

APPENDIX 1

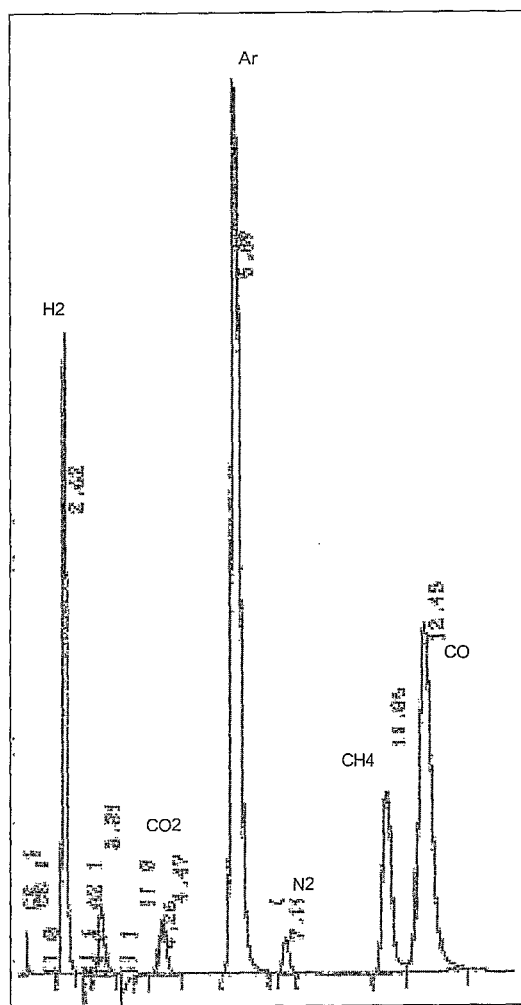
GC – GAS ANALYSES

This appendix will show typical GC analyses obtained on the gas phase product and feed streams of the ChemFT catalyst. Data shown is that of the first reference condition of Experiment 3 used during the kinetic investigation.

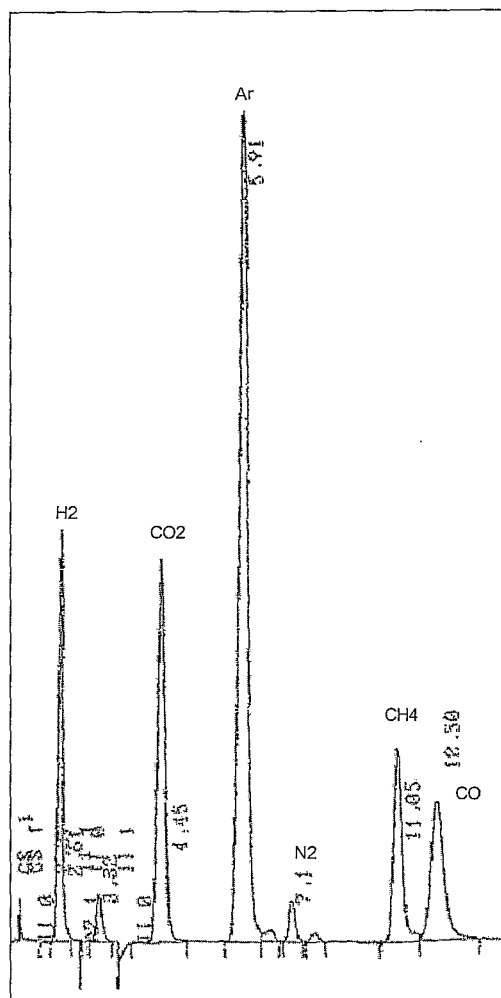
Typical TCD analyses:

TCD analyses are used for the calculation of gas conversion and reaction rates. Argon is used as tracer gas and will therefore appear in both the feed and outlet analyses.

Reactor Feed



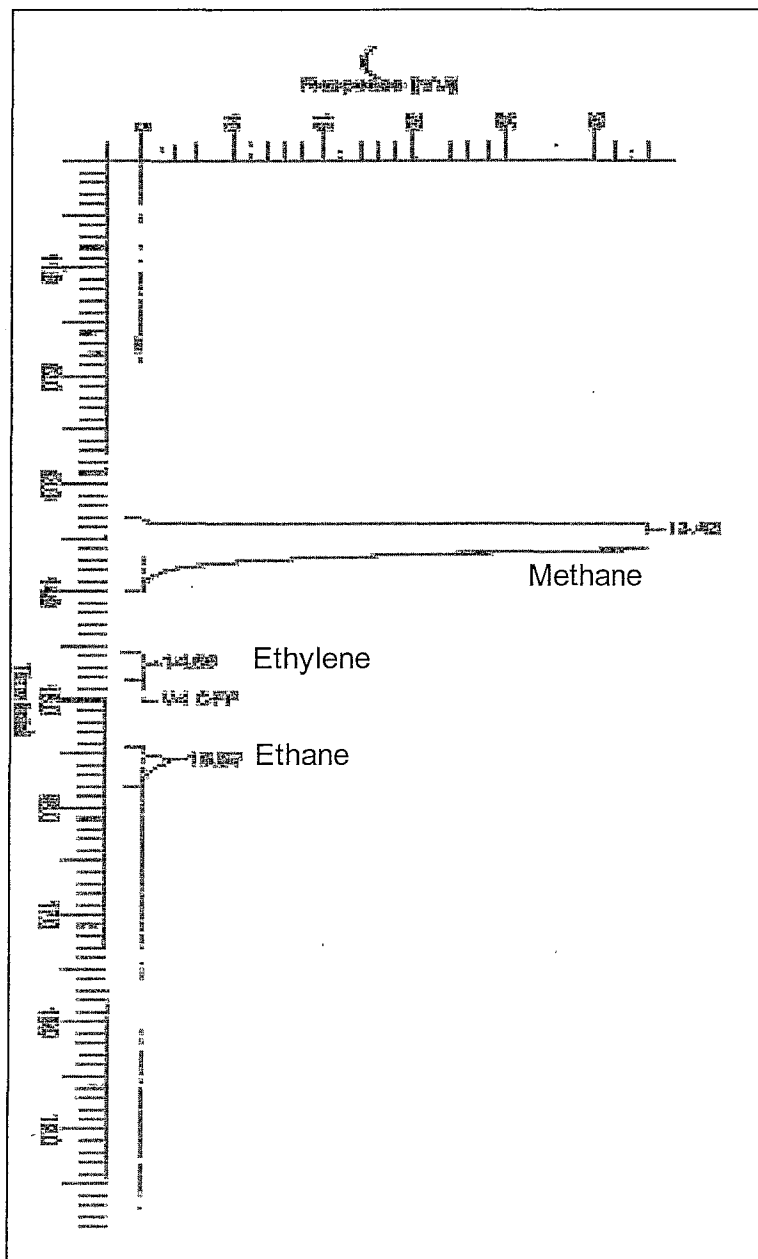
Reactor outlet



Typical FID analyses of ChemFT gas feed and product streams:

FID analyses will pick up all hydrocarbons present in the feed and product streams. These analyses are used to calculate the product selectivity of the catalyst.

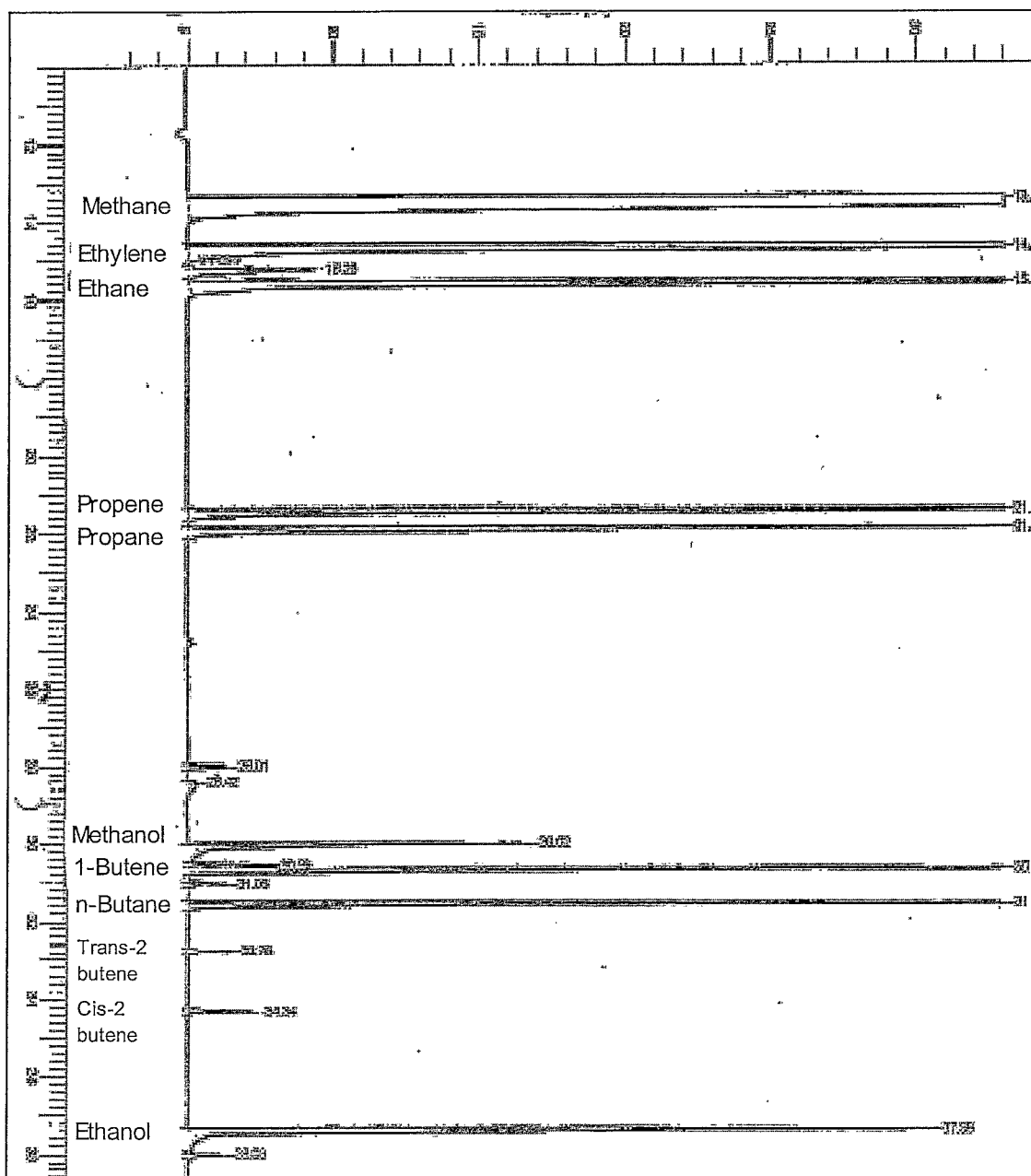
Typical FID feed analysis:



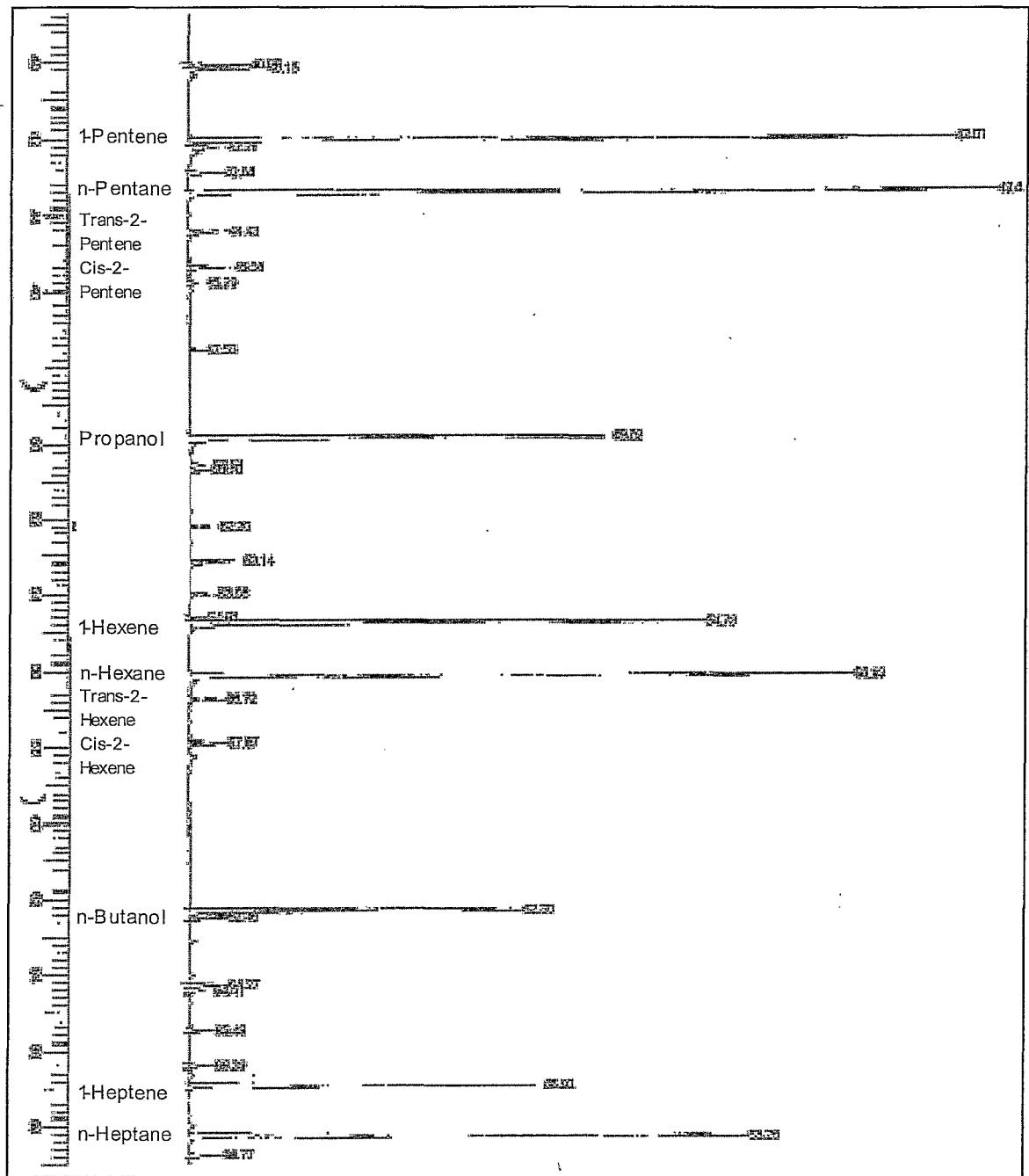
Typical FID analysis of ChemFT reactor outlet gas analysis.

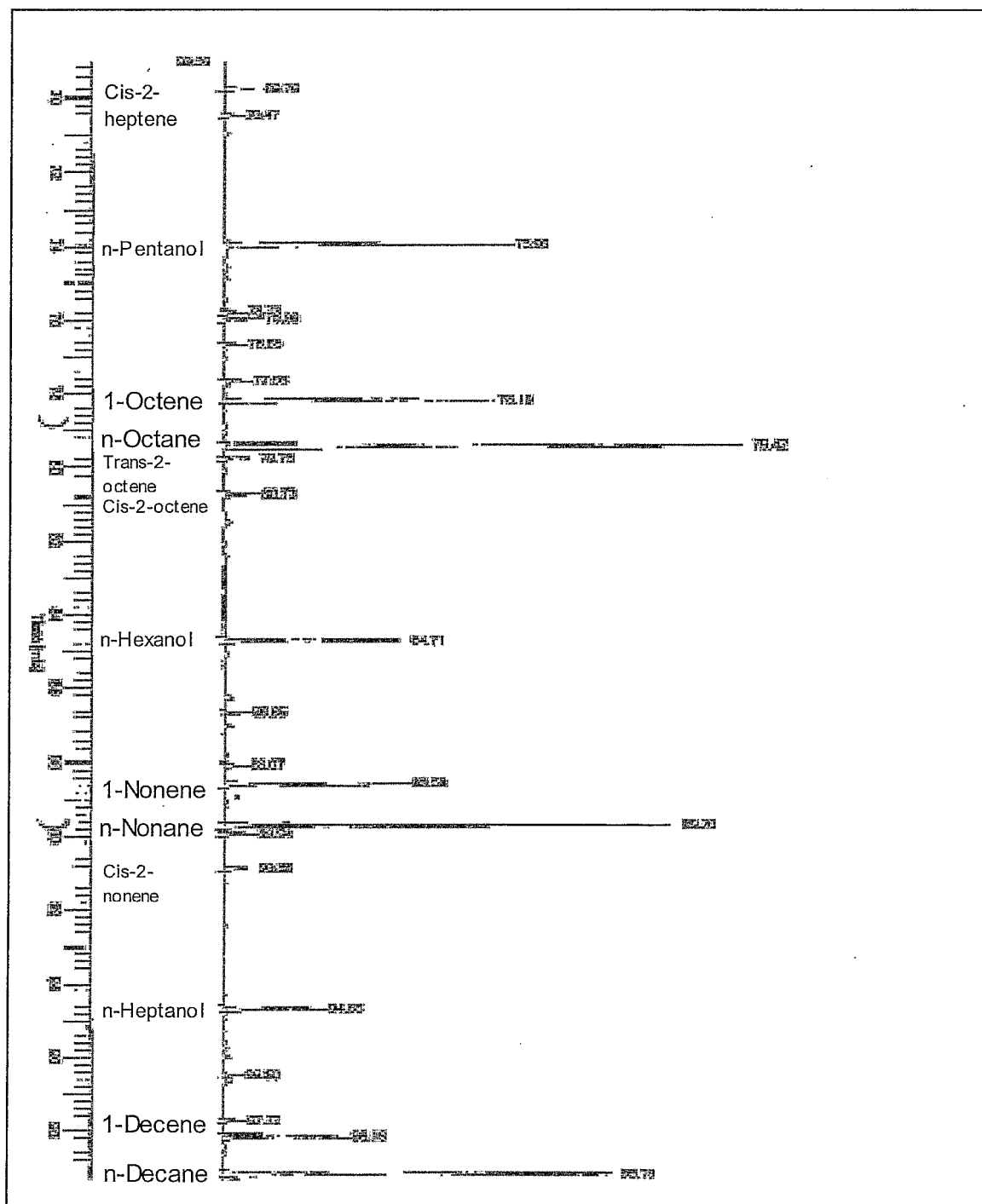
The product spectrum of the ChemFT catalyst as shown in the outlet gas FID trace appears to be relatively “clean”. Prominent 1-olefin, n-paraffin and n-alcohol peaks indicate very few branched products. Such a product trace will normally indicate easy product separation.

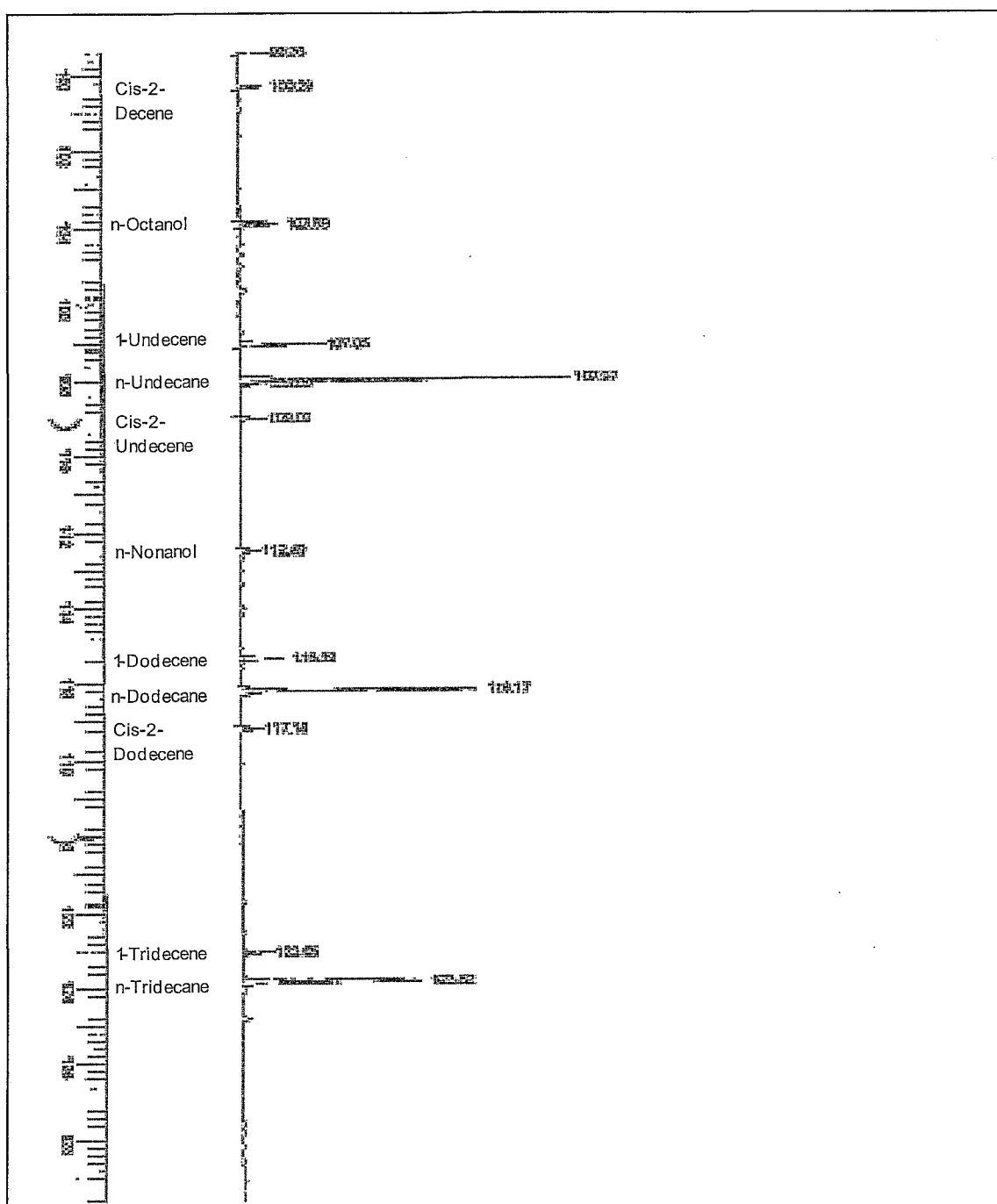
(part 1)



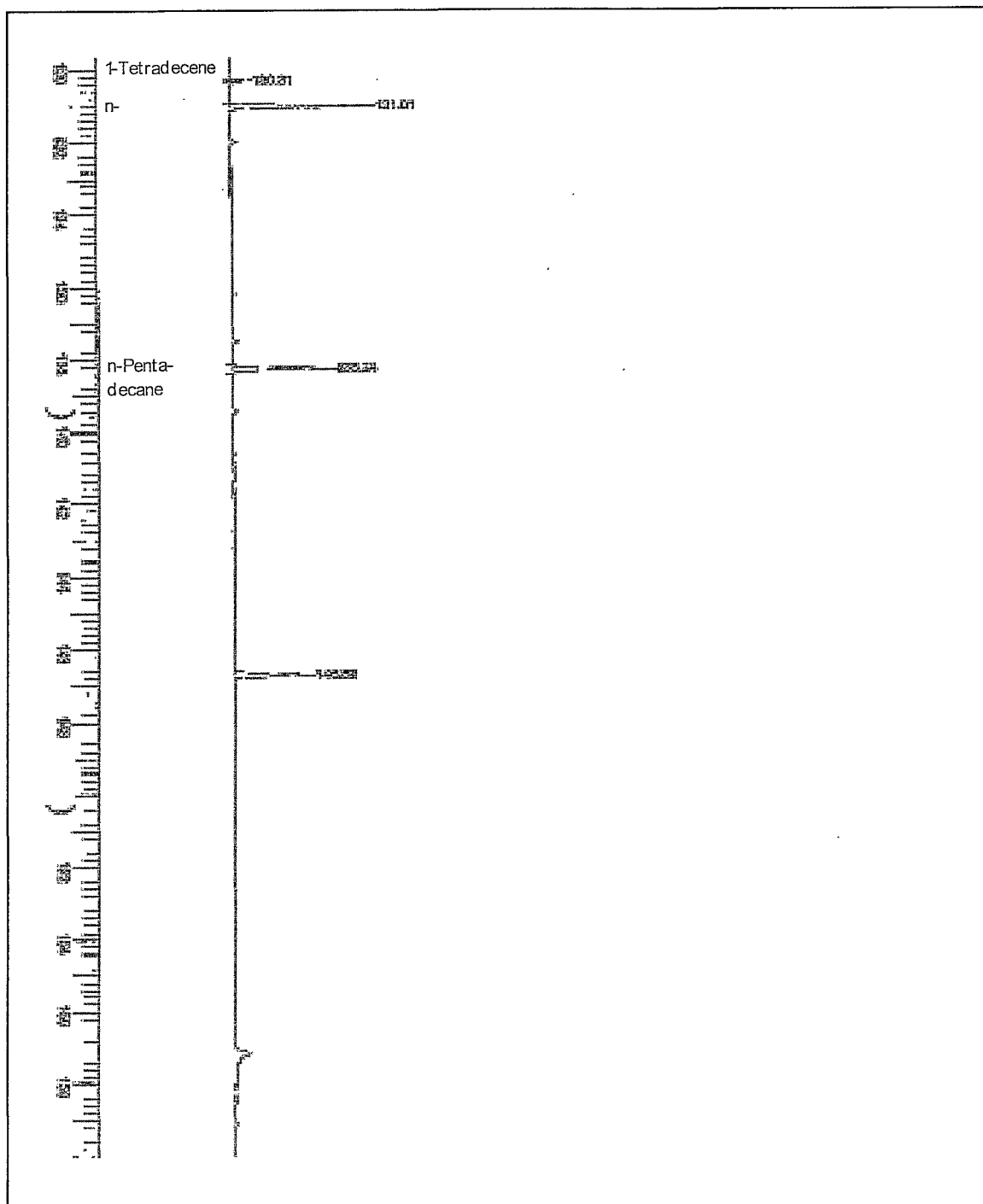
(part 2)







(part 5)



APPENDIX 2

CATALYST PREPARATION PROCEDURE

A large batch of the ChemFT catalyst was prepared from which all the laboratory and pilot plant experimentation was done. Preparation of the final ChemFT catalyst entailed the following:

- 57.87 kg of $\text{Fe}(\text{NO}_3)_3$, 8.18 kg of $\text{Zn}(\text{NO}_3)_2$, 13.7 kg of $\text{Mn}(\text{NO}_3)_3$, 1.55 kg KNO_3 and 1.37 kg $\text{Cu}(\text{NO}_3)_2$ were dissolved in distilled water (chemicals were purchased from Aldrich chemicals and used as received – analytical grade).
- 12.89 kg of FeC_2O_4 was dissolved separately in dilute HNO_3 . This solution was added to the other metal salt solution and the volume of the solution adjusted to give a Fe concentration of 60 g/l. The volume of metal salt solution was about 200 litre.
- The solution was heated up to 70°C.
- A 70 litre solution of ammonia (25 % NH_3 in H_2O) was co-fed with the metal solution into a precipitation vessel with the feed adjusted such that the precipitation pH was about 8 and the temperature 70°C.
- The precipitate was filtered and washed to a conductivity of between 300 and 1500 μs , followed by the re-slurrying of the precipitate. The elemental composition of the slurry was determined via ICP.
- Zn, K and Cu were re-added to the slurry in order to obtain the target promoter levels.
- SiO_2 (5 g/100 g Fe) was added to the slurry as binder.
- The catalyst was spraydried to obtain spherical particles of between 38 and 150 microns.

Finally the catalyst was calcined at 450°C for a period of 16 hours.

APPENDIX 3

EXPERIMENTAL RESULTS: INFLUENCE OF CALCINATION TEMPERATURE (IN-SITU REDUCTION)

Reduced in-situ at 240°C, 20bar(g), switch over to synthesis by lowering Temperature to 200°C					
Synthesis at 20 bar(g) and 240°C. H ₂ /CO feed ratio = 2.00					
Catalyst description	400°C/5 hrs calc	400°C/16 hrs calc	450°C/16 hrs calc	500°C/16 hrs calc	600°C/16 hrs calc
GHSV calculated (ml(n)/gcat/h)	2852	2846	2893	2813	1232
H ₂ /CO reactor ratio	3.01	4.03	3.6	4.4	4.27
Reactor partial pressures (bar(g))					
H ₂	8.95	9.32	9.45	9.49	9.6
CO	2.97	2.31	2.63	2.16	2.25
H ₂ O	1.28	1.09	0.9	0.67	1.03
CO ₂	1.5	1.81	1.79	2.02	1.82
% Conversion					
H ₂	33.35	29.3	29.01	28.41	31.87
CO	56.85	65.48	61.56	67.03	66.09
Synthesis gas	41.32	41.49	40.06	41.17	42.81
CO+CO ₂	37.75	40.85	37.37	38.66	40.8
CO+CO ₂ conversion (mmol/gcat/h)	16.06	17.57	15.75	15.90	5.54
% CO (of total reacted) converted to CO ₂	33.60	37.61	39.30	42.3	38.3
% CH ₄ Selectivity (C-atom)	16.1	16.6	17.58	24.7	22.7
Drainings: (per gram catalyst)					
Hot condensate – Wax (mg/gcat/h)	3.75	0.02	0.00	10.20	0.27
Cold condensate – Oil (mg/gcat/h)	61.20	61.20	57.50	73.50	14.25
Cold condensate – Water (mg/gcat/h)	101.75	89.65	73.90	82.25	26.35
Alcohol oil (mg/gcat/h)	9.19	16.44	18.60	23.92	4.08
1-Olefin oil (mg/gcat/h)	12.23	10.47	13.31	11.03	2.63
Cold condensate – Oil (mass %)					
1-Olefins	10.99	10.40	18.98	9.09	15.45
Internal olefins	9.00	6.70	4.17	5.92	2.99
n-Paraffins	53.23	44.85	32.31	41.01	41.29
Alcohols	15.02	26.86	32.34	32.54	28.65
Ketones	1.55	1.37	1.81	1.63	2.40
I-Paraffins + I-Olefins	10.07	9.80	10.35	9.79	9.02
NAC – water (mass %)					
Methanol	1.40	6.83	2.86	5.71	4.17
Ethanol	3.51	10.85	5.85	14.20	9.30
Propanol	1.12	2.96	1.52	3.39	2.15
Butanol	0.39	1.04	0.54	1.34	0.78
Acid number:	1.67	1.25	4.08	1.43	3.16
Total selectivity (C ₁ – C ₃₀ mass %):					
1-Olefins	27.40	23.83	29.84	19.50	23.49
n-Paraffins	55.70	52.72	49.60	56.72	60.53
Alcohols	7.30	14.88	11.36	16.29	10.83
Growth parameter (Alpha-1) :Alcohols	0.65	0.63	0.69	0.65	0.78

APPENDIX 4

EXPERIMENTAL RESULTS: INFLUENCE OF CALCINATION TEMPERATURE (EX-SITU REDUCTION)

Reduced ex-situ at 340°C and 1 bar(g), switch over to synthesis by lowering T to 200°C. Synthesis 20 bar(g) and 240°C. H ₂ /CO feed ratio = 2.00			
Catalyst description	450°C/16 hrs calc	600°C/16 hrs calc	700°C/16 hrs calc
GHSV calculated (ml(n)/gcat/h)	4332	1259	2203
H ₂ /CO reactor ratio	2.97	3.29	2.73
Reactor partial pressures (bar(g))			
H ₂	9.56	9.29	9.56
CO	3.22	2.82	3.5
H ₂ O	0.86	1.03	1.02
CO ₂	1.2	1.26	1.16
% Conversion			
H ₂	17.01	23.92	24.97
CO	46.92	52.68	45.13
H ₂ +CO	27.32	33.36	31.69
CO+CO ₂	30.59	35	30.54
CO + CO ₂ conv (mmol/ g cat/ hr)	18.45	4.93	11.96
% CO (of total reacted) converted to CO ₂	36.7	33.6	32.3
% CH ₄ Selectivity (C-atom)	9.9	8.7	7.4
Drainings: (per gram catalyst)			
Hot condensate – Wax (mg/gcat/h)	6.47	27.95	119.75
Cold condensate – Oil (mg/gcat/h)	86.19	11.71	15.23
Cold condensate – Water (mg/gcat/h)	92.53	36.27	37.24
Alcohol oil (mg/gcat/h)	28.82	2.38	3.78
Olefins oil (mg/gcat/h)	20.41	3.65	3.68
Cold condensate – Oil (mass %)			
1-Olefins	21.96	28.75	21.34
Internal olefins	1.72	2.43	2.81
n-Paraffins	31.09	32.73	36.82
Alcohols	33.44	20.37	24.82
Ketones	3.4	2.36	2.73
I-Paraffins + I-Olefins	8.37	13.32	11.37
NAC – water (mass %)			
Methanol	2.06	0.93	1.45
Ethanol	8.41	3.21	3.63
Propanol	1.66	0.81	1.03
Acid number:	14.66	21.15	Not available
Total selectivity (C ₁ -C ₃₀ – mass %):			
1-Olefins	29.21	40.54	41.52
n-Paraffins	42.35	39.02	41.61
Alcohols	20.65	8.93	8.57
Growth parameter (Alpha-1) : Alcohols	0.77	0.78	0.77

APPENDIX 5

LIQUID OIL PRODUCT BREAKDOWN

Liquid product (oil fraction) carbon number breakdowns are shown for the ChemFT catalyst operating at 20 bar(g) and 45 bar(g). A similar product breakdown obtained from a standard commercially used Fe-catalyst is also given for comparison. The discussion of the data forms part of Section 2.4.3.1.

The product breakdowns as given in Tables A.5.1 to A.5.3 were obtained from a liquid GC.

Table A.5.1: Liquid oil fraction analysis (mass %) – 20 bar(g) ChemFT catalyst

20 bar(g)						
Mass %						
C#	1 – Olefins	Int-olefins	n – Paraffins	Alcohols	Ketones	Iso-products
1	0.00	0.00	0.00	1.23	0.00	0.00
2	0.00	0.00	0.00	5.11	0.00	0.00
3	0.00	0.00	0.06	4.00	0.00	0.00
4	0.24	0.03	0.19	4.25	0.15	0.00
5	0.74	0.13	0.67	4.36	0.33	0.48
6	1.61	0.29	1.59	3.64	0.29	0.69
7	2.39	0.39	2.55	2.73	0.21	0.88
8	2.73	0.50	3.11	1.89	0.17	1.52
9	2.50	0.53	3.16	1.47	0.22	1.69
10	2.16	0.52	3.02	1.15	0.18	1.30
11	1.79	0.50	2.82	0.82	0.08	1.11
12	1.38	0.45	2.57	0.55	0.05	0.85
13	1.03	0.21	2.49	0.41	0.04	0.56
14	0.76	0.19	2.15	0.28	0.03	0.48
15	0.54	0.13	1.78	0.18	0.03	0.35
16	0.39	0.10	1.40	0.11	0.01	0.19
17	0.27	0.07	1.07	0.07	0.01	0.11
18	0.18	0.05	0.80	0.04	0.00	0.08
19	0.11	0.03	0.60	0.02	0.00	0.04
20	0.07	0.02	0.45	0.02	0.00	0.02
21	0.04	0.02	0.34	0.01	0.00	0.00
22	0.02	0.01	0.26	0.01	0.00	0.00
23	0.02	0.01	0.21	0.00	0.00	0.00
24	0.01	0.00	0.17	0.00	0.00	0.00
25	0.01	0.00	0.16	0.00	0.00	0.00
26	0.00	0.00	0.14	0.00	0.00	0.00
27	0.00	0.00	0.13	0.00	0.00	0.00
28	0.00	0.00	0.11	0.00	0.00	0.00
29	0.00	0.00	0.10	0.00	0.00	0.00
30	0.00	0.00	0.08	0.00	0.00	0.00
31	0.00	0.00	0.07	0.00	0.00	0.00
32	0.00	0.00	0.05	0.00	0.00	0.00
Totals	18.98	4.17	32.31	32.34	1.81	10.35

Table A.5.2: Liquid oil fraction analysis (mass %) – 45 bar(g) ChemFT catalyst

45 bar(g)						
Mass %						
C #	1 – Olefins	Int-olefins	n – Paraffins	Alcohols	Ketones	Iso-products
1	0.00	0.00	0.00	3.51	0.00	0.00
2	0.00	0.00	0.01	7.37	0.00	0.00
3	0.00	0.00	0.11	5.55	0.00	0.00
4	0.31	0.07	0.51	5.50	0.17	0.00
5	0.90	0.30	1.76	5.32	0.17	0.81
6	1.49	0.54	3.54	4.18	0.20	1.05
7	1.50	0.62	4.73	3.13	0.12	1.07
8	1.14	0.64	4.77	2.03	0.09	1.30
9	0.75	0.56	4.21	1.50	0.13	1.28
10	0.48	0.46	3.55	1.08	0.11	1.02
11	0.30	0.36	2.97	0.72	0.05	0.72
12	0.19	0.27	2.49	0.46	0.04	0.56
13	0.12	0.09	2.18	0.31	0.02	0.40
14	0.09	0.06	1.76	0.20	0.02	0.30
15	0.06	0.04	1.36	0.12	0.02	0.25
16	0.01	0.03	0.99	0.07	0.01	0.18
17	0.04	0.02	0.69	0.04	0.01	0.06
18	0.04	0.01	0.45	0.02	0.00	0.03
19	0.02	0.01	0.28	0.01	0.00	0.00
20	0.01	0.00	0.18	0.00	0.00	0.00
21	0.00	0.00	0.11	0.00	0.00	0.00
22	0.00	0.00	0.08	0.00	0.00	0.00
23	0.00	0.00	0.07	0.00	0.00	0.00
24	0.00	0.00	0.07	0.00	0.00	0.00
25	0.00	0.00	0.07	0.00	0.00	0.00
26	0.00	0.00	0.06	0.00	0.00	0.00
27	0.00	0.00	0.05	0.00	0.00	0.00
28	0.00	0.00	0.04	0.00	0.00	0.00
29	0.00	0.00	0.03	0.00	0.00	0.00
30	0.00	0.00	0.02	0.00	0.00	0.00
31	0.00	0.00	0.02	0.00	0.00	0.00
32	0.00	0.00	0.00	0.00	0.00	0.00
Totals	7.45	4.08	37.17	41.09	1.17	9.04

Table A.5.3: Liquid oil fraction analysis (mass %) – standard Fe catalyst

Standard – 20 bar(g)						
Mass %						
C #	1 – Olefins	Int-olefins	n – Paraffins	Alcohols	Ketones	Iso-products
1	0.00	0.00	0.00	0.09	0.00	0.00
2	0.00	0.00	0.00	0.35	0.00	0.00
3	0.00	0.00	0.02	0.43	0.00	0.00
4	0.09	0.01	0.06	0.98	0.03	0.00
5	0.40	0.06	0.25	1.74	0.06	0.09
6	1.18	0.22	0.81	1.93	0.13	0.14
7	2.30	0.47	1.85	1.69	0.04	0.36
8	3.08	0.83	2.98	1.30	0.11	0.60
9	3.06	1.10	3.69	1.11	0.16	0.83
10	2.62	1.29	4.08	0.98	0.14	0.75
11	2.05	1.33	4.27	0.72	0.08	0.78
12	1.53	1.30	4.34	0.52	0.06	0.63
13	1.11	0.58	4.95	0.43	0.05	0.67
14	0.77	0.50	4.73	0.31	0.04	0.58
15	0.52	0.40	4.31	0.22	0.03	0.53
16	0.40	0.30	3.69	0.15	0.03	0.38
17	0.26	0.22	2.94	0.11	0.02	0.36
18	0.22	0.14	2.21	0.07	0.01	0.18
19	0.07	0.10	1.57	0.04	0.01	0.17
20	0.08	0.06	1.08	0.02	0.01	0.07
21	0.04	0.04	0.70	0.01	0.00	0.06
22	0.02	0.02	0.42	0.01	0.00	0.04
23	0.01	0.01	0.25	0.00	0.00	0.01
24	0.01	0.00	0.14	0.00	0.00	0.00
25	0.00	0.00	0.09	0.00	0.00	0.00
26	0.00	0.00	0.06	0.00	0.00	0.00
27	0.00	0.00	0.05	0.00	0.00	0.00
28	0.00	0.00	0.05	0.00	0.00	0.00
29	0.00	0.00	0.04	0.00	0.00	0.00
30	0.00	0.00	0.03	0.00	0.00	0.00
31	0.00	0.00	0.03	0.00	0.00	0.00
32	0.00	0.00	0.03	0.00	0.00	0.00
Totals	19.85	8.98	49.70	13.20	1.01	7.22

APPENDIX 6

CHEMFT TOTAL PRODUCT DISTRIBUTION

Total C-atom product distribution of the ChemFT catalyst operating at 240°C, 20 bar(g) and 45 bar(g). See Section 2.3.3.4. for explanation of how products are sorted.

Table A.6.1: ChemFT product distribution 20 bar(g), 240°C

TOTAL PRODUCT DISTRIBUTION (C atom selectivity %)							
C #	1 - Olefins	Internal Olefins	n - Paraffins	Alcohols	Ketones, acids + aldehydes	I-Paraffins & I-Olefins	Total %
1	0.00	0.00	18.19	0.56	0.00	0.00	18.75
2	5.31	0.00	8.76	1.99	0.00	0.00	16.07
3	9.72	0.00	4.61	1.08	0.14	0.00	15.55
4	5.29	0.77	3.53	0.97	0.03	0.79	11.38
5	3.54	0.48	2.74	0.95	0.07	1.15	8.92
6	2.20	0.35	2.03	0.79	0.06	0.78	6.21
7	1.40	0.10	1.46	0.72	0.05	0.42	4.14
8	0.98	0.13	1.03	0.42	0.04	0.59	3.20
9	0.99	0.22	1.01	0.33	0.05	0.74	3.36
10	0.69	0.13	1.03	0.26	0.04	0.53	2.68
11	0.63	0.13	1.04	0.19	0.02	0.83	2.85
12	0.45	0.12	0.84	0.13	0.01	0.22	1.77
13	0.27	0.05	0.64	0.10	0.01	0.14	1.21
14	0.20	0.05	0.55	0.07	0.01	0.12	1.00
15	0.14	0.03	0.46	0.04	0.01	0.09	0.77
16	0.10	0.03	0.36	0.03	0.00	0.05	0.57
17	0.07	0.02	0.27	0.02	0.00	0.03	0.41
18	0.05	0.01	0.21	0.01	0.00	0.02	0.30
19	0.03	0.01	0.15	0.01	0.00	0.01	0.21
20	0.02	0.01	0.12	0.00	0.00	0.01	0.15
21	0.01	0.00	0.09	0.00	0.00	0.00	0.10
22	0.01	0.00	0.07	0.00	0.00	0.00	0.08
23	0.00	0.00	0.05	0.00	0.00	0.00	0.06
24	0.00	0.00	0.04	0.00	0.00	0.00	0.05
25	0.00	0.00	0.04	0.00	0.00	0.00	0.04
26	0.00	0.00	0.04	0.00	0.00	0.00	0.04
27	0.00	0.00	0.03	0.00	0.00	0.00	0.03
28	0.00	0.00	0.03	0.00	0.00	0.00	0.03
29	0.00	0.00	0.03	0.00	0.00	0.00	0.03
30	0.00	0.00	0.02	0.00	0.00	0.00	0.02
30+	0.00	0.00	0.03	0.00	0.00	0.00	0.03
TOTAL	32.10	2.64	49.52	8.68	0.54	6.52	100.00

Table A.6.2: ChemFT product distribution 45 bar(g), 240°C

TOTAL PRODUCT DISTRIBUTION (C atom selectivity %)							
C #	1 - Olefins	Internal Olefins	n - Paraffins	Alcohols	Ketones,acids + aldehydes	I-Paraffins & I-Olefins	Total %
1	0.00	0.00	19.05	2.55	0.00	0.00	21.61
2	2.30	0.00	11.22	4.75	0.67	0.00	18.94
3	8.13	0.00	7.48	2.14	0.00	0.00	17.75
4	4.05	0.88	5.30	1.47	0.03	0.35	12.09
5	2.44	0.54	3.90	1.21	0.03	0.84	8.96
6	1.30	0.38	2.77	0.89	0.04	0.44	5.82
7	0.66	0.25	1.95	0.63	0.03	0.25	3.77
8	0.36	0.15	1.42	0.42	0.02	0.31	2.67
9	0.18	0.13	1.09	0.31	0.03	0.30	2.05
10	0.11	0.11	0.84	0.23	0.02	0.24	1.55
11	0.07	0.09	0.70	0.15	0.01	0.17	1.19
12	0.05	0.06	0.59	0.10	0.01	0.13	0.94
13	0.03	0.02	0.51	0.07	0.01	0.09	0.73
14	0.02	0.01	0.42	0.04	0.00	0.07	0.57
15	0.02	0.01	0.32	0.03	0.00	0.06	0.44
16	0.00	0.01	0.23	0.02	0.00	0.04	0.30
17	0.01	0.00	0.16	0.01	0.00	0.02	0.20
18	0.01	0.00	0.11	0.00	0.00	0.01	0.13
19	0.00	0.00	0.07	0.00	0.00	0.00	0.08
20	0.00	0.00	0.04	0.00	0.00	0.00	0.04
21	0.00	0.00	0.03	0.00	0.00	0.00	0.03
22	0.00	0.00	0.02	0.00	0.00	0.00	0.02
23	0.00	0.00	0.02	0.00	0.00	0.00	0.02
24	0.00	0.00	0.02	0.00	0.00	0.00	0.02
25	0.00	0.00	0.02	0.00	0.00	0.00	0.02
26	0.00	0.00	0.01	0.00	0.00	0.00	0.01
27	0.00	0.00	0.01	0.00	0.00	0.00	0.01
28	0.00	0.00	0.01	0.00	0.00	0.00	0.01
29	0.00	0.00	0.01	0.00	0.00	0.00	0.01
30	0.00	0.00	0.01	0.00	0.00	0.00	0.01
30+	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TOTAL	19.73	2.66	58.34	15.03	0.91	3.33	100.00

APPENDIX 7

RESULTS FROM PILOT PLANT EVALUATION

This section contains summaries of the data used for the pilot plant evaluation performed within Chapter 3. Table A.7.1 is the result from the pilot plant operating in a once-through operation, while Table A.7.2 is the recycle operation result. Table A.7.3 is a summary of the laboratory result used for comparison within Chapter 3.

Table A.7.1: Once-Through pilot plant operation result – Data point 1

Reactor & Run Name		MPR 77	Balance mass:					
Catalyst Name & Description		OLE 116 450°C calc/16 hours	IN: Feed gas (g/hr)		(Fresh Feed)	12009.55		
Run Period		Once-through : data point 1						
			OUT: Tail gas (g/hr)			10027.26		
Reactor Pressure (bar)		45.10	Hot condensate/wax (g/hr)			210.83		
Reactor Temperature (°C)		240.00	Cold condensate - oil (g/hr)			665.00		
Unreduced Catalyst Mass (g)		5000.00	Cold condensate - water fraction (g/hr)			1051.67		
			Total (g/hr)			11954.76		
			Mass balance percentage (%)			99.54		
Reactor Feed Gas Flow Rate (ml(n) / s)			Reactor Partial Pressures (bar)					
H2		3696.61		H2		23.35		
CO		1883.42		CO		7.70		
SYNGAS		5580.02		H2O		4.08		
CH4		800.92		CO2		3.61		
CO2		40.59	% Conversion					
				H2		34.71		
Total Reactor Feed Gas Flow Rate (ml(n) / s)		6421.54		CO		57.73		
Total Reactor Tail Gas Flow Rate (ml(n) / s)		4662.03		SYNGAS		42.48		
				CO+CO2		40.06		
H2/CO Ratio of Fresh Feedgas		1.96						
H2CO Ratio of Total Feedgas		1.96	% CH4-Selectivity (C-atom)			5.30		
H2/CO-Reactor Ratio		3.03	% CH4-Selectivity (Mass %)			5.73		
TOTAL PRODUCT DISTRIBUTION (MASS % OF TOTAL PRODUCT, excl H2O and CO2)								
Mass % of total product								
	1 - Olefins	Internal	n - Paraffins	Alcohols	Ketones	I-Paraffins	Cyclic	Total
C #	Olefins				+ aldehydes	& I-Olefins	compounds	%
1	0.000	0.000	5.727	3.260	0.000	0.000	0.000	8.99
2	3.126	0.000	6.150	5.354	0.000	0.000	0.000	14.63
3	6.657	0.000	4.185	2.652	0.420	0.000	0.000	13.91
4	4.133	0.296	3.373	2.520	0.171	0.400	0.000	10.89
5	2.797	0.167	2.488	2.577	0.141	0.338	0.000	8.51
6	1.801	0.139	1.872	2.189	0.152	0.315	0.000	6.47
7	1.284	0.089	1.595	1.781	0.126	0.233	0.000	5.11
8	1.010	0.141	1.610	1.196	0.096	0.419	0.000	4.47
9	0.878	0.170	1.681	0.889	0.093	0.470	0.000	4.18
10	0.686	0.170	1.730	0.660	0.145	0.333	0.000	3.72
11	0.505	0.152	1.572	0.475	0.129	0.337	0.000	3.17
12	0.328	0.119	1.416	0.402	0.096	0.256	0.000	2.62
13	0.223	0.052	1.288	0.375	0.075	0.174	0.000	2.19
14	0.146	0.033	1.118	0.368	0.040	0.143	0.000	1.85
15	0.092	0.015	0.944	0.332	0.081	0.103	0.000	1.57
16	0.026	0.007	0.855	0.301	0.072	0.054	0.000	1.32
17	0.011	0.004	0.728	0.255	0.066	0.043	0.000	1.11
18	0.004	0.000	0.624	0.204	0.065	0.030	0.000	0.93
19	0.004	0.000	0.535	0.159	0.060	0.024	0.000	0.78
20	0.000	0.000	0.456	0.121	0.056	0.019	0.000	0.65
21	0.000	0.000	0.390	0.091	0.047	0.016	0.000	0.54
22	0.000	0.000	0.354	0.067	0.030	0.013	0.000	0.46
23	0.000	0.000	0.322	0.050	0.025	0.011	0.000	0.41
24	0.000	0.000	0.298	0.037	0.021	0.009	0.000	0.36
25	0.000	0.000	0.266	0.018	0.027	0.007	0.000	0.32
26	0.000	0.000	0.213	0.012	0.026	0.000	0.000	0.25
27	0.000	0.000	0.162	0.009	0.021	0.000	0.000	0.19
28	0.000	0.000	0.117	0.006	0.016	0.000	0.000	0.14
29	0.000	0.000	0.078	0.000	0.015	0.000	0.000	0.09
30	0.000	0.000	0.052	0.000	0.010	0.000	0.000	0.06
30+	0.000	0.000	0.080	0.000	0.026	0.000	0.000	0.11
TOTAL	23.71	1.55	42.28	26.36	2.35	3.75	0.00	100.00

Table A.7.2: Recycle pilot plant operation result – Data point 2

Reactor & Run Name		MPR 77	Balance mass:					
Catalyst Name & Description		OLE 116 450°C calc/16 hours	IN: Feed gas (g/hr)		(Fresh Feed)	4970.12		
Run Period		Recycle : Data point 2						
			OUT: Tail gas (g/hr)			3725.54		
Reactor Pressure (bar)		45.10	Hot condensate/wax (g/hr)			108.33		
Reactor Temperature (°C)		240.00	Cold condensate - oil (g/hr)			315.83		
Unreduced Catalyst Mass (g)		5000.00	Cold condensate - water fraction (g/hr)			879.17		
			Total (g/hr)			5028.88		
			Mass balance percentage (%)			101.18		
Reactor Feed Gas Flow Rate (ml(n) / s)			Reactor Partial Pressures (bar)					
H2		3312.01		H2		18.65		
CO		1164.09		CO		3.56		
SYNGAS		4476.10		H2O		1.83		
CH4		1561.83		CO2		7.54		
CO2		703.07	% Conversion					
				H2		64.61		
Total Reactor Feed Gas Flow Rate (ml(n) / s)		6741.00		CO		86.88		
Total Reactor Tail Gas Flow Rate (ml(n) / s)		1363.70		SYNGAS		72.17		
				CO+CO2		62.23		
H2/CO Ratio of Fresh Feedgas		1.94						
H2CO Ratio of Total Feedgas		2.84	% CH4-Selectivity (C-atom)			8.05		
H2/CO-Reactor Ratio		5.24	% CH4-Selectivity (Mass %)			7.02		
TOTAL PRODUCT DISTRIBUTION (MASS % OF TOTAL PRODUCT, excl H2O and CO2)								
Mass % of total product								
C #	1 - Olefins	Internal Olefins	n - Paraffins	Alcohols	Ketones + aldehydes	I-Paraffins & I-Olefins	Cyclic compounds	Total %
1	0.000	0.000	7.015	7.133	0.000	0.000	0.000	14.15
2	1.936	0.000	11.749	7.178	0.000	0.000	0.000	20.86
3	4.659	0.000	10.129	2.743	0.000	0.000	0.000	17.53
4	1.816	1.779	6.023	1.890	0.025	0.569	0.000	12.10
5	1.066	1.066	4.172	1.437	0.031	0.721	0.000	8.49
6	0.589	0.638	2.745	0.906	0.036	0.473	0.000	5.39
7	0.318	0.369	1.779	0.668	0.029	0.388	0.000	3.55
8	0.176	0.241	1.223	0.404	0.022	0.358	0.000	2.43
9	0.129	0.200	1.002	0.275	0.038	0.346	0.000	1.99
10	0.091	0.158	0.888	0.192	0.073	0.239	0.000	1.64
11	0.066	0.116	0.771	0.111	0.032	0.216	0.000	1.31
12	0.040	0.079	0.652	0.078	0.007	0.150	0.000	1.01
13	0.024	0.023	0.578	0.064	0.007	0.102	0.000	0.80
14	0.016	0.015	0.495	0.050	0.019	0.082	0.000	0.68
15	0.009	0.007	0.431	0.043	0.015	0.073	0.000	0.58
16	0.009	0.004	0.374	0.045	0.020	0.036	0.000	0.49
17	0.005	0.002	0.331	0.036	0.019	0.024	0.000	0.42
18	0.003	0.001	0.312	0.032	0.021	0.015	0.000	0.38
19	0.001	0.000	0.327	0.017	0.035	0.010	0.000	0.39
20	0.000	0.000	0.379	0.020	0.036	0.005	0.000	0.44
21	0.000	0.000	0.451	0.023	0.037	0.005	0.000	0.52
22	0.000	0.000	0.522	0.028	0.035	0.007	0.000	0.59
23	0.000	0.000	0.592	0.030	0.037	0.007	0.000	0.67
24	0.000	0.000	0.634	0.031	0.038	0.000	0.000	0.70
25	0.000	0.000	0.620	0.031	0.041	0.000	0.000	0.69
26	0.000	0.000	0.552	0.032	0.036	0.000	0.000	0.62
27	0.000	0.000	0.444	0.028	0.030	0.000	0.000	0.50
28	0.000	0.000	0.328	0.023	0.023	0.000	0.000	0.37
29	0.000	0.000	0.226	0.018	0.017	0.000	0.000	0.26
30	0.000	0.000	0.147	0.014	0.012	0.000	0.000	0.17
30+	0.000	0.000	0.218	0.032	0.029	0.000	0.000	0.28
TOTAL	10.95	4.70	56.11	23.61	0.80	3.83	0.00	100.00

Table A.7.3: Laboratory micro reactor result – Data point A

Reactor & Run Name		E007 Laboratory	Balance mass:				
Catalyst Name & Description		OLE 116 450°C calc/16 hours	IN: Feed gas (g/hr)	(Fresh Feed)			42.19
Run Period		Laboratory: Data Point A					
			OUT: Tail gas (g/hr)				36.76
Reactor Pressure (bar)		45.10	Hot condensate/wax (g/hr)				0.00
Reactor Temperature (°C)		239.00	Cold condensate - oil (g/hr)				1.85
Unreduced Catalyst Mass (g)		19.90	Cold condensate - water fraction (g/hr)				3.35
			Total (g/hr)				41.96
			Mass balance percentage (%)				99.46
Reactor Feed Gas Flow Rate (ml(n)/s)			Reactor Partial Pressures (bar)				
H2		13.31	H2				20.85
CO		6.56	CO				5.01
SYNGAS		19.88	H2O				3.40
CH4		2.90	CO2				3.92
CO2		0.13	% Conversion				
Ar		2.21	H2				34.31
Total Reactor Feed Gas Flow Rate (ml(n)/s)		25.12	CO				68.00
Total Reactor Tail Gas Flow Rate (ml(n)/s)		18.91	SYNGAS				45.44
			CO+CO2				44.86
H2/CO Ratio of Fresh Feedgas		2.03					
H2CO Ratio of Total Feedgas		2.03	% CH4-Selectivity (C-atom)				16.31
H2/CO-Reactor Ratio		4.16	% CH4-Selectivity (Mass %)				16.69
TOTAL PRODUCT DISTRIBUTION (MASS % OF TOTAL PRODUCT, excl H2O and CO2)							
Mass % of total product							
	1 - Olefins	Internal	n - Paraffins	Alcohols	Ketones	I-Paraffins	% Cyclic
C #		Olefins			+ aldehydes	& I-Olefins	compounds
1	0.000	0.000	16.686	5.767	0.000	0.000	0.000
2	2.261	0.000	10.452	7.274	0.000	0.000	0.000
3	6.948	0.000	6.766	2.814	0.000	0.000	0.000
4	3.462	0.652	4.697	1.923	0.042	0.481	0.000
5	2.082	0.397	3.344	1.564	0.041	0.650	0.000
6	1.136	0.306	2.382	1.147	0.051	0.377	0.000
7	0.620	0.217	1.781	0.837	0.032	0.249	0.000
8	0.361	0.152	1.377	0.533	0.024	0.355	0.000
9	0.255	0.137	1.163	0.401	0.034	0.320	0.000
10	0.126	0.115	0.953	0.295	0.028	0.244	0.000
11	0.079	0.092	0.759	0.199	0.012	0.182	0.000
12	0.049	0.070	0.674	0.131	0.011	0.146	0.000
13	0.030	0.025	0.572	0.092	0.007	0.107	0.000
14	0.026	0.018	0.480	0.061	0.007	0.081	0.000
15	0.019	0.011	0.394	0.038	0.005	0.069	0.000
16	0.002	0.008	0.310	0.025	0.003	0.056	0.000
17	0.015	0.005	0.233	0.014	0.002	0.025	0.000
18	0.012	0.003	0.165	0.008	0.000	0.013	0.000
19	0.007	0.002	0.111	0.004	0.000	0.006	0.000
20	0.004	0.001	0.070	0.002	0.000	0.001	0.000
21	0.001	0.000	0.042	0.000	0.000	0.000	0.000
22	0.000	0.000	0.024	0.000	0.000	0.000	0.000
23	0.000	0.000	0.016	0.000	0.000	0.000	0.000
24	0.000	0.000	0.012	0.000	0.000	0.000	0.000
25	0.000	0.000	0.010	0.000	0.000	0.000	0.000
26	0.000	0.000	0.009	0.000	0.000	0.000	0.000
27	0.000	0.000	0.007	0.000	0.000	0.000	0.000
28	0.000	0.000	0.005	0.000	0.000	0.000	0.000
29	0.000	0.000	0.004	0.000	0.000	0.000	0.000
30	0.000	0.000	0.003	0.000	0.000	0.000	0.000
30+	0.000	0.000	0.000	0.000	0.000	0.000	0.000
TOTAL	17.50	2.21	53.50	23.13	0.30	3.36	0.00

APPENDIX 8

RESULTS FROM KINETIC EXPERIMENTS 1 TO 16

This section contains summaries of the data used for the kinetic investigation performed on the ChemFT catalyst within Chapter 4. Table A.8.1 shows the results from Experiments 1 to 5, while Table A.8.2 contains the results of Experiments 6 to 16.

Table A.8.1: Results from kinetic investigation - Experiments 1 to 5

Experiment	Exp 1	Exp 1	Exp 1	Exp 1	Exp 1	Exp 1	Exp 1
Data point	1	2	3	4	5	6	7
Time on line (hr)	33.50	45.00	56.00	66.00	76.00	86.00	211.00
Reactor Pressure (bar)	45.10	45.70	44.50	45.10	45.70	44.50	45.20
Reactor Temperature (°C)	239.40	239.10	239.30	239.00	239.40	239.00	238.80
Mass of catalyst (unreduced) (g)	20.00	20.00	20.00	20.00	20.00	20.00	20.00
H2/CO Feed Ratio	1.97	2.06	2.02	2.03	1.96	2.02	2.02
Reactor Partial Pressures (bar)							
H2	19.38	20.15	19.16	19.39	19.62	19.26	19.74
CO	5.31	5.42	5.01	4.66	5.55	4.99	5.34
H2O	2.43	1.92	2.12	3.16	2.09	1.51	2.74
CO2	3.93	3.90	4.34	3.65	3.87	4.29	3.68
% Conversion							
H2	34.05	36.02	34.87	34.31	36.18	37.94	35.20
CO	64.36	64.20	65.69	68.00	64.61	67.53	64.50
Syngas	44.25	45.17	45.09	45.44	45.78	47.74	44.89
CO+CO2	40.35	41.17	38.88	44.86	43.36	42.39	41.37
FT Reaction Rate (mole CO to products excl. CO2/gcat/s)	6.0E-06	6.1E-06	5.6E-06	6.6E-06	6.5E-06	6.4E-06	6.6E-06
WGS Reaction Rate (mol CO2/gcat/s)	3.6E-06	3.4E-06	3.9E-06	3.4E-06	3.2E-06	3.8E-06	3.7E-06
Experiment	Exp 1	Exp 1	Exp 1	Exp 1	Exp 2	Exp 2	Exp 2
Data point	8	9	10	11	12	13	14
Time on line (hr)	328.00	353.00	478.00	500.00	90.00	114.00	138.00
Reactor Pressure (bar)	44.40	44.20	44.60	44.50	44.80	45.00	45.00
Reactor Temperature (°C)	239.50	239.20	239.00	239.10	229.10	229.30	229.30
Mass of catalyst (unreduced) (g)	20.00	20.00	20.00	20.00	20.00	20.00	20.00
H2/CO Feed Ratio	1.89	2.03	1.99	2.00	2.09	1.96	1.94
Reactor Partial Pressures (bar)							
H2	18.53	20.12	19.64	20.12	20.68	20.00	20.36
CO	5.35	5.31	5.61	5.76	7.00	7.29	7.31
H2O	2.36	2.21	1.92	1.50	2.28	2.46	2.67
CO2	4.01	3.54	3.65	3.56	2.53	2.69	2.58
% Conversion							
H2	33.61	33.22	33.10	31.00	27.51	28.80	27.25
CO	63.73	61.44	61.90	60.43	48.81	48.99	49.37
Syngas	44.02	42.07	42.72	40.80	34.41	35.61	34.78
CO+CO2	39.87	38.75	39.53	38.39	32.73	33.09	33.92
FT Reaction Rate (mole CO to products excl. CO2/gcat/s)	5.6E-06	5.5E-06	5.9E-06	5.6E-06	4.1E-06	4.3E-06	4.9E-06
WGS Reaction Rate (mol CO2/gcat/s)	3.3E-06	3.2E-06	3.3E-06	3.2E-06	2.0E-06	2.1E-06	2.2E-06
Experiment	Exp 2	Exp 3	Exp 3	Exp 4	Exp 4	Exp 5	Exp 5
Data point	15	16	17	18	19	20	21
Time on line (hr)	162.00	405.00	430.00	440.00	451.00	403.00	427.00
Reactor Pressure (bar)	45.10	44.60	44.40	26.60	26.80	26.70	26.70
Reactor Temperature (°C)	229.30	219.20	219.30	239.40	239.10	219.20	219.20
Mass of catalyst (unreduced) (g)	20.00	20.00	20.00	20.00	20.00	20.00	20.00
H2/CO Feed Ratio	1.90	1.95	1.99	1.97	1.99	2.05	2.00
Reactor Partial Pressures (bar)							
H2	18.91	21.29	21.04	11.99	10.73	12.80	13.11
CO	7.67	9.51	9.50	3.77	4.14	5.80	5.62
H2O	3.01	1.58	1.44	0.96	1.33	0.81	0.80
CO2	2.58	1.34	1.37	2.13	2.25	0.80	0.75
% Conversion							
H2	33.91	19.35	20.27	28.48	41.03	20.87	15.52
CO	49.46	27.94	28.37	55.60	54.80	26.48	25.92
Syngas	39.30	22.94	22.98	37.60	45.64	22.71	18.93
CO+CO2	34.65	20.24	20.70	33.30	32.93	19.29	18.78
FT Reaction Rate (mole CO to products excl. CO2/gcat/s)	4.8E-06	3.1E-06	3.1E-06	3.7E-06	3.6E-06	2.1E-06	2.0E-06
WGS Reaction Rate (mol CO2/gcat/s)	2.1E-06	1.2E-06	1.1E-06	2.5E-06	2.4E-06	7.8E-07	7.7E-07

Table A.8.2: Results from kinetic investigation - Experiments 6 to 16

Experiment	Start-up	Exp 6	Exp 7	Exp 7	Exp 8	Exp 9	Exp 10	Exp 10	Exp 11
		Ref 1				Ref 1			
Data point		1	2	3	4	5	6	7	8
Time on line (hr)	23.42	93.42	113.75	138.75	186.50	210.83	258.50	282.67	329.42
Reactor Pressure (bar)	50.10	50.20	50.30	50.30	50.20	50.30	50.30	50.20	50.20
Reactor Temperature (°C)	239.00	239.90	238.50	239.70	239.70	239.70	239.50	239.90	238.70
Mass of catalyst (unreduced) g	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Total Reactor Feed Gas Flow Rate (ml(n) / s)	23.34	28.38	28.96	28.30	27.81	27.59	28.16	28.04	27.25
Total Reactor Tail Gas Flow Rate (ml(n) / s)	18.77	24.05	24.30	24.04	22.71	23.71	24.01	24.19	23.59
Reactor Feedgas composition (vol %)									
H2	50.03	47.49	52.96	52.12	62.69	47.25	46.03	45.91	46.40
CO	24.97	23.02	21.99	22.30	22.41	22.94	28.93	28.91	33.22
CH4	10.95	9.34	9.58	9.73	9.19	9.17	9.10	9.25	9.27
CO2	0.77	0.68	0.59	0.63	0.61	0.63	0.65	0.57	0.58
Ar	13.28	19.47	14.87	15.21	5.10	20.01	15.30	15.36	10.53
H2/CO-Feed Ratio	2.00	2.06	2.41	2.34	2.80	2.06	1.59	1.59	1.40
H2/CO-Reactor Ratio	3.44	3.30	4.61	4.20	5.01	3.14	1.95	2.04	1.56
Reactor Partial Pressures (bar)									
H2	20.46	19.63	22.85	22.23	27.26	19.71	18.83	19.11	18.98
CO	5.95	5.95	4.96	5.29	5.45	6.29	9.64	9.36	12.17
H2O	2.85	2.46	2.78	2.81	3.12	2.44	2.69	2.64	2.77
CO2	3.35	2.93	2.81	2.74	2.63	2.46	2.50	2.52	2.49
% Conversion									
H2	34.37	30.21	28.00	27.97	29.28	28.73	30.67	28.48	29.49
CO	61.73	56.34	62.35	59.97	60.47	53.17	43.54	44.36	36.85
SYNGAS	43.48	38.74	38.08	37.56	37.49	36.72	35.64	34.62	32.56
CO+CO2	43.28	37.80	43.72	42.03	44.09	37.58	31.13	31.37	25.68
FT Reaction Rate (mole CO to products excl CO2/ g-cat/s)	5.6E-06	5.5E-06	6.2E-06	5.9E-06	6.1E-06	5.3E-06	5.7E-06	5.7E-06	5.2E-06
WGS reaction rate (mole CO2/gcat/s)	2.4E-06	2.7E-06	2.6E-06	2.5E-06	2.3E-06	2.2E-06	2.3E-06	2.4E-06	2.3E-06
Experiment	Exp 12	Exp 12	Exp 13	Exp 13	Exp 14	Exp 15	Exp 15	Exp 16	Exp 16
	Ref 1	Ref 1						Ref 2	Ref 2
Data point	9	10	11	12	13	14	15	16	17
Time on line (hr)	354.58	378.58	395.00	418.33	467.42	490.33	515.33	538.17	562.00
Reactor Pressure (bar)	50.10	50.20	25.20	25.30	25.50	25.50	25.40	25.40	25.50
Reactor Temperature (°C)	237.80	238.70	239.70	238.50	240.00	240.10	238.20	238.10	238.40
Mass of catalyst (unreduced) g	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00	20.00
Total Reactor Feed Gas Flow Rate (ml(n) / s)	27.97	27.73	18.62	18.17	16.25	18.20	18.18	18.44	18.27
Total Reactor Tail Gas Flow Rate (ml(n) / s)	23.97	23.53	16.30	15.99	14.21	16.04	15.48	15.97	15.87
Reactor Feedgas composition (vol %)									
H2	47.71	47.40	47.52	46.74	49.33	48.19	49.31	48.01	47.67
CO	22.80	22.96	22.58	23.04	24.82	23.16	22.66	22.19	22.21
CH4	9.07	9.06	9.39	9.15	10.27	9.60	9.47	9.06	9.23
CO2	0.66	0.63	0.63	0.68	9.98	3.51	3.30	0.66	0.62
Ar	19.76	19.94	19.89	20.39	5.60	15.55	15.26	20.08	20.27
H2/CO-Feed Ratio	2.09	2.06	2.10	2.03	1.99	2.08	2.18	2.16	2.15
H2/CO-Reactor Ratio	3.31	3.17	3.53	3.49	3.06	3.17	3.23	3.31	3.28
Reactor Partial Pressures (bar)									
H2	20.21	19.80	10.67	10.49	10.99	10.75	10.63	10.45	10.38
CO	6.11	6.25	3.02	3.00	3.59	3.40	3.30	3.15	3.16
H2O	2.29	2.30	0.82	0.86	1.35	1.06	1.05	1.00	1.01
CO2	2.53	2.56	1.36	1.42	3.89	2.03	2.11	1.36	1.36
% Conversion									
H2	27.53	29.37	22.01	21.92	23.61	22.86	27.75	25.75	25.80
CO	54.17	54.01	53.50	54.64	50.46	49.32	51.27	51.52	51.47
SYNGAS	36.14	37.41	32.15	32.72	32.60	31.45	35.15	33.89	33.96
CO+CO2	38.06	37.92	35.43	36.16	36.92	34.12	34.68	33.67	33.37
FT Reaction Rate (mole CO to products excl CO2/ g-cat/s)	5.4E-06	5.4E-06	3.3E-06	3.4E-06	3.3E-06	3.2E-06	3.2E-06	3.1E-06	3E-06
WGS reaction rate (mole CO2/gcat/s)	2.3E-06	2.3E-06	1.7E-06	1.7E-06	1.2E-06	1.4E-06	1.5E-06	1.6E-06	1.6E-06