Supplementary: Kinetic Study Based on the Carbide Mechanism of a Co-Pt/γ-Al_2O_3 Fischer-Tropsch Catalyst Tested in a Laboratory-Scale Tubular Reactor

Marco Marchese, Niko Heikkinen, Emanuele Giglio, Andrea Lanzini, Juha Lehtonen and Matti Reinikainen

A - Kinetic model

Kinetic mechanistic steps

Catalytic site expressed as "*" in the reaction steps

FT-1) reaction paths

MARR=49%

Reaction number	Reaction step	Constant parameter
0	H_2 + 2* ↔ 2H*	K0
1 rds	CO + H* → CO H*	k1
	CO + CH_3* → CO CH_3*	
	CO + C_NH_{2N+1}* → CO C_NH_{2N+1}*	
2	CO H* + H_2 ↔ H C* + H_2O	K2
	CO CH_3* + H_2 ↔ CH_3 C* + H_2O	
	C_NH_{2N+1} CO* + H_2 ↔ C_NH_{2N+1} C* + H_2O	
3	H C* + H_2 ↔ H *CH_2	K3
	CH_3 C* + H_2 ↔CH_3 *CH_2	
	C_NH_{2N+1} C* + H_2 ↔ C_NH_{2N+1} *CH_2	
4	C_NH_{2N+1} *CH_2 ↔ C_NH_{2N+1} CH_2*	K4
5 rds	CH_3* + H_2 → CH_4 + H*	k5M
	C_NH_{2N+1}* + H_2 → C_NH_{2N+2} + H*	k5
6 rds	C_2H_5* → C_2H_4 + H*	k6E
	C_NH_{2N+1}* → C_NH_{2N} + H*	k6

Resolution of the mechanism to get the Rates expressions. Description of the probability growths as the ratio of the growth over the growth and termination, through alpha values for each of the products.

$R_{CH4} = k_{5M}\,[CH_3^*]\,P_{H2}$		$\alpha_1 = \frac{k_1 P_{CO}}{k_1 P_{CO} + k_{5M} P_{H_2}}$

$R_{C2H4} = k_{6E}\ e^{2c}\ [C_2H_5*]$		$\alpha_2 = \frac{k_1 P_{CO}}{k_1 P_{CO} + k_5 P_{H_2} + k_{6E} e^{2c}}$
$R_{CnH2n+1} = k_5\ [C_nH_{2n+1}*]\ P_{H2}$	Paraffins n>=2	$\alpha_n = \frac{k_1 P_{CO}}{k_1 P_{CO} + k_5 P_{H_2} + k_6 e^{nc}}$
$R_{CnH2n} = k_6\ e^{nc}\ [C_2H_{2n+1}*]$	Olefins n>=3	

It is possible to apply the Quasi Steady-State Assumption (QSSA) to derive the formulation of the growth probabilities. For n=1 we apply it on $[CH_3*]$ species, for n=2 for $[C_2H_5*]$ and for n>2 we apply it over $[C_NH_{2N+1}*]$.

$\frac{d[CH_3^*]}{dt} = 0 = Intermediate\ generation - intermediate\ termination$ $= k_1 P_{CO}[H^*] - k_1 P_{CO}[CH_3^*] - k_{5M} P_{H_2}[CH_3^*]$
$\frac{d[C_2H_5^*]}{dt} = 0 = k_1 P_{CO}[CH_3^*] - k_1 P_{CO}[C_2H_5^*] - k_5 P_{H_2}[C_2H_5^*] - k_{6E} e^{2c}[C_2H_5^*]$
$\frac{d[C_nH_{2n+1}^*]}{dt} = 0$ $= k_1 P_{CO}[C_{n-1}H_{2n-1}{}^*] - k_1 P_{CO}[C_nH_{2n+1}{}^*] - k_5 P_{H_2}[C_nH_{2n+1}{}^*]$ $- k_6 e^{nc}[C_nH_{2n+1}{}^*]$

From the above formulation, we find the same definition of alphas as previously expressed. Thus, we can express concentrations for the balance of active sites.

$[\mathrm{CH_3^*}] = \alpha_1[H^*]$
$[\mathrm{C_2H_5^*}] = \alpha_2[CH_3^*]$
$[\mathrm{C_nH_{2n+1}}{}^*] = \alpha_n[C_{n-1}H_{2n-1}{}^*]$

From the different reaction steps I can then express values for kinetic and equilibrium constants for the balance of the active sites. The site balance can be expressed as follows:

$$1 = [*] + [H^*] + [CH_3^*] + [C_2H_5^*] + [C_{n-1}H_{2n-1}^*] + [H\ CO^*] + [CH_3\ CO^*] + [C_{n-1}H_{2n-1}\ CO^*] + [H\ C^*] + [CH_3\ C^*] + [C_{n-1}H_{2n-1}\ C^*] + [H^*CH_2] + [CH_3^*CH_2] + [C_{n-1}H_{2n-1}{}^*CH_2]$$

The above expression assumes that no active catalytic site decreases over time.

$[H^*]^2 = K_0 P_{H_2}[*]^2 \rightarrow [H^*] = \sqrt{(K_0 P_{H_2})}\,[*]$
$[H^* CH_2] = \frac{1}{K_4}\,[CH_3^*] = \frac{1}{K_4}\,\alpha_1 \sqrt{(K_0 P_{H_2})}\,[*]$
$[CH_3^* CH_2] = \frac{1}{K_4}\,[C_2H_5^*] = \frac{1}{K_4}\,\alpha_1\alpha_2 \sqrt{(K_0 P_{H_2})}\,[*]$
$[C_{n-1}H_{2n-1}{}^* CH_2] = \frac{1}{K_4}\,[C_n H_{2n}^*] = \frac{1}{K_4}\,\alpha_1\alpha_2 \prod_{n=3}^{n} \alpha_n \sqrt{(K_0 P_{H_2})}\,[*]$
$[HC^*] = \frac{1}{K_3 P_{H_2}}\,[H\,CH_2^*] = \frac{1}{K_3 K_4 P_{H_2}}\,\alpha_1 \sqrt{(K_0 P_{H_2})}\,[*]$
$[CH_3\,C^*] = \frac{1}{K_3 P_{H_2}}\,[CH_3\,CH_2^*] = \frac{1}{K_3 K_4 P_{H_2}}\,\alpha_1\alpha_2 \sqrt{(K_0 P_{H_2})}\,[*]$
$[C_{n-1}H_{2n-1}\,C^*] = \frac{1}{K_3 P_{H_2}}\,[C_{n-1}H_{2n-1}\,CH_2^*] = \frac{1}{K_3 K_4 P_{H_2}}\,\alpha_1\alpha_2 \prod_{n=3}^{n} \alpha_n \sqrt{(K_0 P_{H_2})}\,[*]$
$[H\,CO^*] = \frac{1}{K_2}\frac{P_{H_2O}}{P_{H_2}}\,[H\,C^*] = \frac{1}{K_2 K_3 K_4}\,\frac{P_{H_2O}}{P_{H_2}^2}\alpha_1 \sqrt{(K_0 P_{H_2})}\,[*]$
$[CH_3\,CO^*] = \frac{1}{K_2}\frac{P_{H_2O}}{P_{H_2}}\,[CH_3\,C^*] = \frac{1}{K_2 K_3 K_4}\,\frac{P_{H_2O}}{P_{H_2}^2}\alpha_1\alpha_2 \sqrt{(K_0 P_{H_2})}\,[*]$
$[C_{n-1}H_{2n-1}\,CO^*] = \frac{1}{K_2}\frac{P_{H_2O}}{P_{H_2}}\,[C_{n-1}H_{2n-1}\,C^*] = \frac{1}{K_2 K_3 K_4}\,\frac{P_{H_2O}}{P_{H_2}^2}\alpha_1\alpha_2 \prod_{n=3}^{n} \alpha_n \sqrt{(K_0 P_{H_2})}\,[*]$

I can substitute these expression and get all in terms of [*].

$[*] = \frac{1}{DENOM1}$
$DENOM1 = 1 + \sqrt{(K_0 P_{H_2})} + \sqrt{(K_0 P_{H_2})}\left(1 + \frac{1}{K_4} + \frac{1}{K_3 K_4 P_{H_2}} + \frac{1}{K_2 K_3 K_4}\,\frac{P_{H_2O}}{P_{H_2}^2}\right)(\alpha_1 + \alpha_1\alpha_2 + \alpha_1\alpha_2 \sum_{j=3}^{n_c} \prod_{n=3}^{j} \alpha_n)$

Substituting the expression of [*] in the expressions of the different active sites and back to the definition of the reactions rates, it is possible to write the latter as follows.

$R_{CH_4} = k_{5M}\, K_0^{0.5}\, P_{H_2}^{1.5}\, \alpha_1\, [*]$	
$R_{C_2H_4} = k_{6E}\, e^{2c} \sqrt{(K_0 P_{H_2})}\ \alpha_1\, \alpha_2\, [*]$	
$R_{C_nH_{2n+2}} = k_5\, K_0^{0.5}\, P_{H_2}^{1.5}\, \alpha_1\, \alpha_2 \prod_{n=3}^{n} \alpha_n\ [*]$	Paraffins n>=2
$R_{C_2H_4} = k_6\, e^{nc} \sqrt{(K_0 P_{H_2})}\ \alpha_1\, \alpha_2 \prod_{n=3}^{n} \alpha_n\ [*]$	Olefins n>=3

The same procedure is applied to the definition of all the mechanisms.

FT-2) reaction mechanism

MARR=41.2%

Reaction number	Reaction step	Constant parameter
0	$H_2 + 2^* \leftrightarrow 2H^*$	K0
1 RDS	$CO + H^* \leftrightarrow COH^*$	k1
	$CO + CH_3^* \leftrightarrow C_2OH_3^*$	
	$CO + C_NH_{2N+1}^* \leftrightarrow C_{N+1}OH_{2N+1}^*$	
2	$COH^* + H^* \leftrightarrow CH^* + OH^*$	K2
	$C_2OH_3^* + H^* \leftrightarrow C_2H_3^* + OH^*$	
	$C_{N+1}OH_{2N+1}^* + H^* \leftrightarrow C_NH_{2N-1}^* + OH^*$	
3	$C_NH_{2N-1}^* + H^* \leftrightarrow C_NH_{2N}^* + *$	K3
4	$C_NH_{2N}^* + H^* \leftrightarrow C_NH_{2N+1}^* + *$	K4
5	$OH^* + H^* \leftrightarrow H_2O + 2^*$	K5
6RDS	$CH_3^* + H_2 \rightarrow CH_4 + H^*$	k6M
	$C_NH_{2N+1}^* + H_2 \rightarrow C_NH_{2N+2} + H^*$	k6
7RDS	$C_2H_5^* \rightarrow C_2H_4 + H^*$	k7E
	$C_NH_{2N+1}^* \rightarrow C_NH_{2N} + H^*$	k7

Definition of the rates and probability growth values.

$R_{CH_4} = k_{6M}[CH_3]P_{H2}$	$\alpha_1 = \dfrac{k_1 P_{CO}}{k_1 P_{CO} + k_{6M} P_{H2}}$
$R_{C_2H_4} = k_{7E}\, e^{2c}\, [C_2H_5]$	$\alpha_2 = \dfrac{k_1 P_{CO}}{k_1 P_{CO} + k_6 P_{H2} + k_{7E} e^{c2}}$
$R_{C_nH_{2n+2}} = k_6[C_N H_{2N+1}]P_{H2}$	$\alpha_N = \dfrac{k_1 P_{CO}}{k_1 P_{CO} + k_6 P_{H2} + k_7\, e^{cN}}$

$R_{C_NH_{2N}} = k_7\, e^{nc}\, [C_NH_{2N+1}]$	

QSSA for the expression of the probability growth.

$\frac{d[C_nH^*_{2n+1}]}{dt} = 0 = Intermediate\ generation - intermediate\ termination$ $= k_1P_{CO}[C_{N-1}H_{2N-1}] - k_1P_{CO}\,[C_NH_{2N+1}] - k_7P_{H2}[C_NH_{2N+1}] - K_7e^{nc}[C_NH_{2N+1}]$

Same applies to C=1 and C=2 to express alpha1 and alpha2.

$[CH^*_3] = \alpha_1[H^*]$
$[C_2H^*_5] = \alpha_2[CH^*_3]$
$[C_nH_{2n+1}{}^*] = \alpha_n[C_{n-1}H_{2n-1}{}^*]$

Balance:

$$1 = [*] + [H] + [COH] + [CH_3] + [C_2OH_3] + [CH] + [C_2H_3] + [OH] + [C_2H_5] + [CH_2] + [C_2H_4] + \sum_3^N[C_nH^*_{2N+1}] + \sum_3^N[C_nH^*_{2N-1}] + \sum_3^N[C_nH^*_{2N}] + \sum_3^N[C_nOH^*_{2N-1}]$$

$[H] = \sqrt{(K_0P_{H_2})}\,[*]$
$[CH] = \frac{1}{K_3}\frac{[CH_2]}{[H]}[*] = \frac{\alpha_1}{K_3\,K_4}\frac{1}{\sqrt{(K_0P_{H_2})}}[*]$
$[C_2H_3] = \frac{1}{K_3}\frac{[C_2H_4]}{[H]}[*] = \frac{\alpha_1\alpha_2}{K_3\,K_4}\frac{1}{\sqrt{(K_0P_{H_2})}}[*]$
$[CH_2] = \frac{1}{K_4}\frac{[CH_3]}{[H]}[*] = \frac{1}{K_4}\frac{\alpha_1\sqrt{(K_0P_{H_2})}}{\sqrt{(K_0P_{H_2})}}[*] = \frac{\alpha_1}{K_4}[*]$
$[C_2H_4] = \frac{1}{K_4}\frac{[C_2H_5]}{[H]}[*] = \frac{\alpha_1\alpha_2}{K_4}[*]$
$[C_2H_5] = \alpha_1\,\alpha_2\sqrt{(K_0P_{H_2})}\,[*]$
$[OH] = P_{H_2O}\frac{[*]^2}{[H]K_5} = \frac{1}{K_5}\frac{P_{H_2O}}{\sqrt{(K_0P_{H_2})}}[*]$
$[COH] = \frac{1}{K_2}\frac{[CH][OH]}{[H]} = \frac{\alpha_1}{K_2\,K_3\,K_4\,K_5}\frac{P_{H_2O}}{(K_0P_{H_2})^{1.5}}[*]$
$[C_2OH_3] = \frac{1}{K_2}\frac{[C_2H_3][OH]}{[H]} = \frac{\alpha_1\alpha_2}{K_2\,K_3\,K_4\,K_5}\frac{P_{H_2O}}{(K_0P_{H_2})^{1.5}}[*]$
$\sum_3^N[C_nH^*_{2N+1}] = \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\sqrt{(K_0P_{H_2})}\,[*]$
$\sum_3^N[C_nH^*_{2N-1}] = \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\frac{1}{K_3\,K_4\sqrt{(K_0P_{H_2})}}[*]$

$\sum_{3}^{N}[C_nH_{2N}^*] = \frac{\alpha_1\alpha_2}{K_4}\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\ [*]$
$\sum_{3}^{N}[C_nOH_{2N-1}^*] = \frac{\alpha_1\alpha_2}{K_2\ K_3\ K_4\ K_5}\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\ \frac{P_{H_2O}}{(K_0P_{H_2})^{1.5}}\ [*]$

From this I can extract [*] and the value of DENOM2.

$$DENOM2=1+\sqrt{(K_0P_{H_2})}*\left(1+(\alpha_1+\alpha_1\alpha_2+\alpha_1\alpha_2\textstyle\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n)\right)+\left((\alpha_1+\alpha_1\alpha_2+\alpha_1\alpha_2\textstyle\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n)\right)\left[\frac{1}{K_4}+\frac{1}{\sqrt{(K_0P_{H_2})}\ K_3K_4}+\frac{P_{H2O}}{(K_0P_{H_2})\text{^}(1.5)\ K_2K_3K_4K_5}\right]+\frac{1}{K_5}\frac{P_{H2O}}{\sqrt{(K_0P_{H_2})}}$$

$R_{CH_4} = k_{7M}\alpha_1\sqrt{(K_9P_{H_2})}\ P_{H2}\ [vac]$	$\alpha_1 = \frac{k_1P_{CO}}{k_1P_{CO}+k_{7M}P_{H2}}$
$R_{C_2H_4} = k_{8E}\ e^{2c}\alpha_1\alpha_2\sqrt{(K_9P_{H_2})}\ [vac]$	$\alpha_2 = \frac{k_1P_{CO}}{k_1P_{CO}+k_7P_{H2}+k_{8E}e^{c2}}$
$R_{C_nH_{2n+2}} = k_7\alpha_1\alpha_2\prod_{n=3}^{n}\alpha_n\sqrt{(K_9P_{H_2})}\ P_{H2}\ [vac]$	$\alpha_N = \frac{k_1P_{CO}}{k_1P_{CO}+k_7P_{H2}+k_{8E}\ e^{cN}}$
$R_{C_NH_{2N}} = k_8\ e^{nc}\ \alpha_1\alpha_2\prod_{n=3}^{n}\alpha_n\sqrt{(K_9P_{H_2})}\ [vac]$	

FT-3) reaction path

MARR=70%

Reaction number	Reaction step	Constant parameter
0	H_2 + 2* ↔ 2H*	K0
1	CO + * ↔ CO*	K1
2	CO* + H_2 ↔ H_2CO*	K2
3	H_2CO* + H_2 ↔ CH_2* + H_2O	K3
4 RDS	CH_2* + H* → CH_3* + *	k4
	CH_2* + CH_3* → C_2H_5* + *	
	CH_2* + C_NH_{2N+1}* → $C_{N+1}H_{2N+3}$* + *	
5 RDS	CH_3* + H* → CH_4 + 2*	k5M
	C_NH_{2N+1}* + H* → C_NH_{2N+2} + 2*	k5
6 RDS	C_2H_5* → C_2H_4 + H*	k6E
	C_NH_{2N+1}* → C_2H_{2N} + H*	k6

$R_{CH_4} = k_{5M}[CH_3][H]$		$\alpha_1 = \dfrac{k_4[CH_2][CH_3]}{k_4[CH_2][CH_3] + k_{5M}[CH_3][H]}$
$R_{C_2H_4} = k_{6E}\, e^{2c}\, [C_2H_5]$		$\alpha_2 = \dfrac{k_4[CH_2][C_2H_5]}{k_4[CH_2][C_2H_5] + k_5[C_2H_5][H] + k_{6E}e^{c2}\, [C_2H_5]}$
$R_{C_nH_{2n+2}} = k_5[C_NH_{2N+1}][H]$	Paraffins n>=2	$\alpha_n = \dfrac{k_4[CH_2][C_NH_{2N+1}]}{k_4[CH_2][C_NH_{2N+1}] + k_5[C_NH_{2N+1}][H] + k_6e^{nc}\, [C_NH_{2N+1}]}$
$R_{C_2H_4} = k_6\, e^{nc}\, [C_NH_{2N+1}]$	Olefins n>=3	

Application of the QSSA.

$\dfrac{d[CH_3^*]}{dt} = 0 = Intermediate\ generation - intermediate\ termination = k_4\,[CH_2]\,[H] - [CH_3](k_4[CH_2] + k_{5M}[H])$
$\dfrac{d[C_2H_5^*]}{dt} = 0 = k_4\,[CH_2]\,[CH_3] - [C_2H_5](k_4[CH_2] + k_5[H] + k_{6E}e^{2c})$
$\dfrac{d[C_nH_{2n+1}^*]}{dt} = 0 = k_4\,[CH_2]\,[C_{N-1}H_{2N-1}] - [C_NH_{2N+1}](k_4[CH_2] + k_5[H] + k_6e^{nc})$

$[\mathrm{CH_3^*}] = \alpha_1[H^*]$
$[\mathrm{C_2H_5^*}] = \alpha_2[CH_3^*]$
$[\mathrm{C_nH_{2n+1}}^*] = \alpha_n[C_{n-1}H_{2n-1}{}^*]$

Balance:

$$1 = [*] + [H] + [CH_3] + [C_2H_5] + \sum_3^N [C_nH_{2N+1}^*] + [CO] + [H_2CO] + [CH_2]$$

1) $k_{1d}P_{CO}[*] = k_{1r}[CO] \rightarrow [CO] = K_1P_{CO}[*]$
2) $k_{2d}P_{H_2}[CO] = k_{2r}[H_2CO] \rightarrow [H_2CO] = K_2P_{H_2}[CO] = K_1K_2\,P_{H_2}P_{CO}[*]$
3) $k_{3d}P_{H_2}[H_2CO] = k_{3r}[CH_2]\,P_{H_2O} \rightarrow [CH_2] = K_3\,\frac{P_{H_2}}{P_{H_2O}}[H_2CO] = K_1K_2K_3\,\frac{P_{CO}\,P_{H_2}^2}{P_{H_2O}}\,[*]$

4) $[H] = \sqrt{(K_0 P_{H_2})}\,[*]$

And from the definition of the probability growths I can obtain

$$[\mathrm{CH_3^*}] = \alpha_1 \sqrt{(K_0 P_{H_2})}\,[*]$$

$$[\mathrm{C_2H_5^*}] = \alpha_1\,\alpha_2 \sqrt{(K_0 P_{H_2})}\,[*]$$

$$[\mathrm{C_nH_{2n+1}}^*] = \alpha_1\,\alpha_2 \prod_{n=3}^{n} \alpha_n \sqrt{(K_0 P_{H_2})}[*]$$

$$[*] = \frac{1}{DENOM3}$$

$$DENOM3 = 1 + K_1 P_{CO} + K_1 K_2 P_{H_2} P_{CO} + K_1 K_2 K_3 \frac{P_{CO}\,P_{H_2}^2}{P_{H_2O}} + \sqrt{(K_0 P_{H_2})}(1 + \alpha_1 + \alpha_1\alpha_2 + \alpha_1\alpha_2 \textstyle\sum_{j=3}^{n_c} \prod_{n=3}^{j} \alpha_n)$$

$R_{CH_4} = k_{5M}\,K_0\,P_{H_2}\,\alpha_1\,[*]^2$	
$R_{C_2H_4} = k_{6E}\,e^{2c} \sqrt{(K_0 P_{H_2})}\;\alpha_1\,\alpha_2\,[*]$	
$R_{C_nH_{2n+2}} = k_5\,K_0\,P_{H_2}\,\alpha_1\,\alpha_2 \prod_{n=3}^{n} \alpha_n\,[*]^2$	Paraffins n>=2
$R_{C_2H_4} = k_6\,e^{nc} \sqrt{(K_0 P_{H_2})}\;\alpha_1\,\alpha_2 \prod_{n=3}^{n} \alpha_n\;[*]$	Olefins n>=3

It is possible to check how the derivation of [*] must pass from an iterative solution.

FT-4) mechanism path

MARR=77.4%

Reaction number	Reaction step	Constant parameter
0	H_2 + 2* ↔ 2H*	K0
1	CO + * ↔ CO*	K1
2	CO* + H_2 ↔ H_2CO*	K2
3	H_2CO* + H_2 ↔ CH_2* + H_2O	K3

4 RDS	$CH_2^* + H^* \rightarrow CH_3^* + ^*$	k4
	$CH_2^* + CH_3^* \rightarrow C_2H_5^* + ^*$	
	$CH_2^* + C_NH_{2N+1}^* \rightarrow C_{N+1}H_{2N+3}^* + ^*$	
5 RDS	$CH_3^* + H_2^* \rightarrow CH_4 + 2^*$	k5M
	$C_NH_{2N+1}^* + H_2^* \rightarrow C_NH_{2N+2} + 2^*$	k5
6 RDS	$C_2H_5^* \rightarrow C_2H_4 + H^*$	k6E
	$C_NH_{2N+1}^* \rightarrow C_2H_{2N} + H^*$	k6

$R_{CH_4} = k_{5M}[CH_3]P_{H_2}$		$\alpha_1 = \dfrac{k_4[CH_2]}{k_4[CH_2] + k_{5M}P_{H_2}}$
$R_{C_2H_4} = k_{6E}\, e^{2c}\, [C_2H_5]$		$\alpha_2 = \dfrac{k_4[CH_2]}{k_4[CH_2] + k_5P_{H_2} + k_{6E}e^{c2}}$
$R_{C_nH_{2n+2}} = k_5[C_NH_{2N+1}]P_{H_2}$	Paraffins n>=2	$\alpha_n = \dfrac{k_4[CH_2]}{k_4[CH_2] + k_5P_{H_2} + k_6e^{nc}}$
$R_{C_2H_4} = k_6e^{nc}\, [C_NH_{2N+1}]$	Olefins n>=3	

Balance:

$$1 = [*] + [H] + [CH_3] + [C_2H_5] + \sum_{3}^{N}[C_nH_{2N+1}^*] + [CO] + [H_2CO] + [CH_2]$$

$[CO] = K_1P_{CO}[*]$
$[H_2CO] = K_2P_{H_2}[CO] = K_1K_2\, P_{H_2}P_{CO}[*]$
$[CH_2] = K_3\,\frac{P_{H_2}}{P_{H_2O}}[H_2CO] = K_1K_2K_3\,\frac{P_{CO}\,P_{H_2}^2}{P_{H_2O}}\,[*]$
$[H] = \sqrt{(K_0P_{H_2})}\,[*]$

And from the definition of the probability growths I can obtain

$[\mathrm{CH}_3^*] = \alpha_1\sqrt{(K_0P_{H_2})}\,[*]$
$[\mathrm{C_2H}_5^*] = \alpha_1\,\alpha_2\sqrt{(K_0P_{H_2})}\,[*]$
$[\mathrm{C_nH_{2n+1}}^*] = \alpha_1\,\alpha_2\prod_{n=3}^{n}\alpha_n\,\sqrt{(K_0P_{H_2})}[*]$

Substituting I can then find the balance value.

$[*] = \frac{1}{DENOM4}$
$DENOM4 = 1 + K_1 P_{CO} + K_1 K_2 P_{H_2} P_{CO} + K_1 K_2 K_3 \frac{P_{CO} P_{H_2}^2}{P_{H_2O}} + \sqrt{(K_0 P_{H_2})}(1 + \alpha_1 + \alpha_1\alpha_2 + \alpha_1\alpha_2 \sum_{j=3}^{n_c} \prod_{n=3}^{j} \alpha_n)$

$R_{CH_4} = k_{5M} \sqrt{(K_0 P_{H_2})}\ P_{H_2}\ \alpha_1\ [*]$	
$R_{C_2H_4} = k_{6E}\ e^{2c} \sqrt{(K_0 P_{H_2})}\ \alpha_1\ \alpha_2\ [*]$	
$R_{C_nH_{2n+2}} = k_5 \sqrt{(K_0 P_{H_2})}\ P_{H_2}\ \alpha_1\ \alpha_2 \prod_{n=3}^{n} \alpha_n\ [*]$	Paraffins n>=2
$R_{C_2H_4} = k_6\ e^{nc} \sqrt{(K_0 P_{H_2})}\ \alpha_1\ \alpha_2 \prod_{n=3}^{n} \alpha_n\ [*]$	Olefins n>=3

It is possible to check how the derivation of [*] must pass from an iterative solution.

FT-5) reaction mechanism

MARR=98%

Reaction number	Reaction step	Constant parameter
1	$CO + * \leftrightarrow CO*$	K1
2	$CO* + H_2 \leftrightarrow H_2CO*$	K2
3	$H_2CO* + H_2 \leftrightarrow CH_2* + H_2O$	K3
4	$H_2 + 2* \leftrightarrow 2H*$	K4
5 RDS	$CH_2* + CH_2* \rightarrow C_2H_4* + *$	k5
	$CH_2* + C_NH_{2N}* \rightarrow C_{N+1}H_{2N+2}* + *$	
6	$CH_2* + H* \rightarrow CH_3* + *$	k6
	$C_NH_{2N}* + H* \rightarrow C_NH_{2N+1}* + *$	
7 RDS	$CH_3* + H* \rightarrow CH_4 + *$	k7M
	$C_NH_{2N+1}* + H* \rightarrow C_NH_{2N+2} + *$	k7
8 RDS	$C_2H_5* \rightarrow C_2H_4 + H*$	k8E
	$C_NH_{2N+1}* \rightarrow C_2H_{2N} + H*$	k8

$R_{CH_4} = k_{7M}[CH_3][H]$		$\alpha_1 = \frac{k_5[CH_2]^2}{k_5[CH_2]^2 + k_{7M}P_{H_2}}$
$R_{C_2H_4} = k_{8E}\ e^{2c}\ [C_2H_5]$		$\alpha_2 = \frac{k_5[CH_2][C_2H_4]}{k_5[CH_2][C_2H_4] + k_7[C_2H_5][H] + k_{8E}e^{c2}[C_2H_5]}$

$R_{C_nH_{2n+2}} = k_7[C_NH_{2N+1}][H]$	Paraffins n>=2	$\alpha_N = \frac{k_5[CH_2][C_NH_{2N}]}{k_5[CH_2][C_NH_{2N}] + k_7[C_NH_{2N+1}][H] + k_{8E}e^{c2}[C_2H_5]}$
$R_{C_2H_4} = k_8\, e^{nc}\, [C_NH_{2N+1}]$	Olefins n>=3	

Balance from other reactions, we obtain

$[CO] = K_1P_{CO}[*]$
$[H_2CO] = K_2P_{H_2}[CO] = K_1K_2\, P_{H_2}P_{CO}[*]$
$[CH_2] = K_3\, \frac{P_{H_2}}{P_{H_2O}}[H_2CO] = K_1K_2K_3\, \frac{P_{CO}\, P_{H_2}^2}{P_{H_2O}}\, [*]$
$k_{4d}P_{H_2}[*]^2 = k_{4r}[H]^2 \;\rightarrow\; [H] = \sqrt{(K_4P_{H_2})}\, [*]$
$[CH_3] = K_6\, \frac{[CH_2][H]}{[*]} = K_1K_2K_3\, K_6\sqrt{(K_4)}\, \frac{P_{CO}\, P_{H_2}^{2.5}}{P_{H_2O}}\, [*]$ // $[C_NH_{2N+1}] = K_1K_2K_3\, \frac{P_{CO}\, P_{H_2}^2}{P_{H_2O}}\, [*]\prod_{n=2}^{n}\alpha_n$

Balance:

$$1 = [*] + [H] + [CH_3] + \sum_2^N [C_NH_{2N+1}^*] + \sum_2^N [C_NH_{2N}^*] + [CO] + [H_2CO] + [CH_2]$$

With substitution of the previous expressions we can then get a value of

$$1 = [*] + P_{CO}[*]\left(K_1 + K_1K_2\, P_{H_2} + K_1K_2K_3\, \frac{P_{H_2}^2}{P_{H_2O}}\right) + \sqrt{(K_4P_{H_2})}\, [*] + K_1K_2K_3\, K_6\sqrt{(K_4)}\, \frac{P_{CO}\, P_{H_2}^{2.5}}{P_{H_2O}}\, [*] + K_1K_2K_3\, K_6\sqrt{(K_4)}\, \frac{P_{CO}\, P_{H_2}^{2.5}}{P_{H_2O}}\, [*]\prod_{n=2}^{n}\alpha_n + K_1K_2K_3\, \frac{P_{CO}\, P_{H_2}^2}{P_{H_2O}}\, [*]\prod_{n=2}^{n}\alpha_n$$

$[*] = \frac{1}{DENOM5}$
$DENOM5 = 1 + P_{CO}\left(K_1 + K_1K_2\, P_{H_2} + K_1K_2K_3\, \frac{P_{H_2}^2}{P_{H_2O}}\right) + \sqrt{(K_4P_{H_2})} + K_1K_2K_3\, K_6\sqrt{(K_4)}\, \frac{P_{CO}\, P_{H_2}^{2.5}}{P_{H_2O}} + K_1K_2K_3\, K_6\sqrt{(K_4)}\, \frac{P_{CO}\, P_{H_2}^{2.5}}{P_{H_2O}}\prod_{n=2}^{n}\alpha_n + K_1K_2K_3\, \frac{P_{CO}\, P_{H_2}^2}{P_{H_2O}}\prod_{n=2}^{n}\alpha_n$

Application of the QSSA.

$\frac{d[CH_2^*]}{dt} = 0 = Intermediate\ generation - intermediate\ termination = -k_5\,[CH_2]^2 + k_5[CH_2]^2 + k_{7M}[CH_3][H])\ (would\ actually\ get\ a\ null\ value)$

$\frac{d[C_2H_4^*]}{dt} = 0 = -k_5\,[CH_2]\,[C_2H_4] + k_5[CH_2][C_2H_4] + k_7[C_2H_5][H] + k_{8E}e^{2c}[C_2H_5]$
$\frac{d[C_nH_{2n}^*]}{dt} = 0 = -k_5\,[CH_2]\,[C_NH_{2N}] + k_5[CH_2][C_NH_{2N}] + k_7[C_NH_{2N+1}][H] + k_8e^{nc}[C_NH_{2N+1}]$

$R_{CH_4} = k_{7M}K_1K_2K_3\,K_6K_4\,\frac{P_{CO}\,P_{H_2}^3}{P_{H_2O}}\,[*]^2$	
$R_{C_2H_4} = k_{8E}\,e^{2c}\,K_1K_2K_3\,\frac{P_{CO}\,P_{H_2}^2}{P_{H_2O}}\,\alpha_2$	
$R_{C_nH_{2n+2}} = k_7K_1K_2K_3\,K_6K_4\,\frac{P_{CO}\,P_{H_2}^3}{P_{H_2O}}\,[*]^2\prod_{n=2}^{n}\alpha_n$	Paraffins n>=2
$R_{C_nH_{2n}} = k_8\,e^{nc}\,K_1K_2K_3\,\frac{P_{CO}\,P_{H_2}^2}{P_{H_2O}}\prod_{n=2}^{n}\alpha_n$	Olefins n>=3

There is the need of an iterative procedure in order to get values of [*] and of the different alphas.

FT-6) reaction mechanism

MARR=77.8%

Reaction number	Reaction step	Constant parameter
0	H_2 + 2* ↔ 2H*	K0
1	CO + * ↔ CO*	K1
2	CO* + H* ↔ HCO* + *	K2
3	HCO* + H* ↔ C* + H_2O*	K3
4	H_2O* ↔ H_2O + *	K4
5	C* + H* ↔ CH* + *	K5
6	CH* + H* ↔ CH_2* + *	K6
7 RDS	CH_2* + H* → CH_3* + *	k7
	CH_2* + CH_3* → C_2H_5* + *	
	CH_2* + C_NH_{2N+1}* → $C_{N+1}H_{2N+3}$* + *	
8 RDS	CH_3* + H* → CH_4 + 2*	k8M
	C_NH_{2N+1}* + H* → C_NH_{2N+2} + 2*	k8
9 RDS	C_2H_5* → C_2H_4 + *	k9E
	C_NH_{2N+1}* → C_NH_{2N} + 2*	k9

Definition of the rates and probability growth values.

$R_{CH_4} = k_{8M}[CH_3][H]$	$\alpha_1 = \dfrac{k_7[CH_2]}{k_7[CH_2] + k_{8M}[H]}$
$R_{C_2H_4} = k_{9E}\, e^{2c}\, [C_2H_5]$	$\alpha_2 = \dfrac{k_7[CH_2]}{k_7[CH_2] + k_8[H] + k_{9E}e^{c2}}$
$R_{C_nH_{2n+2}} = k_8[C_NH_{2N+1}][H]$	$\alpha_N = \dfrac{k_7[CH_2]}{k_7[CH_2] + k_8[H] + k_9e^{cn}}$
$R_{C_2H_4} = k_9\, e^{nc}\, [C_NH_{2N+1}]$	

Application of the QSSA.

$\dfrac{d[CH_3^*]}{dt} = 0 = Intermediate\ generation - intermediate\ termination$ $= k_7[CH_2]\,[H] - [CH_3](k_7[CH_2] + k_{8M}[H])$
$\dfrac{d[C_2H_5^*]}{dt} = 0 = k_7[CH_2]\,[CH_3] - [C_2H_5](k_7[CH_2] + k_8[H] + k_{9E}e^{2c})$
$\dfrac{d[C_nH_{2n+1}^*]}{dt} = 0 = k_7[CH_2]\,[C_{N-1}H_{2N-1}] - [C_NH_{2N+1}](k_7[CH_2] + k_8[H] + k_9e^{nc})$

$[\mathrm{CH_3^*}] = \alpha_1[H^*]$
$[\mathrm{C_2H_5^*}] = \alpha_2[CH_3^*]$
$[\mathrm{C_nH_{2n+1}}^*] = \alpha_n[C_{n-1}H_{2n-1}{}^*]$

Balance:

$$1 = [*] + [H] + [CO] + [HCO] + [H_2O] + [C] + [CH] + [CH_2] + [CH_3] + [C_2H_5] + \sum_3^N [C_nH_{2N+1}^*]$$

$[H] = \sqrt{(K_0P_{H_2})}\,[*]$
$[CO] = K_1P_{CO}[*]$
$[HCO] = K_2\dfrac{[CO][H]}{[*]} = K_1K_2P_{CO}\sqrt{(K_0P_{H_2})}\,[*]$
$[C] = K_3\frac{[HCO][H]}{[H_2O]} = K_1\, K_2\, K_3\, K_4\, K_0\, \frac{P_{H_2}\ P_{CO}}{P_{H_2O}}\,[*]$
$[H_2O] = \dfrac{1}{K_4}\, P_{H_2O}\,[*]$
$[CH] = K_5\frac{[C][H]}{[*]} = K_1\, K_2\, K_3\, K_4\, K_5\, K_0^{1.5}\, \frac{P_{H_2}^{1.5}\ P_{CO}}{P_{H_2O}}\,[*]$

$[CH_2] = K_6 \frac{[CH][H]}{[*]} = K_1\, K_2\, K_3\, K_4\, K_6\, K_5\, K_0^2\, \frac{P_{H_2}^2\, P_{CO}}{P_{H_2O}}\, [*]$

Substitute all in the balance of sites to get the expression for the free site fraction/concentration.

$$1 = [*] + \sqrt{(K_0 P_{H_2})}\, [*] + K_1 P_{CO}[*] + K_1 K_2 P_{CO} \sqrt{(K_0 P_{H_2})}\, [*] + \frac{1}{K_4}\, P_{H_2O}\, [*] + K_1\, K_2\, K_3\, K_4\, K_0\, \frac{P_{H_2}\, P_{CO}}{P_{H_2O}}\, [*] + K_1\, K_2\, K_3\, K_4\, K_5\, K_0^{1.5}\, \frac{P_{H_2}^{1.5}\, P_{CO}}{P_{H_2O}}\, [*] + K_1\, K_2\, K_3\, K_4\, K_6\, K_5\, K_0^2\, \frac{P_{H_2}^2\, P_{CO}}{P_{H_2O}}\, [*] + \alpha_1 \sqrt{(K_0 P_{H_2})}\, [*] + \alpha_1 \alpha_2 \sqrt{(K_0 P_{H_2})}\, [*] + \alpha_1 \alpha_2 \sum_{j=3}^{n_c} \prod_{n=3}^{j} \alpha_n \sqrt{(K_0 P_{H_2})}\, [*]$$

From this I can extract [*] and the value of DENOM6.

There is the need of an iterative process to find the solution.

FT-7) reaction mechanism

MARR=52.38%

Reaction number	Reaction step	Constant parameter
0	$H_2 + 2^* \leftrightarrow 2H^*$	K0
1	$CO + H^* \leftrightarrow COH^*$	K1
	$CO + CH_3^* \leftrightarrow C_2OH_3^*$	
	$CO + C_NH_{2N+1}^* \leftrightarrow C_{N+1}OH_{2N+1}^*$	
2 RDS	$COH^* + H_2 \rightarrow CH^* + H_2O$	k2
	$C_2OH_3^* + H_2 \rightarrow C_2H_3^* + H_2O$	
	$C_NOH_{2N-1}^* + H_2 \rightarrow C_NH_{2N-1}^* + H_2O$	
3	$CH^* + H_2 \rightarrow CH_3^*$	K3
	$C_2H_3^* + H_2 \rightarrow C_2H_5^*$	
	$C_NH_{2N-1}^* + H_2 \rightarrow C_NH_{2N+1}^*$	
5 rds	$CH_3^* + H_2 \rightarrow CH_4 + H^*$	k5M
	$C_NH_{2N+1}^* + H_2 \rightarrow C_NH_{2N+2} + H^*$	k5
6 rds	$C_2H_5^* \rightarrow C_2H_4 + H^*$	k6E
	$C_NH_{2N+1}^* \rightarrow C_NH_{2N} + H^*$	k6

Definition of the rates and probability growth values.

$R_{CH_4} = k_{5M}[CH_3]P_{H_2}$	$\alpha_1 = \frac{k_2[C_2OH_3]}{k_2[C_2OH_3] + k_{5M}[CH_3]}$

$R_{C_2H_4} = k_{6E}\, e^{2c}\, [C_2H_5]$	$\alpha_2 = \frac{k_2[C_3OH_4]}{k_2[C_3OH_4] + k_5[C_2H_5] + k_{6E}e^{c2}}$
$R_{C_nH_{2n+2}} = k_5[C_NH_{2N+1}]P_{H_2}$	$\alpha_N = \frac{k_2[C_NOH_{2N-1}]}{k_2[C_NOH_{2N-1}] + k_5[C_NH_{2N+1}] + k_6e^{cn}}$
$R_{C_NH_{2N}} = k_6\, e^{nc}\, [C_NH_{2N+1}]$	

QSSA application.

$\frac{d[CH_3^*]}{dt} = 0 = generation - termination = \ k_{5m}[CH_3]\, P_{H_2} - P_{H_2}k_2[COH] + \ P_{H_2}k_2[C_2OH_3])$
$\frac{d[C_2H_5^*]}{dt} = 0 == K_5[C_2H_5]P_{H_2} + K_6e^{2c}[C_2H_5] + K_2K_1P_{CO}[C_2H_5]P_{H_2} - K_2K_1P_{CO}[CH_3]P_{H_2}$
$\frac{d[C_nH_{2n+1}^*]}{dt} = 0 = K_5[C_NH_{2N+1}]P_{H_2} + K_6e^{nc}[C_NH_{2N+1}] + K_2K_1P_{CO}[C_NH_{2N+1}]P_{H_2} - K_2K_1P_{CO}[C_{N-1}H_{2N-1}]P_{H_2}$

$[\mathrm{CH_3^*}] = \ \alpha_1[H^*]$
$[\mathrm{C_2H_5^*}] = \ \alpha_2[CH_3^*]$
$[\mathrm{C_nH_{2n+1}}^*] = \ \alpha_n[C_{n-1}H_{2n-1}{}^*]$

$\alpha_1 = \frac{k_2K_1P_{CO}}{k_2K_1P_{CO}+k_{5M}}$
$\alpha_2 = \frac{k_2K_1P_{CO}P_{H_2}}{k_2K_1P_{CO}P_{H_2} + k_5P_{H_2} + k_{6E}e^{c2}}$
$\alpha_N = \frac{k_2K_1P_{CO}P_{H_2}}{k_2K_1P_{CO}P_{H_2} + k_5P_{H_2} + k_6e^{cn}}$

Balance:

$$1 = [*] + [H] + [CO] + [CH_3] + [C_2OH_3] + [C_2H_5] + \sum_3^N [C_nH_{2N+1}^*] + \sum_3^N [C_nOH_{2N-1}^*] + [CH] + [C_2H_3] + \sum_3^N [C_nH_{2N-1}^*]$$

$[H] = \sqrt{(K_0P_{H_2})}\,[*]$
$[COH] = K_1P_{CO}[H] = K_1P_{CO}\sqrt{(K_0P_{H_2})}\,[*]$
$[CH_3] = \alpha_1[H^*] = \ \alpha_1\sqrt{(K_0P_{H_2})}\,[*]$

$[C_2OH_3] = K_1P_{CO}[CH_3] = K_1P_{CO}\ \alpha_1\ \sqrt{(K_0P_{H_2})}\ [*]$
$[C_2H_5] = \alpha_1\alpha_2[CH_3] = \alpha_1\ \alpha_2\sqrt{(K_0P_{H_2})}\ [*]$
$[CH] = \frac{1}{K_3\ P_{H_2}}[CH_3] = \frac{1}{K_3\ P_{H_2}}\ \alpha_1\ \sqrt{(K_0P_{H_2})}\ [*]$
$[C_2H_3] = \frac{1}{K_3\ P_{H_2}}[C_2H_5] = \frac{1}{K_3\ P_{H_2}}\ \alpha_1\ \alpha_2\ \sqrt{(K_0P_{H_2})}\ [*]$
$\sum_3^N[C_nH_{2N-1}^*] = \frac{1}{K_3\ P_{H_2}}\ \sqrt{(K_0P_{H_2})}\ [*]\ \alpha_1\ \alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n$
$\sum_3^N[C_nOH_{2N-1}^*] = K_1P_{CO}\ \sqrt{(K_0P_{H_2})}\ [*]\ \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n$
$\sum_3^N[C_nH_{2N+1}^*] = \sqrt{(K_0P_{H_2})}\ [*]\ \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n$

From this I can extract [*] and the value of DENOM7.

NO iteration needed.

FT-8) reaction mechanim

MARR=60.7%

Reaction number	Reaction step	Constant parameter
0	$H_2 + 2^* \leftrightarrow 2H^*$	0
1	$CO + H^* \leftrightarrow COH^*$	K1
	$CO + CH_3^* \leftrightarrow C_2OH_3^*$	
	$CO + C_NH_{2N+1}^* \leftrightarrow C_{N+1}OH_{2N+1}^*$ (As C_NOH_{2N-1})	
2	$COH^* + H_2 \rightarrow CH^* + H_2O$	K2
	$C_2OH_3^* + H_2 \rightarrow C_2H_3^* + H_2O$	
	$C_NOH_{2N-1}^* + H_2 \rightarrow C_NH_{2N-1}^* + H_2O$	
3 RDS	$CH^* + H_2 \rightarrow CH_3^*$	k3
	$C_2H_3^* + H_2 \rightarrow C_2H_5^*$	
	$C_NH_{2N-1}^* + H_2 \rightarrow C_NH_{2N+1}^*$	
5 rds	$CH_3^* + H_2 \rightarrow CH_4 + H^*$	k5M
	$C_NH_{2N+1}^* + H_2 \rightarrow C_NH_{2N+2} + H^*$	k5

6 rds	$C_2H_5^* \rightarrow C_2H_4 + H^*$	k6E
	$C_NH_{2N+1}^* \rightarrow C_NH_{2N} + H^*$	k6

Definition of the rates and probability growth values.

$R_{CH_4} = k_{5M}[CH_3]P_{H_2}$	$\alpha_1 = \dfrac{k_3[C_2H_3]\,P_{H_2}}{k_3[C_2H_3]\,P_{H_2} + k_{5M}[CH_3]\,P_{H_2}}$
$R_{C_2H_4} = k_{6E}\ e^{2c}\ [C_2H_5]$	$\alpha_2 = \dfrac{k_3[C_3H_5]\,P_{H_2}}{k_3[C_3H_5]\,P_{H_2} + k_5[C_2H_5]P_{H_2} + k_{6E}e^{c2}[C_2H_5]}$
$R_{C_nH_{2n+2}} = k_5[C_NH_{2N+1}]P_{H_2}$	$\alpha_N = \dfrac{k_3[C_NH_{2N-1}]\,P_{H_2}}{k_3[C_NH_{2N-1}]\,P_{H_2} + k_5[C_NH_{2N+1}+1]P_{H_2} + k_6e^{cN}[C_NH_{2N+1}]}$
$R_{C_NH_{2N}} = k_6\ e^{nc}\ [C_NH_{2N+1}]$	

By substitution of the different species expressions, based on the reactions

$$[C_2H_3] = K_2\frac{P_{H_2}}{P_{H_2O}}\ [C_2OH_3]\ ;\ [C_2OH_3] = K_1P_{CO}\ [CH_3]\ ;\ [C_3H_5] = K_1K_2P_{CO}P_{H_2}\ [C_2H_5]$$

$$\alpha_1 = \frac{K_1\ K_2\ k_3\dfrac{P_{CO}P_{H_2}^2}{P_{H_2O}}}{K_1\ K_2\ k_3\dfrac{P_{CO}P_{H_2}^2}{P_{H_2O}} + k_{5M}\ P_{H_2}}$$

$$\alpha_2 = \frac{K_1\ K_2\ k_3\dfrac{P_{CO}P_{H_2}^2}{P_{H_2O}}}{K_1\ K_2\ k_3\dfrac{P_{CO}P_{H_2}^2}{P_{H_2O}} + k_5P_{H_2} + k_{6E}e^{c2}}$$

$$\alpha_N = \frac{K_1\ K_2\ k_3\dfrac{P_{CO}P_{H_2}^2}{P_{H_2O}}}{K_1\ K_2\ k_3\dfrac{P_{CO}P_{H_2}^2}{P_{H_2O}} + k_5P_{H_2} + k_6e^{cN}}$$

QSSA application.

$$\frac{d[C_nH_{2n+1}^*]}{dt} = 0 = -k_5[C_NH_{2N+1}]\,P_{H_2} - k_6e^{nc}\ [C_NH_{2N+1}] - k_{1D}P_{CO}[C_NH_{2N+1}] + K_3[C_NH_{2N-1}]$$

$$\frac{d[C_nH^*_{2n+1}]}{dt} = -k_5[C_NH_{2N+1}]\,P_{H_2} - k_6e^{nc}\,[C_NH_{2N+1}] - k_3K_2K_1\,[C_NH_{2N+1}]\,\frac{P_{CO}P^2_{H_2}}{P_{H_2O}} + k_3K_2K_1P_{CO}\,[C_{N-1}H_{2N-1}]\,\frac{P_{H_2}}{P_{H_2O}}$$

Same applies to C=1 and C=2 to express alpha1 and alpha2. Considering always

$[\mathrm{CH}^*_3] = \alpha_1[H^*]$
$[\mathrm{C_2H}^*_5] = \alpha_2[CH^*_3]$
$[\mathrm{C_nH_{2n+1}}^*] = \alpha_n[C_{n-1}H_{2n-1}{}^*]$

Balance:

$$1 = [*] + [H] + [CO] + [CH_3] + [C_2OH_3] + [C_2H_5] + \sum_3^N[C_nH^*_{2N+1}] + \sum_3^N[C_nOH^*_{2N-1}] + [CH] + [C_2H_3] + \sum_3^N[C_nH^*_{2N-1}]$$

$[H] = \sqrt{(K_0P_{H_2})}\,[*]$
$[COH] = K_1P_{CO}[H] = K_1P_{CO}\sqrt{(K_0P_{H_2})}\,[*]$
$[CH_3] = \alpha_1[H^*] = \alpha_1\sqrt{(K_0P_{H_2})}\,[*]$
$[C_2OH_3] = K_1P_{CO}[CH_3] = K_1P_{CO}\,\alpha_1\sqrt{(K_0P_{H_2})}\,[*]$
$[C_2H_5] = \alpha_2[CH_3] = \alpha_1\,\alpha_2\sqrt{(K_0P_{H_2})}\,[*]$
$[CH] = K_2\frac{P_{H_2}}{P_{H_2O}}\,[COH] = K_1K_2\,\frac{P_{H_2}}{P_{H_2O}}\sqrt{(K_0P_{H_2})}\,[*]$
$[C_2H_3] = \alpha_1K_1K_2\,\frac{P_{CO}P_{H_2}}{P_{H_2O}}\sqrt{(K_0P_{H_2})}\,[*]$
$\sum_3^N[C_nH^*_{2N-1}] = K_1K_2\,\frac{P_{CO}P_{H_2}}{P_{H_2O}}\sqrt{(K_0P_{H_2})}\,[*]\,\alpha_1\,\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n$
$\sum_3^N[C_nOH^*_{2N-1}] = K_1P_{CO}\sqrt{(K_0P_{H_2})}\,[*]\,\alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n$
$\sum_3^N[C_nH^*_{2N+1}] = \sqrt{(K_0P_{H_2})}\,[*]\,\alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n$

From this I can extract [*] and the value of DENOM8.

This time I have NO iteration needed.

FT-9) reaction mechanism

MARR=85.1%

Reaction number	Reaction step	Constant parameter
1	$CO + * \leftrightarrow CO*$	K1
2	$CO* + * \leftrightarrow C* + O*$	K2
3	$C* + H_2 \leftrightarrow CH_2*$	K3
4	$O* + H_2 \leftrightarrow H_2O + *$	K4
5	$H_2 + 2* \leftrightarrow 2H*$	K5
6 rds	$CH_2* + H* \rightarrow CH_3* + *$	k6
	$CH_2* + CH_3* \rightarrow C_2H_5* + *$	
	$CH_2* + C_NH_{2N-1}* \rightarrow C_{N+1}H_{2N+3}* + *$	
7RDS	$CH_3* + H* \rightarrow CH_4 + 2*$	k7M
	$C_NH_{2N+1}* + H* \rightarrow C_NH_{2N+2} + 2*$	k7
8RDS	$C_2H_5* \rightarrow C_2H_4 + H*$	k8E
	$C_NH_{2N+1}* \rightarrow C_NH_{2N} + H*$	k8

Definition of the rates and probability growth values.

$R_{CH_4} = k_{7M}[CH_3][H]$	$\alpha_1 = \dfrac{k_6[CH_2]}{k_6[CH_2] + k_{7M}[H]}$
$R_{C_2H_4} = k_{8E}\, e^{2c}\, [C_2H_5]$	$\alpha_2 = \dfrac{k_6[CH_2]}{k_6[CH_2] + k_{7M}[H] + k_{8E}e^{c2}}$
$R_{C_nH_{2n+2}} = k_7[C_NH_{2N+1}][H]$	$\alpha_N = \dfrac{k_6[CH_2]}{k_6[CH_2] + k_7[H] + k_{8E}\, e^{cN}}$
$R_{C_NH_{2N}} = k_8\, e^{nc}\, [C_NH_{2N+1}]$	

$[CH_2] = K_3[C]P_{H_2}\,;\,[C] = K_2\frac{[CO][*]}{[O]}\,;\,[O] = \frac{P_{H_2O}[*]}{K_4P_{H_2}};\,[CO] = K_1P_{CO}[*];[H] = \sqrt{(K_5P_{H_2})}[*]$
$\alpha_1 = \dfrac{K_1\,K_2\,K_3\,K_4\,k_6\frac{P_{CO}P_{H_2}^2}{P_{H_2O}}}{K_1\,K_2\,K_3\,K_4\,k_6\frac{P_{CO}P_{H_2}^2}{P_{H_2O}} + k_{7M}\sqrt{(K_5P_{H_2})}}$
$\alpha_2 = \dfrac{K_1\,K_2\,K_3\,K_4\,k_6\frac{P_{CO}P_{H_2}^2}{P_{H_2O}}\,[*]}{K_1\,K_2\,K_3\,K_4\,k_6\frac{P_{CO}P_{H_2}^2}{P_{H_2O}}[*] + k_7\sqrt{(K_5P_{H_2})}\,[*] + k_{8E}e^{c2}}$

$$\alpha_N = \frac{K_1\ K_2\ K_3\ K_4\ k_6 \frac{P_{CO}P_{H_2}^2}{P_{H_2O}}\ [*]}{K_1\ K_2\ K_3\ K_4\ k_6 \frac{P_{CO}P_{H_2}^2}{P_{H_2O}}\ [*] + k_7\sqrt{(K_5P_{H_2})}\ [*] + k_8e^{cn}}$$

QSSA for the expression of the probability growth.

$$\frac{d[C_nH_{2n+1}^*]}{dt} = 0 = k_6[CH_2][C_{N-1}H_{2N-1}] - k_6[CH_2]\ [C_NH_{2N+1}] - k_7[H][C_NH_{2N+1}] - K_8e^{nc}[C_NH_{2N+1}]$$

Same applies to C=1 and C=2 to express alpha1 and alpha2. Considering always

$[\mathrm{CH}_3^*] = \alpha_1[H^*]$
$[\mathrm{C_2H}_5^*] = \alpha_2[CH_3^*]$
$[\mathrm{C_nH_{2n+1}}^*] = \alpha_n[C_{n-1}H_{2n-1}{}^*]$

Balance:

$$1 = [*] + [H] + [CO] + [CH_3] + [C_2H_5] + [C] + [0] + [CH_2] + \sum_3^N [C_nH_{2N+1}^*]$$

$[H] = \sqrt{(K_5P_{H_2})}\ [*]$
$[CO] = K_1P_{CO}[*]$
$[C] = K_2\frac{[CO][*]}{[O]} = K_1\ K_2\ K_4\ \frac{P_{CO}P_{H_2}}{P_{H_2O}}\ [*]$
$[CH_2] = K_1\ K_2\ K_3\ K_4\ \frac{P_{CO}P_{H_2}^2}{P_{H_2O}}\ [*]$
$[O] = \frac{P_{H_2O}}{K_4P_{H_2}}\ [*]$
$[CH_3] = \alpha_1\ [H] = \alpha_1\ \sqrt{(K_5P_{H_2})}\ [*]$
$[C_2H_5] = \alpha_1\ \alpha_2\ \sqrt{(K_7P_{H_2})}\ [*]$
$\sum_3^N [C_nH_{2N+1}^*] = \sqrt{(K_7P_{H_2})}\ [*]\ \alpha_1\alpha_2 \sum_{j=3}^{n_c}\prod_{n=3}^{j} \alpha_n$

From this I can extract [*] and the value of DENOM9.

Iteration needed.

FT-10) reaction mechanism

MARR=74%

Reaction number	Reaction step	Constant parameter
0	$H_2 + 2^* \leftrightarrow 2H^*$	K0
1 RDS	$CO + H^* \leftrightarrow COH^*$	k1
	$CO + CH_3^* \leftrightarrow C_2OH_3^*$	
	$CO + C_NH_{2N+1}^* \leftrightarrow C_{N+1}OH_{2N+1}^*$	
2	$COH^* + H^* \leftrightarrow CH^* + OH^*$	K2
	$C_2OH_3^* + H^* \leftrightarrow C_2H_3^* + OH^*$	
	$C_{N+1}OH_{2N+1}^* + H^* \leftrightarrow C_NH_{2N-1}^* + OH^*$	
3	$C_NH_{2N-1}^* + H^* \leftrightarrow C_NH_{2N}^* + ^*$	K3
4	$C_NH_{2N}^* + H^* \leftrightarrow C_NH_{2N+1}^* + ^*$	K4
5	$OH^* + H^* \leftrightarrow H_2O + 2^*$	K5
6RDS	$CH_3^* + H^* \rightarrow CH_4 + 2^*$	k6M
	$C_NH_{2N+1}^* + H^* \rightarrow C_NH_{2N+2} + 2^*$	k6
7RDS	$C_2H_5^* \rightarrow C_2H_4 + H^*$	k7E
	$C_NH_{2N+1}^* \rightarrow C_NH_{2N} + H^*$	k7

Definition of the rates and probability growth values.

$R_{CH_4} = k_{6M}[CH_3][H]$	$\alpha_1 = \dfrac{k_1P_{CO}}{k_1P_{CO} + k_{6M}[H]}$
$R_{C_2H_4} = k_{7E}\, e^{2c}\, [C_2H_5]$	$\alpha_2 = \dfrac{k_1P_{CO}}{k_1P_{CO} + k_6[H] + k_{7E}e^{c2}}$
$R_{C_nH_{2n+2}} = k_6[C_NH_{2N+1}][H]$	$\alpha_N = \dfrac{k_1P_{CO}}{k_1P_{CO} + k_6[H] + k_{7E}\, e^{cN}}$
$R_{C_NH_{2N}} = k_7\, e^{nc}\, [C_NH_{2N+1}]$	

QSSA for the expression of the probability growth.

$$\frac{d[C_nH_{2n+1}^*]}{dt} = 0 = k_1P_{CO}[C_{N-1}H_{2N-1}] - k_1P_{CO}\,[C_NH_{2N+1}] - k_7[H][C_NH_{2N+1}] - K_8e^{nc}[C_NH_{2N+1}]$$

Same applies to C=1 and C=2 to express alpha1 and alpha2. Considering always

$[\mathrm{CH}_3^*] = \alpha_1[H^*]$
$[\mathrm{C_2H}_5^*] = \alpha_2[CH_3^*]$
$[\mathrm{C_nH}_{2n+1}^*] = \alpha_n[C_{n-1}H_{2n-1}^*]$

Balance:

$$1 = [*] + [H] + [COH] + [CH_3] + [C_2OH_3] + [CH] + [C_2H_3] + [OH] + [C_2H_5] + [CH_2] + [C_2H_4] + \sum_3^N [C_nH_{2N+1}^*] + \sum_3^N [C_nH_{2N-1}^*] + \sum_3^N [C_nH_{2N}^*] + \sum_3^N [C_nOH_{2N-1}^*]$$

$[H] = \sqrt{(K_0 P_{H_2})}\,[*]$
$[CH] = \frac{1}{K_3}\frac{[CH_2]}{[H]}[*] = \frac{\alpha_1}{K_3\,K_4}\frac{1}{\sqrt{(K_0P_{H_2})}}[*]$
$[C_2H_3] = \frac{1}{K_3}\frac{[C_2H_4]}{[H]}[*] = \frac{\alpha_1\alpha_2}{K_3\,K_4}\frac{1}{\sqrt{(K_0P_{H_2})}}[*]$
$[CH_2] = \frac{1}{K_4}\frac{[CH_3]}{[H]}[*] = \frac{1}{K_4}\frac{\alpha_1\sqrt{(K_0P_{H_2})}}{\sqrt{(K_0P_{H_2})}}[*] = \frac{\alpha_1}{K_4}[*]$
$[C_2H_4] = \frac{1}{K_4}\frac{[C_2H_5]}{[H]}[*] = \frac{\alpha_1\alpha_2}{K_4}[*]$
$[C_2H_5] = \alpha_1\,\alpha_2\sqrt{(K_0P_{H_2})}\,[*]$
$[OH] = P_{H_2O}\frac{[*]^2}{[H]K_5} = \frac{1}{K_5}\frac{P_{H_2O}}{\sqrt{(K_0P_{H_2})}}[*]$
$[COH] = \frac{1}{K_2}\frac{[CH][OH]}{[H]} = \frac{\alpha_1}{K_2\,K_3\,K_4\,K_5}\frac{P_{H_2O}}{(K_0P_{H_2})^{1.5}}[*]$
$[C_2OH_3] = \frac{1}{K_2}\frac{[C_2H_3][OH]}{[H]} = \frac{\alpha_1\alpha_2}{K_2\,K_3\,K_4\,K_5}\frac{P_{H_2O}}{(K_0P_{H_2})^{1.5}}[*]$
$\sum_3^N [C_nH_{2N+1}^*] = \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\sqrt{(K_0P_{H_2})}\,[*]$
$\sum_3^N [C_nH_{2N-1}^*] = \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\frac{1}{K_3\,K_4\sqrt{(K_0P_{H_2})}}[*]$
$\sum_3^N [C_nH_{2N}^*] = \frac{\alpha_1\alpha_2}{K_4}\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\,[*]$
$\sum_3^N [C_nOH_{2N-1}^*] = \frac{\alpha_1\alpha_2}{K_2\,K_3\,K_4\,K_5}\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\frac{P_{H_2O}}{(K_0P_{H_2})^{1.5}}[*]$

From this I can extract [*] and the value of DENOM10.

This time I have iteration needed.

FT-11) reaction mechanism

MARR=93.9%

Reaction number	Reaction step	Constant parameter
0	$H_2 + 2^* \leftrightarrow 2H^*$	K0
1	$CO + H^* \leftrightarrow COH^*$	k1
	$CO + CH_3^* \leftrightarrow C_2OH_3^*$	
	$CO + C_NH_{2N+1}^* \leftrightarrow C_{N+1}OH_{2N+1}^*$	
2 rds	$COH^* + H^* \leftrightarrow CH^* + OH^*$	k2
	$C_2OH_3^* + H^* \leftrightarrow C_2H_3^* + OH^*$	
	$C_NOH_{2N-1}^* + H^* \leftrightarrow C_NH_{2N-1}^* + OH^*$	
3	$C_NH_{2N-1}^* + H^* \leftrightarrow C_NH_{2N}^* + ^*$	K3
4	$C_NH_{2N}^* + H^* \leftrightarrow C_NH_{2N+1}^* + ^*$	K4
5	$OH^* + H^* \leftrightarrow H_2O + 2^*$	K5
6RDS	$CH_3^* + H^* \rightarrow CH_4 + 2^*$	k6M
	$C_NH_{2N+1}^* + H^* \rightarrow C_NH_{2N+2} + 2^*$	k6
7RDS	$C_2H_5^* \rightarrow C_2H_4 + H^*$	k7E
	$C_NH_{2N+1}^* \rightarrow C_NH_{2N} + H^*$	k7

Definition of the rates and probability growth values.

$R_{CH_4} = k_{6M}[CH_3][H]$	$\alpha_1 = \frac{k_2[C_2OH_3]}{k_2[C_2OH_3] + k_{7M}[CH_3]}$
$R_{C_2H_4} = k_{7E}\, e^{2c}\, [C_2H_5]$	$\alpha_2 = \frac{k_2[C_3OH_5][H]}{k_2[C_3OH_5][H] + k_6[C_2H_5][H] + k_{7E}e^{c2}[C_2H_5]}$
$R_{C_nH_{2n+2}} = k_6[C_NH_{2N+1}][H]$	$\alpha_N = \frac{k_2[C_{N+1}OH_{2N+1}][H]}{k_2[C_{N+1}OH_{2N+1}][H] + k_6[C_NH_{2N+1}][H] + k_7e^{cN}[C_NH_{2N+1}]}$
$R_{C_NH_{2N}} = k_7\, e^{nc}\, [C_NH_{2N+1}]$	

Given that I can express the intermediates as

$$[C_2OH_3] = K_1[CH_3]P_{CO}\,;\, [C_3OH_5] = K_1[C_2H_5]P_{CO}\,;\, [H] = \sqrt{(K_9P_{H_2})}\,[*]$$

QSSA for the expression of the probability growth.

$$\frac{d[C_nH_{2n+1}^*]}{dt} = 0 = -k_{1D}P_{CO}[C_{N+1}H_{2N+1}] + k_2[C_{N-1}OH_{2N-1}][H] - k_6[H][C_NH_{2N+1}] - K_7e^{nc}[C_NH_{2N+1}]$$

Same applies to C=1 and C=2 to express alpha1 and alpha2. Considering always

$[\mathrm{CH_3^*}] = \alpha_1[H^*]$
$[\mathrm{C_2H_5^*}] = \alpha_2[CH_3^*]$
$[\mathrm{C_nH_{2n+1}}^*] = \alpha_n[C_{n-1}H_{2n-1}^*]$

Balance:

$$1 = [*] + [H] + [COH] + [CH_3] + [C_2OH_3] + [CH] + [C_2H_3] + [OH] + [C_2H_5] + [CH_2] + [C_2H_4] + \sum_3^N [C_nH_{2N+1}^*] + \sum_3^N [C_nH_{2N-1}^*] + \sum_3^N [C_nH_{2N}^*] + \sum_3^N [C_nOH_{2N-1}^*]$$

Get values of other intermediates concentration with respect to the reactions

$[H] = \sqrt{(K_0 P_{H_2})}\,[*]$
$[CH] = \frac{1}{K_3}\frac{[CH_2]}{[H]}\,[*] = \frac{\alpha_1}{K_3\,K_4}\frac{1}{\sqrt{(K_0P_{H_2})}}\,[*]$
$[C_2H_3] = \frac{1}{K_3}\frac{[C_2H_4]}{[H]}\,[*] = \frac{\alpha_1\alpha_2}{K_3\,K_4}\frac{1}{\sqrt{(K_0P_{H_2})}}\,[*]$
$[CH_2] = \frac{1}{K_4}\frac{[CH_3]}{[H]}\,[*] = \frac{\alpha_1}{K_4}\,[*]$
$[C_2H_4] = \frac{1}{K_4}\frac{[C_2H_5]}{[H]}\,[*] = \frac{\alpha_1\alpha_2}{K_4}\,[*]$
$[C_2H_5] = \alpha_1\,\alpha_2\sqrt{(K_0P_{H_2})}\,[*]$
$[OH] = P_{H_2O}\frac{[*]^2}{[H]K_5} = \frac{1}{K_5}\frac{P_{H_2O}}{\sqrt{(K_0P_{H_2})}}\,[*]$
$[COH] = K_1P_{CO}[H] = K_1P_{CO}\sqrt{(K_0P_{H_2})}\,[*]$
$[C_2OH_3] = K_1[CH_3]P_{CO} = K_1P_{CO}\,\alpha_1\sqrt{(K_0P_{H_2})}\,[*]$
$\sum_3^N [C_nH_{2N+1}^*] = \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\sqrt{(K_0P_{H_2})}\,[*]$
$\sum_3^N [C_nH_{2N-1}^*] = \alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\frac{1}{K_3\,K_4\sqrt{(K_0P_{H_2})}}\,[*]$
$\sum_3^N [C_nH_{2N}^*] = \frac{\alpha_1\alpha_2}{K_4}\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\,[*]$
$\sum_3^N [C_nOH_{2N-1}^*] = K_1P_{CO}\,\alpha_1\alpha_2\sum_{j=3}^{n_c}\prod_{n=3}^{j}\alpha_n\sqrt{(K_0P_{H_2})}\,[*]$

From this I can extract [*] and the value of DENOM11. This time I have iteration needed.

B - Catalyst testing

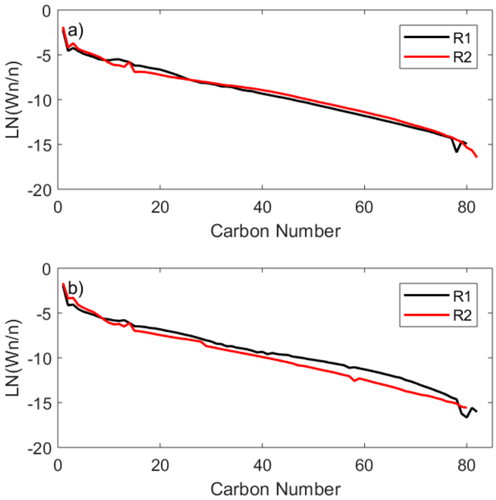

Figure B1. Products distribution data reproducibility: a) 483K, 20bar, H_2/CO 2.09, X_{CO} R1: 12.31%, X_{CO} R2: 11.96%; b) 493K, 20bar, H_2/CO 1.06, X_{CO} R1: 9.34%, X_{CO} R2: 9.2%.