CHAPTER IX.B.

ANALYSIS OF FISCHER-TROPSCH SYNTHESIS PRODUCTS

Product Calculation Procedure

The following describes the gas chromatographic systems utilized for the analysis of Fischer-Tropsch (FT) products. An on-line analytical procedure was used for the characterization of the gas phase products and an off-line analysis was used for the condensed liquid phase generated during FT catalyst evaluation studies.

The hydrogen and carbon monoxide flow rates to the FT reactor are controlled by a thermal mass flow regulator (Brooks Instrument); after flow regulation, the two gases are mixed in a 0.5 L pressure vessel prior to entering the reactor. For mass balance calculations, the carbon and hydrogen gases entering the reactor are calculated as:

$$[CO\ in\ (g/hr)] = \frac{CO\ feed\ (mole\ \%)}{100} \times flow\ rate\ in \times \frac{1\ lb\ mole}{359\ SCF} \times MW\ (CO)\left(\frac{454\ gm}{1\ lb}\right) \quad (1)$$

$$[H_2\ in\ (g/hr)] = \frac{H_2\ feed\ (mole\ \%)}{100} \times flow\ rate\ in \times \frac{1\ lb\ mole}{359\ SCF} \times MW\ (H_2)\left(\frac{454\ gm}{1\ lb}\right) \quad (2)$$

$$Total\ (CO + H_2) = [CO\ in] + [H_2\ in] \quad (3)$$

The CSTR is operated so that a gas stream (at 270°C) exits the reactor through a tube fitted with a metal porous filter (0.5 μm). The flow rate of the exit gas, containing noncondensible products and unconverted reactants, is measured periodically using a soap film flow-meter.

The exit gas stream consisting of hydrocarbon products that remain in the vapor phase are conducted through a heated (80°C) GC sample loop to avoid condensation. The exit gas sample that contains C_4-C_9 hydrocarbons and the aqueous phase sample, which is analyzed for water and oxygenates, are analyzed separately using a GC fitted with a thermal conductivity detector (TCD) and a Porpack Q column operated at 100°C for 1 min., then programmed at 8°C/min, to 245°C. A factor is determined to normalize the data from the Porpak Q column and the Carle Analyzer using the analysis for the C_4 hydrocarbons. The olefin and paraffin compounds are not separated using this column. The analysis of the water sample provides the amount of C_1-C_4 oxygenates.

The Carle Gas Analyzer is utilized for quantitative determinations of CO, H_2, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8 and the butane/butene compounds. The instrument is calibrated using a standard mixture of the gases that are to be analyzed (supplied by Matheson Gas Products, Inc.) to obtain response factors to use to calculate the moles of each of the above compounds in the exit gas stream. Any components above C_4 elute together as a C_{5+} backflush. This instrument is used primarily to determine H_2, CO, and CO_2, which usually constitute more than 90 percent of the product stream; hydrocarbons and oxygenated species make up the balance.

The system allows collection of condensible products in three traps. Two hot traps, one at a temperature set at 200°C and the other at 100°C, are followed by a cold trap held at 1°C. The gas exiting the 1°C trap passes through a Tescom pressure regulator and is reduced to atmospheric pressure. The depressurized gas stream is sampled by on-line injection into either a Carle Gas Analyzer or a GC fitted with a column consisting of polystyrene cross-linked with divinylbenzene (Porpak Q) column for C_4 - C_9 hydrocarbon analysis. The gaseous sample contains unconverted reactants, CO_2, and products with carbon numbers from C_1 to C_9 in addition to water vapor. The quantity of these gaseous products exiting the reactor are calculated through Eqs (4-11).

$$\text{Partial Pressure of } H_2O\ (\chi_{H_2O}) = \frac{(\text{Vapor Pressure}/(760) \times 14.7)}{\text{System Pressure} + 14.7} \tag{4}$$

$$\text{Vapor Pressure (mmHg)} = 0.375 \times \text{Cold Trap Temp. } ^\circ C + 4.688 \tag{5}$$

$$\begin{aligned}\text{Total Gas Product (mol\%)} &= CO + H_2 + CO_2 + C_1 + C_2 + C_{2=} + C_3 + C_{3=} \\ &+ i\text{-}C_4 + n\text{-}C_4 + 1\text{-}C_{4=} + t\text{-}C_{4=} + c\text{-}C_{4=} + C_5 + C_6 + C_7 + C_8 + C_9\end{aligned} \tag{6}$$

$$\text{Gas Product Normalized } (J) = \text{Gas Product (mol\%) } (J) \times \frac{100}{\text{Total Gas Product}} \tag{7}$$

$$\text{Dry Basis Gas Product } (J) = \text{Gas Product Normalized}(J) \times (1-\chi_{H_2O}) \tag{8}$$

$$\text{Gas Product Mole Fraction } (J) = \frac{\text{Wet Gas Product}}{100} \tag{9}$$

$$\begin{aligned}\text{Gas Product (mol/hr) } (J) &= \text{Gas Product Mole Fraction } (J) \\ &\times \text{Flow Rate Out}\left(\frac{454}{359}\right)\end{aligned} \tag{10}$$

$$\text{Gas Product (gm/hr) } (J) = \text{Gas Product (mol/hr) } (J) \times MW\ (J) \tag{11}$$

where J is a matrix of all gas components.

The material collected in the cold trap separates into two phases - an aqueous layer which contains water plus soluble oxygenates and an oil layer which contains mostly hydrocarbons. Care must be taken to protect the samples during storage; thus, refrigeration is required to protect loss of volatile components. Products condensible in the 200°C hot trap include high molecular weight waxes; this fraction is not included in the chromatographic analysis to prevent plugging of the chromatographic injection valve and column. These non-volatile components are included in the mass balance calculations through Eqs. 12-17.

$$H_2O\ (gm/hr) = \left(\frac{aqueous\ wt.}{sample\ time\ period}\right) \tag{12}$$

$$Oil\ (gm/hr) = \left(\frac{oil\ wt.}{sample\ time\ period}\right) \tag{13}$$

$$Wax\ (gm/hr) = \left(\frac{wax\ wt.}{sample\ time\ period}\right) \tag{14}$$

$$Rewax\ (gm/hr) = \left(\frac{rewax\ wt.}{sample\ time\ period}\right) \tag{15}$$

$$Total\ Sample\ (gm/hr) = \left(\frac{total\ sample\ wt.}{sample\ time\ period}\right) \tag{16}$$

$$\begin{aligned} Total\ (gm/hr) = Total\ C_1\text{-}C_9\ (gm/hr) + \\ (H_2O + Oil + Wax + Rewax)\ (gm/hr) \end{aligned} \tag{17}$$

Product Analysis

Two gas chromatographic systems are employed to analyze the condensible fractions (figure 1). Components in the oil phase consist of hydrocarbons starting with carbon number C_4. The liquid samples from the cold trap and the hot trap (100°C) are combined, based upon the mass balance, and diluted with 50 volume% carbon disulfide, which effectively dissolves the hydrocarbons. The samples are analyzed using a Hewlett-Packard 5890A gas chromatograph. This instrument is equipped with a fused-silica capillary DB-5 column (60m X 0.32mm i.d., purchased from J&W Scientific, Inc.), a dual flame ionization detector and a Hewlett-Packard 7673A auto-sampler, with a constant volume size of 3 μL. The column head pressure is kept at about 20 psi by adjusting the retention time of CH_4. During an analysis, the oven temperature is maintained initially at 35°C for 10 min, is then programmed at 4°C/min to a final temperature of 325°C and held at this temperature until all detectable components elute. Injection of standards verified that, to avoid split-discrimination effects and condensation of higher boiling components in the injection ports, an injector temperature of 375°C is required, with the detector maintained at 350°C. The high FID temperature reduces the amount of material condensing onto the detector parts. A FID is used because of its identical response factor of essentially unity for all hydrocarbons. Helium is used as the carrier gas for the column (flow rate of 30 cm^3/min); following the exit from the column, air and hydrogen (450 and 30 cm^3/min, respectively) are added before the detector.

With column use, peaks of oxygenated species (most notably alcohols) broaden and their retention time shifts relative to hydrocarbon peaks. This is likely due to washing with each injection of the stationary phase from the beginning of the column and this eventually exposes the bare silica. Since the oxygenates spend a disproportionate amount of time in the beginning of the column because of the initially low temperature, they interact with the polar exposed silica surface and resolution deteriorates.

Mass Balance and Product Selectivity

Hydrocarbons are classified by carbon number, and the major ones within each carbon number fraction, such as normal α-olefins, normal β-olefins, and normal paraffins, are quantified and combined with the total area of the smaller peaks (branched paraffins and/or olefins) to obtain the total area for each C_n fraction. During a period of about 90 min, components up to C_{40} elute. Chromatographic peak area integration is performed by a Hewlett-Packard 3390A GC integrator. The mass closures for carbon, hydrogen, and oxygen are calculated to estimate the accuracy of the combined data. Good material balance closures (± 3%) are nearly always obtained even though four separate samples must be analyzed. For an overall material balance, the weights of the oil, wax, and water samples that are collected in each trap over an interval of about 24h are determined. This information is combined with the on-line gas analyses of the lighter products and the effluent gas flow rate to calculate the overall mass balance using Eq. (20).

$$\textit{Mass Balance} = \frac{\textit{GasProduct}(gm/hr)(CO) + \textit{Gas Product}(gm/hr)(H_2) + \textit{Gas Product}\ (gm/hr)(CO_2) + \textit{Total}(gm/hr)}{\textit{Total}\ (CO+H_2)\ in} \tag{18}$$

FT synthesis information, such as conversion and product selectivity, can be calculated using Eqs. (19)-(44).

$$\textit{Total}\ (CO+H_2 in)(m^3) = \textit{gas flow in}\ X\ 0.0283168 \tag{19}$$

$$\begin{gathered}\textit{Total HC} = [\textit{mass of C in} - \textit{mass of C in}\ CO_2\ \textit{out} - \\ \textit{mass of C in CO out}]\left(\frac{14.02709}{12.01115}\right)\end{gathered} \tag{20}$$

The $\left(\frac{14.02709}{12.01115}\right)$ ratio assumes the hydrocarbon is $(CH_2)_n$. This ratio is changed to

reflect the appropriate $\overline{MW_n}$ based upon the determined α values.

$$\begin{gathered}\textit{Total}\ C_{3+} = \textit{Total HC} - \textit{Gas Product}\ (gm/hr)\ (CH_4) - \\ \textit{Gas Product}\ (gm/hr)\ (C_2 + C_{2=})\end{gathered} \tag{21}$$

$$\text{Total HC per } m^3 (CO+H_2 \text{ converted}) \ (g/m^3) = \frac{\text{Total HC}}{\text{Total } (CO+H_2 \text{ converted}) (m^3)} \tag{22}$$

$$\text{Total } C_{3+} \ (g/m^3) = \frac{\text{Total } C_{3+}}{\text{Total } (CO+H_2 \text{ converted}) (m^3)} \tag{23}$$

$$\frac{C_2 \text{ alkane fraction}}{C_2 \text{ alkane} + C_2 \text{ alkene}} = \frac{\text{Dry Gas Product } (C_2)}{\text{Dry Gas Product } (C_2) + \text{Dry Gas Product } (C_{2=})} \tag{24}$$

$$\frac{C_3 \text{ alkane fraction}}{C_3 \text{ alkane} + C_3 \text{ alkene}} = \frac{\text{Dry Gas Product } (C_3)}{\text{Dry Gas Product } (C_3) + \text{Dry Gas Product } (C_{3=})} \tag{25}$$

$$\frac{C_4 \text{ alkane fraction}}{C_4 \text{ alkane} + C_4 \text{ alkene}} = \frac{\text{Dry Gas Product } (C_4)}{\text{Dry Gas Product } (C_4) + \text{Dry Gas Product } (C_{4=})} \tag{26}$$

$$\frac{C_4 \text{ 1-alkene}}{C_4 \text{ Total Alkene}} = \frac{\text{Dry Gas Product } (C_4 \text{ 1-alkene})}{\text{Dry Gas Product } (C_4 \text{ 1-alkene}) + \text{Dry Gas Product } (C_4 \text{ c-2-alkene}) + \text{Dry Gas Product } (C_4 \text{ t-2-alkene})} \tag{27}$$

$$\text{WHSV} \left(\frac{\text{g of inlet gas}}{\text{hr. g of cat}} \right) = \left(\frac{454}{\text{catalyst wt.}} \right) x \ \frac{\text{flow rate in}}{359} \ x \left(\frac{\text{CO feed (mol\%)} x \text{CO MW}}{100} + \frac{H_2 \text{ feed (mol\%)} x H_2 \text{ MW}}{100} \right) \tag{28}$$

$$\text{Space Velocity} \left(\frac{\text{SCF of inlet gas}}{\text{ft.}^3 \text{ of cat-hr.}} \right) = \frac{\text{flow rate in}}{\text{catalyst volume } x \ 0.00003532} \tag{29}$$

$$[H_2] = \frac{\text{Dry Gas Product } (H_2)}{100} \ x \text{ flow rate out} \tag{30}$$

$$[CO_2] = \frac{\text{Dry Gas Product } (CO_2)}{100} \ x \text{ flow rate out} \tag{31}$$

$$[CO] = \frac{\textit{Dry Gas Product (CO)}}{100}\ x\ \textit{flow rate out} \qquad (32)$$

$$[H_2O] = \left(\frac{\textit{aqueous wt.}}{\textit{sample time period}}\right) x \left(\frac{1\ lb}{454\ gm}\right) x \left(\frac{1\ \textit{lb-mol}\ H_2O}{18\ lb}\right) x \left(\frac{359\ SCF}{1\ \textit{lb-mol}}\right) + (\chi_{H_2O}\ x\ \textit{flow rate out}) \qquad (33)$$

$$CO\ conv.\% = \frac{(\textit{gas flow in x CO feed} - \textit{Dry Gas Product}(CO)\textit{x gas flow out})}{\textit{gas flow in x CO feed}}\ X\,100 \qquad (34)$$

$$H_2\ conv.\% = \frac{(\textit{gas flow in x } H_2 \textit{ feed} - \textit{Dry Gas Product}(H_2)\textit{x gas flow out})}{\textit{gas flow in x } H_2 \textit{ feed}}\ X\,100 \qquad (35)$$

$$CO + H_2\ conv.\% = \frac{(\textit{gas flow in x } (\textit{CO feed} + H_2 \textit{ feed}) - \textit{Dry Gas Product}(CO + H_2)\textit{x gas flow out})}{\textit{gas flow in x } (\textit{CO feed} + H_2 \textit{ feed})}\ X\,100 \qquad (36)$$

where CO and H_2 feed is defined as CO and H_2 mole fraction.

$$\textit{Mass of C in} = \left[\left(\frac{\textit{CO feed}}{100}\right) x \left(\frac{\textit{flow rate in}}{359}\right) x (CO\ MW * 454)\right]\ x\ \frac{12.01115}{CO\ MW} \qquad (37)$$

$$\textit{Mass of C in } CO_2 \textit{ out} = \left[\left(\frac{\textit{Dry Gas Product } (CO_2)}{100}\right) x \left(\frac{\textit{flow rate out}}{359}\right) x (CO_2\ MW * 454)\right]\ x\ \frac{12.01115}{CO_2\ MW} \qquad (38)$$

$$\textit{Mass of C in CO out} = \left[\left(\frac{\textit{Dry Gas Product (CO)}}{100}\right) x \left(\frac{\textit{flow rate out}}{359}\right) x (CO\ MW * 454)\right]\ x\ \frac{12.01115}{CO\ MW} \qquad (39)$$

$$\textit{Mass of } CH_4 = \left[\left(\frac{\textit{Dry Gas Product } (CH_4)}{100}\right) x \left(\frac{\textit{flow rate out}}{359}\right) x (C_1\ MW * 454)\right] \qquad (40)$$

$$\textit{Mass of } C_2H_6 = \left[\left(\frac{\textit{Dry Gas Product } (C_2H_6)}{100}\right) x \left(\frac{\textit{flow rate out}}{359}\right) x (C_2\ MW * 454)\right] \qquad (41)$$

$$CH_4\% = \left[\frac{(Mass\ of\ CH_4 x12.01115/16.04303)}{Mass\ of\ C in - Mass\ C\ in\ CO_2\ out - Mass\ of\ C\ in CO out} \right] x100 \qquad (42)$$

$$(CH_4 + C_2H_6)\% = \left[\frac{(Mass\ of\ CH_4 x12.01115/16.04303)\ +\ (Mass\ of\ C_2H_6 x24.0223)/30.07012}{Mass\ of\ C in - Mass\ C\ in\ CO_2\ out - Mass\ of\ C\ in CO out} \right] x100 \qquad (43)$$

$$\frac{CO_2}{CO} = \frac{Mass\ of\ C\ in\ CO_2\ out}{Mass\ C\ in - Mass\ C\ in\ CO\ out} \qquad (44)$$

The chromatographic system and analytical procedure that has been described is a viable method for the characterization of products from indirect coal liquefaction studies. Because of the quantity and complexity of the data that are generated using the analyses that are described, a data collection and analysis automation system utilizes the capabilities of an internal RS-232 serial communication line. All functions, such as column oven temperature programming, heated zone temperatures, etc., are stored within the computer system as part of the analysis method; the raw data are also stored for reintegration purposes. This means that the chromatograph can be completely "set-up" for a particular analysis by proper selection of a stored method (IX.B-1). This ability is utilized in the automation of the oil analyses. The auto sampler will inject samples only when the chromatograph shows a ready condition. Each day of the catalyst test has been assigned a separate library of files. It is only necessary, therefore, to specify the data number and sequence number of the desired data when accessing the data from a particular analysis. A complete analysis contains five files; these consist of all analyses performed for the products from the reactor at any particular sampling period. The five files are the results from the two analyses of the gas samples, the analysis of the aqueous phase sample, analysis of the organic phase (oil) sample, and the operator log sheet. Each of these files has been assigned a separate suffix. A provision has been made to transfer the data to a mainframe Vax computer as an archive for the data.

REFERENCE

IX.B-1. Bauer, J. V. and Dyer, P. N., *Chemical and Engineering Progress*, September, 51 (1982).