-C**H2**-OH	D
6	~ 2	R-C**H2**-CH=CH2	E
7	~ 1.6	**H2**O, R-CH=CH-C**H3**	Not included
8	1.25	R-C**H2**-R′	F
9	0.90	R-C**H3**	G
10	9.80	R-C**H**O	H
11	8.10	Contamination from vial lid (formates)	Not applicable

The protons in the hydrocarbon structure that are assigned to peaks in the ^{1}H NMR spectra are indicated in bold text and are underlined

This shows that ^{1}H NMR analysis gave higher values for 1-olefin, 2-olefin and 1-alcohol compared to 1D-GC and GCxGC which is to be expected due the problems already discussed with GC sensitivity and peak resolution. The average carbon numbers derived from ^{1}H NMR and 1D-GC were similar.

The ^{1}H NMR data also supports the assessment from the 1D-GC data showing 1-olefin to decrease more significantly with increasing carbon number compared to the 2-olefin and the 1-alcohol. The average number of each class group per carbon chain has been calculated for the LHcL1 and Wax1 samples and these are summarised along with ratio of the Wax1:LHcL1 values in Table 11. These ratios were 0.20 for the 1-olefin, 0.77 for the 2-olefin and 0.78 for the 1-alcohol indicating that the higher Mw material (Wax1) had lower values that the lower Mw material (LHLc1).

A series of wax and light hydrocarbon liquid samples produced on pilot plants and waxes produced on microreactors, all again from Co based TiO₂ catalysts, were analysed by ^{1}H NMR and GC-GC for 1-alcohols and the results are compared in Additional file 1: Figure S9. This showed that the ^{1}H NMR analysis consistently gave slightly higher values than the GCxGC analysis which was likely caused by the limited carbon range of the latter analysis. However, this also confirmed the robustness of the GCxGC analysis over the carbon range of the analysis.

Comparison of acidity of light hydrocarbon liquid by GC-MS and KOH titration methods

Acidity analysis of a light hydrocarbon liquid (LHc2), from an earlier pilot plant trial of a Co-based TiO₂ catalyst, was quantified by both GC-MS and KOH titration methods. This confirmed that both analytical techniques gave

Table 8 ^{13}C NMR Peak assignments

Peak	^{13}C NMR Peak (ppm)	Assignment	Input to calculations given in Additional file 1
1	139.2	R-**C**H=CH2	A
2	114.2	R-CH=**C**H2	B
3	131.8	R-**C**H=CH-CH3 (*trans*)	C
4	124.6	R-CH=**C**H-CH3 (*trans*)	D
5	131.1	R-**C**H=CH-CH3 (*cis*)	E
6	123.7	R-CH=**C**H-CH3 (*cis*)	F
7	62.9	R-**C**H2-OH	G
8	17.9	R-CH=CH-**C**H3 (*trans*)	H
9	12.8	R-CH=CH-**C**H3 (*cis*)	I
10	14.2	R-**C**H3	J
11	22.8–32.1	R-**C**H2-R′ (incl. β, γ, δ, ε)	K

The carbon atoms in the hydrocarbon structure that are assigned to peaks in the ^{13}C NMR spectra are indicated in bold text and are underlined

Table 9 Class group quantification across the NMR and GC techniques, LHcL1

	^{1}H NMR	^{13}C NMR	1D-GC	GCxGC	GC-MS
1-Olefin (mmol/g)	0.581	0.463	0.471	–	–
2-Olefin (mmol/g)	0.447	0.368	0.303	–	–
1-Alcohol (mmol/g)	0.262	0.198	0.111	0.184	–
Aldehyde (mmol/g)	0.003	–	–	–	–
Carboxylic acid (mmol/g)	–	–	–	–	0.0035
Average Cn	9.60	10.25	10.0	–	–
Average Mw	137	145	142	–	–

similar acidity results when this was calculated on a common unit basis, e.g. mg KOH/g as shown in Table 12. The calculation used for converting the carboxylic acids concentrations determined from the GC-MS analysis to an equivalent acidity value expected from a KOH titration is given in Eq. 5 and assumes that monobasic carboxylic acids are neutralised effectively by a molar equivalent of KOH.

$$\text{Acidity equivalent (mg KOH/g)} \quad (5)$$
$$= \sum_{n=1}^{\infty} (Carboxylic \ acid \ Cn, \%w/w)$$
$$\times 56/(100,000 \times Mw)$$

The conclusion from these results was that the acidity present in FT products made over the Co/TiO$_2$ catalyst was due to linear carboxylic acids with little, or no, contribution from any other acidic function since the GC-MS method used was specific to the carboxylic acid class group.

Summary and conclusions

Comprehensive two-dimensional gas chromatography analysis (GCxGC) of 1-alcohols and gas chromatography–mass spectrometry (GC-MS) analysis of

Table 10 Class group quantification across the NMR and GC techniques, Wax1

	^{1}H NMR	^{13}C NMR	1D-GC	GCxGC	GC-MS
1-Olefin (mmol/g)	0.048	–	0.014	–	–
2-Olefin (mmol/g)	0.114	–	–	–	–
1-Alcohol (mmol/g)	0.087	–	–	0.052	–
Aldehyde (mmol/g)	–	–	–	–	–
Carboxylic acid (mmol/g)	–	–	–	–	0.0013
Average Cn	22.98	–	24.3	–	–
Average Mw	324	–	343	–	–

Table 11 Average number of class groups per chain in LHcL1 and Wax1–^{1}H NMR

	LHcL1	Wax1	Ratio Wax1/LHcL1
1-Olefin	0.080	0.016	0.20
2-Olefin	0.061	0.047	0.77
1-Alcohol	0.036	0.028	0.78
Aldehyde	0.0004	0	0

derivatised carboxylic acids, as their methyl esters, have demonstrated accurate quantification of Fischer-Tropsch hydrocarbon liquid and wax products.

The GCxGC and GC-MS methods in combination with conventional one-dimensional GC analysis of the aqueous, gas, liquid hydrocarbon and wax products plus conventional HPLC analysis of the aqueous phase allowed a detailed and quantified class compound distribution to be demonstrated for a Fischer-Tropsch product from a Co-based TiO$_2$ catalyst operating in a fixed bed gas phase pilot plant. Comparison of GCxGC versus ^{1}H NMR and GC-MS versus KOH titration confirmed the applicability of the chromatographic methods for quantitative analysis of FT oxygenated compounds.

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, ^{1}H NMR and ^{13}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.

Table 12 Acidity of a light hydrocarbon liquid, LHcL2

	GC-MS (acidity equivalent, mg KOH/g)	KOH titration (mg KOH/g)
Acidity	0.17	0.15

Supplementary information

Additional file 1: Table S1. Relative standard deviation of response established for FAME analytes at a concentration of 10.0 μgmL^{-1} over 10 analyses in GC-MS analysis. **Table S2.** Recovery of carboxylic acid standards in GC-MS analysis. **Table S3.** Example of a duplicate sample preparations of a liquid hydrocarbon for carboxylic acid analysis. **Table S4.** ^1H NMR of C_{14} standards, calculation of average carbon number and class compound per carbon chain. **Table S5.** Concentration of class compounds in repeat analyses of a wax sample. **Figure S1.** Linearity of response of selected FAMEs in GC-MS analysis. **Figure S2.** GC chromatogram of aqueous phase, Aq1. **Figure S3.** HPLC chromatogram of aqueous phase, Aq1. **Figure S4.** 1D GC analysis of wax, Wax1. **Figure S5.** Comparison of 1-alcohols in LHcL1 using 1D-GC and GCxGC. **Figure S6.** McLafferty rearrangement of long chain methyl ester to form the McLafferty ion. **Figure S7.** ^1H NMR of C_{14} standards, 1%w/w in $CDCl_3$. **Figure S8.** Repeatability of ^1H NMR analysis of a wax sample. **Figure S9.** Comparison of ^1H NMR and GCxGC analysis of 1-alcohols in FT waxes and light hydrocarbons.

Abbreviations
FT: Fischer-Tropsch; MSW: Municipal solid waste; GC: Gas chromatography; 1D-GC: One-dimensional gas chromatography; GCxGC: Comprehensive two-dimensional gas chromatography analysis; GC-MS: Gas chromatography–mass spectrometry; HPLC: High-performance liquid chromatography; ^1H NMR: Proton nuclear magnetic resonance; ^{13}C NMR: Carbon 13 nuclear magnetic resonance; DEPT: Distortionless enhancement by polarisation transfer; ASF: Anderson-Schultz-Flory; TAN: Total acid number; FAME: Fatty acid methyl ester

Acknowledgements
Not applicable.

Authors' contributions
JC oversaw the operation of the pilot plant. JW and KS analysed the Fischer-Tropsch products. JP provided technical insight of Fischer Tropsch processes and products. RP collated and interpreted the results and drafted the manuscript. All authors read and approved the final manuscript.

Funding

Availability of data and materials
All data generated or analysed during this study are included in this published article.

Competing interests
The authors declare that they have no competing interests.

Author details
[1]BP Group Research, BP International, Saltend Chemicals Park, Hull HU12 8DS, UK. [2]Johnson Matthey, Princeton Drive, Thornaby, Stockton-on-Tees TS17 6PY, UK. [3]BP Chemicals, Saltend Chemicals Park, Hull HU12 8DS, UK.

References
Anderson RR, White CM. Analysis of Fischer-Tropsch by-product waters by gas chromatography. J High Resolut Chromatogr. 1994;17(4):245–50.

Bell GH. Solubilities of normal aliphatic acids, alcohols and alkanes in water. Chem Phys Lipids. 1973;10(1):1–10.

Bertoncini F, Marion MC, Brodusch N, Esnault S. Unravelling molecular composition of products from cobalt catalysed Fischer-Tropsch reaction by comprehensive gas chromatography: methodology and application. Oil & gas Science and technology - rev. IFP. 2009;64(1):79–90.

Burger JL, Widegren JA, Lovestead TM, Bruno TJ. ^1H and ^{13}C NMR analysis of gas turbine fuels as applied to the advanced distillation curve method. Energy Fuel. 2015;29(8):4874–85.

Coe A, Paterson J. Back to the future. Chem Eng. 2019;937:30–4.

Collins JP, Font Freide JJHM, Nay B. A history of Fischer-Tropsch wax upgrading at BP—from catalyst screening studies to full scale demonstration in Alaska. J Nat Gas Chem. 2006;15(1):1–10.

Cookson DJ, Smith BE. Determination of the structures and abundances of alkanes and olefins in Fischer-Tropsch products using ^{13}C and ^1H n.m.r. methods. Fuel. 1989;68(6):776–81.

Day ME. The Fischer–Tropsch process: 1950–2000. Catal Today. 2002;71:227–41.

de Klerk A (2011) Fischer–Tropsch Synthesis. In: Fischer-Tropsch Refining, Wiley-VCH Verlag GmbH & Co. KGaA. ISBN: 9783527326051.

Fernandes DR, Pereira VB, Stelzer KT, Gomes AO, Aquino Neto FR, Azevedo DA. Quantification of trace O-containing compounds in GTL process samples via Fischer–Tropsch reaction by comprehensive two-dimensional gas chromatography/mass spectrometry. Talanta. 2015;144(1):627–35.

Fu T, Li Z. Review of recent development in co-based catalysts supported on carbon materials for Fischer–Tropsch synthesis. Chem Eng Sci. 2015;135:3–20.

Gamblin TD (2014) Fischer-Tropsch Process in a Radial Reactor. US Patent 8906970 (B2), 9 Dec 2014.

Gholami Z, Tišler Z, Rubáš V. Recent advances in Fischer-Tropsch synthesis using cobalt-based catalysts: a review on supports, promoters, and reactors. Catal Rev. 2020. https://doi.org/10.1080/01614940.2020.1762367.

Gnanamani MK, Shafer WD, Pendyala VRR, Chakrabarti D, de Klerk A, Keogh RA, et al. ^{14}C-labeled alcohol tracer study: comparison of reactivity of alcohols over cobalt and ruthenium Fischer–Tropsch catalysts. Top Catal. 2015;58:343–9.

Grobler T, Claeys M, van Steen E, van Vuuren MJJ. GC × GC: a novel technique for investigating selectivity in the Fischer–Tropsch synthesis. Catal Commun. 2009;10(13):1674–80.

Iglesia E. Design, synthesis, and use of cobalt-based Fischer-Tropsch synthesis catalysts. Appl Catal A-Gen. 1997;161:59–78.

JM press release (2018): JM and BP license waste-to-fuels technology to Fulcrum BioEnergy. https://matthey.com/en/news/2018/jm-and-bp-license-waste-to-fuels-technology-to-fulcrum-bioenergy. Accessed 22 June 2020.

Khodakov A, Chu W, Fongarland P. Advances in the development of novel cobalt Fischer–Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels. Chem Rev. 2007;10(5):1692–744.

Krylova AY. Products of the Fischer–Tropsch synthesis (a review). Solid Fuel Chem. 2014;48(1):22–35.

Ma H, Pedersen CM, Zhao Q, Lyu Z, Chang H, Qiao Y, et al. NMR analysis of the Fischer-Tropsch wastewater: combination of 1D selective gradient TOCSY, 2D DOSY and qNMR. Anal Chim Acta. 2019;1066:21–7.

Martínez B, Miranda JM, Franco CM, Cepeda A, Rodríguez JL. Development of a simple method for the quantitative determination of fatty acids in milk with special emphasis on long-chain fatty acids. CYTA J Food. 2012;10(1):27–35.

Oukaci R, Singleton AH, Goodwin JG. Comparison of patented Co F–T catalysts using fixed-bed and slurry bubble column reactors. Appl Catal A-Gen. 1999; 186:129–44.

Peacock M, Paterson J, Reed L, Davies S, Carter S, Coe A, et al. Innovation in Fischer–Tropsch: developing fundamental understanding to support commercial opportunities. Top Catal. 2020. https://doi.org/10.1007/s11244-020-01239-6.

Pei Y, Ding Y, Zhu H, Du H. One-step production of C_1–C_{18} alcohols via Fischer-Tropsch reaction over activated carbon-supported cobalt catalysts: promotional effect of modification by SiO_2. Chinese J Catal. 2015;36:355–61.

Peña D, Griboval-Constant A, Lancelot C, Quijada M, Visez N, Stéphan O, et al. Molecular structure and localization of carbon species in alumina supported cobalt Fischer–Tropsch catalysts in a slurry reactor. Catal Today. 2014;228:65–76.

Potgieter H, van der Westhuizen R, Rohwer E, Malan D. Hyphenation of supercritical fluid chromatography and two-dimensional gas chromatography–mass spectrometry for group type separations. J Chromatogr A. 2013;1294:137–44.

Seomoon K. On-line GC and GC–MS analyses of the Fischer–Tropsch products synthesized using ferrihydrite catalyst. J Ind Eng Chem. 2013;19(6):2108–14.

Shafer WD, Gnanamani MK, Graham UM, Yang J, Masuku CM, Jacobs G, et al. Fischer–Tropsch: product selectivity–the fingerprint of synthetic fuels. Catalysts. 2019;9(3):259.

Silva RSF, Tamanqueir JB, Dias JCM, Passarelli FM, Bidart AMF, Aquino Neto FR, et al. Comprehensive two-dimensional gas chromatography with time of flight mass spectrometry applied to analysis of Fischer-Tropsch synthesis

products obtained with and without carbon dioxide addition to feed gas. J Braz Chem Soc. 2011;22(11):2121–6.

Speight RJ, Rourke JP, Wong A, Barrow NS, Ellis PR, Bishop PT, et al. [1]H and ^{13}C solution- and solid-state NMR investigation into wax products from the Fischer–Tropsch process. Solid State Nucl Magn Reson. 2011;39(3–4):58–64.

Takayama M. Metastable McLafferty rearrangement reaction in the electron impact ionization of stearic acid methyl ester, Int. J. Mass Spectrom. Ion Processes. 1995;144:199–204.

van de Laan GP, Beenackers AACM. Kinetics and selectivity of the Fischer–Tropsch synthesis: a literature review. Catal Rev Sci Eng. 1999;41(3-4):255–318.

van der Westhuizen R, Crous R, de Villiers A, Sandra P. Comprehensive two-dimensional gas chromatography for the analysis of Fischer–Tropsch oil products. J Chromatogr A. 2010;1217(52):8334–9.

Xiao K, Qi X, Wang X, Lv D, Zhu M, Zhong L. Factors associated with accurate analysis of Fischer–Tropsch products. Catal Letters. 2017;147:704–15.

Yang R, Zhou L, Gao J, Hao X, Wu B, Yang Y, et al. Effects of experimental operations on the Fischer-Tropsch product distribution. Catal Today. 2017; 298:77–88.

Publisher's Note