APPENDIX A

Estimation of Concentrations of Various Species in the Catalyst Phase (Yongkeat, 1996)

Isobutane Concentration in the Acid Phase

Isobutane concentration in the acid phase may be calculated by the use of an equation to describe the rate of mass transfer from hydrocarbon to acid phase. At steady state, the rate of mass transfer of isobutane to the acid phase is equal to the rate of consumption of isobutane in the acid phase (Rase, 1977).

$$k_{L,iC4}a_V[(C_{iC4,a})_i - C_{iC4,a}] = (-r_{iC4})_a Ha \qquad \text{(A.1)}$$

or

$$k_{L,iC4}a_V[K_{d,iC4}C_{iC4,h} - C_{iC4,a}] = (-r_{iC4})_a Ha \qquad \text{(A.2)}$$

By rearranging equation A.2, the concentration of isobutane in the acid can be expressed as:

$$C_{iC4,a} = K_{d,iC4}C_{iC4,h} - \frac{(r_{iC4})_a Ha}{k_{L,iC4}a_V} \qquad \text{(A.3)}$$

The term $K_{d,iC4}$ in equation A.3, the distribution coefficient for isobutane, is 0.003 litre/litre, H_2S0_4 (0.0007 lb/lb, H_2S0_4) as used by Langley and Pike (1972). But this coefficient was also found to change with the temperature. The correlated equation used to calculate $K_{d,iC4}$ is as follows (Vichailak, 1995):

$$K_{d,iC4} = 0.008129T^{-0.269136} \qquad \text{(A.4)}$$

The term $k_{L,iC4}\, a_v$ in the equation A.3 is the mass transfer term. This constant term was assumed to be a constant value, $2000 s^{-1}$.

The concentration of isobutane in the hydrocarbon phase is calculated from reactant feed flow rate. The concentration of isobutane in hydrocarbon phase is equal to the molar flow rate of isobutane divided by the volumetric flow rate of hydrocarbon.

The rate of isobutane consumption is calculated from component mass balance in the reactor. This rate value is equal to the rate of consumption of isobutane divided by volume of acid in the reactor

The volume of acid in the reactor can be determined by the definition of olefin space velocity. Olefin space velocity is defined as the volume of olefin charged per hour divided by the volume of acid in reactor.

Olefin Concentration in Acid Phase

Since olefins are well solvated by acid phase, their concentrations in the acid phase would be proportional to their concentrations in the feed (Langley, 1969). Thus the olefin concentration in acid phase was assumed to be:

$$[Olefin]_{acid} = constant[Olefin]_{feed} \qquad \text{(A.5)}$$

The constant term is $1^* 10^{-8}$ (Langley and Pike, 1972). This was found to change with the temperature. By regressing the constant value with the operating temperature, the correlated equation for this constant is as follows (Vichailak, 1995):

$$(constant)=1^* 10^{-8} (18.935742-2.774266\, T + 0.159883\, T^2 - 0.003993\, T^3 + 0.000036\, T^4) \qquad \text{(A.6)}$$

The olefin concentration in feed can be determined from a mass balance equation, similar to that used for isobutane. At steady state, the rate of formation of paraffin (i) in the acid phase must equal to the rate of its mass transfer out of the acid phase.

$$k_{L,Ci} a_V [C_{Ci,a} - (C_{Ci,a})] = (r_{Ci})_a Ha \tag{A.7}$$

or

$$k_{L,Ci} a_V [C_{Ci,a} - K_{d,Ci} C_{Ci,h}] = (r_{Ci})_a Ha \tag{A.8}$$

By rearranging equation A.8, the concentration of isobutane in the acid phase can be

$$C_{Ci,a} = K_{d,Ci} C_{Ci,h} + \frac{(r_{Ci})_a Ha}{k_{L,Ci} a_V} \tag{A.9}$$

expressed as:

The term $K_{d,Ci}$ is the distribution coefficient for paraffin (i). Since only data on the solubility for isobutane in sulfuric acid is available in literature, a relationship must be assumed between the solubilities of paraffins(i) in the acid phase and that of isobutane. As a general rule, the higher the molecular weight of a hydrocarbon, the less soluble it is in water. This should also hold for sulfuric acid, since it is an aqueous medium, but not necessarily in the same proportion as for water (Langley and Pike, 1972). Therefore, the concentration of paraffin (i) in acid phase at equilibrium can be considered to be a function of its molecular weight. Thus, the distribution coefficient for other paraffins (i) can be estimated by the following equation:

The value of the mass transfer coefficient for other paraffins (i), $k_{L,Ci}\ a_v$, is taken

$$K_{d,Ci} = \frac{K_{d,C_{iC4}} \times MW_{iC4}}{MW_{Ci}} \tag{A.10}$$

to be 2000 s^{-1} which is equal to the mass transfer coefficient for isobutane, since no other data is available.

Ionic Intermediate Concentration in the Catalyst Phase

The molar concentrations of carbonium ions in the acid phase can be considered to be a function of the molar concentrations of their parent molecules in acid phase.

$$[C_i^+ X^-]_a = f([C_i]_a) \tag{A.11}$$

The relationship between the molar concentration of the carbonium ions and the molar concentration of their parent molecules used in this study is a simple proportional relationship. Thus, the above equation becomes:

$$[C_i^+ X^-]_a = z([C_i]_a) \tag{A.12}$$

The constant, z, used in this study is $1x10^{-7}$ (Langley and Pike, 1972).

Olefinic Intermediate Concentration in Acid Phase

The concentrations of olefinic intermediates in acid phase depend on the concentrations of the intermediates from which they were formed and the products they form. From the propylene-isobutane alkylation reaction model in Table 2.1, there are three olefinic intermediates involved: iso-butylene ($iC_4^=$), iso-pentylene ($iC_5^=$) and iso-heptylene ($iC_7^=$). The concentrations of these olefinic intermediates are calculated by using the above assumption.

1. Iso-butylene concentration in the acid phase

The reaction involving the formation of iso-butylene is:

$$iC_4^+X^- \rightarrow iC_4^= + HX \tag{A.13}$$

$$[iC_4^=]_a = f([iC_4^+ X^-]_a) \tag{A.14}$$

So, the iso-butylene concentration should be a function of the isobutane carbonium ion.

The consumption of iso-butylene is:

$$iC_4^+X^- + iC_4^= \rightarrow iC_8^+X^- \qquad \text{(A.15)}$$

But the only reaction involved for the iso-octane carbonium ion is:

$$iC_8^+X^- + iC_4^= \rightarrow iC_8 + iC_4^+X^- \qquad \text{(A.16)}$$

Thus it would seem that the concentration of iso-octane is a function of iso-butylene:

$$[iC_8]_a = f([iC_4^=]_a) \qquad \text{(A.17)}$$

But the concentration of iso-octane has been determined by the mass transfer equation, so equation A.14 can be arranged to:

$$[iC_4^=]_a = f([iC_8]_a \qquad \text{(A.18)}$$

From equations A.14 and A.18, the simplest functional form to determine the concentration of iso-butylene is a proportion. So the form to be used for the concentration

$$[iC_4^=]_a = (Y_{iC8})[iC_4^+X^-]_a \qquad \text{(A.19)}$$

of iso-butylene is:

Where Y_{iC8} is the mole fraction of octane in the reaction product (excluding isobutane). Concentrations of the other olefinic intermediates may be derived in a similar way.

2. Iso-pentylene concentration in the acid phase

The reaction forming iso-pentylene is:

$$iC_7^= + iC_4^+X^- \rightarrow iC_5^= + iC_6^+X^- \qquad \text{(A.20)}$$

and

$$iC_{10}^{+}X^{-} \rightarrow iC_5^{=} + iC_5^{+}X^{-} \quad \text{(A.21)}$$

Thus, the concentration of iso-pentylene is a function of the concentrations of isodecane carbonium ion and iso-heptylene.

The consumption of iso-pentylenes is given by:

$$[iC_5^{=}]_a = f([iC_7^{=}]_a + [iC_{10}^{+}X^{-}]_a) \quad \text{(A.22)}$$

$$iC_5^{=} + HX \rightarrow iC_5^{+}X^{-} \quad \text{(A.23)}$$

$$iC_4 + iC_5^{+}X^{-} \rightarrow iC_5 + iC_4^{+}X^{-}$$

$$iC_5^{=} + iC_4^{+}X^{-} \rightarrow iC_9^{+}X^{-} \quad \text{(A.24)}$$

$$iC_4 + iC_9^{+}X^{-} \rightarrow iC_9 + iC_4^{+}X^{-}$$

and

Thus, the concentration of iso-pentylene is a function of isopentane and isononane:

$$[iC_5^{=}]_a = f([iC_5]_a + [iC_9]_a) \quad \text{(A.25)}$$

So, the equation for calculating the iso-pentylene is:

$$[iC_5^{=}]_a = (Y_{iC5} + Y_{iC9})([iC_7^{=}]_a + [iC_{10}^{+}X^{-}]_a) \quad \text{(A.26)}$$

3. Iso-heptylene concentration in the acid phase

The reaction forming iso-heptylene is:

$$iC_7^{+}X^{-} \rightarrow iC_7^{=} + HX \quad \text{(A.27)}$$

Thus the concentration of iso-heptylene is:

The consumption of iso-heptylene is:

$$[iC_7^{=}]_a = f([iC_7^{+}X^{-}]_a) \quad \text{(A.28)}$$

$$iC_7^{=} + iC_4^{+}X^{-} \rightarrow iC_5^{=} + iC_6^{+}X^{-} \quad \text{(A.29)}$$

The other reactions involved for iso-pentylene and isohexane carbonium ions are:

$$iC_5^{=} + HX \rightarrow iC_5^{+}X^{-}$$

$$iC_4 + iC_5^{+}X^{-} \rightarrow iC_5 + iC_4^{+}X^{-} \quad \text{(A.30)}$$

$$[iC_7^{=}]_a = f([iC_5]_a + [iC_6]_a + [iC_9]_a) \quad \text{(A.31)}$$

$$iC_5^{=} + iC_4^{+}X^{-} \rightarrow iC_9^{+}X^{-}$$

$$iC_4 + iC_9^{+}X^{-} \rightarrow iC_9 + iC_4^{+}X^{-}$$

$$iC_4 + iC_6^{+}X^{-} \rightarrow iC_6 + iC_4^{+}X^{-}$$

From the above reactions, it can be concluded that iso-heptylene is a function of isopentane, isohexane and isononane:

From Equations (A.20) and (A.21), the concentration of iso-heptylene is:

$$[iC_7^{=}]_a = (Y_{iC5} + Y_{iC6} + Y_{iC9})([iC_7^{+}X^{-}]_a) \quad \text{(A.32)}$$

In the butylene-isobutane alkylation model, the olefinic intermediates involved are iso-butylene ($iC_4^{=}$), isopentylene ($iC_5^{=}$), and iso-octylene ($iC_8^{=}$). The concentrations of these olefinic intermediates are calculated using the above assumptions.

4. Iso-butylene concentration in the acid phase

$$iC_4^+X^- \rightarrow iC_4^= + HX \tag{A.33}$$

The reaction forming iso-butylene is:

The consumption of iso-butylene is:

$$\begin{aligned} iC_4^+X^- + iC_4^= &\rightarrow iC_8^+X^- \\ iC_8^+X^- + iC_4 &\rightarrow iC_8 + iC_4^+X^- \end{aligned} \tag{A.34}$$

Thus, the equation used to calculate the concentration of iso-butylene is:

$$[iC_4^=]_a = (Y_{iC8})[iC_4^+X^-]_a \tag{A.35}$$

5. Iso-pentylene concentration in the acid phase

The reactions forming iso-pentylene are:

$$iC_8^= + iC_4^+X^- \rightarrow iC_5^= + iC_7^+X^- \tag{A.36}$$

and

$$iC_{11}^+X^- \rightarrow iC_5^= + iC_6^+X^- \tag{A.37}$$

The consumption of iso-pentylene is according to the reactions:

$$\begin{aligned} iC_5^= + HX &\rightarrow iC_5^+X^- \\ iC_4 + iC_5^+X^- &\rightarrow iC_5 + iC_4^+X^- \end{aligned} \tag{A.38}$$

$$iC_5^{=} + iC_4^{+}X^{-} \rightarrow iC_9^{+}X^{-} \quad \text{(A.39)}$$
$$iC_4 + iC_9^{+}X^{-} \rightarrow iC_9 + iC_4^{+}X^{-}$$

and

So, the equation for calculating the iso-pentylene concentration is:

$$[iC_5^{=}]_a = (Y_{iC5} + Y_{iC9})([iC_8^{=}]_a + [iC_{11}^{+}X^{-}]_a) \quad \text{(A.40)}$$

6. Iso-octylene concentration in the acid phase

The reaction forming iso-octylene is:

$$iC_8^{+}X^{-} \rightarrow iC_8^{=} + HX \quad \text{(A.41)}$$

The consumption of iso-octylene is:

$$iC_8^{=} + iC_4^{+}X^{-} \rightarrow iC_5^{=} + iC_7^{+}X^{-} \quad \text{(A.42)}$$

The other reactions involved for iso-pentylene and isoheptane carbonium ions are:

$$iC_5^{=} + HX \rightarrow iC_5^{+}X^{-} \quad \text{(A.43)}$$
$$iC_4 + iC_5^{+}X^{-} \rightarrow iC_5 + iC_4^{+}X^{-}$$
$$iC_5^{=} + iC_4^{+}X^{-} \rightarrow iC_9^{+}X^{-}$$
$$iC_4 + iC_9^{+}X^{-} \rightarrow iC_9 + iC_4^{+}X^{-}$$
$$iC_4 + iC_7^{+}X^{-} \rightarrow iC_7 + iC_4^{+}X^{-}$$
$$C_4^{=} + iC_7^{+}X^{-} \rightarrow iC_{11}^{+}X^{-}$$
$$iC_4 + iC_{11}^{+}X^{-} \rightarrow iC_{11} + iC_4^{+}X^{-}$$

The concentration of iso-octylene is:

$$[iC_8^{=}]_a = (Y_{iC5} + Y_{iC7} + Y_{iC9} + Y_{iC11})([iC_8^{+}X^{-}]_a) \quad \text{(A.44)}$$

In pentylene-isobutane alkylation model, The olefinic intermediates involved are iso-butylene ($iC_4^{=}$), iso-hextylene ($iC_6^{=}$) and iso-nonylene ($iC_9^{=}$). The concentrations of these olefinic intermediates are:

7. Iso-butylene concentration in acid phase

The reaction forming iso-butylene is:

$$iC_4^{+}X^{-} \rightarrow iC_4^{=} + HX \quad \text{(A.45)}$$

The consumption of iso-butylene is according to:

$$\begin{aligned} iC_4^{+}X^{-} + iC_4^{=} &\rightarrow iC_8^{+}X^{-} \\ iC_8^{+}X^{-} + iC_4 &\rightarrow iC_8 + iC_4^{+}X^{-} \end{aligned} \quad \text{(A.46)}$$

Thus, the concentration of iso-butylene can be calculated as:

$$[iC_4^{=}]_a = (Y_{iC8})[iC_4^{+}X^{-}]_a \quad \text{(A.47)}$$

8. Iso-hextylene concentration in the acid phase

The reaction forming iso-hextylene is:

$$iC_9^{=} + iC_4^{+}X^{-} \rightarrow iC_6^{=} + iC_7^{+}X^{-} \quad \text{(A.48)}$$

The reactions consuming iso-hextylene are:

$$\begin{aligned} iC_6^{=} + HX &\rightarrow iC_6^{+}X^{-} \\ iC_4 + iC_6^{+}X^{-} &\rightarrow iC_6 + iC_4^{+}X^{-} \\ C_5^{=} + iC_6^{+}X^{-} &\rightarrow iC_{11}^{+}X^{-} \\ iC_4 + iC_{11}^{+}X^{-} &\rightarrow iC_{11} + iC_4^{+}X^{-} \end{aligned} \quad \text{(A.49)}$$

Thus, the concentration of iso-hextylene can be calculated as:

$$[iC_6^{=}]_a = (Y_{iC6} + Y_{iC11})([iC_9^{=}]_a) \tag{A.50}$$

9. Iso-nonylene concentration in the acid phase

The reaction forming iso-nonylene is:

$$iC_9^{+}X^{-} \rightarrow iC_9^{=} + HX \tag{A.51}$$

The consumption of iso-nonylene is:

$$iC_9^{=} + iC_4^{+}X^{-} \rightarrow iC_6^{=} + iC_7^{+}X^{-} \tag{A.52}$$

The other reactions involved for iso-hextylene and isoheptane carbonium ions are:

$$\begin{aligned} &iC_6^{=} + HX \rightarrow iC_6^{+}X^{-} \\ &iC_4 + iC_6^{+}X^{-} \rightarrow iC_6 + iC_4^{+}X^{-} \\ &iC_4 + iC_7^{+}X^{-} \rightarrow iC_7 + iC_4^{+}X^{-} \\ &C_5^{=} + iC_7^{+}X^{-} \rightarrow iC_{12}^{+}X^{-} \\ &iC_4 + iC_{12}^{+}X^{-} \rightarrow iC_{12} + iC_4^{+}X^{-} \end{aligned} \tag{A.53}$$

The concentration of iso-nonylene is:

$$[iC_9^{=}]_a = (Y_{iC6} + Y_{iC7} + Y_{iC12})([iC_9^{+}X^{-}]_a) \tag{A.54}$$

By following the above procedure, concentrations of all the species in the acid phase were obtained. Substituting these concentrations into the rate equations in Tables 2.1, and 2.2, reaction rates were determined.

Estimation of Concentrations of the contactor components

The concentrations of the contactor components in the acid phase are calculated using the equations in Table 2.2 given the following concentrations

Acid Concentration:

$$C_{C623}^{HX} = \frac{\rho_{AC09} x_{AC09}^{11}}{MW^{11}}$$

Isobutane Concentration:

$$C_{C623}^{3} = \frac{\rho_{AC09} x_{AC09}^{3}}{MW^{3}}$$

Butene Concentration:

$$C_{C623}^{2} = \frac{\rho_{AC09} x_{AC09}^{2}}{MW^{2}}$$