This is our contribution to the COLaN 2022 meeting.

Unfortunately, we cannot attend in person, hence we pre-recorded this presentation.

We hope you find it interesting.

Overview

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- Desire to expose petroleum properties in ChemSep via CAPE-OPEN Property Package
- Though these properties may be covered by the petroleum properties standard, adoption of that standard takes time
- Thermodynamic standard allows for “custom” properties to pragmatically add any property
- We used custom properties to export petroleum properties, accepting that they may not be universally understood
- Such properties can be ‘private’ between Unit Operation and CAPE-OPEN Property Package (COPP)

Recently we added petroleum properties into ChemSep and we wanted to add these to flowsheets. The petroleum properties CAPE-OPEN standard has not yet been universally adopted by all potentially interested parties. However, the thermodynamics standard v1.1 includes the facility to define add any CAPE-OPEN Custom Property (COCP). We decided to use this facility to define our “extra” properties, fully understanding that these will not be universally understood.

History of ChemSep LITE

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ChemSep standalone distributed to universities

- 2005: v5.0: ChemSep LITE first *CAPE-OPEN* version, demonstrated as UnitOp in Pro/II & Aspen+
- 2006: v6.0: integrated CAPE-OPEN from wrapper into GUI and added adaptive icons (in COCO)
- 2015: v7.0: ChemSep CAPE-OPEN property packages
- 2018: v8.0: Parallel Column Model for DWC
- **2022: v8.3: Export of Additional Properties**

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The development of ChemSep started in 1990 and standalone versions have been made available via CACHE (www.cache.org). ChemSep includes both equilibrium and nonequilibrium models. The development of the CAPE-OPEN version of ChemSep was made possible in part by support from BP International. Later, other industrial sponsors joined the ChemSep Consortium.

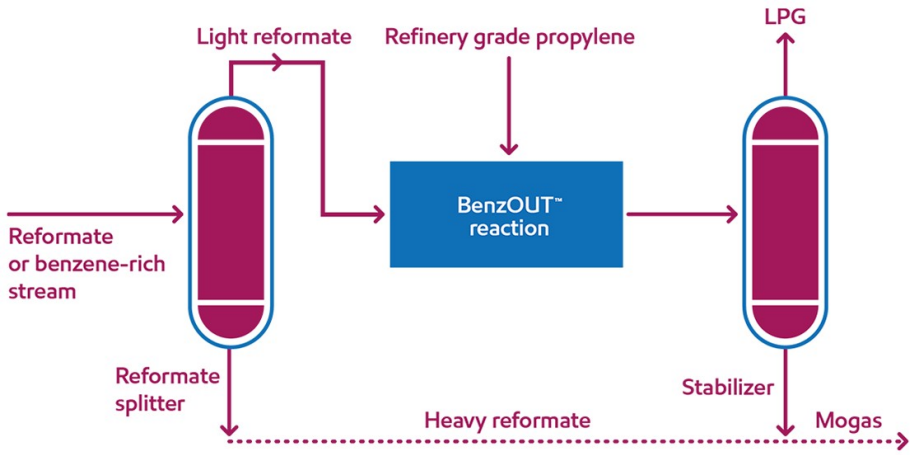
When we started many simulators used keyword-based input files. This changed in the late 90's when user interfaces based on Microsoft Windows came on the market. Around the same time the desire for large companies to use their in-house simulation tools in multiple simulators resulted in the creation of the CAPE-OPEN standard.

A windows interface was developed for ChemSep in 2000 but this was not released to the wider world until 2005 when we released ChemSep LITE, a freely available version of our software that includes our equilibrium-stage column model. This version was tested with commercial flowsheeting software. We have continued developing ChemSep to this day. This resulted into many new developments such as adaptive icons, our own property packages, including one for electrolytes, and unit operations not offered by commercial suppliers such as a single-unit Dividing Wall Columns model.

Now we are adding the export of additional properties.

Example: EXXON-Mobil BenzOUT

- Reduce Benzene in gazoline (Mogas) by reacting with Propylene without causing a loss in octane#
- Includes stabilizer to maintain low vapor pressure
- Patented process US 8,395,006 B2:



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In a refinery all the streams that are blended into automotive gasoline are called “Mogas” streams. (This is to distinguish these streams from those that create avgas – aviation gasoline.) A significant part of the Mogas pool originates with the Catalytic Reformer where light (cyclo-) alkanes in the Naphtha streams are reformed into aromatic components.

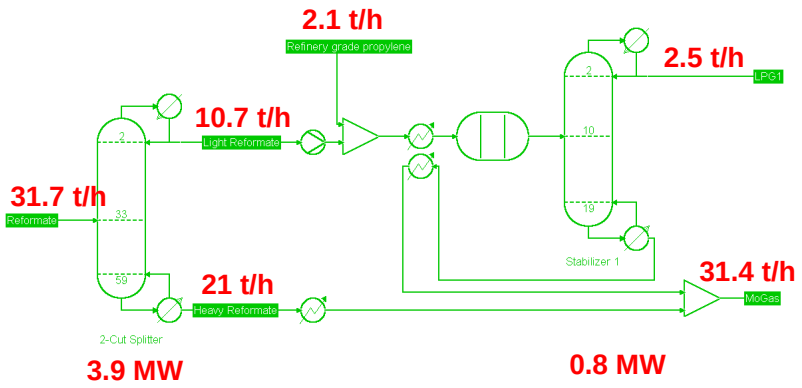
Light unbranched and cyclo- alkanes are not very suitable for gasoline because of their high tendency to “knock” in engines. Aromatics, on the other hand have excellent “knock” properties. The property that characterizes this behavior is called the “Octane number” which varies from 0 (for n-Heptane) to 100 (for a fully branched Octane). The minimum posted octane number at the pump is 95 (in Europe). Note that the dehydrogenation of alkanes in the reformer also produces a lot of hydrogen that gets used in the refinery hydro-cracker, to “upgrade” molecules that would be too heavy to put in the gasoline by breaking them in smaller pieces.

The reforming process produces a considerable quantity of carcinogenic Benzene which must be removed before the Reformate can be used in the Mogas pool (to levels lower than 1%). Since the removal of the Benzene would lower the octane number of the Reformate, the refinery must compensate this by blending in additional components; this can be expensive.

The Exxon Mobile BenzOUT process is a simple process that removes the Benzene from the Reformate by converting it without causing a loss in octane number or increasing the vapor pressure (which would create a problem for tank storage). It does this by separating a light fraction which is reacted with Propylene to create a branched aromatic with high Octane number.

Example: EXXON-Mobil BenzOUT

- Process needs to fulfill petroleum properties specs:
  - Minimize drop in octane number
  - Maintain low Reid Vapor Pressure of product



Stream	Reformate	MoGas	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.0902	°C
Flow rate	343	335.349	kmol / h
Mole frac n-butane	0.0309038	0.00909843	
Mole frac isopentane	0.0819242	0.0835314	
Mole frac n-pentane	0.0580175	0.0592973	
Mole frac 2-methylpentane	0.0862974	0.0882657	
Mole frac n-hexane	0.045481	0.0465187	
Mole frac benzene	0.101458	0.0121412	
Mole frac 3-methylhexane	0.0186589	0.0190846	
Mole frac toluene	0.248397	0.254064	
Mole frac ethylbenzene	0.0306122	0.0313107	
Mole frac p-xylene	0.0370262	0.037871	
Mole frac m-xylene	0.106122	0.108544	
Mole frac o-xylene	0.0478134	0.0489043	
Mole frac m-ethyltoluene	0.0361516	0.0369765	
Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0608322	
Mole frac 1,4-diethylbenzene	0.0116618	0.0119279	
Mole frac Propane	0	6.03384e-07	
Mole frac Propylene	0	6.69168e-07	
Mole frac Cumene	0	0.0596601	
Liquid phase			
OCTN	100.404	98.3165	-
RVP	0.414281	0.315115	bar
TVP100	0.427999	0.333699	bar

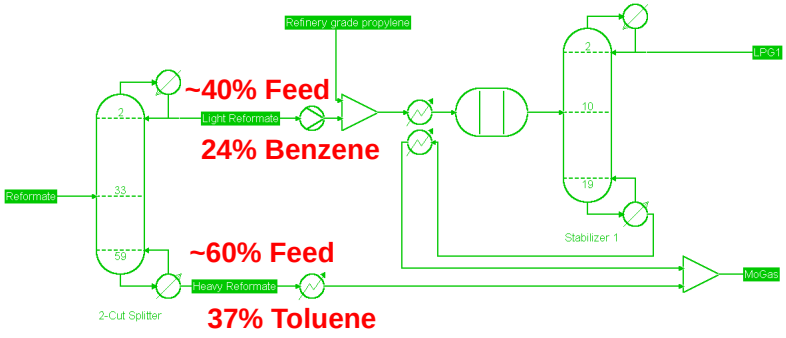
Here is our own implementation of the BenzOUT process inside the flowsheet simulation program COCO (www.cocosimulator.org). Heat inputs and mass flows are shown on the slide.

The reformate splitter is on the left, the reactor in the middle, and the stabilizer on the right. A neat feature of the process is that the feed to the reactor is heat integrated with the bottoms of the stabilizer, reducing the amount of heat wasted.

The refinery properties are now part of the flowsheet since we have used ChemSep as the property package, which includes the octane number (OCTN) and the Reid Vapor Pressure (RVP). These extra properties are highlighted by the red outline that appears bottom right.

Example: EXXON-Mobil BenzOUT

- Process needs to fulfill petroleum properties specs:
  - Minimize drop in octane number
  - Maintain low Reid Vapor Pressure of product



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Mole frac ethylbenzene	0.0306122	0.0313107	
Mole frac p-xylene	0.0370262	0.037871	
Mole frac m-xylene	0.106122	0.108544	
Mole frac o-xylene	0.0478134	0.0489043	
Mole frac m-ethyltoluene	0.0361516	0.0369765	
Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0608322	
Mole frac 1,4-diethylbenzene	0.0116618	0.0119279	
Mole frac Propane	0	6.03384e-07	
Mole frac Propylene	0	6.69168e-07	
Mole frac Cumene	0	0.0596601	
Mole frac P-diisopropylbenzene	0	0.0320708	
Liquid phase			
OCTN	100.404	98.3165	-
RVP	0.414281	0.315115	bar
TVP100	0.427999	0.333699	bar

As you can see, the Reformate is split 40-60% such that the Benzene is present in the overhead, and that Toluene, which has a high Octane number, passes via the bottoms. This way the reactor is minimized in size and the heat duties are reduced.

Example: EXXON-Mobil BenzOUT

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Can we improve the economics of this process while maintaining performance in OCTN & RVP?

Example: EXXON-Mobil BenzOUT

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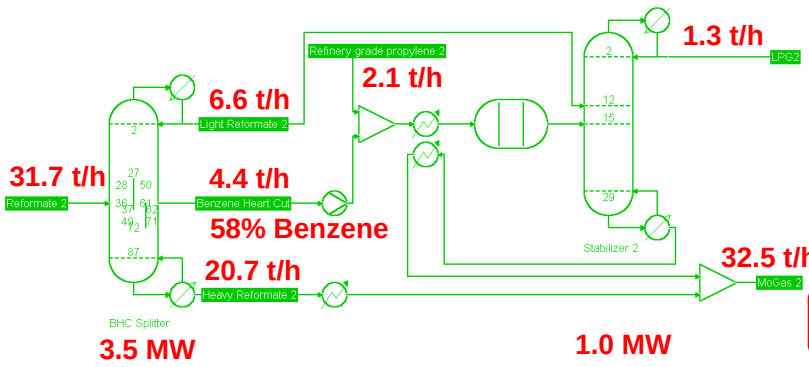
Can we improve the economics of this process while maintaining performance in OCTN & RVP?

- Produce “heart-cut” product in which >99% of the Benzene is recovered, only send this to the reactor: Reduces flow through reactor & stabilizer by 2x
- Use Dividing Wall Column (DWC) technology to revamp the reformate splitter in the same column

Example: EXXON-Mobil BenzOUT

- Advantages:
  - Smaller reactor + stabilizer: TAC -30%
  - No difference in OCTN or RVP
  - 5% lower duty



Stream	Reformate 2	MoGas 2	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.3644	°C
Flow rate	343	334.936	kmol / h
Mole frac n-butane	0.0309038	0.0115992	
Mole frac isopentane	0.0819242	0.0805443	
Mole frac n-pentane	0.0580175	0.0587449	
Mole frac 2-methylpentane	0.0862974	0.0863696	
Mole frac n-hexane	0.045481	0.0465759	
Mole frac benzene	0.101458	0.0120102	
Mole frac 3-methylhexane	0.0186589	0.0191081	
Mole frac toluene	0.248397	0.254377	
Mole frac ethylbenzene	0.0306122	0.0313493	
Mole frac p-xylene	0.0370262	0.0379177	
Mole frac m-xylene	0.106122	0.108678	
Mole frac o-xylene	0.0478134	0.0489646	
Mole frac m-ethyltoluene	0.0361516	0.037022	
Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0609072	
Mole frac 1,4-diethylbenzene	0.0116618	0.0119426	
Mole frac Propane	0	2.02693e-06	
Mole frac Propylene	0	2.25938e-06	
Mole frac Cumene	0	0.0597255	
Liquid phase			
OCTN	100.404	98.3402	-
RVP	0.414281	0.316967	bar
TVP100	0.427999	0.337995	bar

In the improved process, the splitter is replaced by a Dividing Wall Column (DWC) that produces essentially the same bottom product but the overhead is now a smaller, Benzene free stream that is fed directly to the stabilizer. An extra product stream is taken from the middle. This “heart-cut” stream is sent to the reactor. By using a DWC we reduced the stream to the reactor by half, reducing the total annualized cost.

Note that the octane number and vapor pressure of the stream for the Mogas pool have practically not changed from the original process. Further note that regular reformate splitters can be retrofit as DWCs when we use high capacity column internals.

Example: EXXON-Mobil BenzOUT

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Other advantages:

- Flexible co-production of 58% Benzene product

Can we further optimize?

Example: EXXON-Mobil BenzOUT

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Other advantages:

- Flexible co-production of 58% Benzene product

Can we further optimize?

- Extra duty enables co-production of >96% Toluene as separate product with Kaibel configuration
- Maintaining OCTN 95 Mogas

Example: EXXON-Mobil BenzOUT

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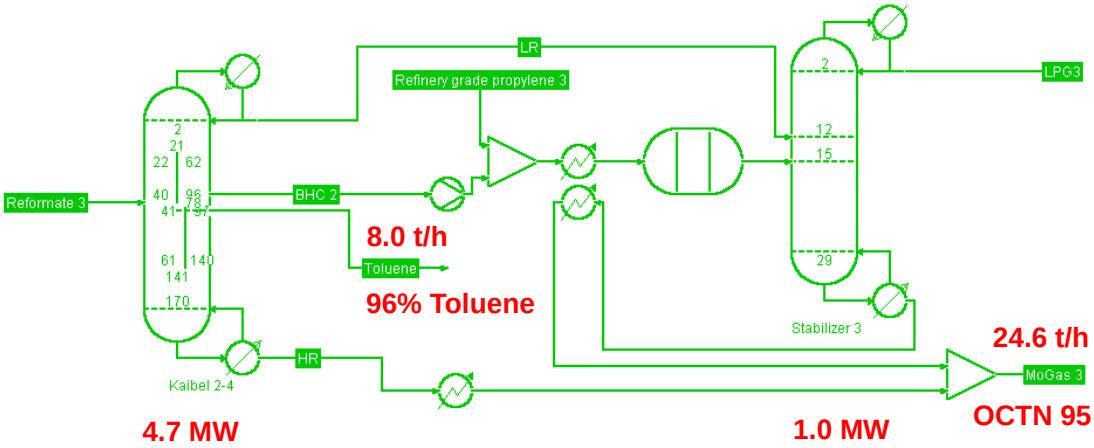
- Existing reformate splitters can be revamped using sloped-wall DWC designs, see Dejanovic *et al.**

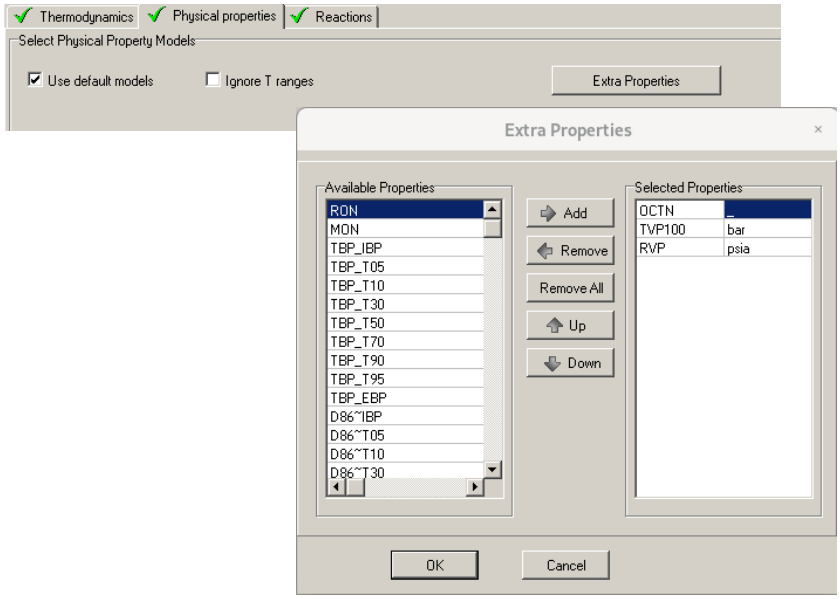


* Dejanović, I., Matijašević, L., Jansen, H., Olujić, Ž., 2011. Designing a Packed Dividing Wall Column for an Aromatics Processing Plant. Industrial & Engineering Chemistry Research 50, 5680–5692. https://doi.org/10.1021/ie1020206

The DWC can be retrofitted with two side streams taken from their own draw-off trays. The extra stream reduces the bottoms stream and the loss of the Toluene causes the octane number to drop to the minimum of 95 allowed for the Mogas pool. Of course this goes at the expense of a considerable amount of extra duty, and it is not likely that this can be retrofitted into an existing splitter at the same capacity. However, if some reboiler/column capacity is available, a smaller Toluene product stream can be drawn off in a fully flexible manner.

Selection of Extra Properties

As part of the physical properties models selection



The petroleum properties are listed as you see in this screen shot. The order of the properties can be changed and the units of measure are taken as set in global units definitions.

Extra Properties Methods

RON & MON: Table values / Estimated from groups or Tb & SG

OCTN: Posted Octane Number = RON/2+MON/2

Flash Point: Riazi (eqn. 3.114/3.115)

TVP100: Antoine vapor pressure model at 100 F
(with Ambrose or Riedel as back-up)

RVP: Approximation using the TVP100, mixtures per Riazi p. 132

TBP: Spline interpolation

D86: Riazi-Daubert 1986 on TBP

API density

K Watson

More to come...

The currently available petroleum properties are summarized here. In the future we will be adding more properties. If you have suggestions please contact us.

RON & MON Estimation

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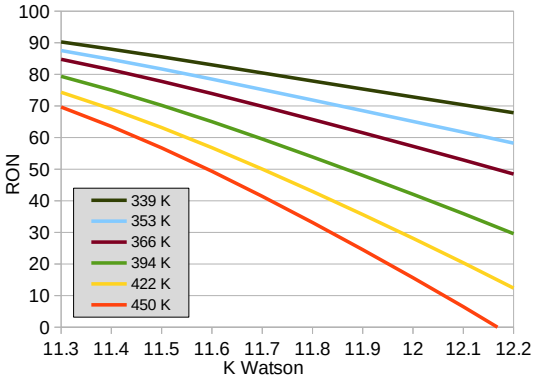
RON:

- UNIFAC groups: Albahri (*Ind.Eng.Chem.Res.* (2003) 42, pp. 657-662 + (2004) 43, p. 7964) and new -OH/=O/-O- groups average error 8.8%

- Pseudo's: Nelson (1969) as *f*(Kw,Tb) for Naphtha's

MON:

Jenkins (1968)
average error 8%



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Most octane numbers are computed from a list of Research and Motor Octane Numbers (RON & MON) that the user can extend by himself. These are text files and each component is identified by its CAS Number. For compounds the user adds the RON and MON are estimated by means of a group contribution method from Albahri using the Modified UNIFAC groups (or from the original UNIFAC groups if the groups for Modified UNIFAC are not available). As the accuracy of the method is dependent on being able to differentiate between cyclic and alkane CH2 groups, it is recommended users ensure the Modified UNIFAc groups are entered. If no group information is known, the RON & MON are estimated by means of boiling point and specific gravity as for refinery Naphtha streams by Nelson (1969). This is only accurate for pseudo components that have a boiling point range and which consist of many compounds.

For the RVP we make use of approximations based on the TVP100 that were published by Campbell.

Extra Properties Results

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Internal Thermo: Show as part of stream table output

Stream	Feed1	L.Feed1	Top	Bottom	Sidestream
Stage	37	37	1	88	61
Pressure (psia)	50.7632	49.5838	39.1602	56.7596	50.8737
Vapour fraction (-)	0.000000	0.000000	0.000000	0.000000	0.000000
Temperature (K)	373.218	373.220	338.862	455.119	391.402
Enthalpy (J/kmol)	-2.212E+07		-1.970E+07	-8.930E+06	-1.622E+07
Entropy (J/kmol/K)	-36044.6		-50096.6	-2814.91	-38012.1
Total molar flow (kmol/s)	0.0952834	0.0952834	0.0255687	0.0576599	0.0120548
Total mass flow (kg/s)	8.81370	8.81370	1.92960	5.89568	0.988422
Vapour std.vol.flow (m3/s)					
Liquid std.vol.flow (m3/s)	0.0111053	0.0111053	0.00302690	0.00681101	0.00126738
Liquid:					
Mole weight (kg/kmol)	92.4999	92.4999	75.4672	102.249	81.9941
Density (kg/m3)	716.579	716.563	587.747	700.750	676.010
Std.density (kg/m3)	793.649	793.649	637.483	865.610	779.892
Viscosity (N/m2.s)	2.3365E-04	2.3365E-04	1.6713E-04	1.4136E-04	1.8449E-04
Heat capacity (J/kmol/K)	200600	200601	188257	237046	189124
Thermal cond. (J/s/m/K)	0.104216	0.104211	0.0959115	0.0931280	0.102774
Surface tension (N/m)	0.0160580	0.0160577	0.0113389	0.0115046	0.0134855
Extra:					
OCTN ( )	100.382	100.382	74.6569	114.685	84.9530
TVP100 (bar)	0.428177	0.428177	1.20952	0.0510031	0.316488
RVP (psia)	6.01158	6.01158	17.1398	0.651681	4.12011

This is how the extra properties are displayed Inside ChemSep: They appear in the stream table of columns. They appear in the same order in which they appear in the selection list.

Extra Properties Results

Clarkson UNIVERSITY defy convention

CS/COPP: As part of the stream table output in COCO

Stream	Reformate	MoGas	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.0902	°C
Flow rate	343	335.349	kmol / h
Mole frac n-butane	0.0309038	0.00909843	
Mole frac isopentane	0.0819242	0.0835314	
Mole frac n-pentane	0.0580175	0.0592973	
Mole frac 2-methylpentane	0.0862974	0.0882657	
Mole frac n-hexane	0.045481	0.0465187	
Mole frac benzene	0.101458	0.0121412	
Mole frac 3-methylhexane	0.0186589	0.0190846	
Mole frac toluene	0.248397	0.254064	
Mole frac ethylbenzene	0.0306122	0.0313107	
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Mole frac 1,3,5-trimethylbenzene	0.0594752	0.0608322	
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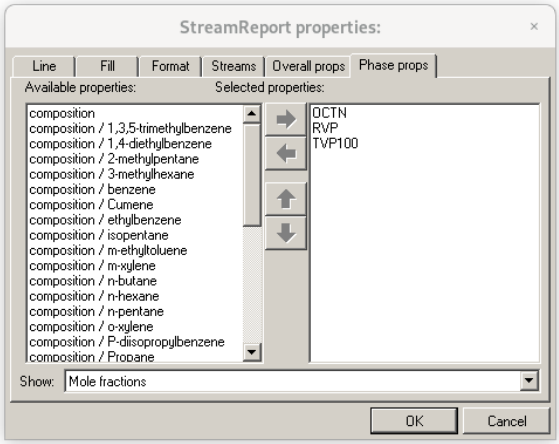
Mole frac Propane	0	6.03384e-07	
Mole frac Propylene	0	6.69168e-07	
Mole frac Cumene	0	0.0595601	
Mole frac P-diisopropylbenzene	0	0.0320708	
Liquid phase			
OCTN	100.404	98.3165	-
RVP	0.414281	0.315115	bar
TVP100	0.427999	0.333599	bar



This is how the extra properties are selected for inside COCO. This is because they were added as part of the ChemSep CAPE-OPEN Property Package (CS/copp).

Extra Properties Results

Clarkson UNIVERSITY defy convention

Units of Measure – Allows conversion of units

Stream	Reformate	MoGas	Unit
Pressure	3.5	2.5	bar
Temperature	100	71.0902	°C
Flow rate	343	335.349	kmol / h
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Liquid phase			
OCTN	100.404	98.3165	-
RVP	0.414281	0.315115	bar
TVP100	0.427999	0.333599	bar

Liquid phase			
OCTN	100.404	98.3165	-
RVP	6.00864	4.57036	psi
TVP100	6.2076	4.83844	psi

The units can be changed in the table as desired.

Code to get the Extra Properties?

Call to Fortran DLL:

```
nex = NumberExtraProps()
do j=1,nex
  i = idExtraProperty(j)
  call EPname (i, Cname)
  call EPdesc (i,iDmns,Desc)
  call EProp (i, Cvalue, T, p, Ffeed, Z, nc, ncmax, iErr)
  if (iErr .eq. 0) then
    write(io,*) Cvalue, ' '//Cname
  else
    write(io,*) 'error calculating '//Cname
  end if
end do
```

See the back-up slides for a description of the function arguments

This is the Fortran code for computing the custom properties directly from our CS/COPP DLL

First, we obtain the number of extra properties defined in the property package.

Then, for each property, we get the property ID. Using the ID we obtain the property name, the units of measure, and its description.

We obtain the property value by calling the EProp function with the Temperature (T), pressure (p) and the vector of the compositions (Z). nc is the number of components and ncmax the length definition for the vector. Upon return, the integer flag iErr is set to a non-zero value if an error was encountered.

Extra Properties Calculation

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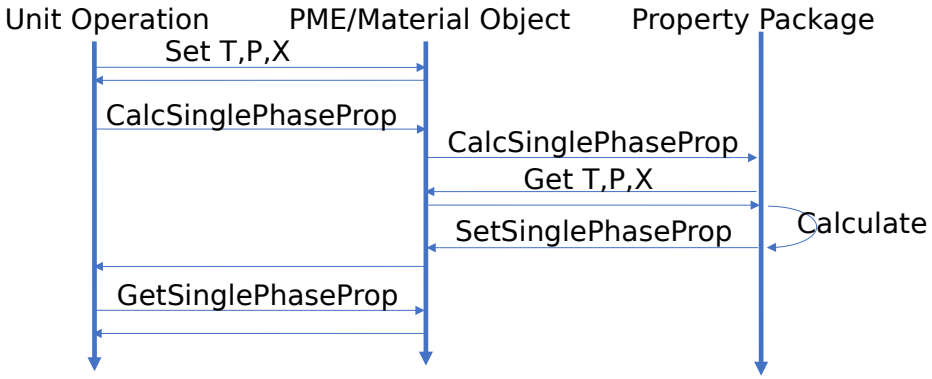
Calling Sequence:



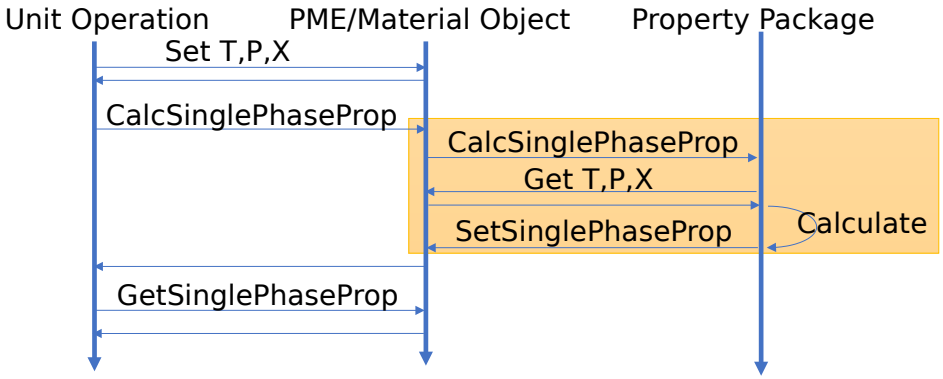
This is to show the calling sequence for the custom properties from within other Unit Operations. It makes use of a CAPE-OPEN Material Object (MO). First the temperature, pressure, and liquid composition must be set (because we defined them as liquid properties).

Then the unit operation sends a request to the Process Modeling Environment (PME) to compute the property. The PME passes the call on to the ChemSep CAPE-OPEN Property Package. The error code is then returned and passed back to the unit operation. If no error is made the value can be picked up.

Extra Properties Calculation

Clarkson UNIVERSITY defy convention

Calling Sequence:



PME can also access the property by itself!

The PME can perform the call itself as well and get access to all the extra properties.

Summary

Clarkson UNIVERSITY defy convention

- CAPE-OPEN Custom Properties (COCP) are useful
- ChemSep uses COCP for Petroleum Properties
  Drawback: Overall properties are missing, exposed as liquid properties
- COCP definition (ChemSep ↔ COCO) via private API
  Drawback: No support by other PMEs

We believe the custom properties are really useful.

Ideally, we would prefer custom properties could also be defined as overall properties, but this is not something we feel is urgent to change/add.

We are planning to allow custom properties to be used as specifications in our column simulations.

If in the future, the petroleum properties standard is fully implemented, we plan to port the petroleum properties to also be accessible via that standard.

Clarkson UNIVERSITY defy convention

Questions?

Backup slides

Code to get the Extra Properties?

Clarkson UNIVERSITY defy convention

integer **NumberExtraProps**()

Returns the number of Extra Properties in the COPP

integer **idExtraProperty**(j)

Returns the type of the j^{th} Extra Property. Each type has its own number

subroutine **EPname** (i, Cname)

Returns the name for the i^{th} Extra Property as string in Cname

subroutine **EPdesc** (i,iDmns,Desc)

Returns the description Desc as string and dimensions array Dmns for the i^{th} Extra Property

Subroutine **EProp** (i, Cvalue, T, p, Ffeed, Z, nc, ncmax, iErr)

Integer i, nc, ncmax, iErr; double Cvalue, T, p, Ffeed; double array Z

Returns the value Cvalue for the i^{th} Extra Property using T,p,Ffeed,Z()

How to Get the Extra Properties?

Clarkson UNIVERSITY defy convention

C/C++ Getting the DLL entry points:

```
NumberExtraProps=(F_NUMBEREXTRAPROPS)GetProcAddress(dllHandle
,"numberextraprops_");

if (!NumberExtraProps) { throw COException(L"Unable to load
NumberExtraProps function from ChemSep DLL"); }

idExtraProperty=(F_IDEXTRAPROPERTY)GetProcAddress(dllHandle,"idext
raproperty_");

if (!idExtraProperty) { throw COException(L"Unable to load
idExtraProperty function from ChemSep DLL"); }

EPdesc=(F_EPDESC)GetProcAddress(dllHandle,"epdesc_");

if (!EPdesc) { throw COException(L"Unable to load EPdesc function from
ChemSep DLL"); }

EProp=(F_EPROP)GetProcAddress(dllHandle,"eprop_");

if (!EProp) { throw COException(L"Unable to load EProp function from
ChemSep DLL"); }
```

How to Get the Extra Properties?

Clarkson UNIVERSITY defy convention

CS/COPP DLL calls in C/C++:

```
int nex=(*NumberExtraProps)();
for (int i=1;i<=nex;i++) {
   int id=(*idExtraProperty)(&i);
   char propName[101];
   propName[100]=' ';
   int dimension[7];
   (*EPdesc)(&id,dimension,propName,100);
   for (int j=100;j>=0;j--) { if (propName[j]!=' ') {propName[j+1]=0; break; }
}
UTF8toUTF16 pName(propName);
propMap[pName]=PropDetails::make((PropertyID)
(PropID_EXTAPROP0+id),0,Deriv_None,massBasisDependent,SinglePhaseProp
erty,pName);
propList1p.emplace_back(pName);
}
```

RON & MON Text-Files

ComponentList RON & MON Applications in Energy and Combustion Science 5 (2021) 100018
CAS Number
RON
MON

1
74-84-0
115
99

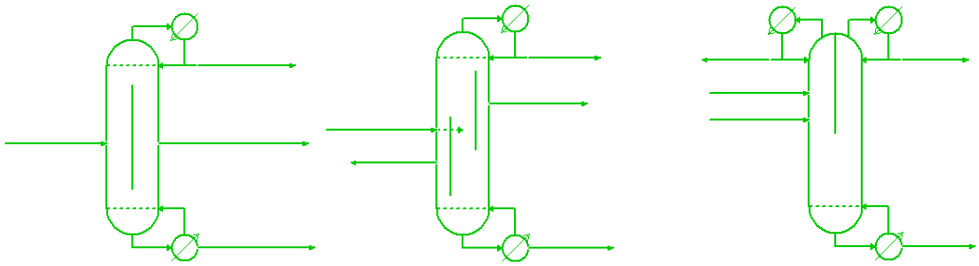
2
74-98-6
111
97

3
106-97-8
94
89

…

DWC Process Simulation in ChemSep

- Parallel Column Model for CAPE-OPEN compliant systems
- Does not require any guesses for streams
- Predefined configurations with single & multiple walls, selection from drop-down list
- Icons reflect actual configuration (in COCO)
- Rapid tray/packing internals design of each column section with selection of any modern type internal
- Column sizing include auxiliaries: CAPEX & OPEX
- Connection to vendor rating tools



Icons in COCO (www.cocosimulator.com)