Kinetics, selectivity and scale up of the Fischer-Tropsch synthesis

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Appendix A
Spinning Basket Reactor, Run A

Table A1 Summary of the experimental conditions and analysis.

Run	TOS	P	F	$\Phi^{in}_{v,0}/W$	$\Phi_{v,0}/W$	y_i			
	(h)	(MPa)		(10^{-3} Nm^3 kg^{-1} s^{-1})		H_2	CO	CO_2	H_2O
A1[1]	240	1.5	2	1.5	1.19	0.584	0.226	0.0537	0.0880
A2	265	1.2	0.5	1.0	0.7	0.245	0.500	0.0978	0.0239
A3	292	1.6	1	1.0	0.69	0.397	0.274	0.1568	0.0537
A4	313	2.4	2	1.0	0.75	0.621	0.138	0.1034	0.0582
A5	361	4.0	4	1.0	0.79	0.771	0.037	0.0341	0.0702
A6[1]	387	1.5	2	1.5	1.23	0.623	0.213	0.0498	0.0407
A7	410	2.0	4	1.0	0.82	0.767	0.073	0.0473	0.0453
A8	450	3.2	1	1.0	0.64	0.317	0.277	0.1699	0.0900
A9	496	3.0	0.5	1.0	0.70	0.194	0.489	0.1593	0.0452
A10	552	2.4	2	0.5	0.34	0.581	0.094	0.1304	0.0569
A11	581	2.4	2	2.0	1.65	0.653	0.191	0.0585	0.0599
A12	622	2.4	2	1.5	1.14	0.599	0.170	0.0739	0.0648
A13[1]	653	1.5	2	1.5	1.24	0.625	0.188	0.0644	0.0502
A14[1]	862	1.5	2	1.5	1.27	0.634	0.233	0.0359	0.0352
A15	889	1.2	2	0.5	0.41	0.624	0.154	0.0912	0.0383
A16	914	1.2	2	2.0	1.80	0.641	0.247	0.0255	0.0205
A17	961	2.4	0.5	2.0	1.65	0.250	0.541	0.0635	0.0251
A18	982	2.4	0.5	0.5	0.36	0.169	0.439	0.2219	0.0562
A19[1]	1011	1.5	2	1.5	1.21	0.630	0.194	0.0626	0.0406
A20	1080	1.2	0.5	2.0	1.70	0.275	0.547	0.0392	0.0117
A21	1101	1.2	2	0.5	0.38	0.586	0.117	0.1243	0.0255
A22	1151	2.0	0.25	1.0	0.81	0.115	0.657	0.0648	0.0072
A23	1177	0.8	1	1.0	0.81	0.423	0.339	0.0919	0.0298
A24[1]	1224	1.5	2	1.5	1.19	0.622	0.188	0.0682	0.0537

[1] Reference experiment

Table A2 On-line mole fractions of paraffins.

Run	Paraffins $10^3 y_i$ (-)									
	1	2	3	4	5	6	7	8	9	10
A1	10.8	1.67	0.687	0.658	0.542	0.382	0.281	0.223	0.187	0.136
A2	5.68	0.861	0.338	0.356	0.318	0.202	0.172	0.142	0.118	0.082
A3	17.6	3.97	1.55	1.44	1.29	0.720	0.613	0.536	0.471	0.431
A4	25.5	5.13	2.27	2.05	1.65	1.15	0.663	0.473	0.387	0.190
A5	18.5	2.90	1.76	1.56	1.19	0.786	0.424	0.351	-	-
A6	11.4	1.88	0.780	0.756	0.573	0.287	0.242	0.196	0.171	0.132
A7	23.85	3.60	1.83	1.60	1.14	0.815	0.386	0.244	0.156	0.114
A8	17.2	4.80	2.15	1.79	1.26	1.02	0.672	0.519	0.506	0.415
A9	6.47	1.32	0.658	0.576	0.502	0.252	0.233	0.195	-	-
A10	31.2	8.14	3.94	2.55	2.17	1.49	1.20	0.880	0.709	0.620
A11	14.3	3.44	1.47	0.998	0.729	0.490	0.384	0.279	0.234	0.189
A12	17.3	4.34	1.84	1.24	0.913	0.645	0.443	0.332	0.269	0.220
A13	14.8	3.33	1.29	0.983	0.687	0.392	0.333	0.273	0.257	-
A14	10.3	1.81	0.713	0.508	0.358	0.249	0.172	0.133	0.115	0.094
A15	24.3	4.96	1.90	1.26	1.02	0.701	0.474	0.336	0.266	0.222
A16	7.44	1.12	0.442	0.276	0.207	0.143	0.107	0.083	0.062	0.063
A17	5.21	0.895	0.430	0.324	0.222	0.162	0.154	0.113	0.105	0.095
A18	9.83	2.39	0.974	0.752	0.678	0.529	0.417	0.301	0.244	0.214
A19	15.6	3.20	1.17	0.784	0.610	0.401	0.284	0.222	0.164	0.139
A20	3.16	0.378	0.192	0.137	0.123	0.080	0.069	0.056	0.052	-
A21	33.3	6.84	2.87	1.82	1.48	0.974	0.697	0.518	0.347	0.294
A22	2.19	0.269	0.165	0.123	0.133	0.094	0.076	0.068	0.054	0.052
A23	11.8	2.20	0.740	0.552	0.487	0.357	0.282	0.264	0.245	-
A24	17.6	3.40	1.28	0.898	0.702	0.461	0.363	0.327	-	-

Table A3 On-line mole fractions of olefins.

Run	Olefins $10^3 y_i$ (-)								
	2	3	4	5	6	7	8	9	10
A1	1.09	2.56	1.63	1.27	0.751	0.542	0.344	0.232	0.178
A2	1.72	2.63	1.73	1.45	0.921	0.648	0.453	0.374	0.224
A3	2.29	6.10	3.68	2.85	1.63	1.03	0.704	0.423	0.336
A4	1.27	5.11	2.97	2.18	1.18	0.613	0.295	0.200	0.090
A5	0.286	1.98	1.05	0.720	0.348	0.120	0.081	-	-
A6	1.24	2.94	1.87	1.34	0.757	0.433	0.284	0.165	0.101
A7	0.535	2.89	1.48	0.933	0.494	0.185	0.123	0.046	0.037
A8	2.95	7.32	4.35	2.96	2.08	1.19	0.714	0.536	0.377
A9	2.53	3.86	2.50	1.88	1.25	0.852	0.599	0.557	-
A10	1.34	6.30	3.02	1.93	1.03	0.651	0.324	0.207	0.138
A11	1.89	4.26	2.28	1.45	0.837	0.440	0.257	0.153	0.107
A12	1.85	4.85	2.50	1.58	0.890	0.468	0.242	0.151	0.088
A13	1.64	3.95	2.04	1.31	0.694	0.402	0.223	0.154	-
A14	1.49	2.62	1.44	0.922	0.524	0.304	0.167	0.115	0.079
A15	1.52	4.79	2.35	1.47	0.777	0.372	0.202	0.119	0.077
A16	1.19	1.84	1.01	0.632	0.371	0.206	0.125	0.077	0.059
A17	1.78	2.40	1.53	1.07	0.738	0.572	0.351	-	0.262
A18	2.81	5.25	3.28	2.42	1.70	1.11	0.727	0.547	0.371
A19	1.56	3.64	1.93	1.21	0.697	0.368	0.290	0.135	0.078
A20	1.19	1.40	0.930	0.687	0.478	0.332	0.228	0.186	0.158
A21	1.34	5.54	2.69	1.66	0.897	0.447	0.259	0.125	0.089
A22	1.15	1.34	0.935	0.744	0.544	0.391	0.282	0.225	0.184
A23	2.13	3.81	2.33	1.66	1.04	0.638	0.428	0.302	-
A24	1.62	3.99	2.25	1.46	0.857	0.512	0.297	0.255	-

Table A4 On-line mole fractions of oxygenates.

Run	1-alcohols $10^3 y_i$ (-)			
	1	2	3	4
A1	1.07	0.662	0.166	-
A2	0.691	0.468	0.101	-
A3	1.05	1.12	0.345	-
A4	2.83	2.34	0.561	0.196
A5	4.42	1.53	-	-
A6	1.16	0.735	0.205	-
A7	1.42	0.922	-	-
A8	1.16	1.30	0.549	0.382
A9	0.882	0.755	0.227	-
A10	4.62	3.89	1.30	0.249
A11	1.55	1.37	0.484	-
A12	1.55	1.51	0.460	0.131
A13	1.11	1.12	0.302	-
A14	1.00	0.854	0.204	-
A15	1.68	1.53	0.387	-
A16	0.793	0.509	-	-
A17	0.552	0.592	0.155	-
A18	0.752	1.14	0.346	-
A19	1.01	1.09	0.285	-
A20	0.247	0.296	0.063	-
A21	1.23	1.50	0.393	-
A22	0.424	0.318	0.076	-
A23	0.690	0.771	0.206	-
A24	1.00	1.10	0.284	-

Appendix B
Slurry Reactor, Run B and C

Table B1 Summary of experimental conditions and results.

Run	TOS	P	F	$\Phi^{in}_{v,0}/W$	$\Phi_{v,0}/W$	y_i			
	(h)	(MPa)		(10^{-3} Nm^3 kg^{-1} s^{-1})		H_2	CO	CO_2	H_2O
B1[1]	156	1.5	0.67	0.51	0.41	0.311	0.503	0.093	0.038
B2	183	1.5	0.67	0.25	0.18	0.270	0.434	0.196	0.035
B3	228	1.5	1	0.51	0.43	0.482	0.390	0.097	0.031
B4[1]	289	1.5	0.67	0.51	0.41	0.310	0.520	0.098	0.030
B5	349	1.5	2	0.51	0.37	0.552	0.174	0.085	0.104
B6	452	2.4	3	0.51	0.39	0.681	0.097	0.071	0.077
B7	520	2.4	1	0.51	0.36	0.340	0.370	0.119	0.079
B8	571	2.4	0.5	0.51	0.39	0.182	0.606	0.100	0.055
B9[1]	643	1.5	0.67	0.51	0.39	0.269	0.512	0.103	0.044
B10	694	1.2	0.5	0.51	0.40	0.220	0.592	0.099	0.026
B11	760	2.4	2	0.51	0.34	0.537	0.114	0.149	0.108
B12	904	2.4	0.5	0.51	0.37	0.165	0.550	0.198	0.034
C1[1]	345	1.5	0.67	0.51	0.38	0.282	0.448	0.136	0.104
C2	385	1.5	0.5	0.51	0.43	0.209	0.542	0.123	0.108
C3	443	1.5	1.0	0.51	0.39	0.378	0.295	0.178	0.076
C4	506	1.5	2.0	0.51	0.40	0.579	0.135	0.122	0.086
C5[1]	552	1.5	0.67	0.51	0.39	0.202	0.475	0.119	0.154
C6	614	1.5	1.0	0.25	0.16	0.346	0.192	0.242	0.143
C7[1]	802	1.5	0.67	0.51	0.39	0.240	0.458	0.136	0.118
C8	875	1.5	1.0	0.25	0.16	0.334	0.194	0.299	0.034
C9	950	1.5	1.0	0.17	0.10	0.332	0.110	0.306	0.163
C10	1001	1.5	1.0	0.77	0.61	0.358	0.393	0.096	0.087
C11	1057	1.5	0.67	0.51	0.39	0.226	0.486	0.148	0.057
C12	1094	1.5	1.0	0.51	0.38	0.357	0.327	0.167	0.057
C13	1139	2.4	2.0	0.51	0.35	0.519	0.090	0.149	0.125
C14[1]	1396	1.5	0.67	0.51	0.41	0.252	0.515	0.093	0.092
C15	1487	1.2	0.5	0.51	0.39	0.195	0.560	0.128	0.075

[1] Reference experiment

Table B2 On-line mole fractions of paraffins.

Run	Paraffins $10^3 y_i$ (-)									
	1	2	3	4	5	6	7	8	9	10
B1	3.98	0.686	0.352	0.316	0.254	0.158	0.120	0.087	0.073	0.068
B2	7.90	1.88	0.741	0.696	0.589	0.319	0.234	0.156	0.113	0.093
B3	7.29	1.48	0.657	0.589	0.470	0.268	0.178	0.137	0.126	0.108
B4	4.92	0.864	0.430	0.385	0.311	0.318	0.220	0.112	0.107	0.098
B5	15.3	3.53	1.67	1.44	1.14	1.04	0.669	0.527	0.426	-
B6	18.3	3.52	1.74	1.56	1.26	1.02	0.759	0.624	0.590	0.415
B7	6.86	1.54	0.793	0.674	0.540	0.394	0.297	0.258	0.216	0.186
B8	3.25	5.83	3.31	2.87	2.35	1.67	0.872	1.14	0.833	-
B9	4.70	0.836	0.398	0.348	0.294	0.217	0.149	0.083	0.082	0.074
B10	3.42	0.519	0.248	0.220	0.207	0.133	0.110	0.068	0.058	0.048
B11	17.9	4.69	2.21	1.88	1.61	1.22	0.925	0.672	-	-
B12	4.60	1.06	0.532	0.454	0.392	0.331	0.196	0.130	0.115	0.094
C1	4.41	0.673	0.355	0.280	0.259	0.190	0.155	0.121	0.085	-
C2	3.13	0.537	0.372	0.205	0.202	-	0.142	0.108	0.081	0.055
C3	7.47	1.68	0.963	0.694	0.618	0.429	0.386	0.322	0.204	0.193
C4	11.7	2.67	1.51	0.969	0.809	0.605	0.401	0.347	0.231	0.210
C5	3.54	0.701	0.498	0.334	0.270	0.157	0.138	0.112	0.093	0.097
C6	3.32	0.641	0.288	0.251	0.211	0.151	0.137	-	0.088	0.056
C7	3.56	0.650	0.287	0.232	0.175	0.161	0.122	0.111	0.098	0.093
C8	13.1	3.70	1.53	1.04	0.964	0.738	0.580	0.429	0.340	0.222
C9	18.8	5.59	2.69	1.62	1.54	1.14	0.872	0.622	0.479	0.340
C10	4.17	0.789	0.340	0.254	0.191	0.132	0.130	0.127	-	-
C11	3.44	0.615	0.265	0.227	0.173	0.123	0.115	0.102	0.104	0.103
C12	6.01	1.25	0.484	0.380	0.279	0.271	0.233	0.186	0.155	0.120
C13	16.3	4.43	2.09	1.30	1.03	0.735	0.524	0.400	0.292	0.199
C14	3.09	0.713	0.312	0.177	0.121	0.084	0.075	-	-	-
C15	2.61	0.478	0.203	0.156	0.103	0.095	0.078	0.062	-	-

Table B3 On-line mole fractions of olefins.

Run	Olefins $10^3 y_i$ (-)								
	2	3	4	5	6	7	8	9	10
B1	1.34	2.07	1.37	1.09	0.718	0.480	0.353	0.246	0.176
B2	1.93	3.84	2.48	1.90	1.11	0.702	0.437	0.295	0.175
B3	1.61	3.01	1.91	1.43	0.843	0.514	0.336	0.209	0.151
B4	1.47	2.35	1.58	1.23	1.00	0.585	0.390	0.286	0.197
B5	1.50	4.38	2.53	1.83	1.26	0.643	0.413	0.235	0.128
B6	0.851	3.46	2.01	1.47	0.970	0.491	0.331	0.216	0.108
B7	2.24	3.69	2.36	1.82	1.21	0.764	0.562	0.359	0.234
B8	1.66	2.06	1.31	0.991	0.640	0.295	0.263	0.201	0.186
B9	1.87	2.48	1.55	1.17	0.810	0.524	0.357	0.268	0.214
B10	1.57	1.92	1.24	0.965	0.656	0.495	0.332	0.250	0.192
B11	2.73	4.59	3.99	2.93	1.84	1.13	0.773	0.384	0.206
B12	2.30	2.86	1.63	1.12	0.800	0.494	0.312	0.236	0.155
C1	0.724	1.26	0.767	0.609	0.381	0.233	0.153	0.108	-
C2	0.838	0.975	0.619	0.511	0.313	0.226	0.162	0.118	0.081
C3	0.788	1.98	1.14	0.871	0.457	0.307	0.201	0.106	0.068
C4	0.510	1.82	0.862	0.585	0.320	0.128	0.070	0.038	0.027
C5	0.808	1.24	0.802	0.633	0.372	0.243	0.169	0.119	0.079
C6	0.641	1.11	0.678	0.525	0.354	0.252	0.120	0.104	0.053
C7	1.02	1.64	1.11	0.900	0.613	0.324	0.299	0.232	0.165
C8	1.29	4.33	2.36	1.69	1.00	0.578	0.340	0.221	0.126
C9	1.01	4.79	2.34	1.61	0.912	0.531	0.259	0.141	0.104
C10	1.08	1.72	1.08	0.752	0.504	0.335	0.261	0.195	-
C11	1.13	1.70	1.15	0.945	0.616	0.424	0.313	0.242	0.165
C12	1.31	2.45	1.56	1.19	0.800	0.562	0.386	0.263	0.184
C13	0.998	3.68	1.81	1.17	0.651	0.308	0.167	0.095	0.055
C14	1.49	1.80	0.992	0.644	0.391	0.253	0.162	0.091	0.065
C15	1.14	1.41	0.857	0.614	0.429	0.316	0.214	-	-

Table B4 On-line mole fractions of oxygenates.

Run	1-alcohols $10^3 y_i$ (-)			
	1	2	3	4
B1	1.25	5.83	1.42	0.800
B2	2.08	1.13	0.299	0.184
B3	1.76	0.930	0.256	0.162
B4	0.986	0.637	0.177	-
B5	2.20	1.28	0.387	0.292
B6	2.43	1.18	0.288	0.086
B7	1.71	0.757	0.225	0.144
B8	0.978	0.394	0.116	0.077
B9	0.992	0.495	0.142	0.108
B10	0.683	0.369	0.091	-
B11	2.13	2.63	0.596	0.235
B12	1.20	0.794	0.091	
C1	0.315	0.468	0.126	-
C2	0.196	0.394	0.075	-
C3	0.241	0.795	0.206	-
C4	0.338	0.828	0.228	-
C5	0.176	0.461	0.097	-
C6	0.406	0.470	0.120	-
C7	0.150	0.404	0.094	-
C8	0.451	0.976	0.287	-
C9	0.513	1.10	0.331	-
C10	0.198	0.418	0.104	-
C11	0.120	0.346	0.086	-
C12	0.240	0.482	0.126	-
C13	0.536	1.14	0.323	-
C14	0.130	0.387	0.084	-
C15	0.119	0.329	0.083	-

List of Symbols

Included in the following list are common symbols employed throughout this thesis. An additional list of symbols is added for Chapter 7.

A_i	integrated GC peak area of component *i*	counts
a,a_∞	kinetic parameters	-
b	kinetic parameter	-
c	kinetic parameter	-
c	exponential constant, eq 4.5	-
C	constant	-
C	concentration	mol m^{-3}
$C^s_{n\ vap}$	saturated vapor phase concentration	mol m^{-3}
C_i	calibration factor GC	-
d	kinetic parameter	-
D	diffusion coefficient	$m^2\ s^{-1}$
D	diameter	m
D_n	diffusivity hydrocarbon with chain length *n*	$m^2\ s^{-1}$
d_P	diameter of catalyst particle	m
d	diameter or film thickness	m
df	degrees of freedom	-
E_A	activation energy	kJ mol^{-1}
E	molar exit ratio H_2 to CO	-
ΔE	potential energy	kJ mol^{-1}
F	molar feed ratio H_2 to CO	-
f	fugacity	Pa
F	molar flow reactor outlet	mol s^{-1}
H	number of competitive models	-
ΔH	reaction enthalpy	kJ mol^{-1}
ΔH_{ad}	heat of adsorption	kJ mol^{-1}
H	height	m
H	Henry's solubility constant	mol Pa^{-1} m^{-3} or Pa
$\Delta G_{1\ phys}$	free energy change of physisorption	kJ mol^{-1}
ΔG_{ox}	free energy change of oxidation	kJ mol^{-1}

k, k_∞	reaction rate constant	-
k_0	reaction rate constant in ideal state	-
k_{dp}	reaction rate constant for depolymerization	-
k_i, k_{ir}	reaction rate for (reverse) initiation	-
k_w	WGS reaction rate constant	-
K_p	equilibrium constant water gas shift	-
K_i	adsorption constant	-
k_R, k_R^*	reaction rate constant readsorption of olefins	-
k_R^2	reaction rate constant readsorption of ethene	-
K_{H_2}	adsorption constant hydrogen	MPa^{-1}
K_i	equilibrium constant (y_i/x_i)	-
L	molar flow liquid phase	mol s^{-1}
m	number of model parameters	-
m	average number of hydrogen atoms	-
m_i	molar selectivity of component i, eq 3.17	-
m_i^{GL}	solubility constant (C_G/C_L)	-
m_n	molar selectivity of hydrocarbon with carbon number n	-
m_O	molar olefin selectivity	-
m_P	molar paraffin selectivity	-
$MARR$	Mean Absolute Relative Residual, eq 3.21	-
M	molecular weight	kg mol^{-1}
n	carbon number	-
n	number of experimental data points	-
N	constant	-
O_n	olefin fraction carbon number n	-
P_n	paraffin fraction carbon number n	-
p	propagation probability	-
P	pressure	Pa
P_n	hydrocarbon vapor pressure with carbon number n	Pa
P_0	vapor pressure constant	Pa
R	reaction rate	mol kg_{cat}^{-1} s^{-1}
R_{FT}	overall Fischer-Tropsch reaction rate	mol kg_{cat}^{-1} s^{-1}
R_{WGS}	water gas shift reaction rate	mol kg_{cat}^{-1} s^{-1}
R	gas constant	8.314 J mol^{-1} K^{-1}
RMR	Relative Molar Response factor	-

RR	Relative Residual, eq 3.23	-
s	catalytic surface site	-
s_{rel}	relative variance, eq 3.22	-
S_{av}^2	average variance of H models	-
S_h^2	total variance of model h	-
STY	space time yield, $-R_{H_2+CO}$	mol kg_{cat}^{-1} s^{-1}
t	time	s
t_O	relative olefin termination probability	-
t_O^2	relative termination probability to ethene	-
t_P^1	relative termination probability to methane	-
t_P^2	relative termination probability to ethane	-
T	temperature	K
V	volume	m^3
V	molar volume	mol m^{-3}
V	molar flow gas phase	mol s^{-1}
$V_{n\ wax}^m$	molar volume waxeous hydrocarbons	mol m^{-3}
w_i	mass component selectivity, eq 3.18	-
w_n	hydrocarbon weight selectivity with carbon number n	-
W	weight of unreduced supported catalyst	kg
X_i	conversion component i	-
X_{CO+H_2}	total synthesis gas conversion	
x	distance	m
x_i	mole fraction liquid phase	-
y_i	mole fraction gas phase	-
z_i	mole fraction	-

Greek symbols

α	chain growth probability	-
α_∞	asymptotical chain growth probability	-
β	termination probability	-
β	vapor pressure coefficient	-
γ	activity coefficients	-
γ_0	relative transport rates of H_2 and CO	-
γ_n	relative transport rates of olefins	-
δ	solubility parameter	-

δ	film thickness	m
θ_i	surface fraction occupied with component *i*	-
μ	viscosity	N s m^{-2}
ρ_L	liquid density	kg m^{-3}
σ^2	function for optimization, eq 4.21	-
$\Phi_{v,0}$	gas flow rate at normal conditions	Nm^3 s^{-1}
χ^2	function for optimization, eq 3.20	-
χ_c^2	critical χ^2 for Bartlett's test	-
χ_t^2	tabulated χ^2 for Bartlett's test	-

Superscripts and Subscripts

A	component A
B	component B
CH_2	methylene
CH_3	methyl
DS	deferred standard
eq	equilibrium
exp	experimental value
G	gas phase
H	hydrogen
i	component, interface, initiation or index
I	activated complex
in	inlet conditions
L	liquid
M	monomer methylene (CH_2)
mod	predicted value
n	carbon number
O	olefins
P	paraffins
p	propagation
ps	physisorption
R	readsorption
R	reactor
S	adsorbed state
s_1	FT catalytic site

s_2	WGS catalytic site
t	termination
v	vacant or free catalytic sites
0	normal conditions, T_0= 273 K, P_0= 0.1013 MPa
1	solute
2	solvent
1	carbon number n= 1
2	carbon number n= 2