

Process Modeling for the Development of Oil Shale Retorting Processes



Rick Sherritt, Jimmy Jia

Jim Schmidt, Meilani Purnomo



28th Oil Shale Symposium
Golden Colorado
13-17 October 2008

General Purpose Process Flowsheet Simulators

- Represent process flowsheet with unit operations connected by streams
- Calculate unknown flow rates, temperatures, pressures, compositions and operation parameters
- Ensure steady-state mass and heat balances for each unit operation and overall process
- Contain built-in models for familiar unit operations
- Contain databank of components and methods to calculate thermodynamic properties
- Aspen Plus[®], Hysys[®], VMGSim[®], Solidsim[®], Metsim[®]

Special Requirements to Simulate Oil Shale Conversion Processes

- Ability to simulate solid, liquid and gas phases
- Ability to create new oil shale specific components and calculate their thermodynamic properties
- Ability to specify reaction stoichiometry and track elemental composition of reacting solids of no fixed molecular formula
- Ability to track particle size distribution

Oil Shale Mineralogy Varies

Group of minerals	Minerals	Kukersite Estonia	Green River USA	El-Lajjun Jordan	Ramsay Cross Rundle Australia	Kerosene Ck Stuart Australia
Clays	Kaolinite			5-10	2.4	6
	Smectite				21.7	27
	Muscovite-illite	12	10.9	5	11.4	5
	Amphibole	1				
Carbonates	Calcite	35	14.1	20-80	4.3	10
	Siderite	Tr	2.4		2.6	3
	Dolomite	15	22.8	2-3.6	1.7	0
Sulphites	Pyrite/Marcasite	5	1.6	5	1.1	2
Sulphates	Gypsum	0.5		5		2
Phosphates	Apatite			4-14		
Plagioclase	Albite	3	13.7		10.7	
	Analcime		0.9			
Oxides and hydroxides	Quartz	12	13.2	10-40	23.2	16
	Rutile	0.3				
	Goethite			5		
	Anatase					1
Feldspars	K-Feldspar	7		5		5
	Orthoclase	15				
Reference		Ots 2003	Brons 1989	Hamareh 2006	Brons 1989	Berkovich 2000

Mineral Reactions

Reaction type	Mineral	Reaction Equation	Reaction Temperature K
Dehydration	Hydrated Smectite	$\text{Ca}_{0.43}\text{K}_{0.24}(\text{Al}_{2.59}\text{Fe}_{0.75}\text{Mg}_{0.65})(\text{Si}_{7.67}\text{Al}_{0.3})\text{O}_{20}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ $\xrightarrow{h_r} \text{smectite} + 2\text{H}_2\text{O}(g)$	446
	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \xrightarrow{h_r} \text{CaSO}_4 + 2\text{H}_2\text{O}(g)$	523
Dehydroxylation	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \xrightarrow{h_r} \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}(g)$	810
	Smectite	$\text{Ca}_{0.43}\text{K}_{0.24}(\text{Al}_{2.59}\text{Fe}_{0.75}\text{Mg}_{0.65})(\text{Si}_{7.67}\text{Al}_{0.3})\text{O}_{20}(\text{OH})_4$ $\xrightarrow{h_r} \text{Ca}_{0.43}\text{K}_{0.24}(\text{Al}_{2.59}\text{Fe}_{0.75}\text{Mg}_{0.65})(\text{Si}_{7.67}\text{Al}_{0.3})\text{O}_{22} + 2\text{H}_2\text{O}(g)$	935
	Illite	$\text{K}_{1.5}(\text{Al}_{3.5}\text{Mg}_{0.5})(\text{Si}_7\text{Al})\text{O}_{20}(\text{OH})_4 \xrightarrow{h_r}$ $0.75\text{K}_2\text{O} \cdot 0.5\text{MgO} \cdot 2.25\text{Al}_2\text{O}_3 \cdot 7\text{SiO}_2 + 2\text{H}_2\text{O}(g)$	750
Carbonate decomposition	Calcite	$\text{CaCO}_3 \xrightarrow{h_r} \text{CaO} + \text{CO}_2$	1023
	Siderite	$\text{FeCO}_3 \xrightarrow{h_r} 1/3\text{Fe}_3\text{O}_4 + 1/3\text{CO} + 2/3\text{CO}_2$	773
	Dolomite	$\text{MgCO}_3 \cdot \text{CaCO}_3 \xrightarrow{h_r} \text{MgO} + \text{CaO} + 2\text{CO}_2$	1023
	Pyrite	$\text{FeS}_2 + \text{H}_2 \xrightarrow{h_r} \text{FeS} + \text{H}_2\text{S}$	773
	Pyrite	$\text{FeS}_2 + 2/3\text{H}_2\text{O} \xrightarrow{h_r} \text{FeS} + 2/3\text{H}_2\text{S} + 1/3\text{SO}_2$	773
Oxidation	Pyrite	$\text{FeS}_2 + 11/4\text{O}_2 \xrightarrow{h_r} 1/2\text{Fe}_2\text{O}_3 + 2\text{SO}_2$	1023
Oxidation	Magnetite	$\text{Fe}_3\text{O}_4 + 1/4\text{O}_2 \xrightarrow{h_r} 3/2\text{Fe}_2\text{O}_3$	1023
Oxidation	Troilite	$\text{FeS} + 7/4\text{O}_2 \xrightarrow{h_r} 1/2\text{Fe}_2\text{O}_3 + \text{SO}_2$	1023
S Capture	Calcium Oxide	$\text{CaO} + \text{SO}_2 + 1/2\text{O}_2 \xrightarrow{h_r} \text{CaSO}_4$	1023
	Hematite	$\text{Fe}_2\text{O}_3 + 1/3\text{H}_2 \xrightarrow{h_r} 2/3\text{Fe}_3\text{O}_4 + 1/3\text{H}_2\text{O}(g)$	773
	Hematite	$\text{Fe}_2\text{O}_3 + 1/3\text{CO} \xrightarrow{h_r} 2/3\text{Fe}_3\text{O}_4 + 1/3\text{CO}_2$	773

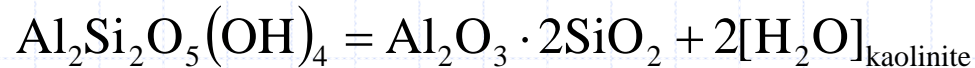
Modeled Mineral Components

Model component	Aspen Plus component type	Analytical determination
Bound H ₂ O	Conventional inert solid (CIS)	MFA water
Bound CO ₂	Conventional inert solid (CIS)	Inorganic carbon as CO ₂
Ash	Non-conventional (NC)	Ultimate analysis ash

Derive thermodynamic properties of modeled components by splitting and lumping pure components.

Properties of Modeled Mineral Components

- Splitting components – example kaolinite



$$c_{p,[\text{H}_2\text{O}]_{\text{kaolinite}}} = \frac{[Mc_p]_{\text{kaolinite}} - [Mc_p]_{\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2}}{2M_{[\text{H}_2\text{O}]_{\text{kaolinite}}}}$$

$$h_{f,[\text{H}_2\text{O}]_{\text{kaolinite}}}^{\circ} = \frac{[Mh_f^{\circ}]_{\text{kaolinite}} - [Mh_f^{\circ}]_{\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2}}{2M_{[\text{H}_2\text{O}]_{\text{kaolinite}}}}$$

- Lumping components – example Bound H₂O

$$\text{BoundH}_2\text{O} = \sum_i x_i$$

$$[xc_p]_{\text{BoundH}_2\text{O}} = \sum_i x_i c_{p_i}$$

$$[xh_f^{\circ}]_{\text{BoundH}_2\text{O}} = \sum_i x_i h_{f_i}^{\circ}$$

c_p = heat capacity, kJ/kg.K

h_f° = standard heat of formation, kJ/kg

M = molecular weight, kg/kmol

x = mass fraction H₂O

i = H₂O of kaolinite, smectite, illite, gypsum,...

Modeled Oil Shale Specific Organic Components

Model component	Aspen Plus component type	Analytical determination
Kerogen	Non-conventional (NC) M=1	CHNOS from ultimate analysis minus inorganic CO ₂ and MFA water
Char	Non-conventional (NC) M=1	Same as Kerogen
Light oil	Mixed component - pseudocomponent	TBP and density curves
Heavy oil	Mixed component pseudocomponent	TBP and density curves

Kerogen Elemental Composition

Element wt%	Kukersite Estonia	Mahogany Zn Green River USA	El Lajjun Jordan	Fushun China	Kerosene Crk Stuart Australia
C	77.45	81.2	75.5	79.07	75.2
H	9.70	10.5	9.5	9.93	9.8
N	0.33	1.4	2.7	2.12	1.4
S	1.76	1.2	10.9	1.86	1.2
O	10.01	5.7	1.4	7.02	12.4
Cl	0.75	-	-	-	-
Reference	Ots 2003	Ingram 1983	-	Qian 2003	Ingram 1983

Properties of Kerogen and Char

- Heat of combustion – Built-in Boie correlation and ultimate analysis

$$h_c^o = a_1 x_C + a_2 x_H + a_3 x_S + a_4 x_O + a_5 x_N + a_6$$

- Standard heat of formation - heat of combustion-based

$$h_f^o = h_c^o + b_1 x_C + b_2 x_H + b_3 x_S + b_4 x_N + b_5 x_{Cl}$$

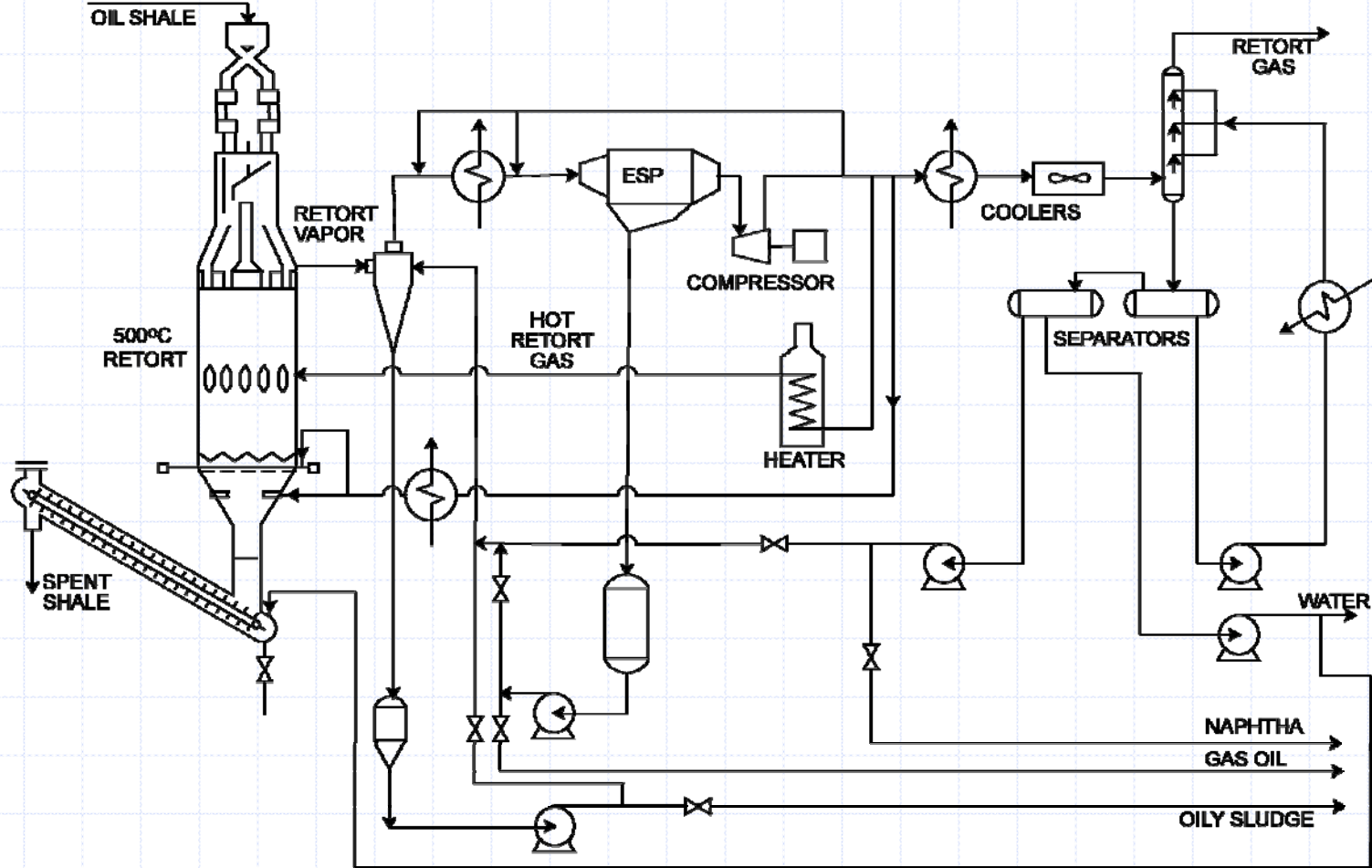
- Heat capacity – Built-in Kirov correlation and proximate analysis

$$C_p = \sum w_j C_{pj}$$

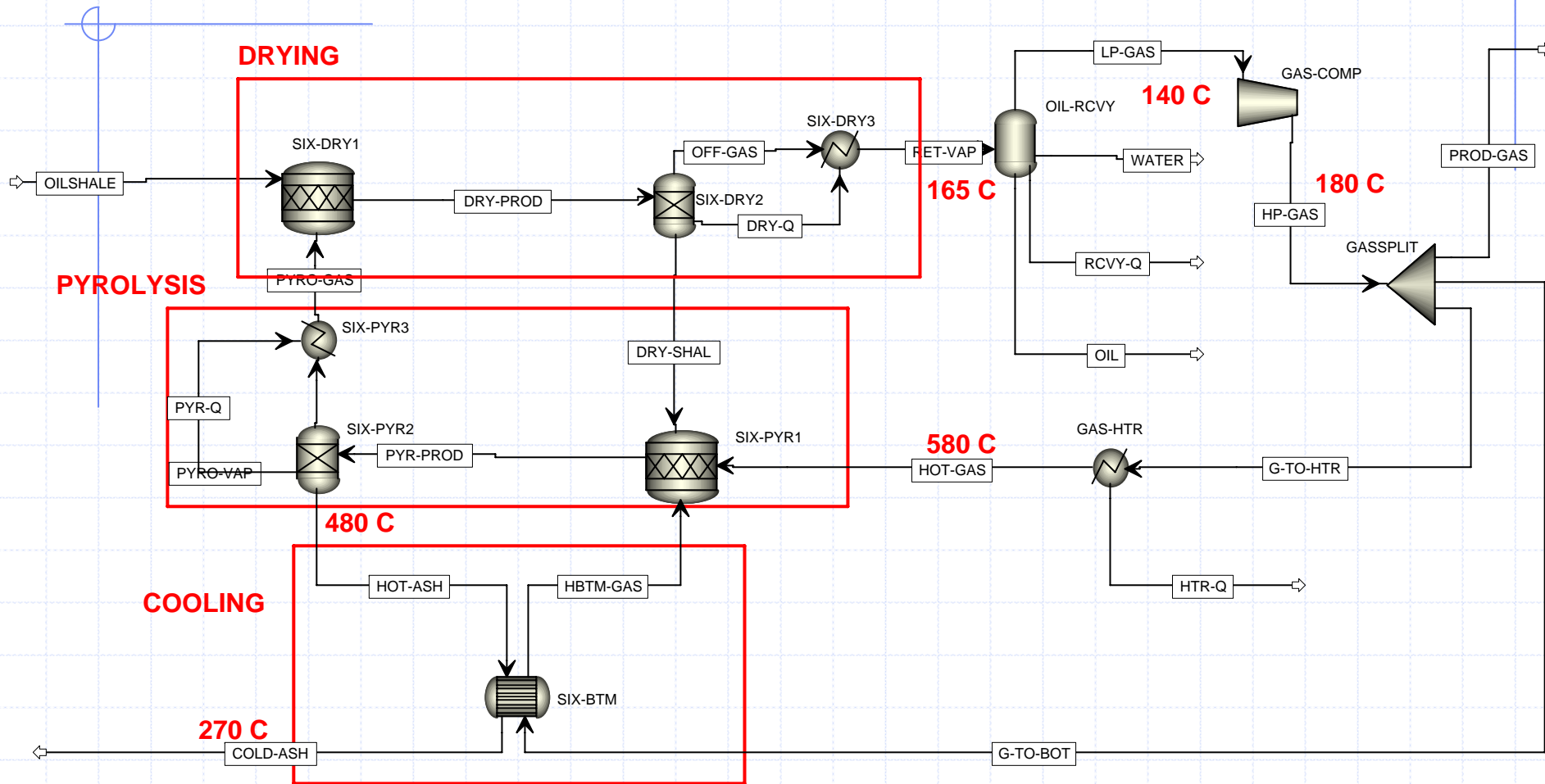
$$C_{pj} = a_{j1} + a_{j2}T + a_{j3}T^2 + a_{j4}T^3$$

$$j = \text{VM, FC}$$

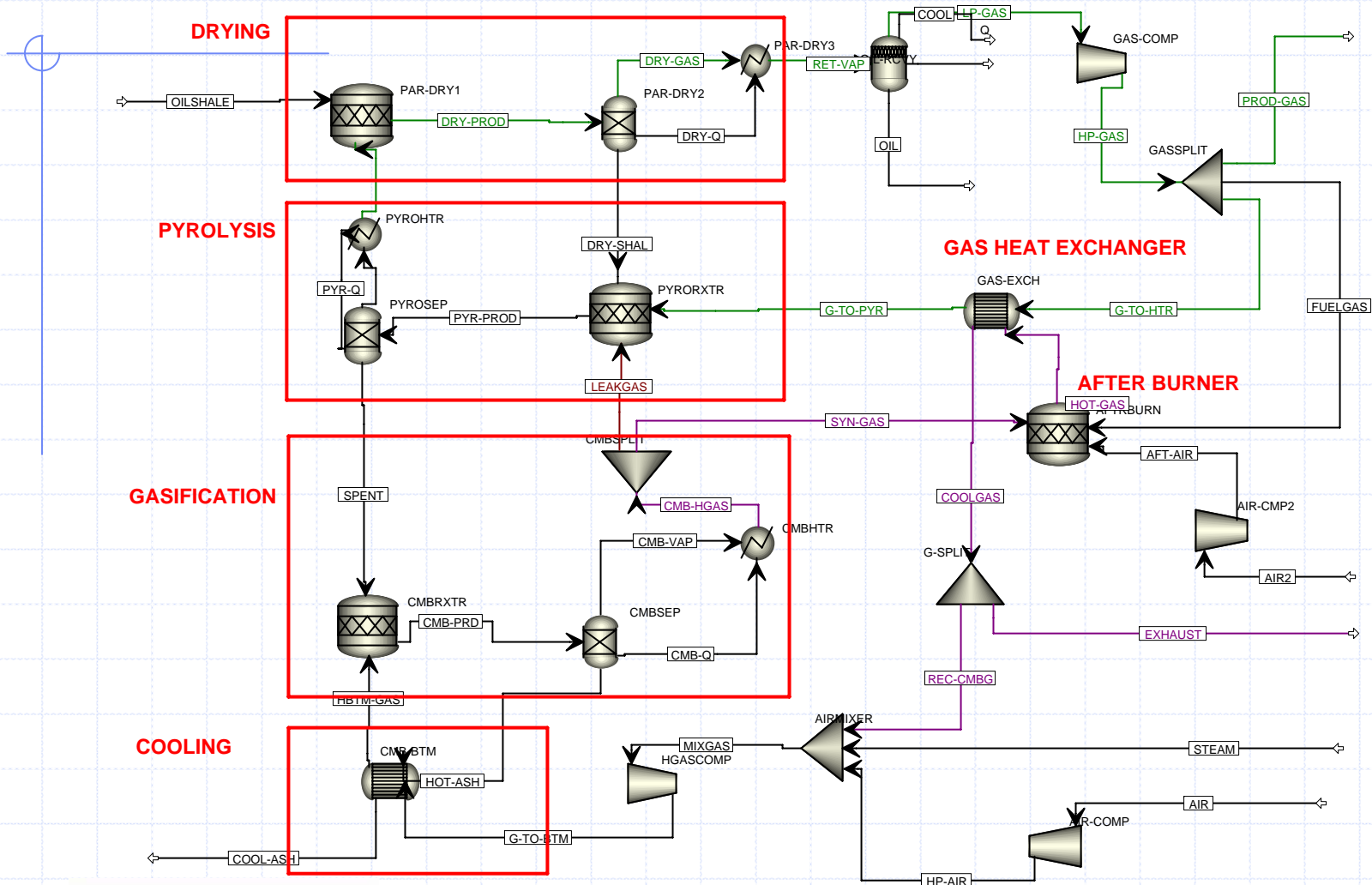
PetroSIX



Externally Heated Recycle Gas



Externally Heated Recycle Gas with Char Gasification



Reaction Modeling

Reactor Model	Description
RYield	Non-stoichiometric reactor based on known yield distribution
RStoic	Stoichiometric reactor based on known fractional conversions or extents of reaction
RCSTR	Rigorous continuous stirred tank reactor with rate-controlled reactions based on known kinetics. Also allows for equilibrium reactions.
RPlug	Rigorous plug flow reactor with rate-controlled reactions based on known kinetics
REquil	Rigorous equilibrium reactor based on stoichiometric approach
RGibbs	Rigorous reaction and/or multiphase equilibrium based on Gibbs free energy minimization

Pyrolysis with Stoichiometric Reactor Model

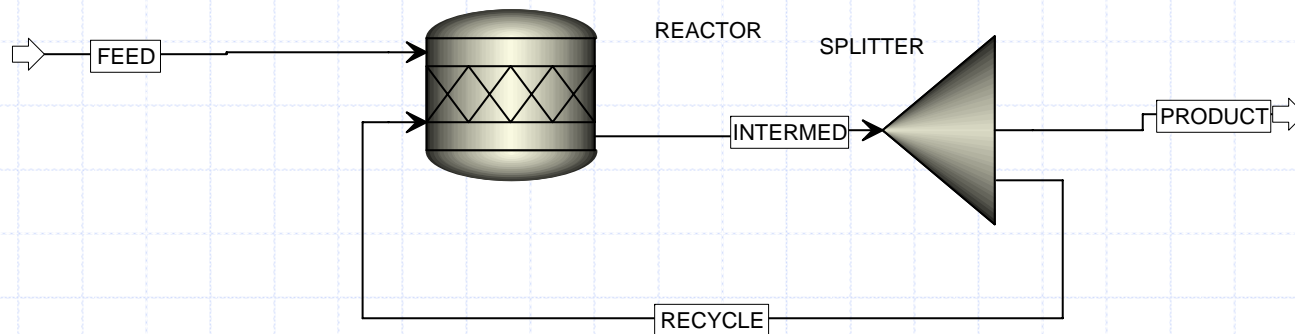
- Pyrolysis reaction stoichiometry
 - Clay dehydroxylation
 - $\text{BoundH}_2\text{O} \rightarrow \text{H}_2\text{O}(\text{g})$
 - Carbonate decomposition
 - $\text{BoundCO}_2 \rightarrow \text{CO}_2(\text{g})$
 - Kerogen decomposition
 - $\text{Kerogen} \rightarrow \text{oil} + \text{gas} + \text{char}$
- Fraction conversion is specified for each reaction
- Elemental balance using ULTANAL attributes and calculator block

Two Solution Approaches

- Sequential modular (SM)
- Equation-oriented (EO)

Sequential Modular Solution Approach

- Input streams and module inputs specified
- Balance each module sequentially
- Output from one module becomes input for next
- Recycle streams solved iteratively

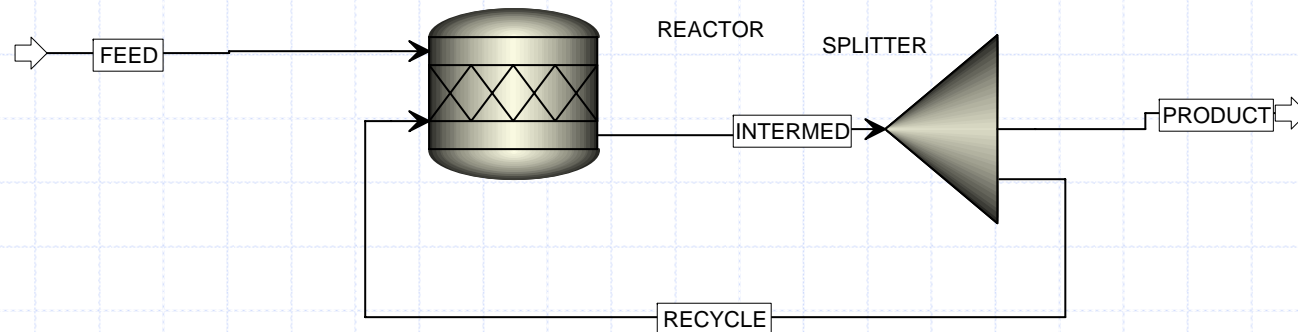


Sequential Modular Solution Approach

- Advantages
 - Used by most modern process simulation packages
 - Any number of streams, modules and components
 - Easy to program and develop
 - Easy to check for completeness and correctness
- Disadvantages
 - Rigid input
 - Slow for process with many recycle streams

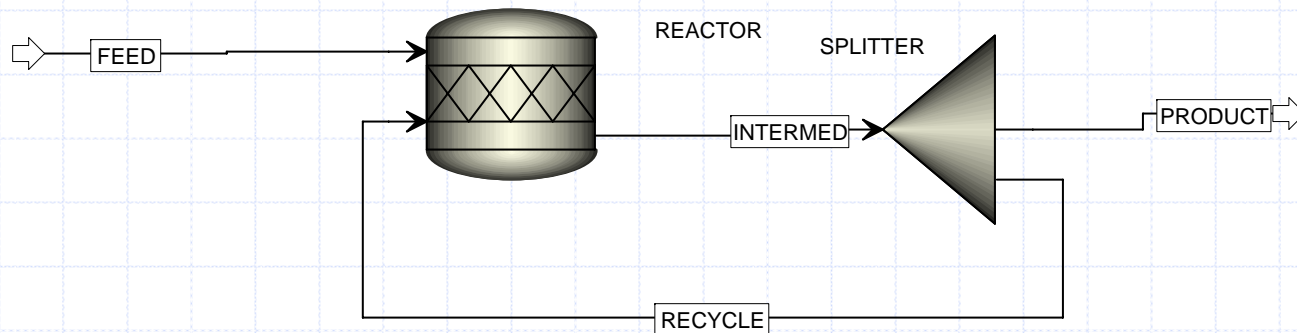
Parameter Estimation using SM

- From tests, feed and products are known and need to calculate module parameters
- Iteratively solved using Aspen Plus 'design spec'



Equation-Oriented Solution Approach

- Equate all balance equations to zero
- Solve all streams including recycles simultaneously



$$\text{Reactor : } -I + R + F = 0$$

$$\text{Splitter : } I - P - R = 0$$

Parameter Estimation using EO

- Develop predictor model in SM mode then switch to EO mode
- Switch to parameter estimation model by re-defining input and calculated variables to maintain same degrees of freedom
- After parameter estimation switch back to predictor model
- EO solution not yet available for 'NC' solids in Aspen Plus 2006.5
- 'NC' solids can be converted to 'CI' solids but kerogen and char composition must be constant

What next?

- Data reconciliation and process optimization
- Sulphur balances
 - Add FeS_2 , Fe_2O_3 , CaSO_4 , CaO , and CaCO_3 as separate components
 - Add pyrite decomposition and sulphur capture reactions
- Replace stoichiometric reactors with kinetic and equilibrium reactors
- Particle size distributions
 - Particle breakage and attrition
 - Separate composition for fines and coarse particles
- Dynamic simulation and automatic control
- Cost estimation and cost optimization
- Couple with CFD-DEM and custom equipment models

Conclusions

- A general purpose process simulator is a useful tool for the development of oil shale conversion processes
- Oil shale specific components and their properties need to be supplied
- Built-in unit operation models are usually adequate but customized models can be developed
- Equation-oriented solution approach is useful for parameter estimation, data reconciliation, optimization and dynamic simulation