HYSYS v8.8 Biocrude Hydrodeoxygenation Refinery Simulation

Simulation Structure: Input of Oxygenates into a HYSYS Hydrotreater Model

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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

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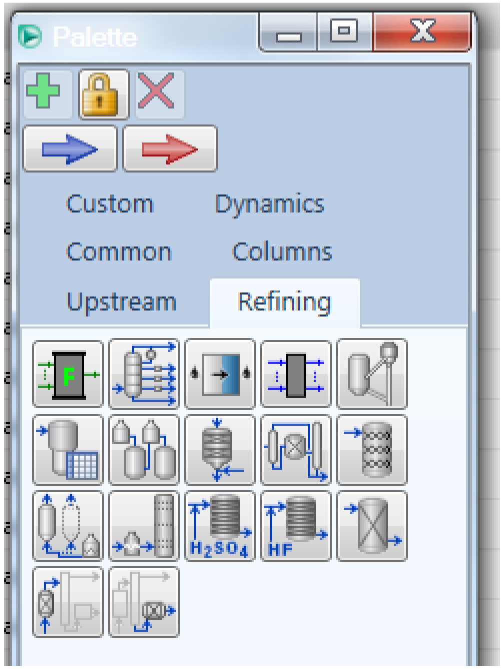
Why Aspen HYSYS® ?

- 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, H2SO4 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

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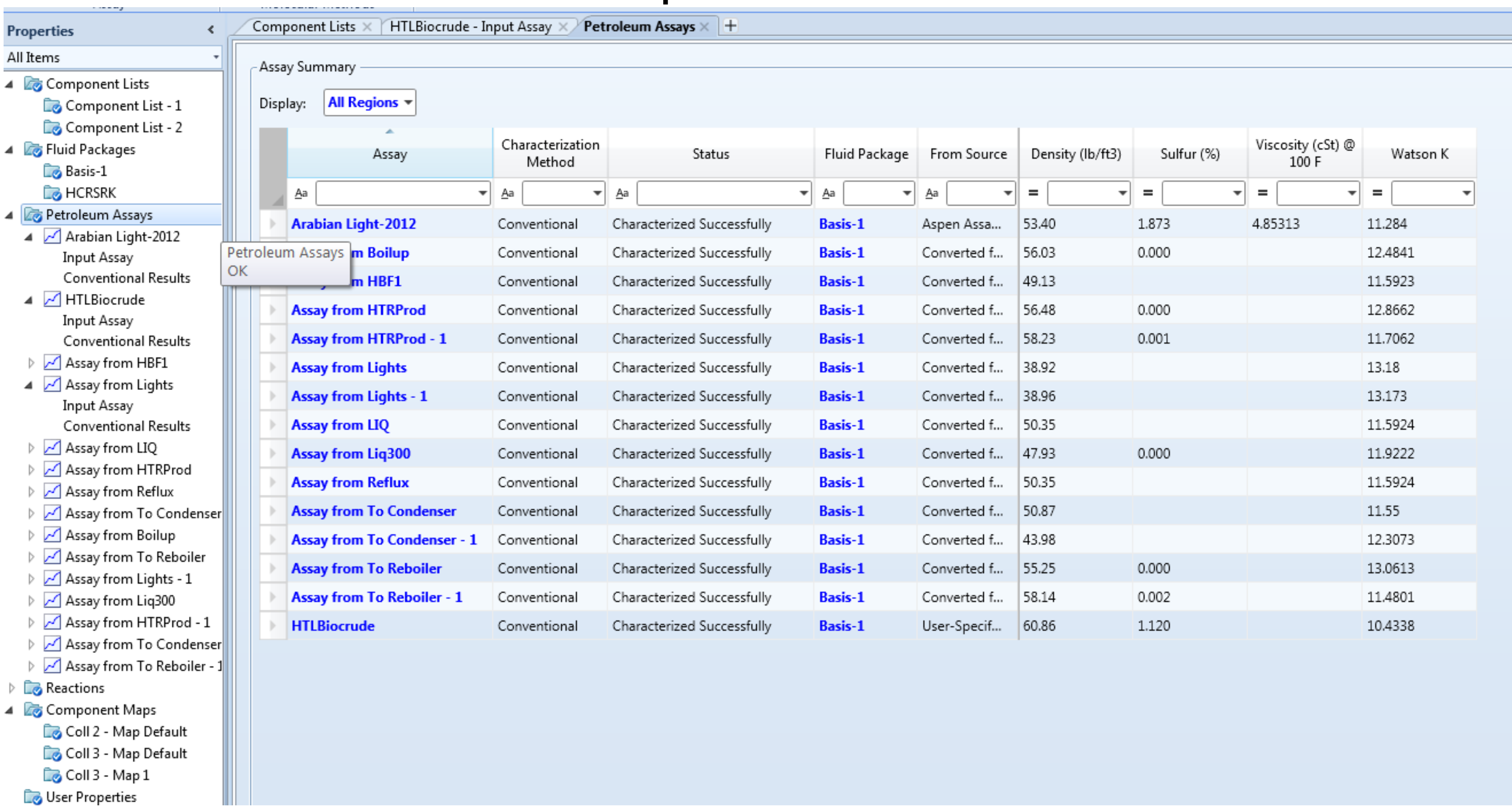
Set up VGO Assay

- Start in HYSYS Properties mode
  - Select Petroleum Assays – for this case “Arabian Light 2012 was from the list options available.



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
m Boilup	Conventional	Characterized Successfully	Basis-1	Converted f...	56.03	0.000		12.4841
m 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;

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Input HTL Biocrude Assay Manually

Properties

All Items

- Component Lists
  - Component List - 1
  - Component List - 2
- Fluid Packages
  - Basis-1
  - HCRSRK
- Petroleum Assays
  - Arabian Light-2012
    - Input Assay
    - Conventional Results
  - HTLBiocrude
    - 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

Conventional Results

Component Lists | HTLBiocrude - Input Assay | Arabian Light-2012 - Input Assay

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	IBP	212.0000	257.0000	302.0000	347.0000	392.0000	437.0000	482.0000	527.0000	572.0000	617.0000	662.0000	707.0000
Final Temperature (F)	FBP	212.0000	257.0000	302.0000	347.0000	392.0000	437.0000	482.0000	527.0000	572.0000	617.0000	662.0000	707.0000	FB
CutYieldByWt (%)		1.14	2.35	10.10	0.38	2.14	2.97	5.20	6.35	5.61	6.28	7.62	5.67	44.19
StdLiquidDensity (lb/ft3)	60.8633	38.8903	49.6792	52.4078	54.3962	55.5065	56.8865	57.1876	58.1159	58.4107	59.6213	59.7719	62.4566	65.8400
SulfurByWt (%)	1.120													
KinematicViscosity (cSt)...														
ParaffinsByVol (%)														
NaphthenesByVol (%)														
OlefinsByVol (%)														
AromByVol (%)														
PourPoint (F)														
FreezePoint (F)														
CloudPoint (F)														
SmokePt (ft)														
NitrogenByWt (%)	4.900													
VanadiumByWt (%)														
ConradsonCarbonByWt...														
RONClear														
MONClear														

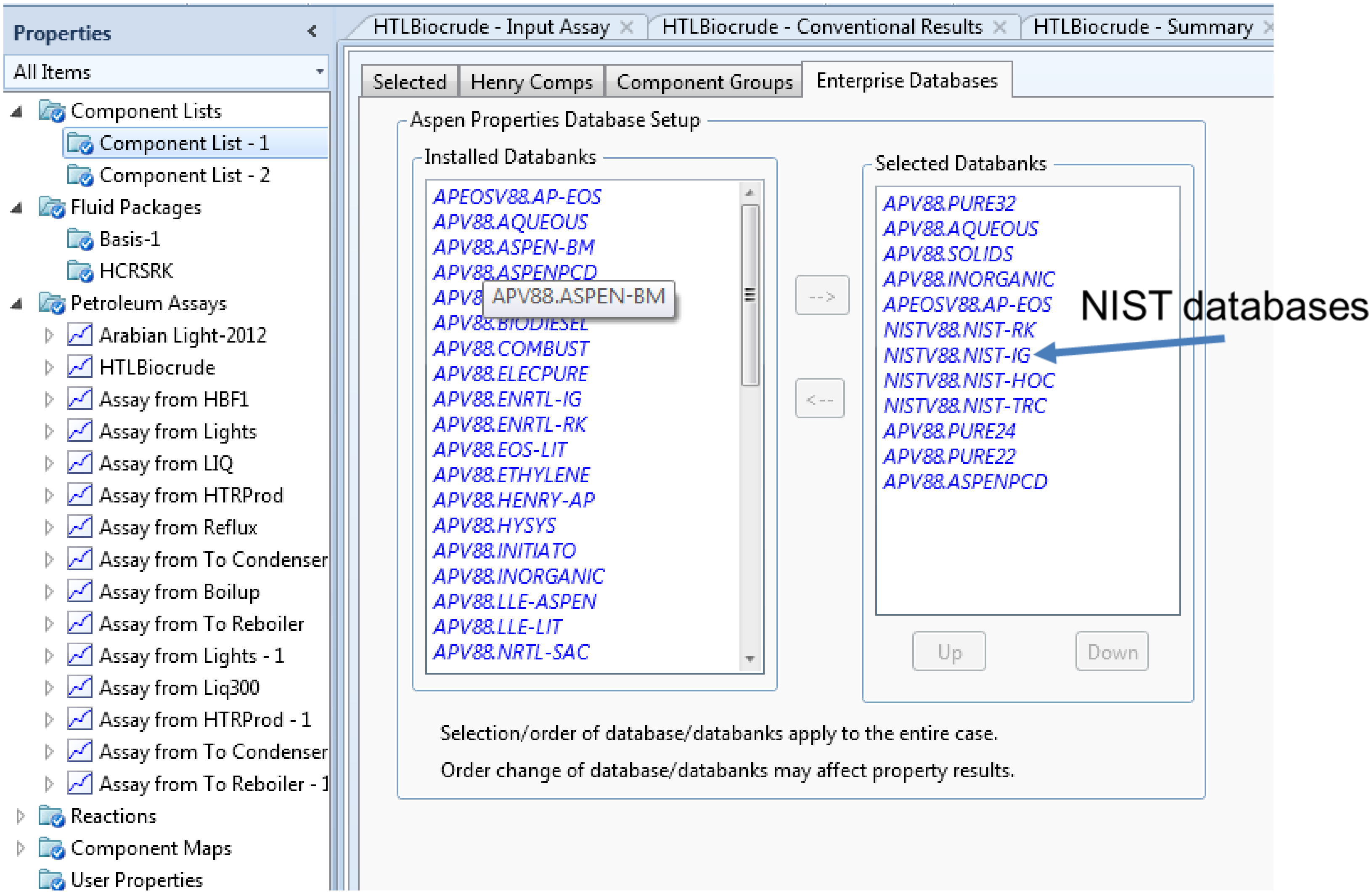
Add the oxygenated test components listed below

- 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**

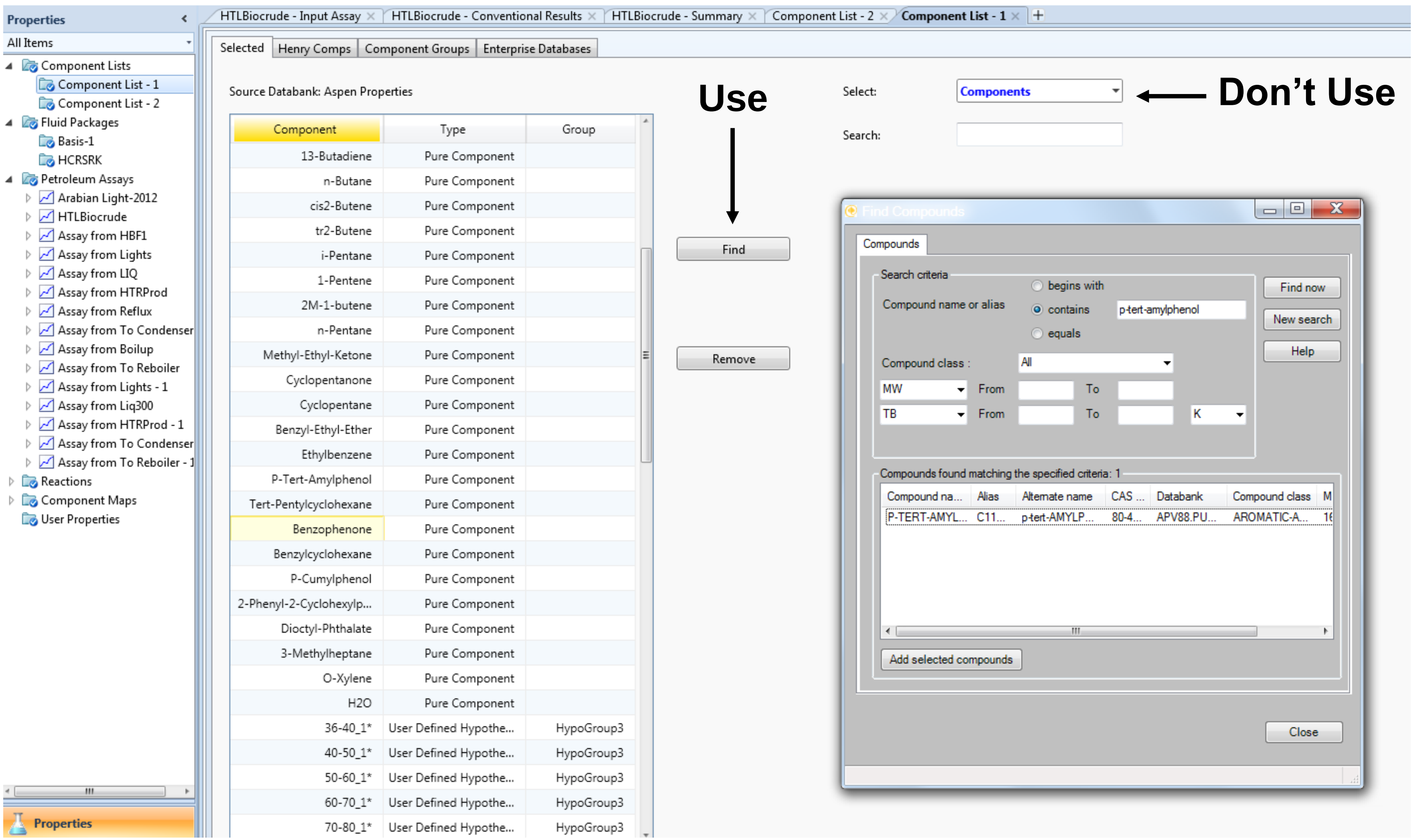
Oxygenates & Products Used in the Simulation

- 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

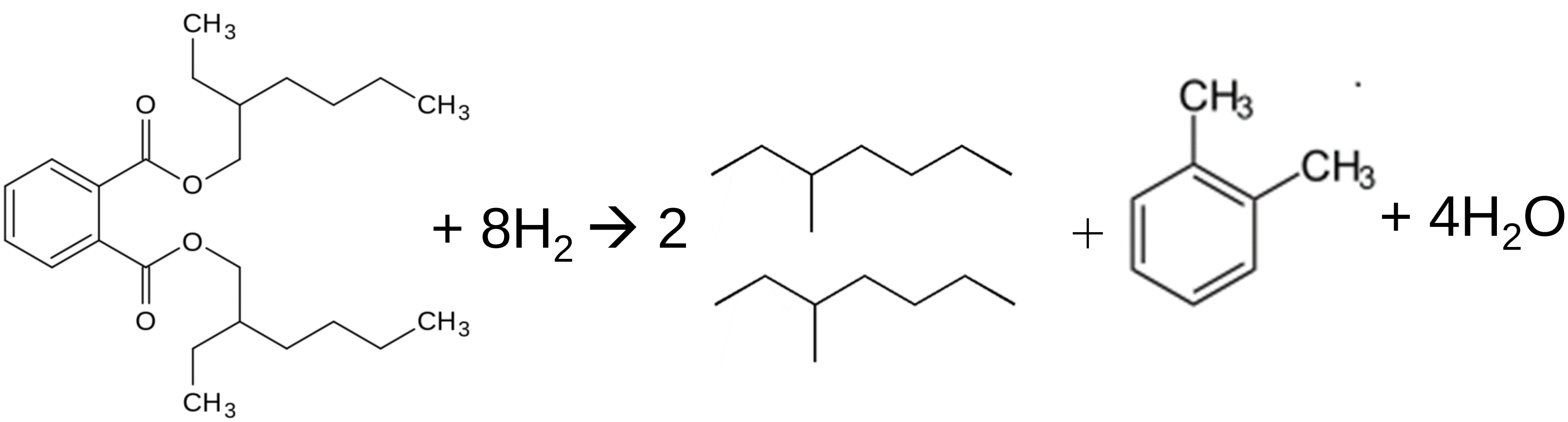


Adding p-tert-amylphenol to component list



Oxygenate Hydrotreating

Dioctyl phthalate 2-methylheptane o-xylene



Build Reaction Set in Property Environment

- For this case 7 reactions
  1. Methyl-Ethyl-Ketone + 2 H_2 → n-Butane + H_2O
  2. Cyclopentanone + 2 H_2 → Cyclopentane + H_2O
  3. Benzyl-ethyl-ether + 2 H_2 → Ethylbenzene + methane + 2 H_2O
  4. P-Tert-Amylphenol + 4 H_2 →Tert-Pentylcyclohexane + H_2O
  5. Benzophenone + 5 H_2 → Benzylcyclohexane + H_2O
  6. P-Cumylphenol + 4 H_2 → 2-Phenyl-2-Cyclohexylpropane + H_2O
  7. Dioctyl-Phthalate + 8 H_2 → 2 3-Methylheptane + O-Xylene + H_2O
- 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."

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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