APPENDIX A

SAMPLE DERIVATION OF KINETIC MODEL (#6)

The objective of this derivation is to develop a mathematical expression for the overall reaction rate, in terms of the sum of molal disappearance of three active reactant species on the basis of unit mass of the catalyst, as a function of observable bulk partial pressures of species at steady state and various kinetic parameters depending on the proposed reaction mechanism.

Let k_j be the forward rate constant for the elementary step j,

k'_j the reverse rate constant for the same elementary step j,

n the number of carbon atoms present in the species i,

p_i the partial pressure of species i in the bulk gaseous stream, in kPa,

r the net reaction rate, in kmols of $(H_2+CO+C_2H_4)$ per hour per kg of catalyst,

r_i the conponent rate of species i, in kmols of i per hour per kg of catalyst,

r_j the intrinsic rate for the elementary step j,

* the unoccupied active site,

i* the adsorbed species i,

and [ ] represent the surface molal concentration.

Following the reaction mechanism proposed in Chapter III, the intrinsic rates for each elementary steps can be written as belows. The equation numbers designated correspond to those given in the summary figure of the mechanism (Figure 3.1).

$$r_2 = k_2 p_{H_2}[*]^2 - k_2'[H*]^2 \quad (A.2)$$

$$r_3 = k_3 p_{CO}[*] - k_3'[*CO] \quad (A.3)$$

$$r_4 = k_4 p_{C_2H_4}[*]^2 - k_4'[*CH_2]^2 \quad (A.4)$$

$$r_5 = k_5[*CO][*] - k_5'[*C][O*] \quad (A.5)$$

$$r_6 = k_6 p_{C_2H_4}[H*] - k_6'[*C_2H_5] \quad (A.6)$$

$$r_7 = k_7[*C][H*]^2 - k_7'[*CH_2][*]^2 \quad (A.7)$$

$$r_8 = k_8[*CH_2][H*] - k_8'[*CH_3][*] \quad (A.8)$$

$$r_9 = k_9[*CH_3][H*] - k_9'[*CH_4][*] \quad (A.9)$$

$$r_{10} = k_{10}[*CH_3][*CH_2] - k_{10}'[*C_2H_5][*] \quad (A.10)$$

$$r_{11} = k_{11}[*C_2H_5][H*] - k_{11}'[*C_2H_6][*] \quad (A.11)$$

$$r_{12} = k_{12}[*CO][H*] - k'_{12}[*COH][*] \qquad (A.12)$$

$$r_{13} = k_{13}[*COH][*CH_2] - k'_{13}[*C(CH_2)OH][*] \qquad (A.13)$$

$$r_{14} = k_{14}[*C(CH_2)OH][H*] - k'_{14}[*CH(CH_2)OH][*] \qquad (A.14)$$

$$r_{15} = k_{15}[*CH(CH_2)OH][H*] - k'_{15}[*CH(CH_3)OH][*] \qquad (A.15)$$

$$r_{16} = k_{16}[*CH(CH_3)OH][H*] - k'_{16}[*CH_2(CH_3)OH][*] \qquad (A.16)$$

$$r_{17} = k_{17}[O*][H*]^2 - k'_{17}[*OH_2][*] \qquad (A.17)$$

$$r_{18} = k_{18}[*CO][O*] - k'_{18}[*CO_2][*] \qquad (A.18)$$

$$r_{19} = k_{19}[*OH_2][*CO][*] - k'_{19}[*CO_2][H*]^2 \qquad (A.19)$$

$$r_{20} = k_{20}[*CH_2C_nH_{2n+1}][*CH_2] - k'_{20}[*CH_2CH_2C_nH_{2n+1}][*]$$

$$\text{for } n \geq 1 \qquad (A.20)$$

$$r_{21} = k_{21}[*CH_2CH_2C_nH_{2n+1}][H*] -$$

$$k'_{21}[*CH_3CH_2C_nH_{2n+1}][*] \qquad (A.21)$$

$$r_{22} = k_{22}[{*CH_2CH_2C_nH_{2n+1}}][{*CH_2}] -$$

$$k'_{22}[{*CH_2CH(CH_3)C_nH_{2n+1}}][*] \quad (A.22)$$

$$r_{23} = k_{23}[{*CH_2CH(CH_3)C_nH_{2n+1}}][H*] -$$

$$k'_{23}[{*CH_3CH(CH_3)C_nH_{2n+1}}][*] \quad (A.23)$$

$$r_{24} = k_{24}[{*CH_2CH_2C_nH_{2n+1}}] -$$

$$k'_{24}[{*CH_2{=}CHC_nH_{2n+1}}][H*] \quad (A.24)$$

$$r_{25} = k_{25}[{*CH(OH)C_nH_{2n+1}}][{*CH_2}] -$$

$$k'_{25}[{*CH(OH)CH_2C_nH_{2n+1}}][*] \quad (A.25)$$

$$r_{26} = k_{26}[{*CH(OH)CH_2C_nH_{2n+1}}][H*] -$$

$$k'_{26}[{*CH_2(OH)CH_2C_nH_{2n+1}}][*] \quad (A.26)$$

$$r_{27} = k_{27}[*CH_4] - k'_{27}p_{CH_4}[*] \tag{A.27}$$

$$r_{28} = k_{28}[*C_2H_6] - k'_{28}p_{C_2H_6}[*] \tag{A.28}$$

$$r_{29} = k_{29}[*CH_3CH_2C_nH_{2n+1}] - k'_{29}p_{C_{n+2}H_{2n+6}}[*] \tag{A.29}$$

$$r_{30} = k_{30}[*CH_3CH(CH_3)C_nH_{2n+1}] -$$

$$k'_{30}p_{C_nH_{2n+1}CH(CH_3)CH_3}[*] \tag{A.30}$$

$$r_{31} = k_{31}[*CH_2{=}CHC_nH_{2n+1}] -$$

$$k'_{31}p_{CH_2=CHC_nH_{2n+1}}[*] \tag{A.31}$$

$$r_{32} = k_{32}[*CH_2(OH)C_{n+1}H_{2n+3}] -$$

$$k'_{32}p_{HOC_{n+2}H_{2n+5}}[*] \tag{A.32}$$

$$r_{33} = k_{33}[*OH_2] - k'_{33}p_{H_2O}[*] \tag{A.33}$$

$$r_{34} = k_{34}[*CO_2] - k'_{34}p_{CO_2}[*] \tag{A.34}$$

Total number of sites, [S], is the sum of vacant sites and adsorbed sites:

$$[S] = [*] + [H*] + [*C] + [O*] + [*CO] + [*CH_2] +$$

$$[*CH_3] + [*C_2H_5] + \sum_{n=1}^{\infty}[*C_{n+2}H_{2n+5}] +$$

$$\sum_{n=1}^{\infty}[*CH_2CH(CH_3)C_nH_{2n+1}] + [*COH] + [*C(OH)CH_2] +$$

$$[*CH(OH)CH_2] + [*CH(OH)CH_3] + \sum_{n=1}^{\infty}[*CH(OH)C_{n+1}H_{2n+3}]$$

$$+ [*CH_4] + [*C_2H_6] + \sum_{n=1}^{\infty}[*C_{n+2}H_{2n+6}] +$$

$$\sum_{n=1}^{\infty}[*CH_3CH(CH_3)C_nH_{2n+1}] + \sum_{n=1}^{\infty}[*CH_2{=}CHC_nH_{2n+1}] +$$

$$\sum_{n=1}^{\infty}[*C_{n+1}H_{2n+3}OH] + [*OH_2] + [*CO_2] \qquad (A.35)$$

The system to be solved involves an infinite number of unknowns (rates and surface activities) and knowns (bulk partial pressures of chemical species and kinetic parameters), in an infinite number of nonlinear algebraic rate equations. Therefore, mathematical simplifications must be imposed so that a solution of practical usefulness can be obtained.

The first simplification is to apply the rate-determining assumption made in the proposed mechanism (in Capter III) to reduce the infinite number of unknown rates to a finite rate expression. The assumption of rate-determining step means that this particular elementary step proceeds much slower than the other steps so that equilibrium conditions can be assumed for all non-rate-determining steps, and thus the net rate of the reaction is sorely governed by the rate-determining step.

By defining a set of equilibrium constants for all non-rate-determining steps, the number of kinetic parameters is hence cut in half. Once the rate-determining simplification is employed, the system becomes more manageable because only those variables in the rate equation for the rate-determining step are of concern and they can be obtained through a sequence of mathematical manipulations of the rate equations of the non-rate-determining steps.

More specifically, [H*] and [$*C_2H_5$] in Eqn. (A.6) are the only two unknown variables considered. [H*] can be determined simply by solving Eqn. (A.2) with the simplification that $r_2 \cong 0$ from the assumption of being the non-rate-determining step. The final form of [H*] is in terms of the bulk hydrogen partial pressure and the concentration of empty sites. Similarly, [$*C_2H_5$] can be obtained by solving Eqns. (A.2), (A.11) and (A.28) simultaneously, as a function of the measureable partial pressure of ethane product and the concentration of empty sites.

Since the concentration of empty sites, [*], is present in both [H*] and [$*C_2H_5$] expressions and it is a nonobservable unknown, [*] must be replaced by the total number of the sites [S] from Eqn. (A.35). Thus, the next task is to find all the intermediates in terms of measureable quantities. Substituting the expressions for the intermediates back into Eqn. (A.35) and solving it for [*], and then plugging [H*], [$*C_2H_5$] and [*] into Eqn. (A.6) will result in the desired rate equation for the rate-determining step, in terms of measureable component partial pressures and kinetic parameters to be determined by the techniques of data fitting. Details of the mathematical manipulations are given in following pages.

Since the elementary step #6 is assumed to be the rate-determining step, all other rates will approach the equilibrium, thus,

$$r_2 = r_3 = r_4 = r_5 = r_7 = r_8 = r_9 = r_{10} = r_{11} =$$

$$r_{12} = r_{13} = r_{14} = r_{15} = r_{16} = r_{17} = r_{18} = r_{19} =$$

$$r_{20}|_{n=1} = \cdots = r_{20}|_{n\to\infty} = r_{21}|_{n=1} = \cdots = r_{21}|_{n\to\infty} =$$

$$r_{22}|_{n=1} = \cdots = r_{22}|_{n\to\infty} = r_{23}|_{n=1} = \cdots = r_{23}|_{n\to\infty} =$$

$$r_{24}|_{n=1} = \cdots = r_{24}|_{n\to\infty} = r_{25}|_{n=1} = \cdots = r_{25}|_{n\to\infty} =$$

$$r_{26}|_{n=1} = \cdots = r_{26}|_{n\to\infty} = r_{27}|_{n=1} = \cdots = r_{27}|_{n\to\infty} =$$

$$r_{28}|_{n=1} = \cdots = r_{28}|_{n\to\infty} = r_{29}|_{n=1} = \cdots = r_{29}|_{n\to\infty} =$$

$$r_{30}|_{n=1} = \cdots = r_{30}|_{n\to\infty} = r_{31}|_{n=1} = \cdots = r_{31}|_{n\to\infty} =$$

$$r_{32}|_{n=1} = \cdots = r_{32}|_{n\to\infty} = r_{33} = r_{34} \cong 0 \qquad \text{(A.36)}$$

Let K_j and K_j' represent the equilibrium constants for step j, and be defined as follows:

$$K_j \equiv \frac{k_j}{k_j'} \tag{A.37}$$

$$K_j' \equiv \frac{k_j'}{k_j} \tag{A.38}$$

Combining Equs. (A.2), (A.36) and (A.37), and solving for [H*] results in:

$$[H^*] = \sqrt{K_2 p_{H_2}}[*] \tag{A.39}$$

Similarly, from Eqns. (A.3), (A.36) and (A.37),

$$[*CO] = K_3 p_{CO}[*] \quad . \tag{A.40}$$

From Eqns. (A.4), (A.36) and (A.37),

$$[{}^*CH_2] = \sqrt{K_4 p_{C_2H_4}}[{}^*] \tag{A.41}$$

The concentrations of all adsorbed product species can be determined from the corresponding termination (desorption) steps, hence,

$$[{}^*CH_4] = K'_{27} p_{CH_4}[{}^*] \tag{A.42}$$

$$[{}^*C_2H_6] = K'_{28} p_{C_2H_6}[{}^*] \tag{A.43}$$

$$[{}^*C_{n+2}H_{2n+6}] = K'_{29} p_{C_{n+2}H_{2n+6}}[{}^*] \quad \text{for } n \geq 1 \tag{A.44}$$

$$[{}^*CH_3CH(CH_3)C_nH_{2n+1}] = K'_{30} p_{C_nH_{2n+1}CH(CH_3)CH_3}[{}^*] \tag{A.45}$$

$$[{}^*CH_2{=}CHC_nH_{2n+1}] = K'_{31} p_{CH_2=CHC_nH_{2n+1}}[{}^*] \tag{A.46}$$

$$[{}^*CH_2(OH)C_{n+1}H_{2n+3}] = K'_{32} p_{C_{n+2}H_{2n+5}OH}[{}^*] \tag{A.47}$$

$$[{*}CO_2] = K'_{34} p_{CO_2} [{*}] \tag{A.48}$$

Combining Eqns. (A.18), (A.36) and (A.38) and solving for [*O] gives,

$$[O{*}] = \frac{K'_{18}[{*}CO_2][{*}]}{[{*}CO]} \tag{A.49}$$

Substituting [*CO] from Eqn. (A.40) and [*CO_2] from Eqn. (A.48) into Eqn. (A.49) ends up,

$$[O{*}] = \left(\frac{K'_{18}K'_{34}}{K_3}\right)\left(\frac{p_{CO_2}}{p_{CO}}\right)[{*}] \tag{A.50}$$

Combining Eqns. (A.5), (A.36) and (A.37) and solving for [*C] yields:

$$[{*}C] = \frac{K_5[{*}CO][{*}]}{[O{*}]} \tag{A.51}$$

Plugging [*CO] from Eqn. (A.40) and [O*] from Eqn. (A.50) into Eqn. (A.51) gives:

$$[*C] = \left(\frac{K_3^2 K_5}{K_{18}' K_{34}'}\right)\left(\frac{p_{CO}^2}{p_{CO_2}}\right)[*] \qquad (A.52)$$

Combining Eqns. (A.9), (A.36) and (A.38) and solving for $[*CH_3]$ results in,

$$[*CH_3] = \frac{K_9'[*CH_4][*]}{[H*]} \qquad (A.53)$$

Substituting [H*] and $[*CH_4]$ from Eqns. (A.39) and (A.42) into Eqn. (A.53) gives,

$$[*CH_3] = \left(\frac{K_9' K_{27}'}{\sqrt{K_2}}\right)\left(\frac{p_{CH_4}}{\sqrt{p_{H_2}}}\right)[*] \qquad (A.54)$$

Combining Eqns. (A.11), (A.36) and (A.38) and solving for $[{}^*C_2H_5]$ produces,

$$[{}^*C_2H_5] = \frac{K'_{11}[{}^*C_2H_6][{}^*]}{[H^*]} \qquad (A.55)$$

Substituting $[H^*]$ and $[{}^*C_2H_6]$ from Eqns. (A.39) and (A.43) into Eqn. (A.55) gives,

$$[{}^*C_2H_5] = \left(\frac{K'_{11}K'_{28}}{\sqrt{K_2}}\right)\left(\frac{p_{C_2H_6}}{\sqrt{p_{H_2}}}\right)[{}^*] \qquad (A.56)$$

Combining Eqns. (A.19), (A.36) and (A.38) and solving for $[H_2O^*]$ results in,

$$[H_2O^*] = \frac{K'_{19}[{}^*CO_2][H^*]^2}{[{}^*CO][{}^*]} \qquad (A.57)$$

Substituting [H*], [*CO] and [*CO_2] from Eqns. (A.39), (A.40) and (A.48) gives,

$$[H_2O^*] = \left(\frac{K_2 K'_{19} K'_{34}}{K_3}\right)\left(\frac{p_{H_2} p_{CO_2}}{p_{CO}}\right)[*] \qquad (A.58)$$

For intermediates of n-alkanes, combining Eqns. (A.20), (A.36) and (A.37) results in:

$$[{}^*C_{n+2}H_{2n+5}] = \frac{K_{20}[{}^*C_{n+1}H_{2n+3}][{}^*CH_2]}{[*]} \quad \text{for } n \geq 1 \qquad (A.59)$$

Assume all rate constants in the propagation phase are independent of the chain length.

For n = 1,

$$[{}^*C_3H_7] = \left(\frac{K_{20}[{}^*CH_2]}{[*]}\right)[{}^*C_2H_5] \qquad (A.60)$$

For n = 2,

$$[{}^*C_4H_9] = \left(\frac{K_{20}[{}^*CH_2]}{[*]}\right)[{}^*C_3H_7] \qquad (A.61)$$

Plugging $[*C_3H_7]$ from Eqn. (A.60) into Eqn. (A.61) gives:

$$[*C_4H_9] = \left(\frac{K_{20}[*CH_2]}{[*]}\right)^2 [*C_2H_5] \qquad (A.62)$$

Similarly, $[*C_{n+2}H_{2n+5}]$ can be determined as below,

$$[*C_{n+2}H_{2n+5}] = \left(\frac{K_{20}[*CH_2]}{[*]}\right)^n [*C_2H_5] \quad \text{for } n \geq 1 \qquad (A.63)$$

For 2-methyl alkane intermediates, Combining Eqns. (A.22), (A.36) and (A.37) yields (for $n \geq 1$),

$$[*CH_2CH(CH_3)C_nH_{2n+1}] = \frac{K_{22}[*C_{n+2}H_{2n+5}][*CH_2]}{[*]} \qquad (A.64)$$

For n = 1,

$$[*CH_2CH(CH_3)_2] = \left(\frac{K_{22}[*CH_2]}{[*]}\right)[*C_3H_7] \qquad (A.65)$$

For n = 2,

$$[{}^*CH_2CH(CH_3)C_2H_5] = \left(\frac{K_{22}[{}^*CH_2]}{[{}^*]}\right)[{}^*CH_2CH(CH_3)_2] \quad (A.66)$$

Plugging $[{}^*CH_2CH(CH_3)_2]$ from Eqn. (A.65) into Eqn. (A.66) gives,

$$[{}^*CH_2CH(CH_3)C_2H_5] = \left(\frac{K_{22}[{}^*CH_2]}{[{}^*]}\right)^2[{}^*C_3H_7] \quad (A.67)$$

Similarly,

$$[{}^*CH_2CH(CH_3)C_nH_{2n+1}] = \left(\frac{K_{22}[{}^*CH_2]}{[{}^*]}\right)^n[{}^*C_3H_7] \quad (A.68)$$

Combining Eqns. (A.12), (A.36) and (A.37), and solving for [*COH] results in,

$$[{}^*COH] = \frac{K_{12}[{}^*CO][H^*]}{[{}^*]} \quad (A.69)$$

Substitute [H*] and [*CO] from Eqns. [A.39] and [A.40],

$$[*COH] = K_2^{\frac{1}{2}} K_3 K_{12} p_{H_2}^{\frac{1}{2}} p_{CO} [*] \tag{A.70}$$

Combining Eqns. (A.13), (A.36) and (A.37), and solving for $[*C(CH_2)OH]$ yields,

$$[*C(CH_2)OH] = \frac{K_{13}[*COH][*CH_2]}{[*]} \tag{A.71}$$

Plugging $[*CH_2]$ and [*COH] from Eqns. (A.41) and (A.70) into Eqn. (A.71) gives,

$$[*C(CH_2)OH] = K_2^{\frac{1}{2}} K_3 K_4^{\frac{1}{2}} K_{13} p_{H_2}^{\frac{1}{2}} p_{CO} p_{C_2H_4}^{\frac{1}{2}} [*] \tag{A.72}$$

Combining Eqns. (A.14), (A.36) and (A.37), and solving for $[*CH(CH_2)OH]$ results in,

$$[*CH(CH_2)OH] = \frac{K_{14}[*C(CH_2)OH][*H]}{[*]} \tag{A.73}$$

Plugging [H*] and [*C(CH$_2$)OH] from Eqns. (A.39) and (A.72) gives,

$$[{*}CH(CH_2)OH] = K_2 K_3 K_4^{\frac{1}{2}} K_{13} K_{14} p_{H_2} p_{CO} p_{C_2H_4}^{\frac{1}{2}} [{*}] \qquad (A.74)$$

Combining Eqns. (A.15), (A.36) and (A.37), and solving for [*CH(CH$_3$)OH] results in,

$$[{*}CH(CH_3)OH] = \frac{K_{15}[{*}CH(CH_2)OH][H{*}]}{[{*}]} \qquad (A.75)$$

Plugging [H*] and [*CH(CH$_2$)OH] from Eqns. (A.39) and (A.74) into Eqn. (A.75) produces,

$$[{*}CH(CH_3)OH] = \sqrt{K_2}^{\,3} K_3 K_4^{\frac{1}{2}} K_{13} K_{14} K_{15} \sqrt{p_{H_2}}^{\,3} p_{CO} p_{C_2H_4}^{\frac{1}{2}} [{*}] \qquad (A.76)$$

For higher oxgenated intermediates, combining Eqns. (A.25), (A.36) and (A.37), and rearranging ends up, for $n \geq 1$,

$$[{*}CH(OH)C_{n+1}H_{2n+3}] = \frac{K_{25}[{*}CH(OH)C_nH_{2n+1}][{*}CH_2]}{[{*}]} \quad (A.77)$$

For n = 1,

$$[{*}CH(OH)C_2H_5] = \left(\frac{K_{25}[{*}CH_2]}{[{*}]}\right)[{*}CH(OH)CH_3] \quad (A.78)$$

For n = 2,

$$[{*}CH(OH)C_3H_7] = \left(\frac{K_{25}[{*}CH_2]}{[{*}]}\right)^2[{*}CH(OH)CH_3] \quad (A.79)$$

For the general n,

$$[{*}CH(OH)C_{n+1}H_{2n+3}] = \left(\frac{K_{25}[{*}CH_2]}{[{*}]}\right)^n[{*}CH(OH)CH_3] \quad (A.80)$$

In order for the propagation steps to proceed, all forward rate constants must be greater than the reverse ones, i.e.,

$$K_{20},\ K_{22},\ K_{25} \geq 1 \qquad \text{(A.81)}$$

However, as soon as initiation starts, all the steps followed will release at least one site, hence,

$$\frac{[{*}CH_2]}{[{*}]} << 1 \qquad \text{(A.82)}$$

Therefore, the combination of Eqns. (A.81) and (A.82) produces,

$$\left|\frac{K_{20}[{*}CH_2]}{[{*}]}\right|,\ \left|\frac{K_{22}[{*}CH_2]}{[{*}]}\right|,\ \left|\frac{K_{25}[{*}CH_2]}{[{*}]}\right| \leq 1 \qquad \text{(A.83)}$$

Summing all alkyl intermediates in Eqns. (A.60), (A.62) and (A.63) and applying the geometric progression rule gives,

$$[{*}C_2H_5] + \sum_{n=1}^{\infty}[{*}C_{n+2}H_{2n+5}] = \frac{[{*}C_2H_5]}{1 - \dfrac{K_{20}[{*}CH_2]}{[{*}]}} \qquad \text{(A.84)}$$

Substituting $[*CH_2]$ and $[*C_2H_5]$ from Eqns. (A.41) and (A.56) into Eqn. (A.84) gives,

$$[*C_2H_5] + \sum_{n=1}^{\infty} [*C_{n+2}H_{2n+5}]$$

$$= \frac{\left(\dfrac{K'_{11}K'_{28}}{K_2^{\frac{1}{2}}}\right)\left(\dfrac{p_{C_2H_6}}{p_{H_2}^{\frac{1}{2}}}\right)[*]}{1 - K_4^{\frac{1}{2}}K_{20}p_{C_2H_4}^{\frac{1}{2}}} \qquad (A.85)$$

Similarly, the sum of all 2-methyl alkane intermediates from Eqns. (A.65), (A.67) and (A.68) becomes,

$$\sum_{n=1}^{\infty} [*CH_2CH(CH_3)C_nH_{2n+1}]$$

$$= \left(\frac{K_{22}[*CH_2][*C_3H_7]}{[*]}\right)\left(\frac{1}{1 - \dfrac{K_{22}[*CH_2]}{[*]}}\right) \qquad (A.86)$$

Combining Eqns. (A.41), (A.56), (A.60) and (A.86) yields,

$$\sum_{n=1}^{\infty} [{}^*CH_2CH(CH_3)C_nH_{2n+1}]$$

$$= \frac{\left(\dfrac{K_4K'_{11}K_{20}K_{22}K'_{23}}{K_2^{\frac{1}{2}}}\right)\left(\dfrac{p_{C_2H_4}p_{C_2H_6}}{p_{H_2}^{\frac{1}{2}}}\right)[*]}{1 - K_4^{\frac{1}{2}}K_{22}p_{C_2H_4}^{\frac{1}{2}}} \quad (A.87)$$

Summing [*CH(OH)CH$_3$] and all higher oxygenate intermediates from Eqns. (A.78), (A.79) and (A.80), and applying the rule of geometric progression ends up,

$$[{*}CH(OH)CH_3] + \sum_{n=1}^{\infty} [{*}CH(OH)C_{n+1}H_{2n+3}]$$

$$= \frac{[{*}CH(OH)CH_3]}{1 - \dfrac{K_{25}[{*}CH_2]}{[{*}]}} \qquad (A.88)$$

Substituting [*CH$_2$] and [*CH(OH)CH$_3$] from Eqns. (A.41) and (A.76) into Eqn. (A.88) gives:

$$[{*}CH(OH)CH_3] + \sum_{n=1}^{\infty} [{*}CH(OH)C_{n+1}H_{2n+3}]$$

$$= \frac{(K_2^{\frac{3}{2}} K_3 K_4^{\frac{1}{2}} K_{13} K_{14} K_{15})(p_{H_2}^{\frac{3}{2}} p_{CO} p_{C_2H_4}^{\frac{1}{2}})[{*}]}{1 - K_4^{\frac{1}{2}} K_{25} p_{C_2H_4}^{\frac{1}{2}}} \qquad (A.89)$$

Combining Eqns. (A.39) through (A.48), (A.50), (A.52), (A.54), (A.58), (A.70), (A.72), (A.74), (A.85), (A.87) and (A.89) with Eqn. (A.35) and solving for [*] results in:

$$[*] = [S]\{1 + \sqrt{K_2 p_{H_2}} + \left(\frac{K_3^2 K_5}{K'_{18} K'_{34}}\right)\left(\frac{p_{CO}^2}{p_{CO_2}}\right) + \left(\frac{K'_{18} K'_{34}}{K_3}\right)\left(\frac{p_{CO_2}}{p_{CO}}\right)$$

$$+ K_3 p_{CO} + \sqrt{K_4 p_{C_2H_4}} + \frac{K'_9 K'_{27} p_{CH_4}}{\sqrt{K_2 p_{H_2}}} + \frac{\dfrac{K'_{11} K'_{28} p_{C_2H_6}}{\sqrt{K_2 p_{H_2}}}}{1 - K_{20}\sqrt{K_4 p_{C_2H_4}}}$$

$$+ \frac{K_4 K'_{11} K_{20} K_{22} K'_{28} p_{C_2H_4} p_{C_2H_6}}{\sqrt{K_2 p_{H_2}}(1 - K_{22}\sqrt{K_4 p_{C_2H_4}})} + \sqrt{K_2} K_3 K_{12} \sqrt{p_{H_2}} p_{CO} +$$

$$+ \sqrt{K_2} K_3 \sqrt{K_4} K_{13} p_{CO} \sqrt{p_{H_2} p_{C_2H_4}} (1 + \sqrt{K_2} K_{14} \sqrt{p_{H_2}}) +$$

$$\frac{\sqrt{K_2}^3 K_3 \sqrt{K_4} K_{13} K_{14} K_{15} \sqrt{p_{H_2}}^3 p_{CO} \sqrt{p_{C_2H_4}}}{1 - K_{25}\sqrt{K_4 p_{C_2H_4}}} + K'_{27} p_{CH_4} +$$

$$K'_{28} p_{C_2H_6} + \sum_{n=1}^{\infty} (K'_{29,n} p_{C_{n+2}H_{2n+6}} + K'_{30,n} p_{C_nH_{2n+1}CH(CH_3)CH_3}$$

$$+ K'_{31,n} p_{CH_2=CHC_nH_{2n+1}} + K'_{32,n} p_{C_{n+2}H_{2n+5}OH}) +$$

$$K_2 K'_{19} K'_{34} p_{H_2} p_{CO_2} / (K_3 p_{CO}) + K'_{34} p_{CO_2}\}^{-1} \qquad \text{(A.90)}$$

Further simplification of Eqn. (A.90) to a more realistic form can be obtained by assuming: (1) higher hydrocarbons, C_{40+} for normal alkanes, C_{30+} for 2-methyl paraffins, C_{20+} for 1-olefins and C_{5+} for 1-oxygenates, are produced in negligible amounts, and (2) [H*], [*C], [O*], [*CO], [$*CH_2$], [$*CH_3$] and [$*C_2H_5$] are the dominant intermediates other than the product species. Thus,

$$[*] = [S]\{1 + \sqrt{K_2 p_{H_2}} + \left(\frac{K_3^2 K_5}{K_{18}' K_{34}'}\right)\left(\frac{p_{CO}^2}{p_{CO_2}}\right) + \left(\frac{K_{18}' K_{34}'}{K_3}\right)\left(\frac{p_{CO_2}}{p_{CO}}\right)$$

$$+ K_3 p_{CO} + \sqrt{K_4 p_{C_2H_4}} + \left(\frac{K_9 K_{27}'}{\sqrt{K_2}}\right)\left(\frac{p_{CH_4}}{\sqrt{p_{H_2}}}\right)$$

$$+ \left(\frac{K_{11}' K_{28}'}{\sqrt{K_2}}\right)\left(\frac{p_{C_2H_6}}{\sqrt{p_{H_2}}}\right) + K_{27}' p_{CH_4} + K_{28}' p_{C_2H_6}$$

$$+ \sum_{n=1}^{40} (K_{29,n}' p_{C_{n+2}H_{2n+6}}) + \sum_{n=1}^{30} (K_{30,n}' p_{C_nH_{2n+1}CH(CH_3)CH_3})$$

$$+ \sum_{n=1}^{20} (K_{31,n}' p_{CH_2=CHC_nH_{2n+1}}) + \sum_{n=1}^{5} (K_{32,n}' p_{C_{n+2}H_{2n+5}OH})$$

$$+ \left(\frac{K_2 K_{19}' K_{34}'}{K_3}\right)\left(\frac{p_{H_2} p_{CO_2}}{p_{CO}}\right) + K_{34}' p_{CO_2}\}^{-1} \qquad \text{(A.91)}$$

The net reaction rate, r, is defined as:

$$r \equiv r_{H_2} + r_{CO} + r_{C_2H_4} \tag{A.92}$$

$$= r_2 + r_3 + r_4 + r_6 \tag{A.93}$$

Applying the assumption of Eqn. (A.36) to Eqn. (A.93) yields,

$$r \cong r_6$$

$$= k_6(p_{C_2H_4}[H^*] - K_6'[^*C_2H_5]) \tag{A.94}$$

Substituting [H*] and $[^*C_2H_5]$ from Eqns. (A.39) and (A.56) into Eqn. (A.94) and rearranging gives,

$$r = \left(\frac{k_6}{\sqrt{K_2 p_{H_2}}}\right)(K_2 p_{H_2} p_{C_2H_4} - K_6' K_{11}' K_{28}' p_{C_2H_6})[^*] \tag{A.95}$$

Combining Eqns. (A.95) and (A.91), rearranging, dissolving k_6 and [S] into the preexponential factor a, and replacing p_{H_2}, p_{CO}, $p_{C_2H_4}$, p_{CH_4}, $p_{C_2H_6}$, $p_{C_{n+2}H_{2n+6}}$, $p_{C_nH_{2n+1}CH(CH_3)CH_3}$, $p_{CH_2=CHC_nH_{2n+1}}$, $p_{C_{n+2}H_{2n+5}OH}$, and p_{CO_2} with p_2, p_3, p_4, p_{27}, p_{28}, $p_{29,n}$, $p_{30,n}$, $p_{31,n}$, $p_{32,n}$, and p_{34} respectively results in,

$$r = ae^{\frac{-E}{RT}}(\sqrt{K_2p_2}p_4 - \frac{K_6'K_{11}'K_{28}'p_{28}}{\sqrt{K_2p_2}})\{1 + \sqrt{K_2p_2} + (\frac{K_3^2K_5}{K_{18}'K_{34}'})(\frac{p_3^2}{p_{34}})$$

$$+ (\frac{K_{18}'K_{34}'}{K_3})(\frac{p_{34}}{p_3}) + K_3p_3 + \sqrt{K_4p_4} + (\frac{K_9K_{27}'}{\sqrt{K_2}})(\frac{p_{27}}{\sqrt{p_2}})$$

$$+ (\frac{K_{11}'K_{28}'}{\sqrt{K_2}})(\frac{p_{28}}{\sqrt{p_2}}) + K_{27}'p_{27} + K_{28}'p_{28} + \sum_{n=1}^{40} K_{29,n}'p_{29,n}$$

$$+ \sum_{n=1}^{30} K_{30,n}'p_{30,n} + \sum_{n=1}^{20} K_{31,n}'p_{31,n} + \sum_{n=1}^{5} K_{32,n}'p_{32,n}$$

$$+ (\frac{K_2K_{19}'K_{34}'}{K_3})(\frac{p_2p_{34}}{p_3}) + K_{34}'p_{34}\}^{-1} \qquad (A.96)$$