3.3.4.8 Fischer-Tropsch Data Calculations

The FTS data and calculations can be broken into several major groups, these being the run and sample conditions, feed and product stream data, conversions, rates, selectivity's, product distributions, and finally alpha values. All the data is stored in raw form in a Microsoft Access database. Any conversions, scaling, and further manipulation of the data is done entirely by SQL query of the database system, with the single exception of the curve fitting for the calculation of alpha values. This curve fitting of is primarily done with the SAS system of Statistical Software. The system has a Microsoft Visual Basic 5.0 front end for data entry with reporting by Crystal Reports Professional Version 6.

Run and Sample Conditions:

The run conditions which are of interest here initial values which will be used for the first and subsequent samples feed gas flow rate (slph) and composition, and the weight of the catalyst (g) and the Active metal (Fe or Co) and its weight percent. Also the date and time of the start of synthesis is recorded.

The sample conditions of interest are the date and time of the sample along with the feed gas (slph) along with its composition, the product gas flow (slph) and the weight of any liquid stream sample which were taken these being the water, light oil, heavy oil, and the wax (rewax) phase all in grams.

Feed and Product Stream Data:

Gas analysis is done on a Carle Gas Analyzer (AGC) which provides the mol percent of Hydrogen, Carbon Monoxide, Carbon Dioxide, Nitrogen, Methane, Ethane, Ethene, Propane, Propene, n-Butane, i-Butane, 1-Butene, iso-Butene, 2-trans-Butene, 2-cis-Butene. This GC is calibrated with a standard gas. The area counts of the olefin

and paraffin's of the carbon numbers from 5 to 10 are provided by the HP 5790 GC. The mol percents of the C5's through C10 will be calculated by multiplying the area count by a response factor. This factor is the sum of the AGC C4 mol percents divided by the sum of the area counts of the C4's from the HP 5790 GC. In summary, the database stores mol percents from the AGC and area counts from the HP 5790 GC. The conversion from area counts to mol percents is done on the fly using SQL queries. Additionally, The SQL will normalize these values after correcting for the vapor pressure of water at 1 atmosphere and 28^{O} C (assumed typical conditions for the laboratory). This results in all gas components being in normalized mol percents.

For the liquid product streams all data is based on the weight percent. Water phase data is from the HP 5790 GC. Both oil phases are combined and analyzed on the HP 5890 GC. Finally the wax (rewax) is analyzed on a High Temperature HP 5890. If the startup wax is one with a very high molecular weight this data must be corrected as the startup wax may not come off the column. For these cases, an internal standard is used to determine the correction factor need to account for this missing mass. This prevents the inflation of the product weight fractions due to the detector not seeing the startup wax which depending on the time on stream may be as high as eighty percent of the wax phase.

Conversions (%)

H_2 and CO Conversions	100 ((component mols in) - (component mols out)) / (component mols in)
(H2 + CO) Conversion	((CO in) (CO Conv.) + (H_2 in) (H_2 Conv.)) / ((H_2 in) + (CO in))

Conversion Rates (Conv. % / g Catalyst)

H_2, CO, Conversion Rates	((Component Conversion) / (weight catalyst {g})) / 100 (Percent Composition of Active Metal)
(H_2 + CO) Conversion Rate	(H2 Conversion Rate) + (CO Conversion Rate)

Rates (mol/h)

CO Rate	(CO Feed {mol/h}) (CO Conversion)
CO_2 Rate	(Gas Product {slph}) (CO_2 {mol %}) / (22.414 {mol/sl}) / 100
FT Rate	(CO Rate) - (CO_2 Rate)
C1-C4 Component Rate	(Gas Product {slph}) (Component {mol %}) / (22.414 {mol/sl}) / 100
C5 Plus Rate	(CO Rate) - (C1 Rate) - (C2 Rate) - (C3 Rate) - (C2 Rate) - (C1 Rate) - (CO_2 Rate)
C5 Plus HC Rate	(C5 Plus Rate) (14.027 {FW of CH_2}) / (Weight Catalyst {g})

Selectivity (Carbon Basis)

C1-C4 Component Selectivity	(Component Rate) / (CO Rate) 100 (Carbon Number)
C5 Plus Selectivity	(CO Selectivity) - (C1 Sel.) - (C2 Sel.) - (C3 Sel.) - (C4 Sel.) - (CO2 Sel.)

Product Distribution (mol fraction by carbon number)

Mol Fraction	For each carbon number C1 to C100 the sum of mol fractions in the gas, oil, wax, and water phases

Olefin / Paraffin Selectivity (per Carbon Number)

Total Alkenes	(1-alkene) + (cis-2-alkene) + (trans-2-alkenes) {all in mols per hour}
Paraffin Ratio	(paraffin {mol/h}) / (total alkenes {mol/h})
Olefin Ratio	(1-olefin {mol/h}) / (total olefins {mol/h})

Mass Balance

Product Gas Effective Molecular Weight	Sum of each of gas components: (Mol Fraction) (Formula Weight)
Water Vapor {g/h}	Product gas is assumed to be saturated at 28^{O} C and 1 atm.
Gas Prod {g/h}	(Gas Prod {slph}) (22.414 {mol/sl}) / (Effective MW {g/mol}) (Water Vapor {g/h})
Gas Feed {g/h}	(Gas Feed {slph}) (22.414 {mol/sl}) (28.01055 {FW of CO}) (CO Fraction) + (2.01594 {FW H_2}) (H_2 Fraction))
Sum Liquid Product {g/h}	(water {g/h}) + (oil {g/h}) + (wax {g/h})
Mass Balance {g/h}	(Gas Feed {g/h}) - (Gas Product {g/h}) - (Sum Liquid products {g/h})
Mass Closure	(Mass Balance {g/h}) / (Gas Feed {g/h})

Alpha Values

Alpha values are primally fitted using the SAS Statistical Software. For a two alpha fit the data is fitted to m(n) = x(1-a_1)a_1^(n-1) + (1-x)(1-a_2)a_2^(n-1) . Where m(n) is the mol fraction at carbon number n, x is the contribution by alpha 1, a_1 is alpha 1, and a_2 is alpha 2. For a single alpha fit: m(n) = (1-a_1)a_1^(n-1). Where m(n) is the mol fraction at carbon number n, and a_1 is the single alpha. For the fitting of data from literature where mol fractions have been reported for ranges of carbon numbers for example C1, C2-C4, C5-C10, C11-C20, and C20+ the internally written Alpha Fitter program was used.

SAS Program for Two Alpha Fit. (with sample data)

```
data a;
      input n y @@;
      cards;
1     0.047791693
2     0.040550869
3     0.035011413
4     0.020920487
5     0.013481663
6     0.010034115
7     0.007725418
8     0.006470921
9     0.005212527
10    0.004101158
11    0.00354337
12    0.002954146
13    0.002458323
14    0.002064626
15    0.001683087
16    0.001356415
17    0.001032646
18    0.000740856
19    0.000473017
20    0.000308679
```

21	0.000161864
22	0.000104361
23	6.27247E-05
24	3.94504E-05
25	2.37152E-05
26	1.61292E-05
27	9.86008E-06
28	6.6132E-06
29	4.34716E-06
30	3.20788E-06
31	2.25648E-06
32	1.7739E-06
33	1.06203E-06
34	8.12232E-07
35	5.66768E-07
36	4.37296E-07
37	3.16018E-07
38	2.50974E-07
39	1.51806E-07
40	1.51413E-07
41	1.21662E-07
42	7.46026E-08
43	6.56068E-08
44	6.40149E-08

45	5.68956E-08
46	5.62721E-08
47	4.98441E-08
48	4.98263E-08
49	4.41901E-08
50	4.37938E-08
51	3.82308E-08
52	3.87464E-08
53	3.29638E-08
54	3.37511E-08
55	2.86092E-08
56	2.9315E-08
57	2.43014E-08
58	2.45553E-08
59	1.97984E-08
60	1.96771E-08
61	1.44268E-08
62	1.56809E-08
63	1.16661E-08
64	1.25362E-08
65	9.49108E-09
66	1.1636E-08
67	8.09836E-09
68	7.88887E-09

```
69      4.77353E-09
70      5.51335E-09
71      2.848E-09
72      3.63534E-09
73      1.38808E-09
74      2.21318E-09
75      8.31286E-10
76      5.83877E-10
77      4.22772E-10
;

data r;
        set a;
        n = n;
        y = log(y);

proc nlin data=r method=dud best=10 smethod=golden;

        parms a1 = 0.5 to .99 by .1
             a2 = 0.5 to .99 by .1
             x  = 0.01 to .99 by .1;

        bounds 0.01<a1<=0.99;
        bounds 0.01<a2<=0.99;
```

```
        bounds 0.01<x<0.99;

        z =  x*(1-a1)*a1**(n-1) + (1-x)*(1-a2)*a2**(n-1);
        model y = log(z);

        output out=b p=yhat r=yresid;

data c;
        set b;
        y    = exp(y);
        yhat = exp(yhat);

proc plot data=b;
        plot y*n='a' yhat*n='p' / overlay vpos=25;
        plot yresid*n / vref=0 vpos=25;


proc univariate plot normal data=b;
        var yresid;

proc capability data=b gout=gseg graphics;

        var yresid;
        histogram yresid / normal;
```

```
run;
quit;
```

Program for Single Alpha Fit (with sample data):

```
data a;
      input n y @@;
      cards;
1     0.047791693
2     0.040550869
3     0.035011413
4     0.020920487
5     0.013481663
6     0.010034115
7     0.007725418
8     0.006470921
9     0.005212527
10    0.004101158
11    0.00354337
12    0.002954146
13    0.002458323
14    0.002064626
```

15	0.001683087
16	0.001356415
17	0.001032646
18	0.000740856
19	0.000473017
20	0.000308679
21	0.000161864
22	0.000104361
23	6.27247E-05
24	3.94504E-05
25	2.37152E-05
26	1.61292E-05
27	9.86008E-06
28	6.6132E-06
29	4.34716E-06
30	3.20788E-06
31	2.25648E-06
32	1.7739E-06
33	1.06203E-06
34	8.12232E-07
35	5.66768E-07
36	4.37296E-07
37	3.16018E-07
38	2.50974E-07

39	1.51806E-07
40	1.51413E-07
41	1.21662E-07
42	7.46026E-08
43	6.56068E-08
44	6.40149E-08
45	5.68956E-08
46	5.62721E-08
47	4.98441E-08
48	4.98263E-08
49	4.41901E-08
50	4.37938E-08
51	3.82308E-08
52	3.87464E-08
53	3.29638E-08
54	3.37511E-08
55	2.86092E-08
56	2.9315E-08
57	2.43014E-08
58	2.45553E-08
59	1.97984E-08
60	1.96771E-08
61	1.44268E-08
62	1.56809E-08

```
63      1.16661E-08
64      1.25362E-08
65      9.49108E-09
66      1.1636E-08
67      8.09836E-09
68      7.88887E-09
69      4.77353E-09
70      5.51335E-09
71      2.848E-09
72      3.63534E-09
73      1.38808E-09
74      2.21318E-09
75      8.31286E-10
76      5.83877E-10
77      4.22772E-10
;


data r;
        set a;
        n = n;
        y = log(y);


proc nlin data=r method=dud best=10 smethod=golden;
```

```
        parms a1 = 0.1 to .99 by 0.01;

        bounds 0.1<a1<=0.99;

        z =  (1-a1)*a1**(n-1);
        model y = log(z);

        output out=b p=yhat r=yresid;

data c;
        set b;
        y    = exp(y);
        yhat = exp(yhat);

proc plot data=b;
        plot y*n='a' yhat*n='p' / overlay vpos=25;
        plot yresid*n / vref=0 vpos=25;


proc univariate plot normal data=b;
        var yresid;

proc capability data=b gout=gseg graphics;
```

```
        var yresid;
        histogram yresid / normal;


run;
quit;
```

3.4.0 Task 5. Reporting - Project Management

All reporting elements have been completed with the submittal of this final report.