Process Chemistry of Petroleum Macromolecules

First Day

1. Characterization of Heavy Oils
   a. Class Separation: Saturates, Aromatics, Resins, Asphaltenes, & Coke
   b. Properties of Classes
   c. Measurement of Asphaltene Molecular Weight
   d. Concept of Asphaltenes
   e. Solvent-Resid Phase Diagram
   f. Scattering Data on Classes
      A. Evidence of Asphaltene Colloid
      B. Evidence of Asphaltene Association
   g. High Performance Liquid Chromatography (HPLC)
      A. Prep Separation of Heavy Coker Gas Oil (HKGO)
      B. Representative HKGO Structures
      C. Prep Separation of Distact Cut of Arabian Heavy Vac Resid

2. Pendant-Core Building Block Model of Petroleum
   a. Approximation to Distribution of Heavy Oil Molecules
   b. Model for Conradson Carbon Residue (CCR)
      A. Related to Hydrogen Content
      B. Evidence of Constant Core and Pendant
      C. Effect of Molecular Weight
      D. Elemental Analysis of CCR (Cores)
      E. Elemental Analysis of Distillable Liq Products (Pendants)
      F. Variation with Processing
   c. Pendant-Core Model Compounds: Discotic Liquid Crystals
      A. Model of CCR and Association
      B. Effect of Multiple Bonds
      C. Implication on CCR Conversion
   d. Future Needs for Building Block Models

3. Phase Behavior of Heavy Oils
   a. Causes of Incompatible Liquids
   b. Basic Features of Heavy Oil Phase Behavior
      A. Flocculation Point
      B. Asymptotic Quantity of Insolubles with Quant. of Nonsolvent
      C. Effect of n-Paraffin Nonsolvent Carbon Number
         i. Asymptotic Quantity of Insolubles
         ii. Maximum in Flocculation Point
   c. Effect of Temperature
      A. Live Oils
      B. Dead Oils
   d. Solubility Parameters
      A. Overall Solubility Parameter
      B. Two-Dimensional Solubility Parameters
         i. Values for Liquids
         ii. Solubility Map for Coal Liquid
         iii. Solubility Maps for Classes
iv. Primary Causes for Heavy Oil Insolubility

e. The Oil Compatibility Model
   A. Colloidal-Solution Hybrid Model of Petroleum
   B. Modes of Asphaltenes Fouling
   C. Flocculation Solubility Parameter
   D. Toluene-Heptane Scale
      i. Insolubility Number
      ii. Solubility Blending Number

E. Measurement of Compatibility Numbers

F. Prediction of Compatibility

G. Oil Compatibility Tests

H. Effect of Blending in Wrong Order

I. Pairs of Incompatible Crude Oils

J. Comparison with P-Test

K. Self-Incompatible Crude Oils

L. Solution to Hydrotreater Plugging Problem

   i. Determining Compatibility Numbers on Oils Without
      Asphaltenes
   ii. Range of Compatibility Numbers
   iii. Root Cause Analysis

M. Effect of n-Paraffin Nonsolvent Carbon Number

   i. Similar Size Solvents and Nonsolvents
   ii. Effective Solubility Parameter

N. Synthetic Asphaltenes Dispersants

f. Limitations and Future Developments in Phase Behavior

4. Separation of Heavy Oils

   a. Desalting
      A. Causes and Mitigation of Stable Oil-Water Emulsions
   b. Distillation
      A. Refinery Distillation
      B. Lab Distact Distillation
   c. Deasphalting
      A. Separation of Resins Fraction
      B. General Resids
      C. Separability of Cold Lake Bitumen
      i. CCR
      ii. Metals
      D. Lab Separability of Arab Heavy Vacuum Resid
      i. Cyclohexene-Attapulgus Clay of Resid
      ii. Cyclohexene-Attapulgus Clay of Visbroken Resid
      E. Molecular Limitations to Separation

5. Thermal Conversion Kinetics

   a. Desirable Attributes for Kinetic Model
   b. Pseudocomponent Model
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  - i. Effect of Resins/Asphaltene Ratio
  - ii. Effect of Metals Deposition on Catalyst

### f. Hydroconversion

- **Ebulated Bed**
  - i. Deposits in Separators
  - ii. IFP Study of Sediments

- **Dispersed Catalyst**
  - i. Formation of Catalyst
  - ii. Microcat-RC Process
  - iii. 90+ Conversion May Not be Optimum
  - iv. Learnings from Microcat Compatibility
  - v. Eni Slurry Technology

### g. Coking

- **Delayed Coking**
- **Fluid Coking**
- **Flexicoking**
- **Optimum Coking**
  - i. Undesirable Reactions
  - ii. Reduction of Secondary Cracking of Products
  - iii. Ideal Coking Potential: Yield vs. Quality
  - iv. Reduction of Feed Degradation

### h. Resid Conversion Can Be Improved

### i. Choosing Resid Process for a Refinery

### j. Heavy Oil Processing in the Future

### 7. Mitigation of Fouling

- **What is fouling?**
- **Fouling Analytical Strategy**
- **Diagnosis & Investigation of Fouling**
  - A. Most Common Causes
  - B. Process Conditions/History
  - C. Analysis of Foulant
  - D. Analysis of Oil
  - E. Evidence of Most Common Causes
- **Innovation & Mitigation**
  - A. Causes of Fouling Suggest Solutions
- **Case Study: Coker Fractionator Fouling**
  - A. Polymerization of Conjugated Olefins
  - B. Measurement of Diene Value
  - C. Mitigation
- **Engineering Methods of Fouling Mitigation**
- **Future Developments in Fouling Mitigation**