Single Event Kinetic Modeling of Hydrocracking Process

Hemendra Khakhar
Gilbert Froment
Texas A & M University

- **Objectives:**

  - **Better balance of gasoline & distillate production**
  - **Greater gasoline yield.**
  - **Improved gasoline pool octane quality**
  - **Supplement FCC to upgrade heavy cracking stocks, aromatics, cycle oils and cocker oils to gasoline, jet fuels & light fuel oils.**
  - **Relative high amount of isobutane production in butane fraction.**

- **Industrial proces:**

- **Feed:**
  - **Vacuum gas oil**
  - **Coker gas oil**
  - **LCO / HCO**

- **Products: Naphtha, jet fuel, diesel, distillates**

- **Operating conditions: 290-400^{0}C , 80-140 atm**

- **Type of reactor :**
  - **Fixed bed reactor**
  - **Single stage / two stage**
  - **Once through / recycling**

- **Bifunctional Catalyst:**

- **Acidic function:**
  - **Amorphous oxide (SiO2/Al2O3)**
  - **zeolites**

- **Metal function:**
  - **Noble metals (Pt / Pd)**
  - **Non Noble metals (Mo ,Co ,Ni etc.)**

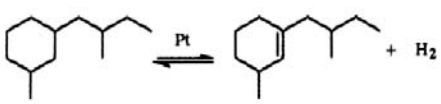
- **Cracking function activity :**

  Zeolite > Si/Al_2O_3 > Al_2O_3 – halogen > Al_2O_3

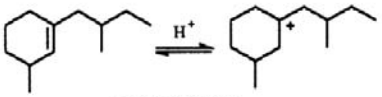
- **Hydrogenation function activity :**

  Pt (Pd) > Ni/W > Ni/Mo > Co / Mo

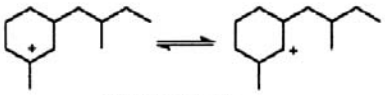
ELEMENTARY STEPS IN HYDROCRACKING



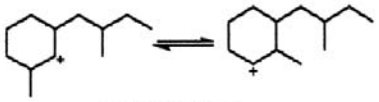
DEHYDROGENATION



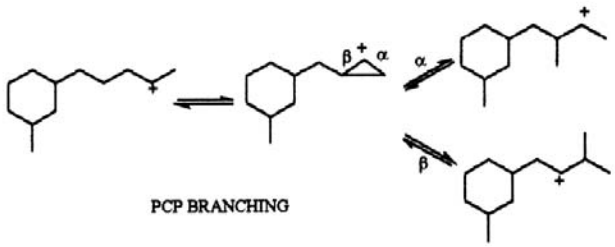
PROTONATION



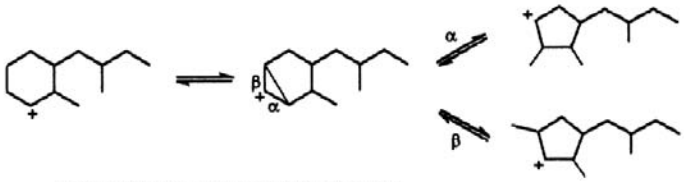
HYDRIDE SHIFT



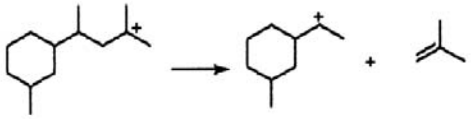
METHYL SHIFT



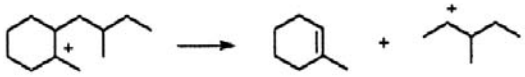
PCP BRANCHING



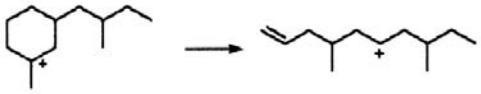
RING CONTRACTION / RING EXPANSION



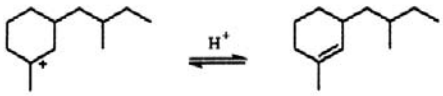
ACYCLIC β - SCISSION



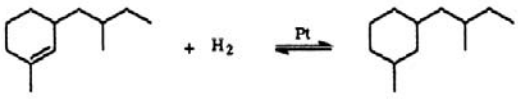
EXOCYCLIC β - SCISSION



ENDOCYCLIC β - SCISSION



DEPROTONATION



HYDROGENATION

- **Kinetic Modeling:**

- **Why ??**

  - **Simulation & Optimization of industrial process**
  - **Design of fixed bed industrial reactors**
  - **Extraction of kinetic data**

1. Three lump model :

Lumps: Gas Oil
Gasoline
Coke + Light Gases

2.Ten Lump Model:

Lumps :G – Gasoline
C – Coke + C_1-C_4 Gases
P – Paraffins
N – Naphthenes
AR – Aromatic ring
AS – Aromatic substituent group
l – low boiling fraction
h – heavier fraction

- **Features:**
  - **Rate coefficient varies with type of Gas Oil**
  - **Extensive experimentation required to characterize gas oil**

Single Event Kinetics

- **Why ??**
  - **Rate of Hydrocracking increase with chain length**
  - **Separate experimental work required for different feeds**
  - **Model depends on reactor configuration**

- **Features:**
  - **Rate parameters invariant with respect to chain length**
  - **Reduction of # of rate parameters to realistic amount**
  - **Independent of type of reactor or type of feed**

- **How it works ???**

- **Effect of structure on ΔS $\longrightarrow$ Single Event Kinetics**
- **Effect of structure on ΔH $\longrightarrow$ Evans Polanyi Relation**

- **Transition State Theory:**

$$k' = \left(\frac{k_b T}{h}\right) \exp\left(\frac{\Delta S^0}{R}\right) \exp\left(\frac{-\Delta H^0}{RT}\right)$$

$$\text{where, } S^0 = S^0_{trans} + S^0_{vib} + S^0_{rot} + S^0_{ele} + S^0_{sym}$$

$$\therefore S^0 = S^0_{intr} - R\ln\left(\sigma_{gl}\right)$$

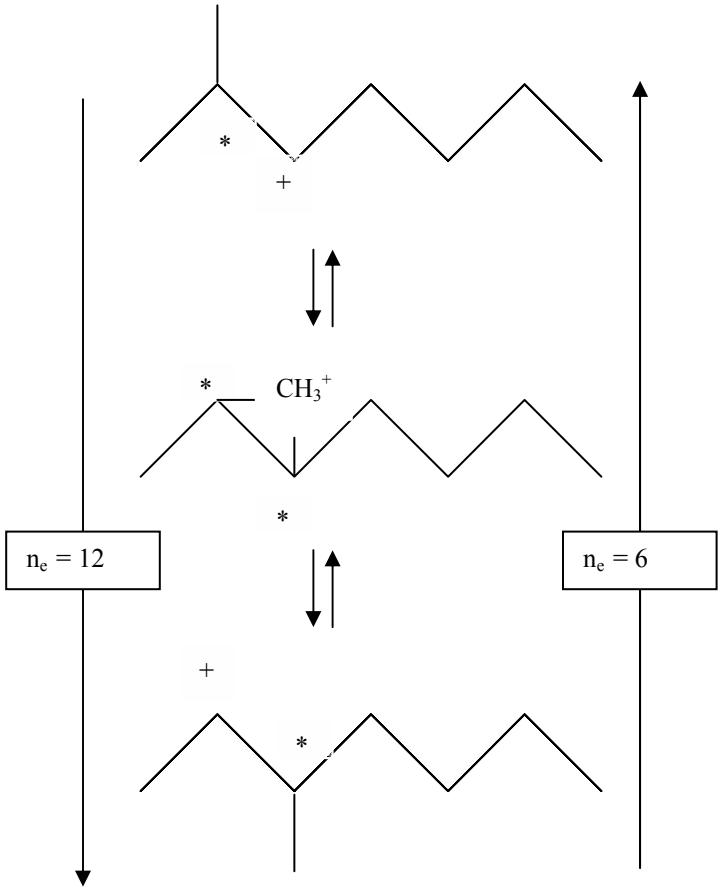
$$\therefore \Delta S^0 = \Delta S^0_{intr} + R\ln\left(\frac{\sigma_{glr}}{\sigma_{gla}}\right)$$

$$\therefore k' = \left(\frac{\sigma_{glr}}{\sigma_{gla}}\right)\left(\frac{k_b T}{h}\right) \exp\left(\frac{\Delta S^0_{intr}}{R}\right) \exp\left(\frac{-\Delta H^0}{RT}\right)$$

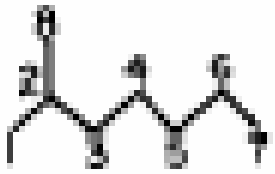
$$\text{where, } \sigma_{gl} = \frac{\sigma}{2^n} \;\&\; n_e = \left(\frac{\sigma_{glr}}{\sigma_{gla}}\right)$$

$$\therefore k' = n_e k$$

HOW TO DETERMINE NO. OF SINGLE EVENTS



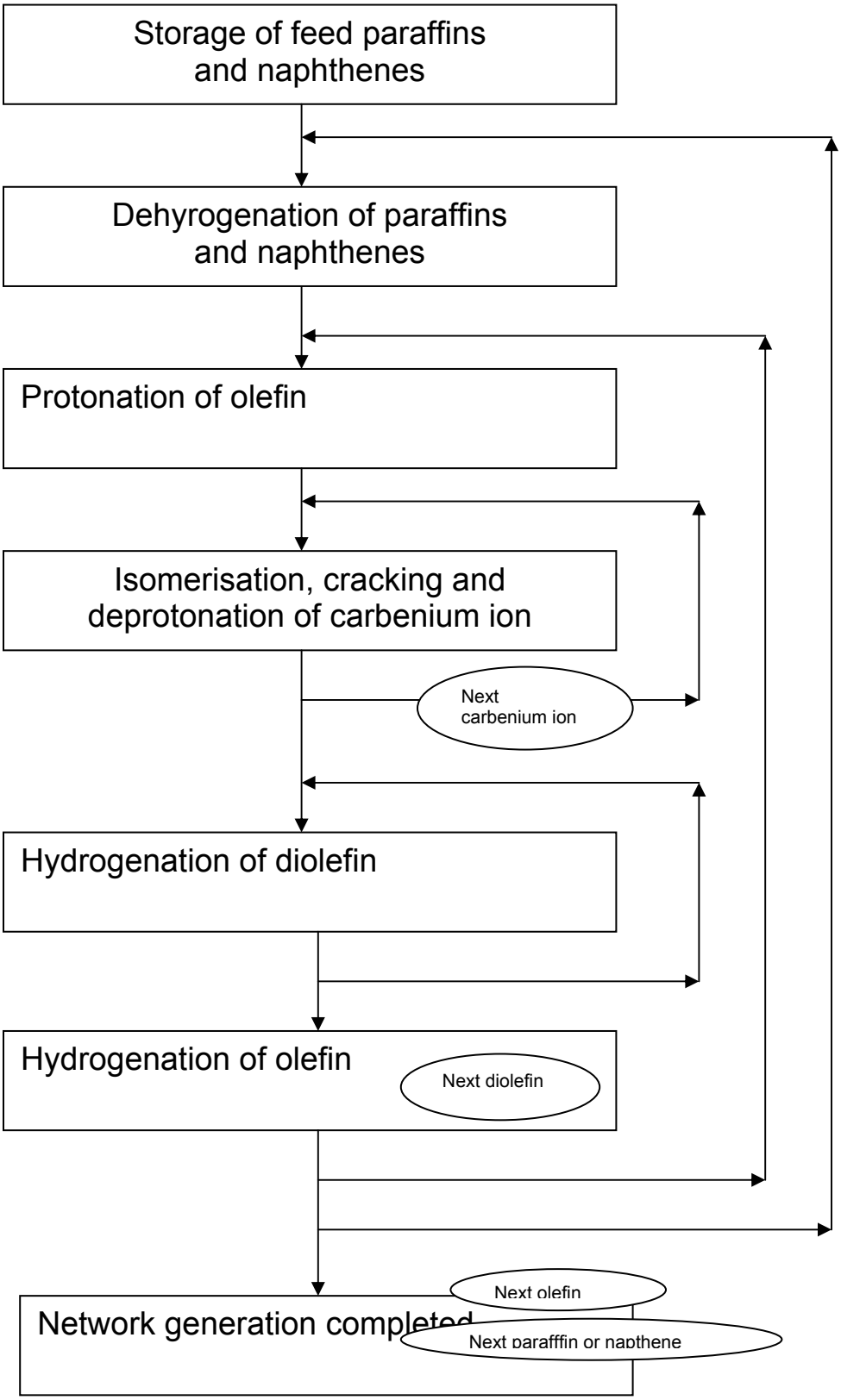
CHARACTERIZATION OF SPECIES
(BOOLEAN MATRICES AND AUXILIARY VECTORS)



$$m_0 \begin{cases} -0 & \text{no C–C bond exists between carbon atoms } i \text{ and } j \\ -1 & \text{a C–C bond exists between carbon atoms } i \text{ and } j. \end{cases}$$

$$M = \begin{array}{c|cccccccc} & 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ \hline 1 & & 1 & & & & & & \\ 2 & & & & & & & & 1 \\ 3 & & & & 1 & & 1 & & \\ 4 & & & 1 & & 1 & & & \\ 5 & & & & 1 & & 1 & & \\ 6 & & & & & 1 & & 1 & \\ 7 & & & & & & 1 & & \\ 8 & & 1 & & & & & & \end{array}$$

NETWORK GENERATION ALGORITHM



NETWORK GENERATION FOR n-OCTANE

- **Mechanism:**

Reaction network generation for Hydrocracking:

- **Feed: n – Octane**

Species: 14 Octanes
5 Paraffinic products
9 olefinic products
49 Octenes
42 Octyl Carbenium ions
6 Carbenium ions with small Carbon no.

- **Total Reactions: 383**

- **Protonation - 75**
- **Deprotonation - 85**
- **Hydride Shift - 88**
- **Methyl Shift - 24**
- **PCP Branching - 96**
- **B – Scission - 15**

- **Characterization of Molecules / Carbenium Ions :**

- **Boolean Matrices (A_{ij})**
- **Auxiliary Vectors:**
- **Three Rows :**
  - **1: Charged / Uncharged**
  - **2: Nature of carbon atom (p/s/t/)**
  - **3: Type of carbon atom**

- **Assumptions:**
  1. **Methyl and primary carbenium ions are so unstable that they can be disregarded in the construction of reaction networks.**
  2. **For Isomerisation single events, only the type of carbenium ion (s or t) not the identity (# of carbon atoms) determines its activity.**
  3. **The rate coefficient of protonation is independent of the olefin.**
  4. **Rate coefficient of deprotonation is independent of the no. of carbon atoms from C_5 onwards.**
  5. **The rate coefficient of cracking is independept of olefin.**
  6. **Rate determining Step occurs on acid sites .**
  7. **Hydrogenation and dehydrogenation steps are in equillibrium.**

- **Reduction of # of Single Event Rate Coefficients:**

1.Thermodynamic Constraint

Deprotonation:

$$k_{De}(m;O_{ij}) = k_{De}(m;O_r)\, k_{isom}(O_r \Leftrightarrow O_j)$$

Isomerisation:

$$\frac{k_{HS}(t;s)}{k_{HS}(s;t)} = \frac{k_{MS}(t;s)}{k_{MS}(s;t)} = \frac{k_{PCP}(t;s)}{k_{PCP}(s;t)} = \frac{k_{Pr}(s)}{k_{Pr}(t)} \frac{k_{De}(t;O_j)}{k_{De}(s;O_j)}$$

2.Evans Polanyi Relation:

$$E_a = E_0 - \alpha|\Delta H_r| \quad \text{.....Exothermic Reaction}$$

$$E_a = E_0 + (1-\alpha)|\Delta H_r| \quad \text{.....Endothermic Reaction}$$

Parameters: E_0 = **Intrinsic Activation Energy**

α = **Transfer Coefficient**

Rate Equations :

$$P_i \Leftrightarrow O_{ij} + H_2$$

$$R_{Pi} = \sum_j [\, k_H(ji)\, C_{Oij} P_{H2} - k_{DH}(ij)\, C_{Pi} \,] \quad \ldots.(1)$$

$$O_{ij} + H^+ \Leftrightarrow \left\{ \begin{matrix} R^+ij,m_1 \\ R^+ij,m_2 \end{matrix} \right\} ; \qquad R_v^+ \rightarrow O_{ij} + R_w^+$$

$$R_{Oij} = k_{DH}(ij) C_{Pi} - k_H(ji) C_{Oij} p_{H2}$$
$$+ k_{De}(m_1, O_{ij}) C_{R^+_{ij,m_1}} + k_{De}(m_2, O_{ij}) C_{R^+_{ij,m_2}}$$
$$- [k_{Pr}(m_1) + k_{Pr}(m_2)\,] C_{Oij} C_{H^+} + k_{Cr}(v; w, O_{ij}) C_{R_v^+} = 0 \quad \ldots..(2)$$

At Pseudo Steady State: $R_{Oij} = 0$

If RDS is on acid sites,

$$R_{Pi} = \sum_j \{\, k_{De}(m_1, O_{ij}) C_{R^+_{ij,m_1}} + k_{De}(m_2, O_{ij}) C_{R^+_{ij,m_2}}$$
$$- [k_{Pr}(m_1) + k_{Pr}(m_2)\,] C_{Oij} C_{H^+} + k_{Cr}(v; w, Oij) C_{R_v^+} \,\} \quad \ldots...(3)$$

$$R_{R_m^+} = \{\sum_O k_{Pr}(m) C_O C_{H^+} + \sum_q k_{HS}(q;m) C_{R_q^+} + \sum_r k_{MS}(r;m) C_{R_r^+} + \sum_u k_{PCP}(u;m) C_{R_u^+} + \sum_v$$

$$-\{\sum_O k_{De}(m;O) + \sum_q k_{HS}(m;q) + \sum_r k_{MS}(m;r) + \sum_u k_{PCP}(m;u) + \sum_z k_{Cr}(m;z,O')\} C_{R_m^+}$$

At Pseudo Steady State: $R_{R_m^+} = 0$

Site Balance: $C_t = C_{H^+} + \sum_m C_{R_m^+}$

Dehydrogenation: $CO_{ij} = \dfrac{C_{Pi} K_{DHij}}{p_{H2}}$

Langmuir Adsorption: $C_{Pi} = \dfrac{C_{s,sat} K_{L,i} p_i}{1 + \sum_m K_{L,m} p_m}$

$$\therefore CO_{ij} = \frac{C_{s,sat} K_{L,i} K_{DHij} p_i}{p_{H2}(1 + \sum_m K_{L,m} p_m)}$$

- **Final Rate Coefficients:**

Elementary Step	Rate Coefficients	#
K_{Pr}	$(O_j;s)$, $(O_j;t)$	2
K_{De}	$(s;O_j)$, $(t;O_j)$	2
K_{HS}	(s;s),(s;t),(t;s),(t;t)	3
K_{MS}	(s;s),(s;t),(t;s),(t;t)	3
K_{PCP}	(s;s),(s;t),(t;s),(t;t)	3
K_{Cr}	$(s; s,O_j)$, $(s; t,O_j)$	4

- **Equillibrium Constants:**
  Benson group contribution method
- **# Of single Events & ΔH_r :**
  Quantum Chemical Packages
  (MOPAC, GAMESS, GAUSSIAN)