Process Modeling for the Development of Oil Shale Retorting Processes

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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				
	Geothite			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	$Ca_{0.43}K_{0.24}(Al_{2.59}Fe_{0.75}Mg_{0.65})(Si_{7.67}Al_{0.3})O_{20}(OH)_4 \cdot 2H_2O \xrightarrow{h_r} \text{smectite} + 2H_2O(g)$	446
	Gypsum	$CaSO_4 \cdot 2H_2O \xrightarrow{h_r} CaSO_4 + 2H_2O(g)$	523
Dehydroxylation	Kaolinite	$Al_2Si_2O_5(OH)_4 \xrightarrow{h_r} Al_2O_3 \cdot 2SiO_2 + 2H_2O(g)$	810
	Smectite	$Ca_{0.43}K_{0.24}(Al_{2.59}Fe_{0.75}Mg_{0.65})(Si_{7.67}Al_{0.3})O_{20}(OH)_4 \xrightarrow{h_r} Ca_{0.43}K_{0.24}(Al_{2.59}Fe_{0.75}Mg_{0.65})(Si_{7.67}Al_{0.3})O_{22} + 2H_2O(g)$	935
	Illite	$K_{1.5}(Al_{3.5}Mg_{0.5})(Si_7Al)O_{20}(OH)_4 \xrightarrow{h_r} 0.75K_2O \cdot 0.5MgO \cdot 2.25Al_2O_3 \cdot 7SiO_2 + 2H_2O(g)$	750
Carbonate decomposition	Calcite	$CaCO_3 \xrightarrow{h_r} CaO + CO_2$	1023
	Siderite	$FeCO_3 \xrightarrow{h_r} 1/3Fe_3O_4 + 1/3CO + 2/3CO_2$	773
	Dolomite	$MgCO_3 \cdot CaCO_3 \xrightarrow{h_r} MgO + CaO + 2CO_2$	1023
	Pyrite	$FeS_2 + H_2 \xrightarrow{h_r} FeS + H_2S$	773
	Pyrite	$FeS_2 + 2/3H_2O \xrightarrow{h_r} FeS + 2/3H_2S + 1/3SO_2$	773
Oxidation	Pyrite	$FeS_2 + 11/4O_2 \xrightarrow{h_r} 1/2Fe_2O_3 + 2SO_2$	1023
Oxidation	Magnetite	$Fe_3O_4 + 1/4O_2 \xrightarrow{h_r} 3/2Fe_2O_3$	1023
Oxidation	Troilite	$FeS + 7/4O_2 \xrightarrow{h_r} 1/2Fe_2O_3 + SO_2$	1023
S Capture	Calcium Oxide	$CaO + SO_2 + 1/2O_2 \xrightarrow{h_r} CaSO_4$	1023
	Hematite	$Fe_2O_3 + 1/3H_2 \xrightarrow{h_r} 2/3Fe_3O_4 + 1/3H_2O(g)$	773
	Hematite	$Fe_2O_3 + 1/3CO \xrightarrow{h_r} 2/3Fe_3O_4 + 1/3CO_2$	773

Modeled Mineral Components

Model component	Aspen Plus component type	Analytical determination
Bound H_2O	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

$$Al_2Si_2O_5(OH)_4 = Al_2O_3 \cdot 2SiO_2 + 2[H_2O]_{kaolinite}$$

$$c_{p,[H2O]kaolinite} = \frac{[Mc_p]_{kaolinite} - [Mc_p]_{Al2O3\cdot 2SiO2}}{2M_{[H2O]kaolinite}}$$

$$h^o_{f,[H2O]kaolinite} = \frac{\left[Mh^o_f\right]_{kaolinite} - \left[Mh^o_f\right]_{Al2O3\cdot 2SiO2}}{2M_{[H2O]kaolinite}}$$

- Lumping components – example Bound H_2O

$$BoundH2O = \sum_i x_i$$

$$[xc_p]_{BoundH2O} = \sum_i x_i c_{p_i}$$

$$[xh^o_f]_{BoundH2O} = \sum_i x_i h^o_{f_i}$$

c_p = heat capacity, kJ/kg.K

h^o_f = standard heat of formation, kJ/kg

M = molecular weight, kg/kmol

x = mass fraction H_2O

i = H_2O 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 - psuedocomponent	TBP and density curves
Heavy oil	Mixed component psuedocomponent	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

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

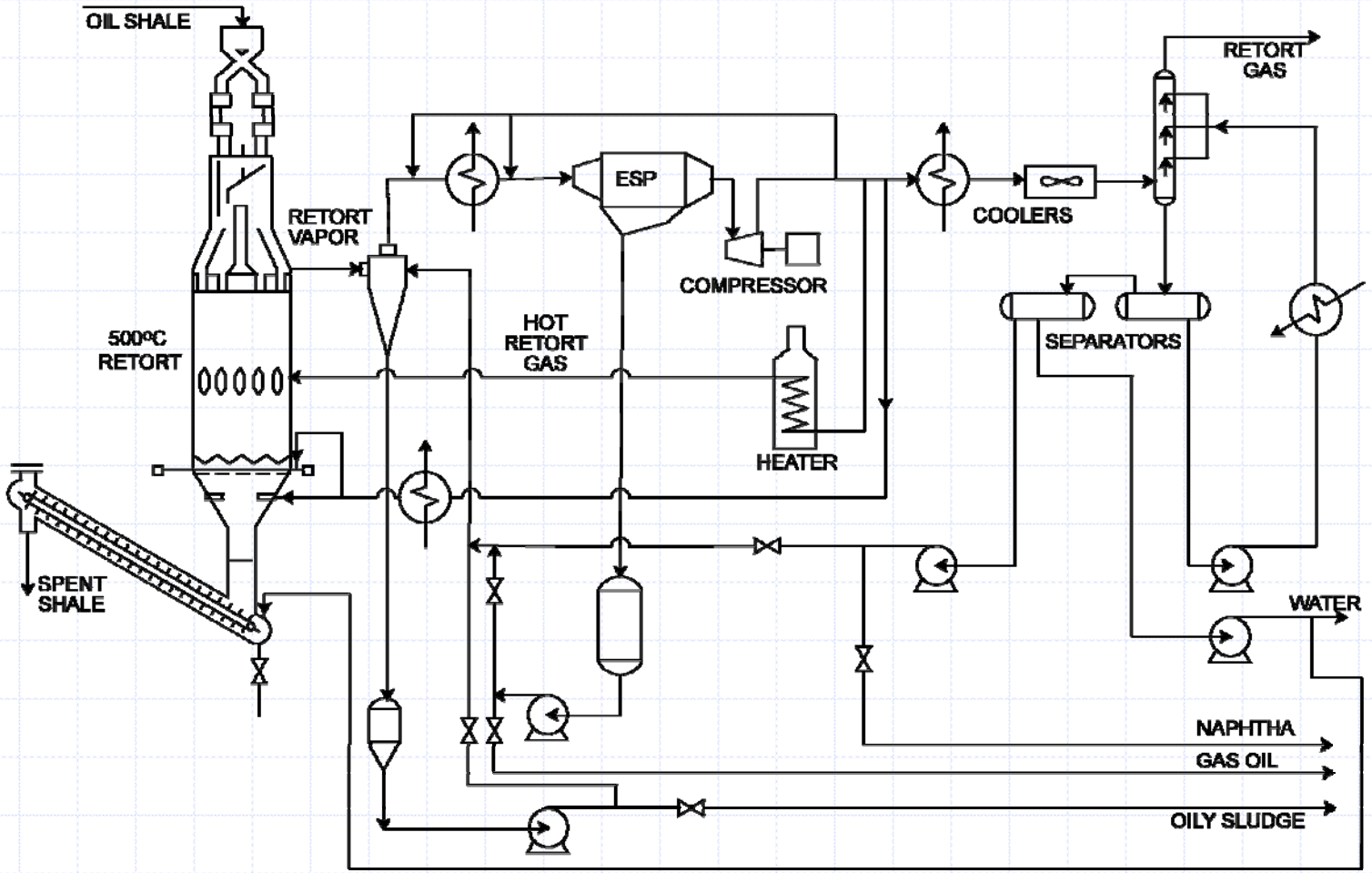
- Heat capacity – Built-in Kirov correlation and proximate analysis

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

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

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

PetroSIX



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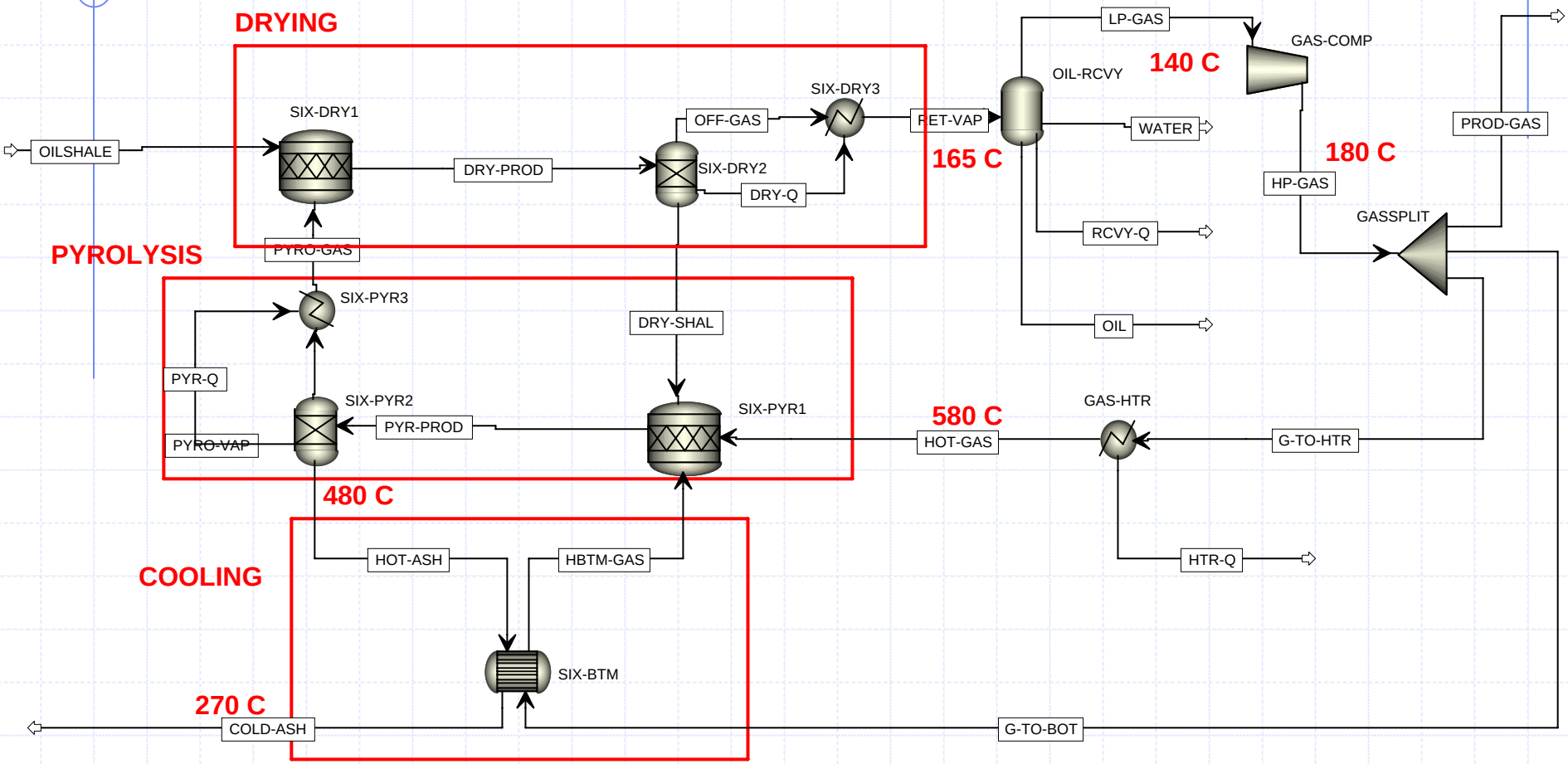
Externally Heated Recycle Gas



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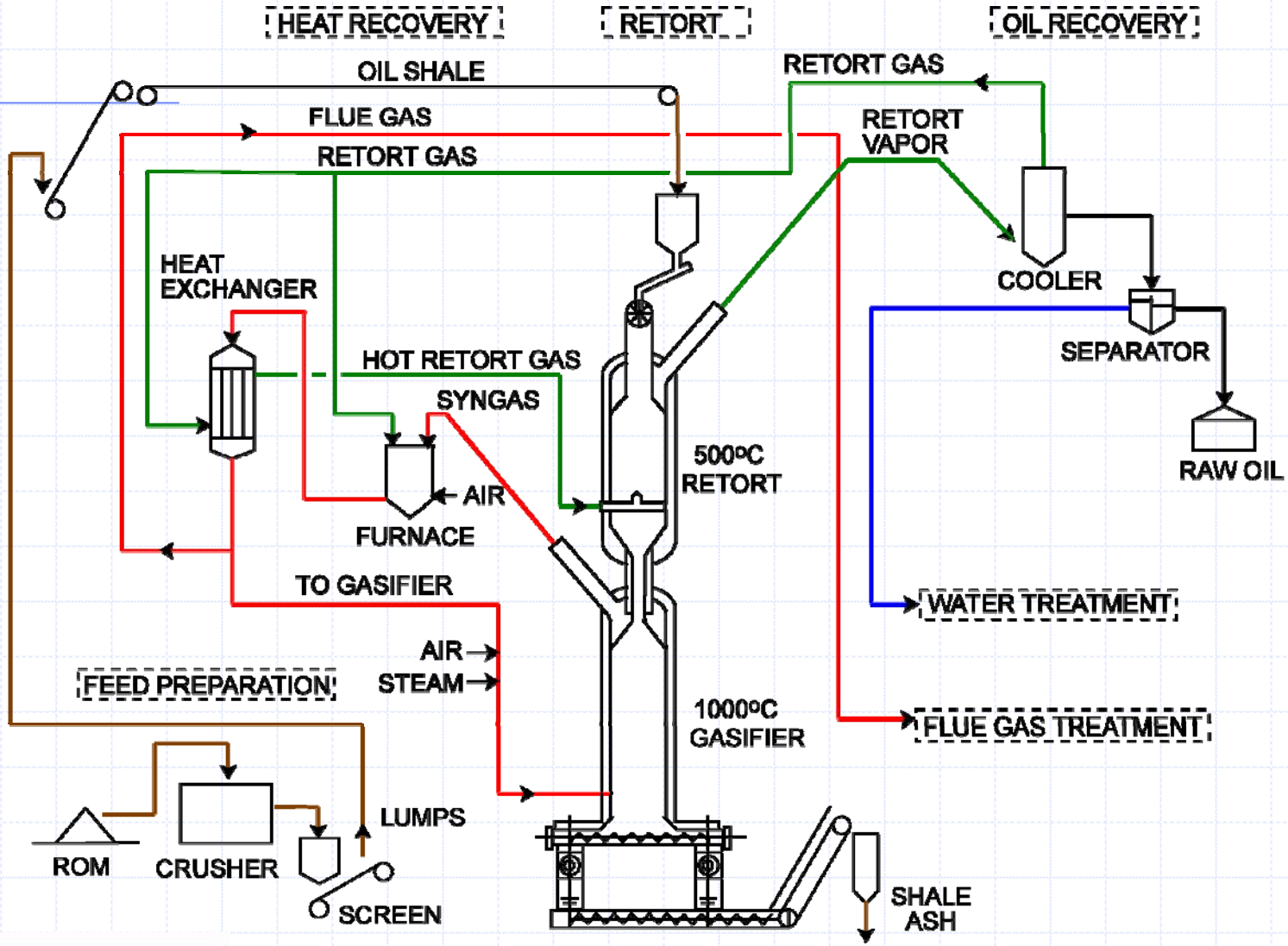

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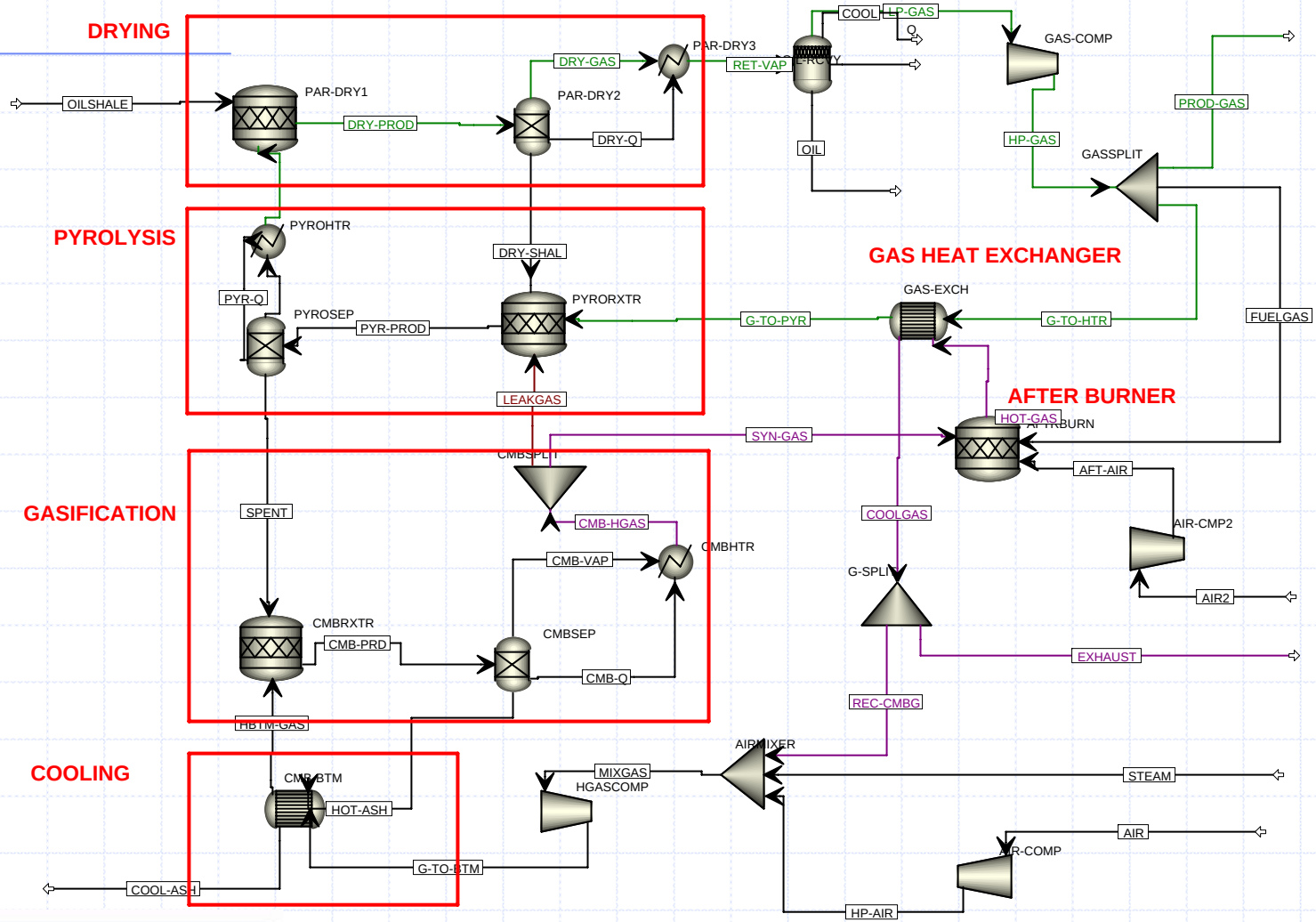
Externally Heated Recycle Gas with Char Gasification



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
    - BoundH_2O → H_2O(g)
  - Carbonate decomposition
    - BoundCO_2 → CO_2(g)
  - Kerogen decomposition
    - Kerogen →oil + gas + char
- Fraction conversion is specified for each reaction
- Elemental balance using ULTANAL attributes and calculator block

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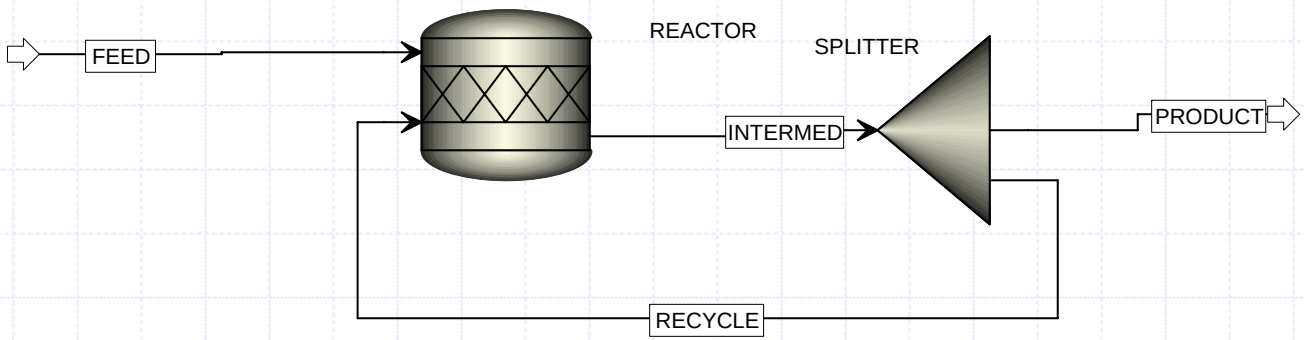
Two Solution Approaches

- 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

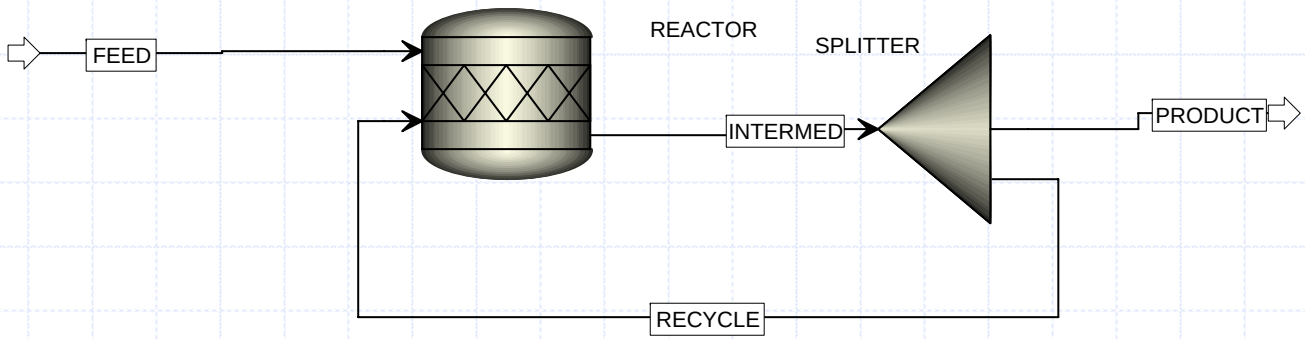


Sequential Modular Solution Approach

- 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

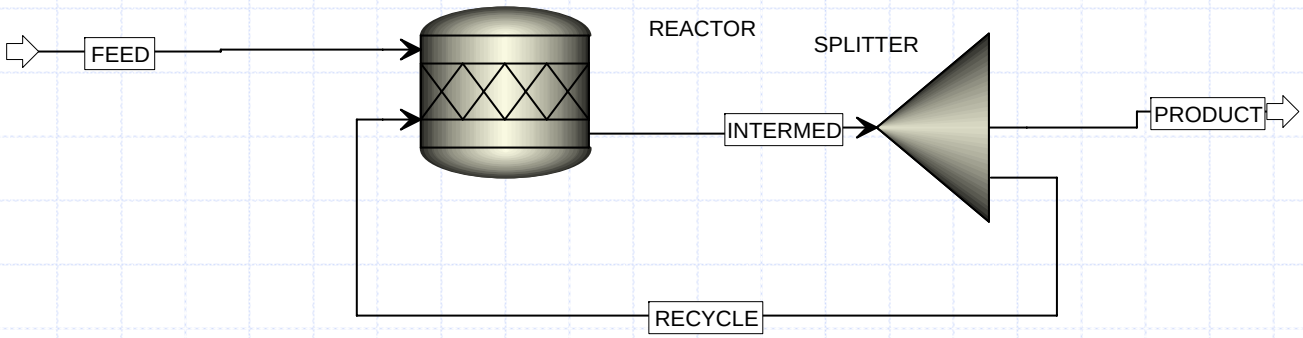
Parameter Estimation using SM

- 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



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

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

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