

HYSYS v8.8 Biocrude Hydrodeoxygenation Refinery Simulation

# **Simulation Structure: Input of Oxygenates into a HYSYS Hydrotreater Model**

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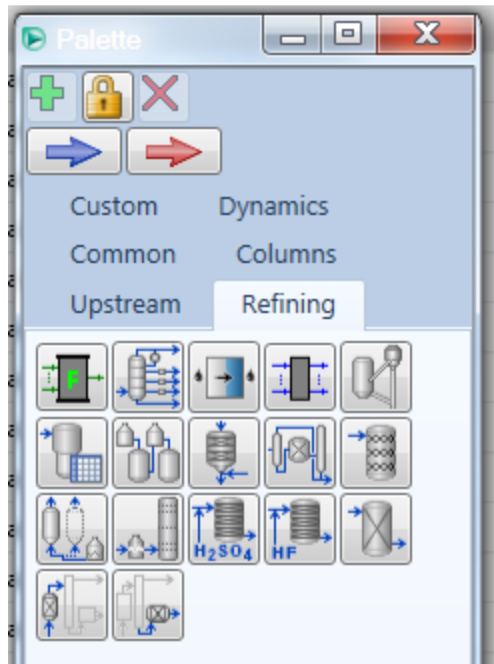
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# Overview of Slide Deck

- ▶ Explanation of why HYSYS was used
- ▶ HYSYS linkage to Aspen Properties
- ▶ Brief intro to setting up the HYSYS hydrotreater model
  - Setting up the petroleum stream assay for the conventional feed stream
  - Setting up the biocrude feed stream
  - Building the stoichiometric reaction set for the oxygenated components

# Why Aspen HYSYS® ?

- ▶ In general HYSYS has historically been used by refiners rather than Aspen Plus.
  - Specialized refinery reactor models have been and are continually being developed in HYSYS
  - Specialized pseudocomponent and property generation are in Aspen Properties, AspenPlus, and Aspen HYSYS



17 Specialized Petroleum unit operations in HYSYS including:

Petroleum Feeder, Petroleum distillation column, Assay manipulator, Product blender, Fluidized Catalytic Cracker, Petroleum shift reactor, Catalytic reformer, Hydrocracker, Isomerization, Hydroprocessor bed, Delayed coker, Visbreaker, H<sub>2</sub>SO<sub>4</sub> alkylation, HF alkylation, Naphtha hydrotreater, Catgas hydrotreater SHU, Catgas hydrotreater HDS

## However - Oxygenates are not handled in HYSYS

- ▶ Petroleum has virtually no oxygenates
- ▶ Hydrodeoxygenation is known to occur over conventional hydrotreating catalysts but oxygenated compounds are rare in petroleum; AspenTech has not (yet) added models or property operations to handle oxygenated feeds within HYSYS.
- ▶ In this simulation a conventional HYSYS stoichiometric reactor model is added to hydrotreat a few oxygenated compounds known to be in Biocrude (hydrothermal liquefaction product).
- ▶ The reactions extent is arbitrarily set to a fixed conversion but kinetics can be added to the reactors if known

## Aspen Physical Properties are required

- ▶ Most of the oxygenate physical properties are not in the HYSYS databank. They are found in Aspen or NIST databanks which can be accessed through linking HYSYS to Aspen Physical Properties. This cannot be done directly by HYSYS
- ▶ **Impact on token usage:**
  - This means 18 more tokens are checked out using this simulation as well as the “layered product” REFSYS (24 more tokens) refining system required for the HBED and other refinery reactor models (in the Refining section of the unit operation palette.
  - Thus this simulation requires HYSYS tokens (14) + Aspen Properties (18) + Aspen Refining System (24) = 56 tokens to run

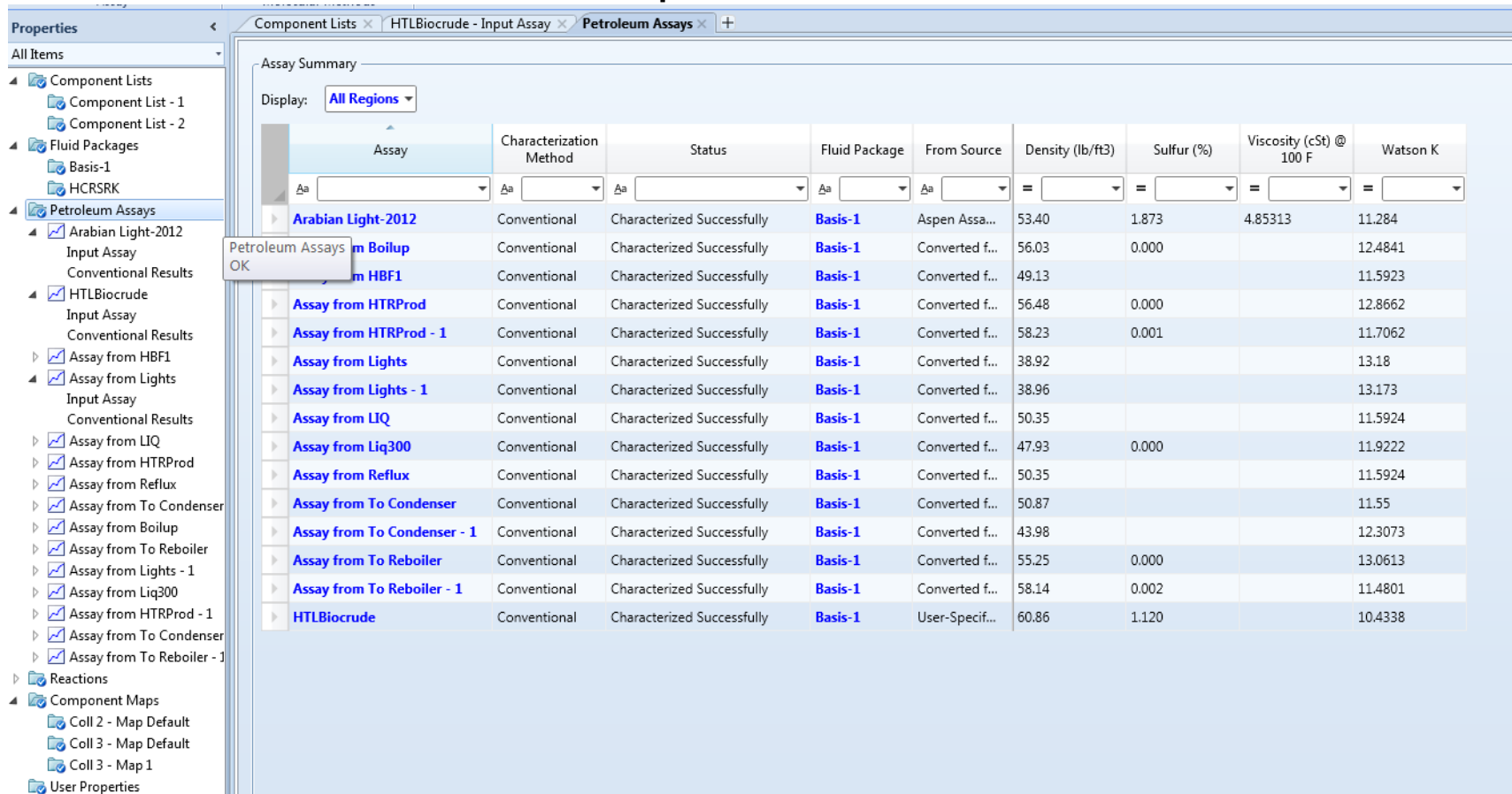
# Create the VGO Assay

- ▶ In Properties Mode
  - Select “Petroleum Assay” on left hand side of screen
  - Select “add assay” from bottom of the screen
  - Select “Middle East Region” (example used in model)
  
- ▶ Screen shots for this shown on next slide

# Set up VGO Assay

## ► Start in HYSYS Properties mode

- Select Petroleum Assays – for this case “Arabian Light 2012 was from the list options available.



The screenshot shows the HYSYS Properties window with the 'Petroleum Assays' tab selected. The 'Assay Summary' table is displayed, showing various assay data for different regions. The table includes columns for Assay, Characterization Method, Status, Fluid Package, From Source, Density (lb/ft³), Sulfur (%), Viscosity (cSt) @ 100 F, and Watson K.

Assay	Characterization Method	Status	Fluid Package	From Source	Density (lb/ft³)	Sulfur (%)	Viscosity (cSt) @ 100 F	Watson K
Arabian Light-2012	Conventional	Characterized Successfully	Basis-1	Aspen Assa...	53.40	1.873	4.85313	11.284
Assay from Boilup	Conventional	Characterized Successfully	Basis-1	Converted f...	56.03	0.000		12.4841
Assay from HBF1	Conventional	Characterized Successfully	Basis-1	Converted f...	49.13			11.5923
Assay from HTRProd	Conventional	Characterized Successfully	Basis-1	Converted f...	56.48	0.000		12.8662
Assay from HTRProd - 1	Conventional	Characterized Successfully	Basis-1	Converted f...	58.23	0.001		11.7062
Assay from Lights	Conventional	Characterized Successfully	Basis-1	Converted f...	38.92			13.18
Assay from Lights - 1	Conventional	Characterized Successfully	Basis-1	Converted f...	38.96			13.173
Assay from LIQ	Conventional	Characterized Successfully	Basis-1	Converted f...	50.35			11.5924
Assay from Liq300	Conventional	Characterized Successfully	Basis-1	Converted f...	47.93	0.000		11.9222
Assay from Reflux	Conventional	Characterized Successfully	Basis-1	Converted f...	50.35			11.5924
Assay from To Condenser	Conventional	Characterized Successfully	Basis-1	Converted f...	50.87			11.55
Assay from To Condenser - 1	Conventional	Characterized Successfully	Basis-1	Converted f...	43.98			12.3073
Assay from To Reboiler	Conventional	Characterized Successfully	Basis-1	Converted f...	55.25	0.000		13.0613
Assay from To Reboiler - 1	Conventional	Characterized Successfully	Basis-1	Converted f...	58.14	0.002		11.4801
HTLBiocrude	Conventional	Characterized Successfully	Basis-1	User-Specif...	60.86	1.120		10.4338



# Biocrude Assay (Manual Entry)

## ► References:

1. Co-processing potential of HTL bio-crude at petroleum refineries – Part 1: Fractional distillation and characterization; Jessica Hoffmann, Claus Uhrenholt Jensen, Lasse A. Rosendahl; Fuel 165 (2016) 526–535.
2. Co-processing potential of HTL bio-crude at petroleum refineries - Part 2: A parametric hydrotreating study; Claus Uhrenholt Jensen, Jessica Hoffmann, Lasse A. Rosendahl;

# Input HTL Biocrude Assay Manually

Properties														
Component Lists														
HTL Biocrude - Input Assay														
Arabian Light-2012 - Input Assay														
All Items														
Component Lists														
Fluid Packages														
Petrochemical Assays														
Arabian Light-2012														
Input Assay														
Conventional Results														
HTL Biocrude														
Input Assay														
Conventional Results														
Assay from HBF1														
Assay from Lights														
Input Assay														
Conventional Results														
Assay from LIQ														
Assay from HTRProd														
Assay from Reflux														
Assay from To Condenser														
Assay from Boilup														
Assay from To Reboiler														
Assay from Lights - 1														
Assay from Liq300														
Assay from HTRProd - 1														
Assay from To Condenser														
Assay from To Reboiler - 1														
Reactions														
Component Maps														
Coll 2 - Map Default														
Input Summary														
Pure Component														
Distillation Data														
Whole Crude														
Cut 1														
Cut 2														
Cut 3														
Cut 4														
Cut 5														
Cut 6														
Cut 7														
Cut 8														
Cut 9														
Cut 10														
Cut 11														
Cut 12														
Cut 13														
Initial Temperature (F)														
IBP														
Final Temperature (F)														
FBP														
CutYieldByWt (%)														
StdLiquidDensity (lb/ft3)														
SulfurByWt (%)														
KinematicViscosity (cSt)...														
ParaffinsByVol (%)														
NaphthenesByVol (%)														
AromaticsByVol (%)														
AromByVol (%)														
PourPoint (F)														
FreezePoint (F)														
CloudPoint (F)														
SmokePt (ft)														
NitrogenByWt (%)														
VanadiumByWt (%)														
ConradsonCarbonByWt...														
RONClear														
MONClear														

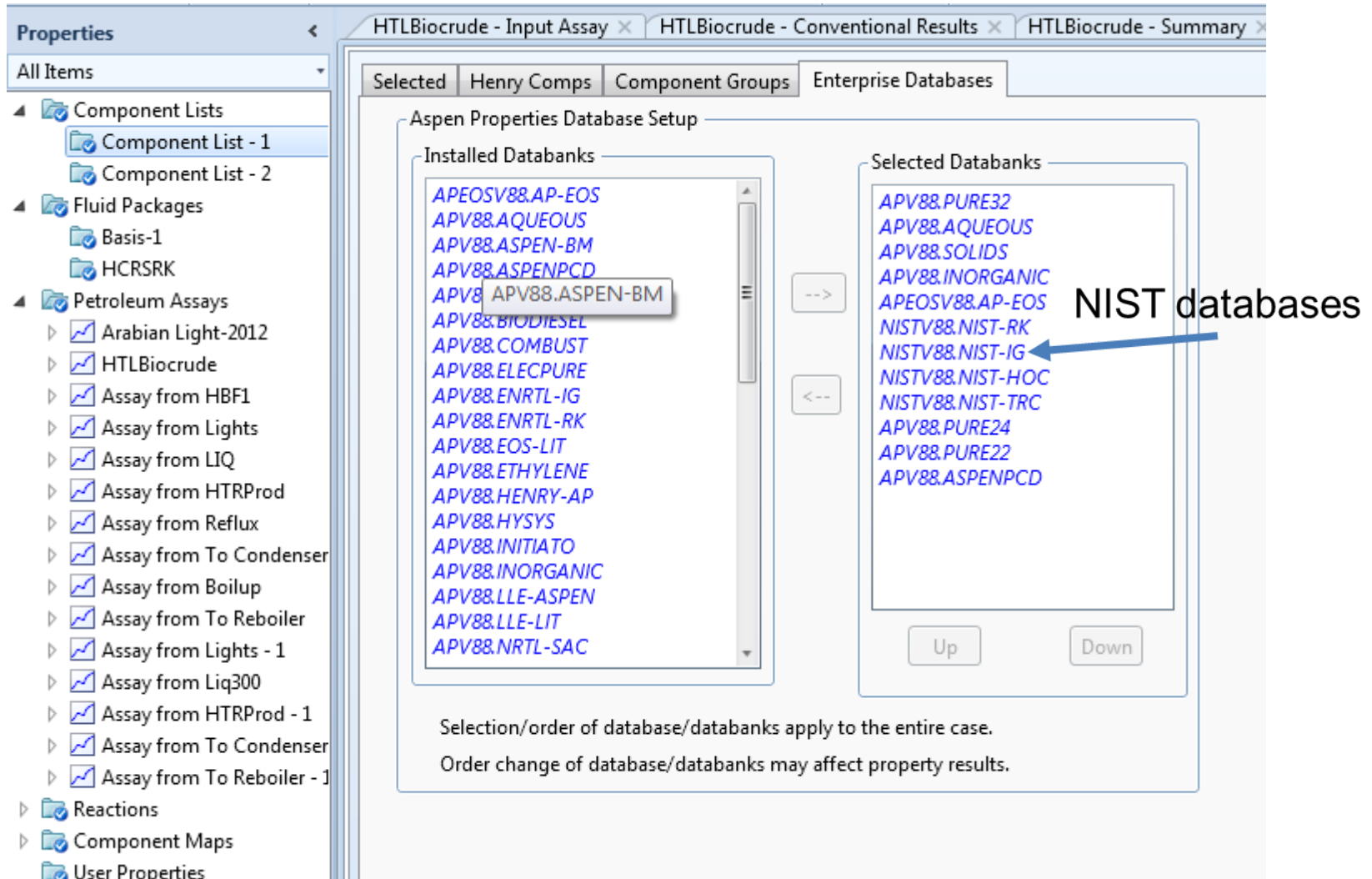
# Add the oxygenated test components listed below

- ▶ Make sure the NIST databases are listed in the Enterprise Database tab of the Components List Window
- ▶ Use “Find” not “Search” to add components
- ▶ Select the component immediately above where you want the new component to go in the list before adding a new component. **HYSYS will not let you reorder the components**

# Oxygenates & Products Used in the Simulation

- ▶ Compounds from Aspen Properties & NIST Databanks
  - Methyl-Ethyl-Ketone
  - Cyclopentanone
    - Cyclopentane
  - Benzyl-Ethyl-Ether
    - Ethylbenzene
  - P-Tert-Amylphenol
    - Tert-Pentylcyclohexane
  - Benzophenone
    - Benzylcyclohexane
  - P-Cumylphenol
    - 2-Phenyl-2-Cyclohexylpropane
  - Dioctyl-Phthalate
    - 3-Methylheptane
    - O-Xylene

# NIST Databases from component list tab



Properties < HTLBiocrude - Input Assay x HTLBiocrude - Conventional Results x HTLBiocrude - Summary >

All Items

- Component Lists
  - Component List - 1
  - Component List - 2
- Fluid Packages
  - Basis-1
  - HCRSRK
- Petroleum Assays
  - Arabian Light-2012
  - HTLBiocrude
  - Assay from HBF1
  - Assay from Lights
  - Assay from LIQ
  - Assay from HTRProd
  - Assay from Reflux
  - Assay from To Condenser
  - Assay from Boilup
  - Assay from To Reboiler
  - Assay from Lights - 1
  - Assay from Liq300
  - Assay from HTRProd - 1
  - Assay from To Condenser
  - Assay from To Reboiler - 1
- Reactions
- Component Maps
- User Properties

Selected Henry Comps Component Groups Enterprise Databases

Aspen Properties Database Setup

Installed Databanks

- APEOSV88.AP-EOS
- APV88.AQUEOUS
- APV88.ASPEN-BM
- APV88.ASPENPCD
- APV88.ASPEN-BM
- APV88.BIODIESEL
- APV88.COMBUST
- APV88.ELECPURE
- APV88.ENRTL-IG
- APV88.ENRTL-RK
- APV88.EOS-LIT
- APV88.ETHYLENE
- APV88.HENRY-AP
- APV88.HYSYS
- APV88.INITIATO
- APV88.INORGANIC
- APV88.LLE-ASPEN
- APV88.LLE-LIT
- APV88.NRTL-SAC

Selected Databanks

- APV88.PURE32
- APV88.AQUEOUS
- APV88.SOLIDS
- APV88.INORGANIC
- APEOSV88.AP-EOS
- NISTV88.NIST-RK
- NISTV88.NIST-IG
- NISTV88.NIST-HOC
- NISTV88.NIST-TRC
- APV88.PURE24
- APV88.PURE22
- APV88.ASPENPCD

Up Down

Selection/order of database/databanks apply to the entire case.  
Order change of database/databanks may affect property results.

NIST databases

# Adding p-tert-amylphenol to component list

Properties

HTLBiocrude - Input Assay x HTLBiocrude - Conventional Results x HTLBiocrude - Summary x Component List - 2 x **Component List - 1** +

Selected Henry Comps Component Groups Enterprise Databases

Source Databank: Aspen Properties

Component	Type	Group
13-Butadiene	Pure Component	
n-Butane	Pure Component	
cis2-Butene	Pure Component	
tr2-Butene	Pure Component	
i-Pentane	Pure Component	
1-Pentene	Pure Component	
2M-1-butene	Pure Component	
n-Pentane	Pure Component	
Methyl-Ethyl-Ketone	Pure Component	
Cyclopentanone	Pure Component	
Cyclopentane	Pure Component	
Benzyl-Ethyl-Ether	Pure Component	
Ethylbenzene	Pure Component	
P-Tert-Amylphenol	Pure Component	
Tert-Pentylcyclohexane	Pure Component	
Benzophenone	Pure Component	
Benzylcyclohexane	Pure Component	
P-Cumylphenol	Pure Component	
2-Phenyl-2-Cyclohexylp...	Pure Component	
Diethyl-Phthalate	Pure Component	
3-Methylheptane	Pure Component	
O-Xylene	Pure Component	
H2O	Pure Component	
36-40_1*	User Defined Hypothe...	HypoGroup3
40-50_1*	User Defined Hypothe...	HypoGroup3
50-60_1*	User Defined Hypothe...	HypoGroup3
60-70_1*	User Defined Hypothe...	HypoGroup3
70-80_1*	User Defined Hypothe...	HypoGroup3

**Use**

Find

Remove

Select: **Components** ← **Don't Use**

Search:

**Find Compounds**

Compounds

Search criteria

Compound name or alias

☐ begins with

☒ contains **p-tert-amylphenol**

☐ equals

Compound class : All

MW From To

TB From To K

Find now

New search

Help

Compounds found matching the specified criteria: 1

Compound na...	Alias	Alternate name	CAS ...	Databank	Compound class	M
P-TERT-AMYL...	C11...	p-tert-AMYP...	80-4...	APV88.PU...	AROMATIC-A...	16

Add selected compounds

Close

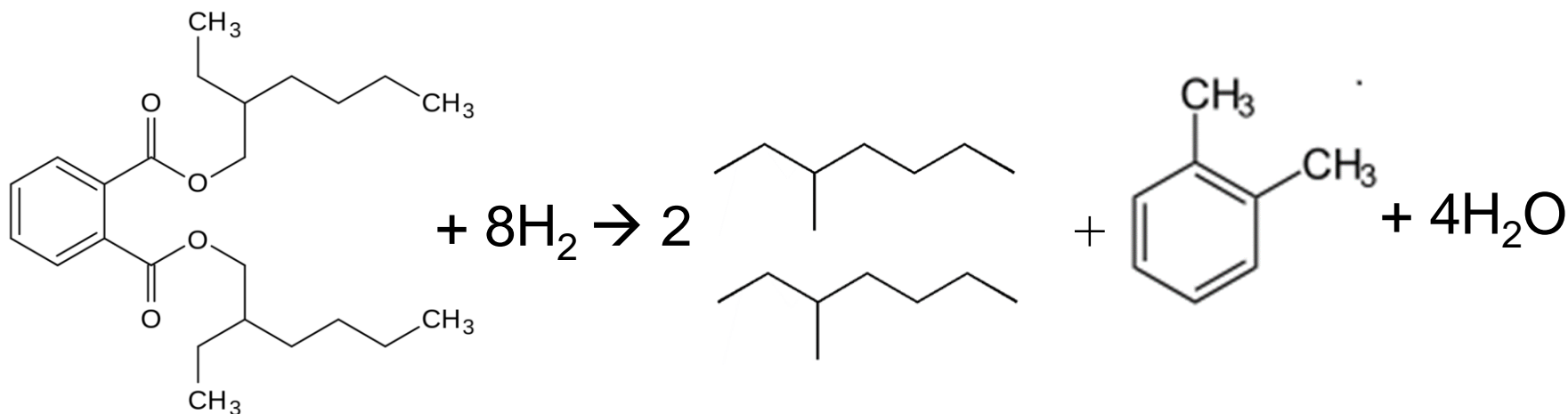
Properties

# Oxygenate Hydrotreating

Diocetyl phthalate

2-methylheptane

o-xylene



# Build Reaction Set in Property Environment

► For this case 7 reactions

1. Methyl-Ethyl-Ketone + 2 H<sub>2</sub> → n-Butane + H<sub>2</sub>O
2. Cyclopentanone + 2 H<sub>2</sub> → Cyclopentane + H<sub>2</sub>O
3. Benzyl-ethyl-ether + 2 H<sub>2</sub> → Ethylbenzene + methane + 2 H<sub>2</sub>O
4. P-Tert-Amylphenol + 4 H<sub>2</sub> → Tert-Pentylcyclohexane + H<sub>2</sub>O
5. Benzophenone + 5 H<sub>2</sub> → Benzylcyclohexane + H<sub>2</sub>O
6. P-Cumylphenol + 4 H<sub>2</sub> → 2-Phenyl-2-Cyclohexylpropane + H<sub>2</sub>O
7. Dioctyl-Phthalate + 8 H<sub>2</sub> → 2 3-Methylheptane + O-Xylene + H<sub>2</sub>O

► Conversion reactions for this case

- Assume 90% conversion
- Reaction kinetics can be added when known



# Hydrotreating System

- ▶ Reference: PETROLEUM REFINING Technology and Economics, Fifth Edition; James H. Gary, Glenn E. Handwerk, Mark J. Kaiser; CRC Press © 2007
  - "Most hydrotreating reactions are carried out below 800° F (427° C) to minimize cracking, and the feed is usually heated to between 500 and 800° F (260 and 427° C). The oil feed combined with the hydrogen-rich gas enters the top of the fixed-bed reactor. In the presence of the metal-oxide catalyst, the hydrogen reacts with the oil to produce hydrogen sulfide, ammonia, saturated hydrocarbons, and free metals.
  - The metals remain on the surface of the catalyst, and the other products leave the reactor with the oil-hydrogen stream. The reactor effluent is cooled before separating the oil from the hydrogen-rich gas. The oil is stripped of any remaining hydrogen sulfide and light ends (i.e. water) in a stripper. The gas may be treated to remove hydrogen sulfide and ammonia, then recycled to the reactor."

# Hydrotreater Reaction Conditions from Handwerk et al. 2007 Reference:

	Reference	Flowsheet	
Temperature	520-800	750	°F
Pressure	100-3000	1,500	psig
Reactor H2 Feed	2,000	1,913	scf/bbl
H2 Consumption	200-800	553	scf/bbl

# HYSYS Simulation Flowsheet

