Advances in Steady-State Process Modeling of Oil Shale Retorting

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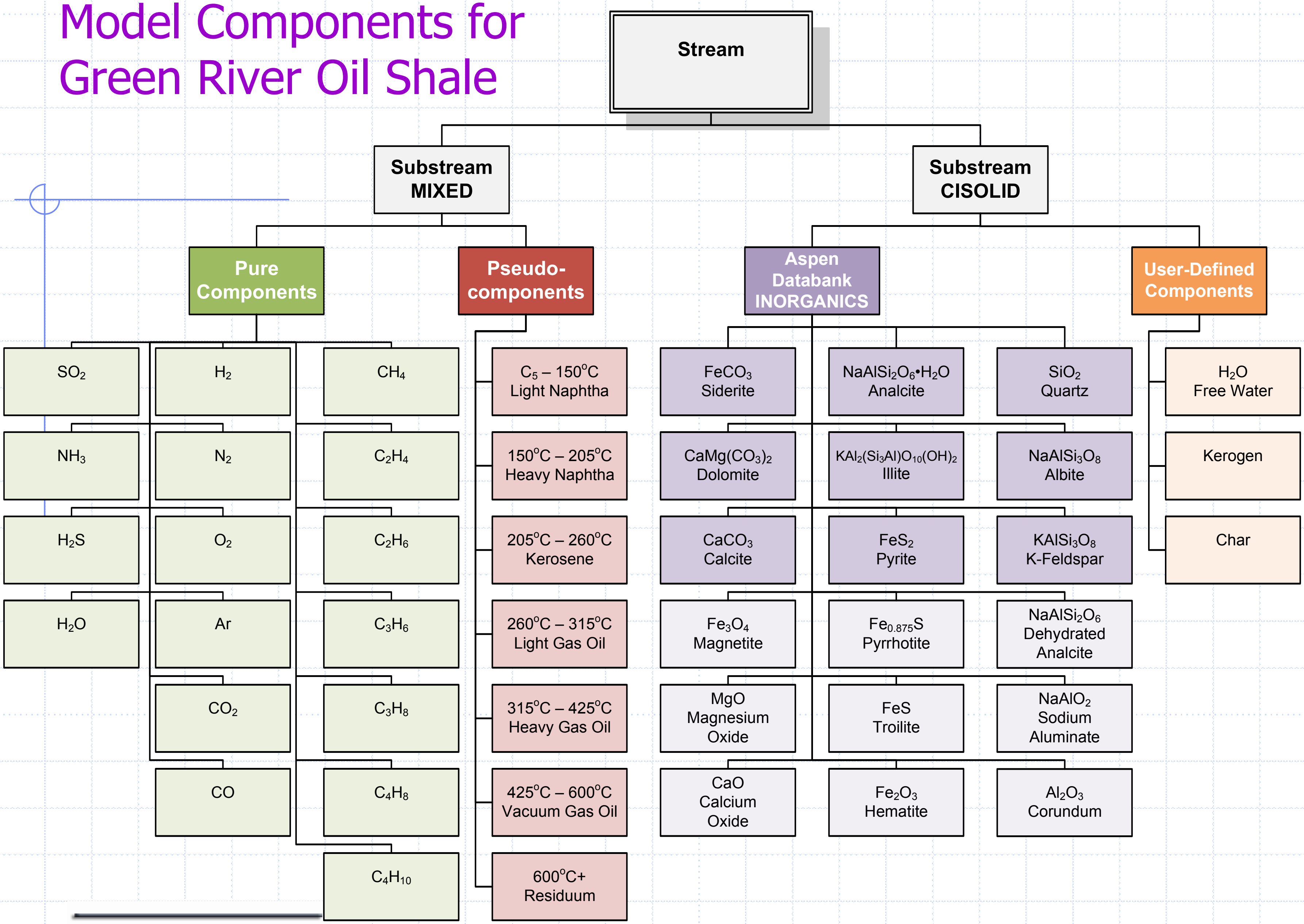
Process Simulators

- Used to develop models of chemical processes that consist of unit operations connected by streams
- Complete mass and heat balance calculations to determine unknown stream flow rates, temperatures, pressures, and compositions
- Contain built-in models for familiar unit operations
- Contain databank of components and methods to calculate thermodynamic properties

Aspen Plus

- Steady-state process simulator with breadth of features needed to simulate oil shale retorting processes
- Built-in libraries of unit operations, components and property methods for both hydrocarbon and mineral processing
- Allows user to create oil shale specific components and define their thermodynamic properties
- Ability to track particle size distribution
- Ability to specify kinetic rates for gas/solid reactions

Model Components for Green River Oil Shale



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Properties of User-Defined Components

- Gross heat of combustion of kerogen and char by Boie (1952)

$$\Delta_c H_{298}^o \left[\text{kJ/kg}\right] = 351.7 w_c + 1162 w_H + 104.7 w_N - 111.0 d w_O + 27 w_S - 439.6$$

- Standard heat of formation from heat of combustion

$$\Delta_f H_{298}^o \left[\text{kJ/kg}\right] = \Delta_c H_{298}^o \left[\text{kJ/kg}\right] - \left(141.8 w_H + 32.78 w_C + 9.26 w_S - 2.42 w_N\right)$$

where w_i = weight percent of element i

Properties of User-Defined Components

Green River Oil Shale

	Kerogen	Char
Formula from Singleton et al. 1986	$CH_{1.5}N_{0.025}O_{0.05}S_{0.005}$	$CH_{0.42}N_{0.056}O_{0.02}S_{0.008}$
Molecular weight, kg/kmol	14.833	13.795
Elemental composition, wt%		
Carbon	80.972	87.066
Hydrogen	10.193	3.069
Nitrogen	2.361	5.686
Oxygen	5.393	2.320
Sulfur	1.081	1.860
Gross heat of combustion, kJ/kg	39549	34042
Standard heat of formation, kJ/kg	-1489.7	1115.9
Standard heat of formation, kJ/kmol	-22097	15394

Properties of User-Defined Components

- Heat capacity

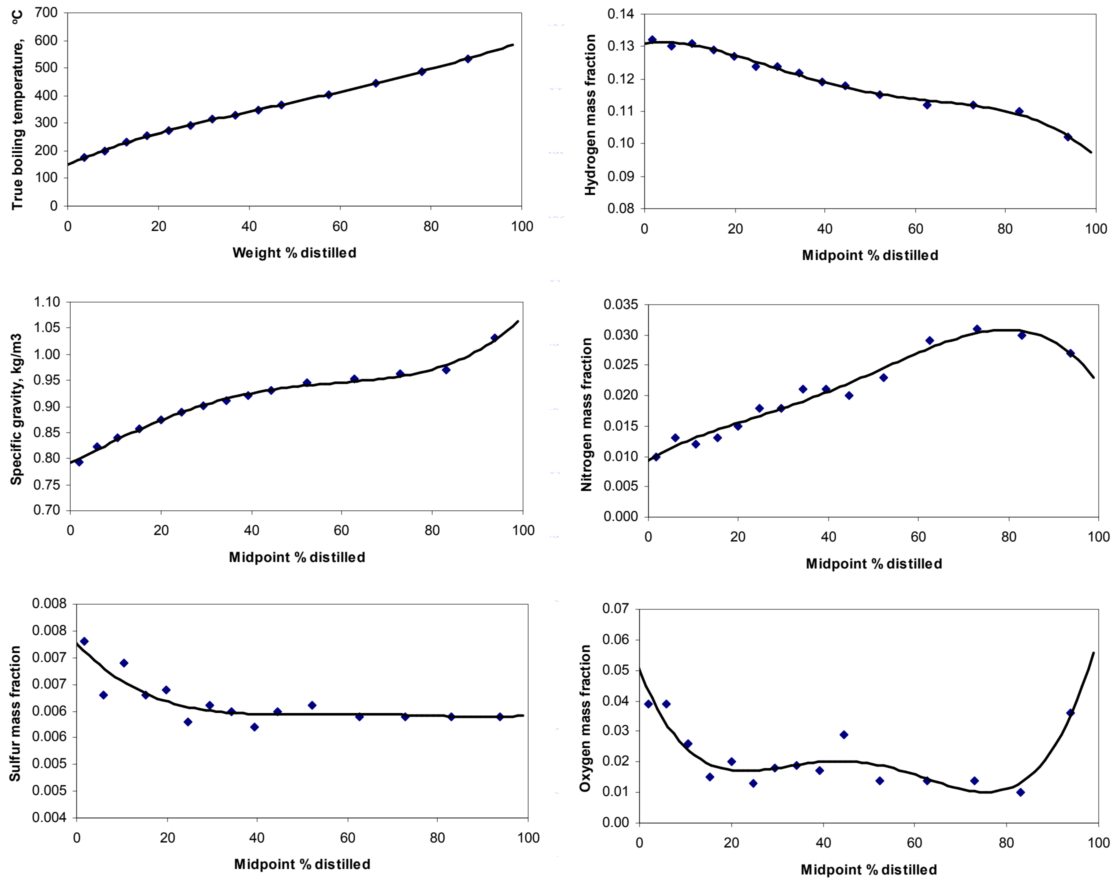
$$C_p[\text{kJ/kmol}\cdot\text{K}] = c_1 + c_2T + c_3T^2 + c_4T^3 + c_5T^4 \quad \text{where} \quad T_{\text{min}} \le T[\text{K}] \le T_{\text{max}}$$

- Green River kerogen and char – Camp (1987)

	Kerogen	**Char**	**Free Water**
MW, kg/kmol	14.833	13.795	18.015
c_1	$3.311\cdot10^{0}$	$-1.626\cdot10^{0}$	$5.084\cdot10^{1}$
c_2	$7.793\cdot10^{-2}$	$5.943\cdot10^{-2}$	$2.131\cdot10^{-1}$
c_3	$-2.453\cdot10^{-5}$	$-2.464\cdot10^{-5}$	$-6.314\cdot10^{-4}$
c_4	0	0	$6.487\cdot10^{-7}$
c_5	0	0	0
T_{min}, K	273	273	273
T_{max}, K	750	1000	623

Data for Pseudo-components

- Green River shale oil - Miknis (1988)



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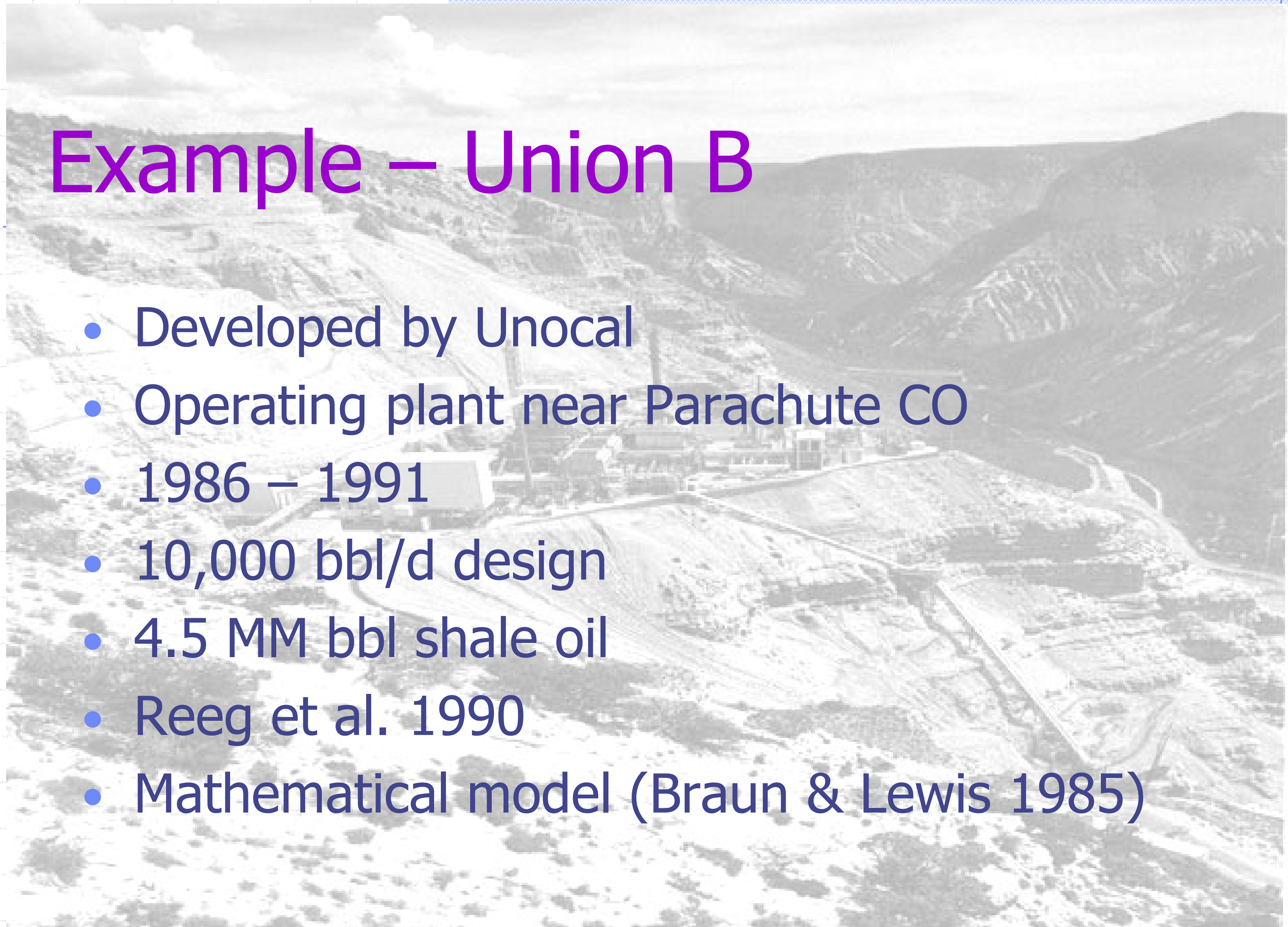
Generated Properties of Psuedo-components

- Green River shale oil

Component	Formula	Mol. Weight g/gmol	Lower Boiling Temperature ºC	Upper Boiling Temperature ºC
Light naphtha	$C_{8.5}H_{16.4}N_{0.10}O_{0.45}S_{0.03}$	128.3	C_5	150
Heavy naphtha	$C_{10.1}H_{19.0}N_{0.18}O_{0.53}S_{0.03}$	152.0	150	205
Kerosene	$C_{13.1}H_{23.4}N_{0.22}O_{0.26}S_{0.04}$	188.9	205	260
Light gas oil	$C_{15.9}H_{27.6}N_{0.37}O_{0.34}S_{0.04}$	231.4	260	315
Heavy gas oil	$C_{21.2}H_{34.4}N_{0.59}O_{0.53}S_{0.06}$	308.5	315	425
Vacuum gas oil	$C_{33.6}H_{51.6}N_{1.3}O_{0.48}S_{0.09}$	483.9	425	600
Residuum	$C_{40.7}H_{56.8}N_{1.4}O_{2.5}S_{0.11}$	609.5	600	700

Composition of Green River Oil Shale Brons & Siskin (1989)

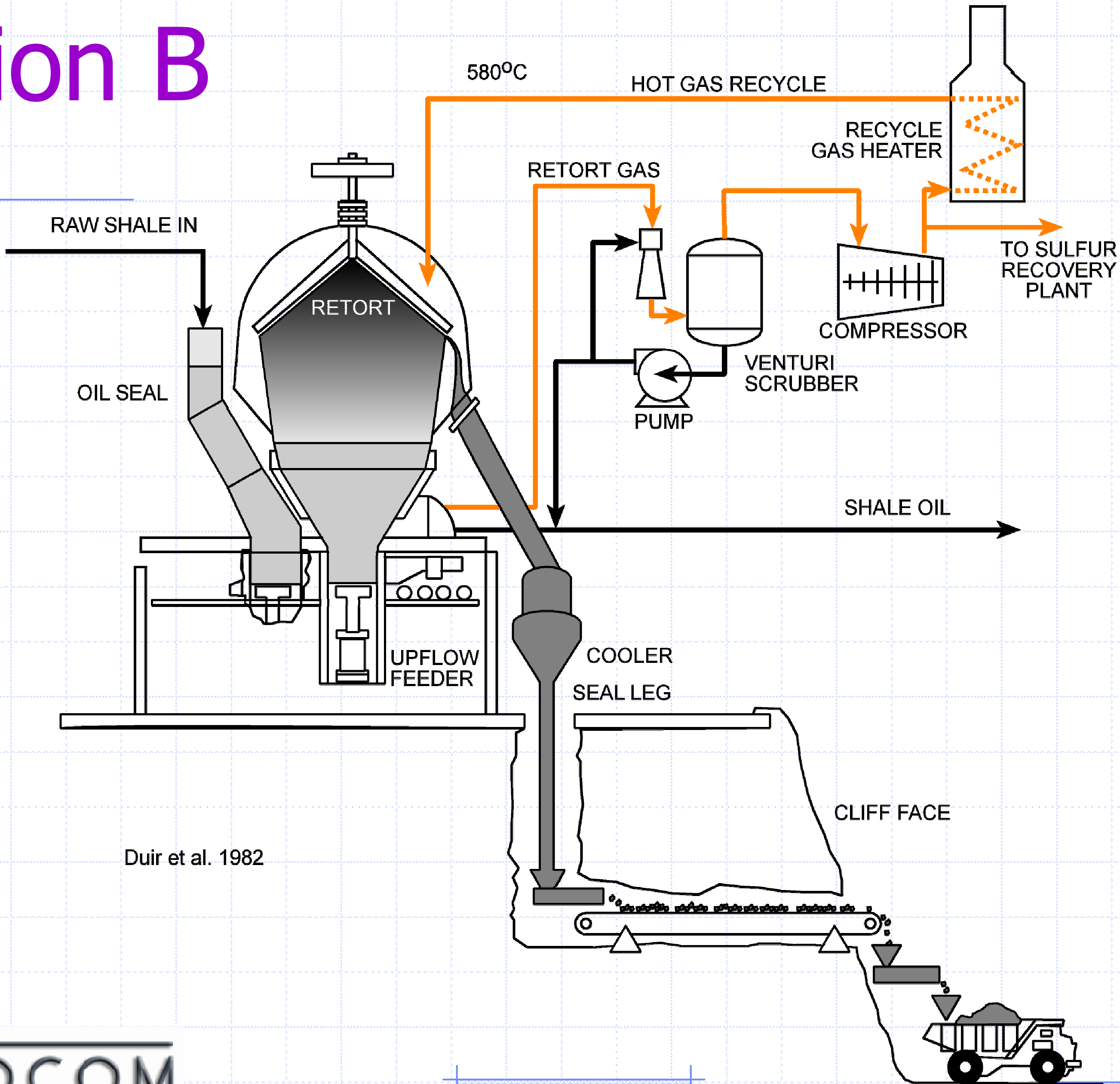
Component	Formula	Mol. Weight g/gmol	wt% dry basis
Kerogen			19.8
Siderite	$FeCO_3$	115.9	2.4
Dolomite	$CaMg(CO_3)_2$	184.4	22.8
Calcite	$CaCO_3$	100.1	14.1
Illite	$K(Al_2)(Si_3Al)O_{10}(OH)_2$	398.3	10.9
Analcime	$NaAlSi_2O_6 \cdot H_2O$	220.2	0.9
Dawsonite	$NaAlCO_3(OH)_2$	144.0	0.6
Pyrite	FeS_2	120.0	1.6
Quartz	SiO_2	60.1	13.2
Albite	$NaAlSi_3O_8$	262.2	13.7
Total			100.0



Example – Union B

- Developed by Unocal
- Operating plant near Parachute CO
- 1986 – 1991
- 10,000 bbl/d design
- 4.5 MM bbl shale oil
- Reeg et al. 1990
- Mathematical model (Braun & Lewis 1985)

Union B



Duir et al. 1982

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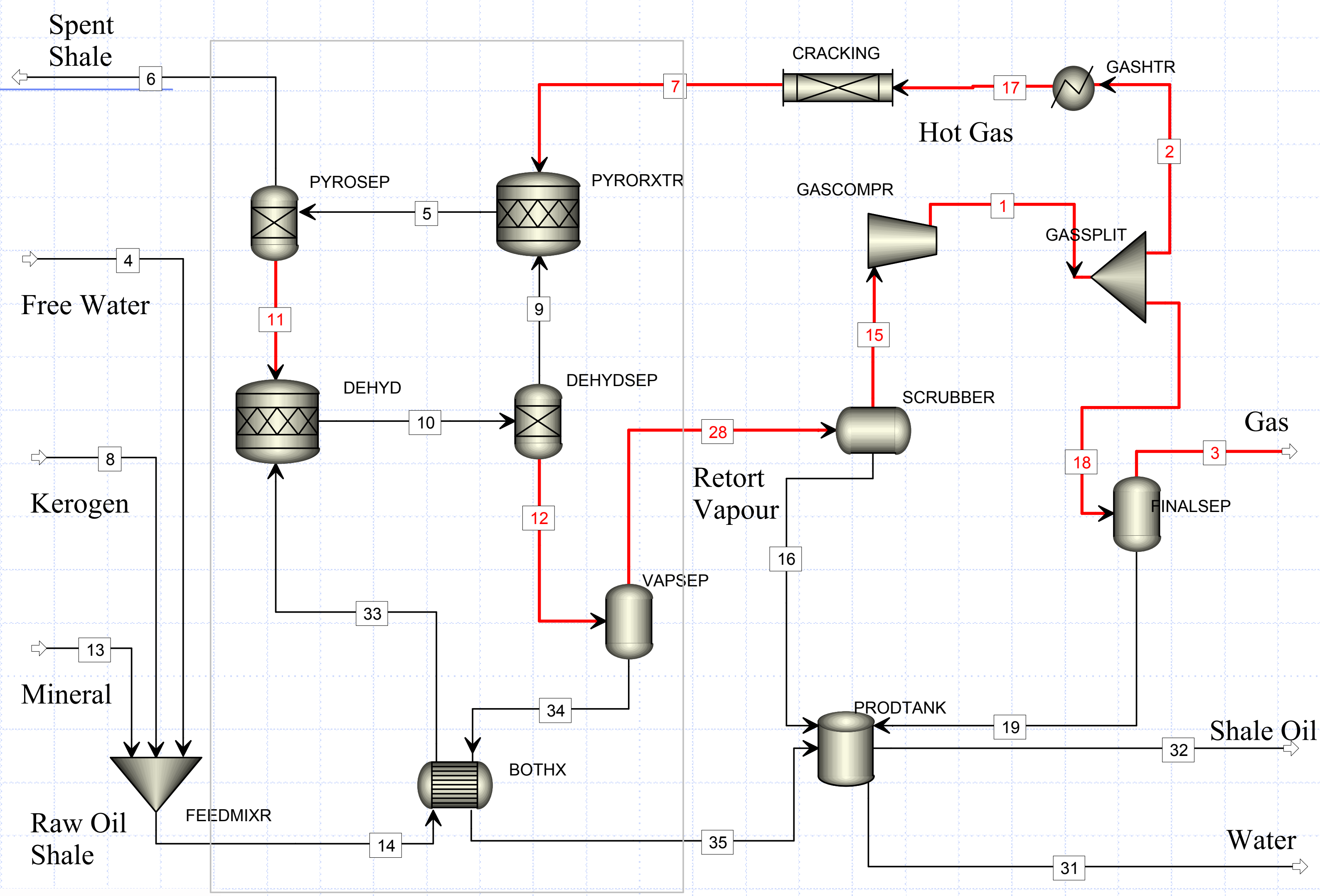
Union B Simulation Flowsheet



Mineral reaction stoichiometry and reaction temperature

Reactant	Reaction Equation	Peak ºC
Analcite	$NaAlSi_2O_6 \cdot H_2O \rightarrow NaAlSi_2O_6 + H_2O$	150-400
Dawsonite	$NaAlCO_3(OH)_2 \rightarrow NaAlO_2 + CO_2 + H_2O$	300, 440
Pyrite	$0.875FeS_2 + 0.75H_2 \rightarrow Fe_{0.875}S + 0.75H_2S$	450-550
Siderite	$3FeCO_3 \rightarrow Fe_3O_4 + CO + 2CO_2$	500-600
Magnetite	$Fe_3O_4 + H_2S \rightarrow FeS + Fe_2O_3 + H_2O$	
Illite	$K(Al_2)(Si_3Al)O_{10}(OH)_2 \rightarrow KAlSi_3O_8 + Al_2O_3 + H_2O$	550, 900
Dolomite	$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2$	790
Calcite	$CaCO_3 \rightarrow CaO + CO_2$	860-1010

Kerogen Pyrolysis Stoichiometry for Green River oil shale from Singleton et al.(1986)

Component	Molecular weight g/gmol	wt% of kerogen	moles per mole kerogen
Kerogen	14.83	**-100.000**	**-1.00000**
Methane	16.04	1.399	0.01293
Hydrogen	2.02	0.297	0.02189
Carbon monoxide	28.01	0.564	0.00298
Carbon dioxide	44.01	3.542	0.01194
Hydrogen sulfide	34.08	0.229	0.00099
Water	18.01	1.208	0.00995
Ethene	28.05	0.304	0.00161
Ethane	30.07	0.894	0.00441
Propene	44.10	0.582	0.00205
Propane	56.11	0.659	0.00222
Butene	58.12	0.519	0.00137
Butane	43.19	0.519	0.00132
Gas subtotal		**10.714**	
Light naphtha	128.3	0.985	0.00114
Heavy naphtha	152.0	5.018	0.00490
Kerosene	188.9	7.267	0.00571
Light gas oil	231.4	9.001	0.00577
Heavy gas oil	308.5	20.626	0.00992
Vacuum gas oil	483.9	22.814	0.00699
Residuum	609.5	3.036	0.00074
Oil subtotal		**68.746**	
Char	13.80	**20.539**	0.22085

Assume Union B retort and laboratory assay have same stoichiometry due to similarity in heating rates and maximum temperatures.

Oil Cracking in Hot Gas Recycle Furnace

- Stoichiometry based on Bissell et al. (1985), Burnham (1980) and Voge and Good (1949)

		Light naphtha		Heavy naphtha		Kerosene	
	MW g/gmol	wt% of light naphtha	moles per mole light naphtha	wt% of heavy naphtha	moles per mole heavy naphtha	wt% of kerosene	moles per mole kerosene
KERO	188.9					-100.0	-1.00000
HNAP	152.0			-100.0	-1.00000	11.6	0.14383
LNAP	128.3	-100.0	-1.00000	23.1	0.27411	11.6	0.17038
CH_4	16.04	5.8	0.46521	4.5	0.42352	4.5	0.52652
H_2	2.02	1.9	1.20483	1.5	1.09686	1.5	1.36360
CO	28.01	3.4	0.15356	2.6	0.13980	2.6	0.17379
C_2H_4	28.05	11.2	0.51132	8.6	0.46550	8.6	0.57871
C_2H_6	30.07	8.1	0.34454	6.2	0.31366	6.2	0.38994
C_3H_6	44.10	10.7	0.32540	8.2	0.29624	8.2	0.36828
C_3H_8	56.11	4.7	0.13767	3.6	0.12533	3.6	0.15581
C_4H_8	58.12	14.1	0.32353	10.9	0.29454	10.9	0.36616
C_4H_{10}	43.19	2.2	0.04897	1.7	0.04459	1.7	0.05543
Coke	13.80	37.9	3.52600	29.1	3.21003	29.1	3.99066

Oil Cracking in Recycle Furnace

- Kinetic Model D from Bissell et al. (1985)
- First-order with same activation energy for each fraction
- Pre-exponential factor depends on average molecular weight

$$\frac{dy_i}{dt} = A_i k y_i \qquad k = f_1 e^{-E_1/T}$$

$f_1 = 1.04 \cdot 10^8\ s^{-1}$ and $E_1 = 19588$ K

Oil fraction	Average molecular weight g/gmol	Relative cracking rate factor A_i
Light naphtha	128.28	2.9
Heavy naphtha	151.97	4.5
Kerosene	188.92	7.6

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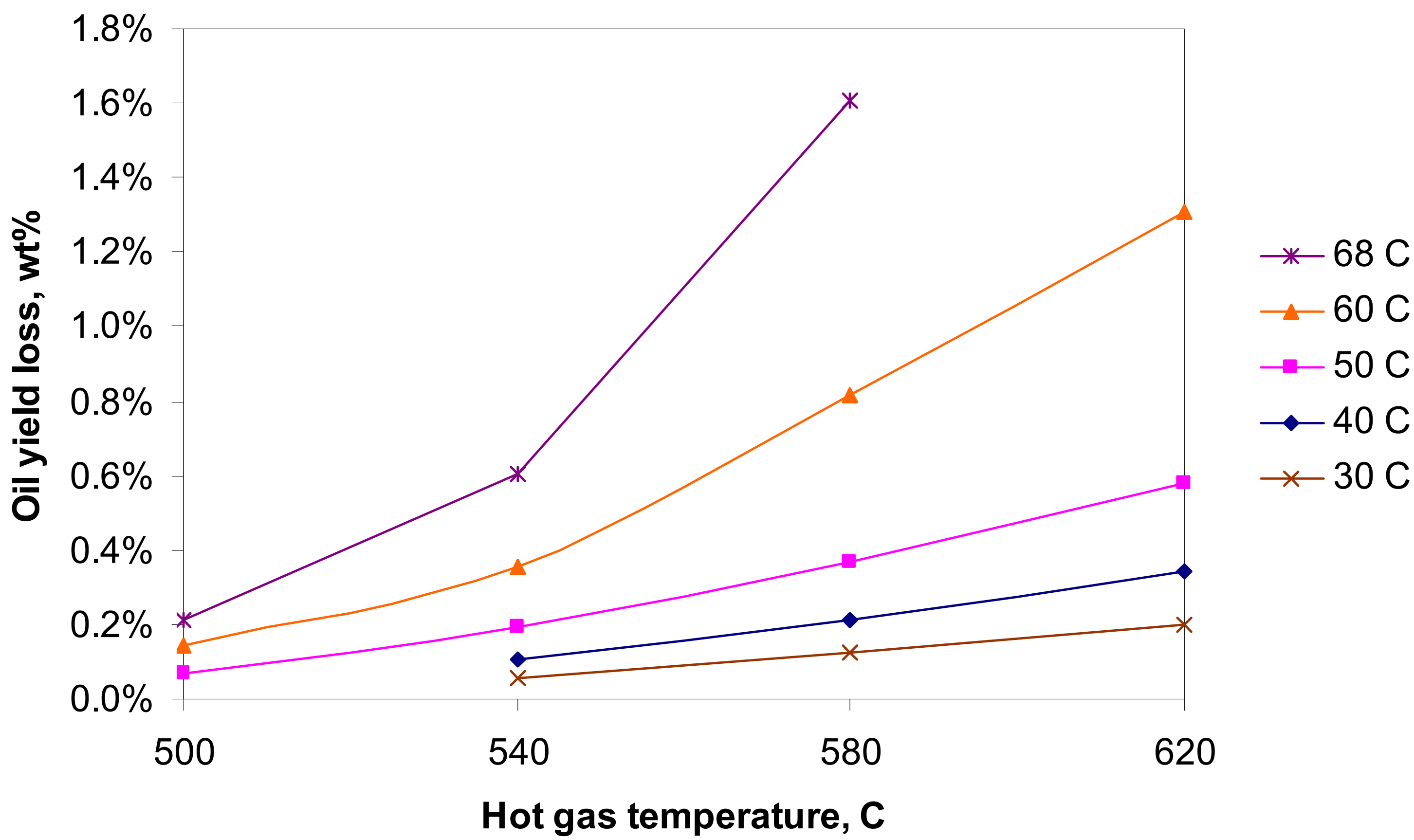
Predicted effect of hot gas temperature and scrubber temperature on oil cracking



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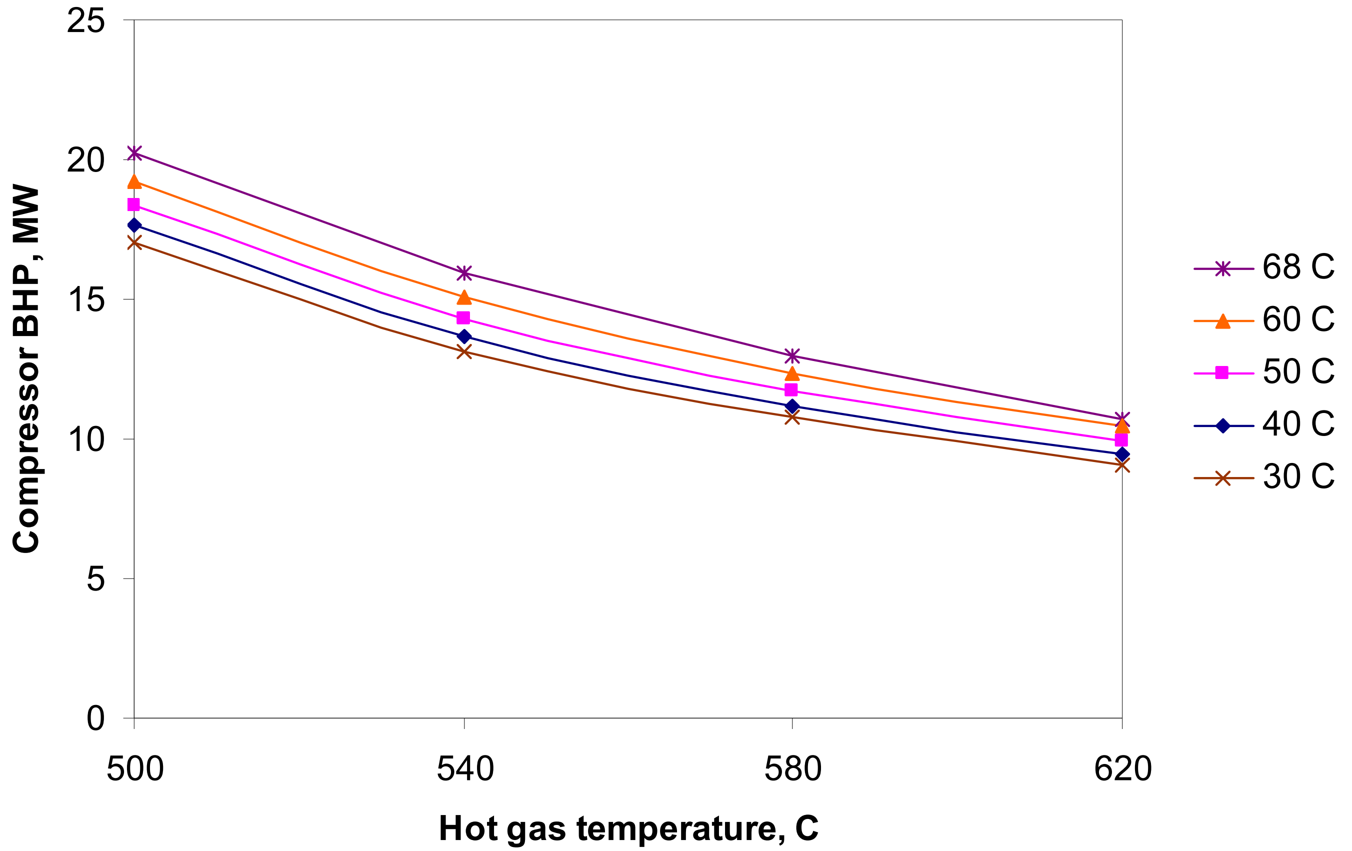
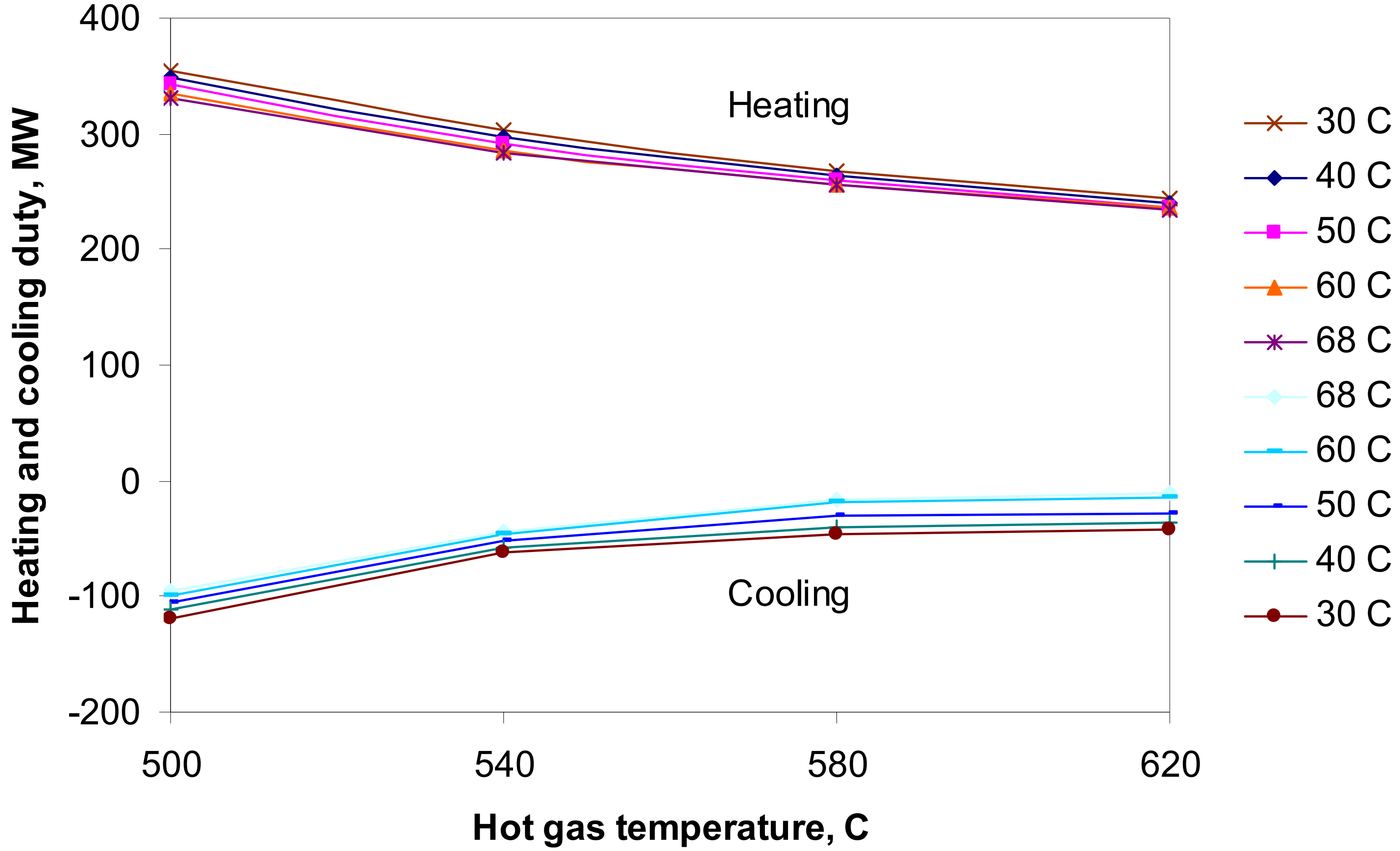
Predicted effect of hot gas temperature and scrubber temperature on compressor power



Predicted effect of hot gas temperature and scrubber temperature on gas heating and cooling



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Conclusions

- A general purpose process simulator is a useful tool for evaluating oil shale conversion processes
- A few oil shale specific components and their properties need to be supplied. Data is available in the literature.
- Built-in unit operation models are usually adequate for steady state mass and heat balances

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