A Simulation-based Protocol for Evaluating Various Shale Processing Options

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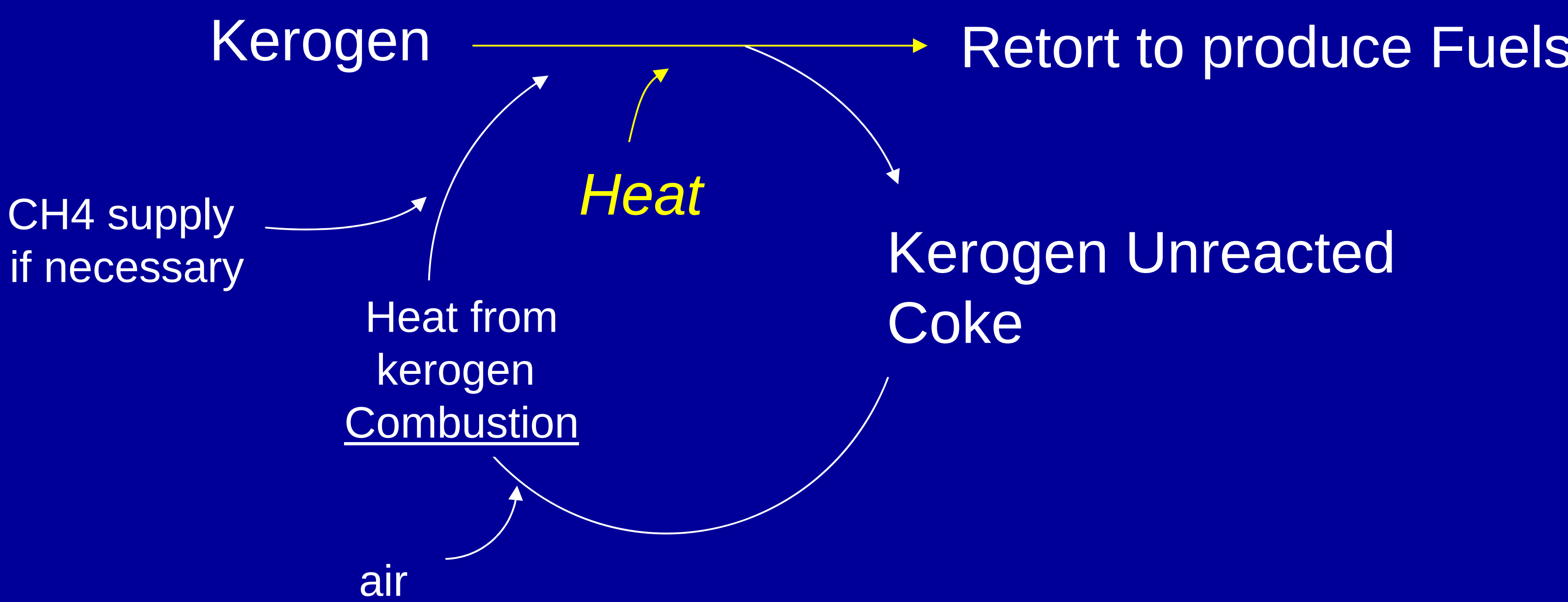
Oil shale

1. Broad definition: Any sedimentary rock that contains solid bituminous material (called **kerogen**)
2. Released as petroleum-like liquid when the rock is heated (process called **retorting**)
3. Surface retorting includes mining and retorting
4. In-situ **retorting** involves heating the oil shale while it is still underground and then pumping the resulting liquid to the surface.
5. Oil recovery varies depending upon the process

Objectives

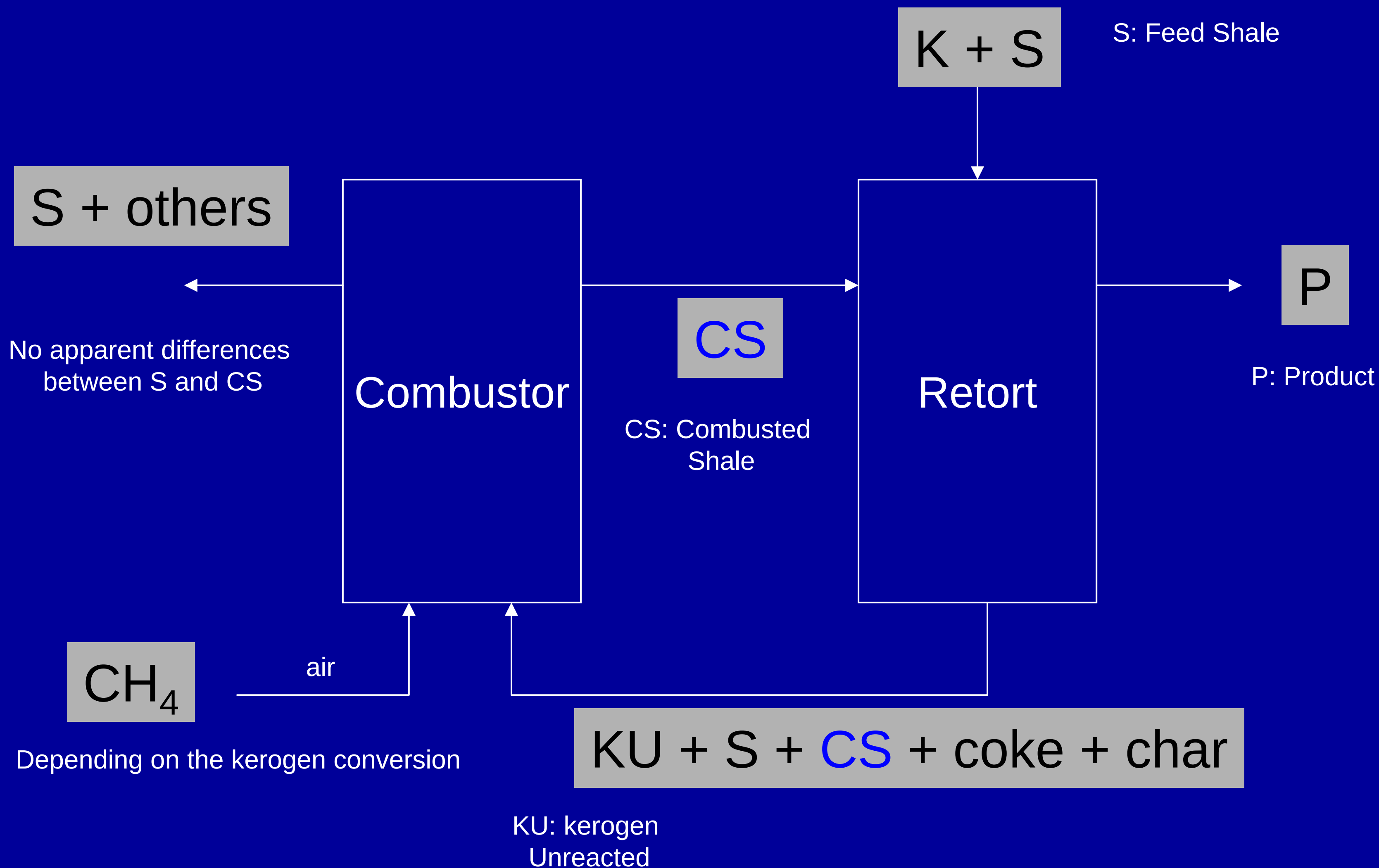
- Need to examine the overall energy requirement of the retorting (oil production) process
- Several process combinations possible (retorting, combustion, gasification, etc.)
- Impact of kerogen content of shale on supplemental energy needs
- Understanding effect of operational parameters

Concept Diagram of Process



*Heat carriers: recycled hot combusted shale, gas, inorganics

Process Diagram



Process Assumptions

- Feed was assumed to be supplied as dry raw shale.
- Operation Temperatures were isothermal for each unit.
  Raw shale feed (298 K)
  Retort (783 K)
  Combustor (1047 K)
- Heat capacity of combusted shale, raw shale and kerogen

$$C_{p,shale} = (906.9 + 506 \cdot w)(1 - f_k) + 827.4 \cdot f_k + \{(0.6184 + 5.56 \cdot w) \cdot (1 - f_k) + 0.922 \cdot f_k\} \cdot (T - 298)$$

here, f_k ; Pyrolyzed kerogen fraction, w : weight fraction of kerogen in raw shale

[Braun,R.L., UCRL-53119 (1981) and , Carley, J.F.,UOPKK 75-28 (1975) Lawrence Livermore Laboratory]

Process Assumptions – cont.

- Retorted product composition

  [Gregoire, 1987 Eastern Oil Shale Symp., 281-289]

- Model Kerogen was used for combustion.: $C_{200}H_{300}N_5SO_{11}$

  [Pan,Feng and Smith, *AIChE* (1985)]

- Kerogen standard heat of formation: -6 MJ/kg

- Combustion with 20% excess of atmospheric air

- Char does not have heating value in combustion.

Stoichiometry for Kerogen Pyrolysis and Oil Cracking (weight basis)

	Primary	Secondary decomposition				
	Kerogen	Naphtha	Distillate	Gas Oil	Bottoms	Product
Naphtha	0.099		0.66	0.4	0.28	**0.2852**
Distillate	0.191			0.4	0.28	**0.1591**
Gas Oil	0.353				0.28	**0.0179**
Bottoms	0.064					**0.0000**
CO2	0.031					**0.0310**
CO	0.005	0.018	0.015	0.014	0.04	**0.0171**
H2O	0.022					**0.0220**
H2	0.002	0.004	0.008	0.0003		**0.0040**
H2S	0.001	0.004	0.004	0.004	0.005	**0.0039**
CH4	0.013	0.040	0.014	0.007		**0.0221**
C2H4	0.003	0.057	0.015	0.010	0.005	**0.0154**
C2H6	0.008	0.142	0.037	0.026	0.018	**0.0395**
C3H6	0.003	0.056	0.015	0.010	0.005	**0.0153**
C3H8	0.008	0.140	0.036	0.025	0.013	**0.0384**
C4H8	0.003	0.047	0.012	0.008	0.004	**0.0130**
C4H10	0.006	0.117	0.03	0.021	0.011	**0.0314**
NH3		0.022	0.01	0.009	0.013	**0.0081**
Char	0.188					**0.1880**
Carbon		0.354	0.145	0.064	0.051	**0.0886**

P
Char
Coke

Source: 1987 Eastern Oil Shale Symposium, pp281-289

Products (based on 100% conversion)

Products	Weight Percent
Naphtha	28.5 %
Distillate	15.9 %
Gas oil	1.8 %
Char	18.8 %
Coke	8.9 %
Others	26.1 %

Heat Capacity

$C_p^{ig}/R = A + BT + CT^2 + DT^{-2}$				
Species	**A**	**B**	**C**	**D**
CO2	5.457	1.045e-3	-	-1.157e5
CO	3.376	0.557e-3	-	-0.031e5
H2O	3.470	1.450e-3	-	0.121e5
H2	3.249	0.422e-3	-	0.083e5
H2S	3.931	1.490e-3	-	-0.232e5
CH4	1.702	9.081e-3	-2.164e-6	-
C2H4	1.424	14.394e-3	-4.392e-6	-
C2H6	1.131	19.225e-3	-5.561e-6	-
C3H6	1.637	22.706e-3	-6.915e-6	-
C3H8	1.213	28.785e-3	-8.824e-6	-
C4H8	1.967	31.630e-3	-9.873e-6	-
C4H10	1.677	37.853e-3	-11.945e-6	-
NH3	3.578	3.020e-3	-	-0.186e5

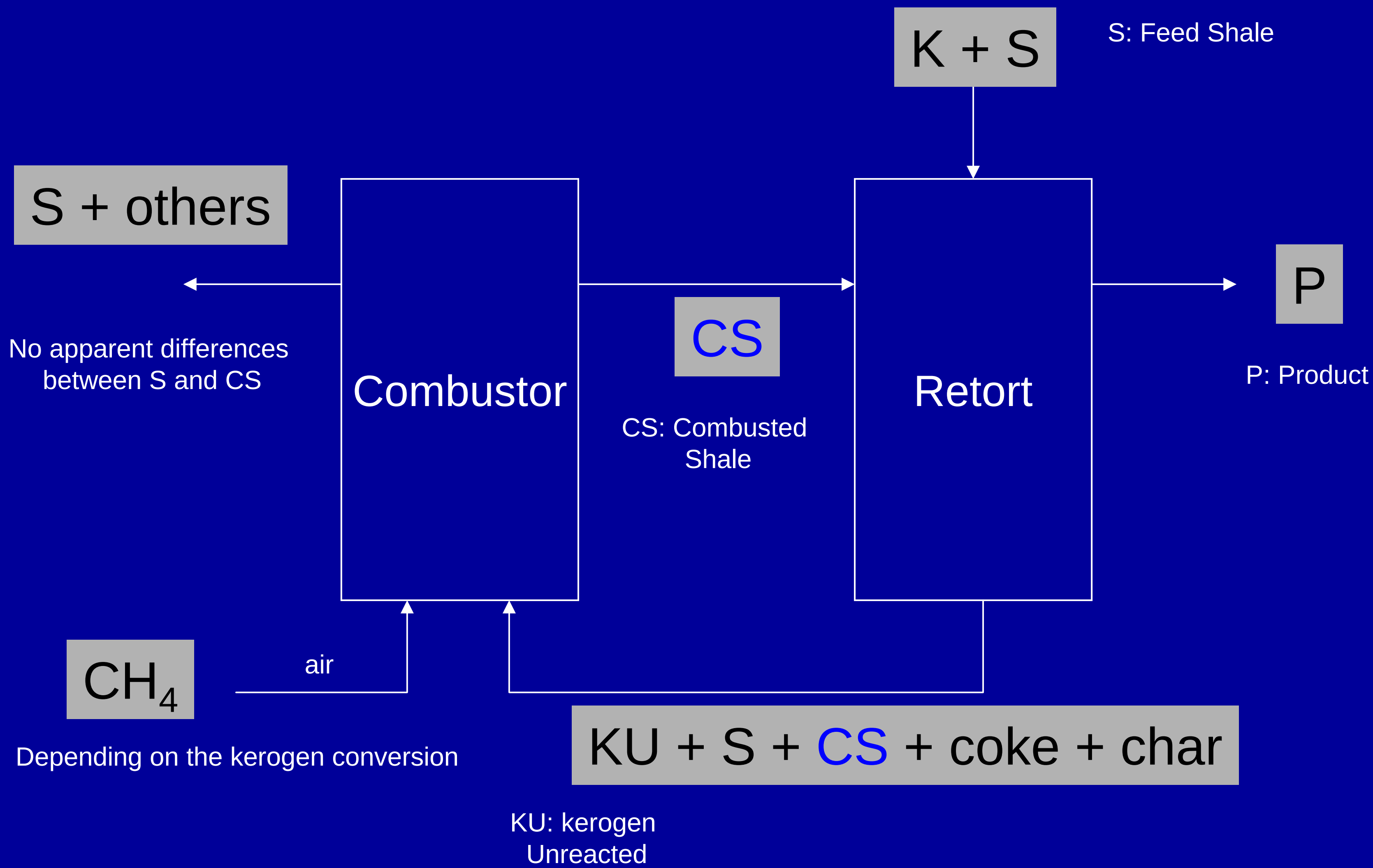
Mean Heat Capacity of Product

$$\int_{T_0}^{T} \frac{C_P}{R} dT = \left[A + \frac{B}{2} T_0(\tau + 1) + \frac{C}{3} T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2} \right] (T - T_0)$$

$$\frac{\langle C_P \rangle_H}{R} = A + \frac{B}{2} T_0(\tau + 1) + \frac{C}{3} T_0^2(\tau^2 + \tau + 1) + \frac{D}{\tau T_0^2}$$

$$\langle C_p^0 \rangle_H = \sum_i n_i \langle C_{P_i}^0 \rangle_H = R \left(\sum_i n_i A_i + \frac{\sum_i n_i B_i}{2} T_0 (\tau + 1) + \frac{\sum_i n_i C_i}{3} T_0^2 (\tau^2 + \tau + 1) + \frac{\sum_i n_i D_i}{\tau T_0^2} \right)$$

Process Diagram

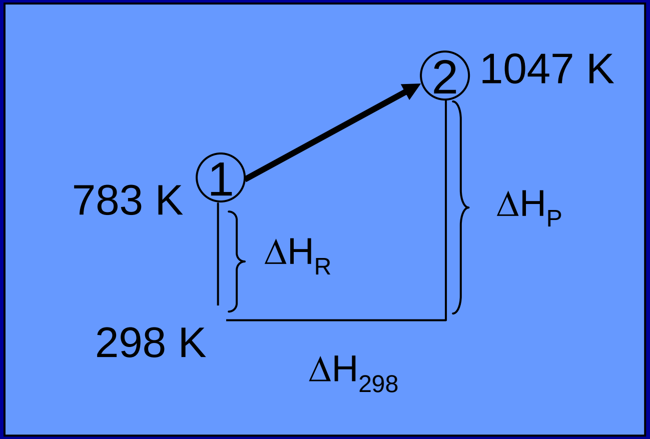


Combustion of Kerogen and Coke

$C_{200}H_{300}SN_5O_{11}$ + 276.5 (1+exc) (O_2 + 3.76 N_2) → 200 CO_2 + 150 H_2O + SO_2 + 5 NO_2 + 276.5exc O2 +276.5(1+exc)(3.76 N_2)

C + (1+exc)(O_2 + 3.76 N_2) → CO_2 + exc O_2 + (1+exc) 3.76 N_2

$$\Delta H = \Delta H_R + \Delta H_{298} + \Delta H_P$$



•exc: excess ratio (0.2 in this work, 20%)

Simulation Procedures

Energy Balance in Retort Process

↓

Amount of Recycle CS (Combusted Shale)

↓

Energy Balance in Combustor

↓

Amount of CH_4

Simulation Results

- Kerogen Conversion, x = 0.6;
  - Mass Balance (Overall)
  - Energy Balance (Retort, Combustor, Overall)
- Kerogen Conversion, x = 0.8;
  - Mass Balance (Overall)
  - Energy Balance (Retort, Combustor, Overall)
- Comparison
  - Recycle ratio
  - CH_4 requirements in combustor

Overall Mass Balance, x=0.6

Retort

Out

P	65.1
coke	8
char	16.9
CS	2801
KU	60
S	850

In

CS	2801
K	150
S	850

Combustor

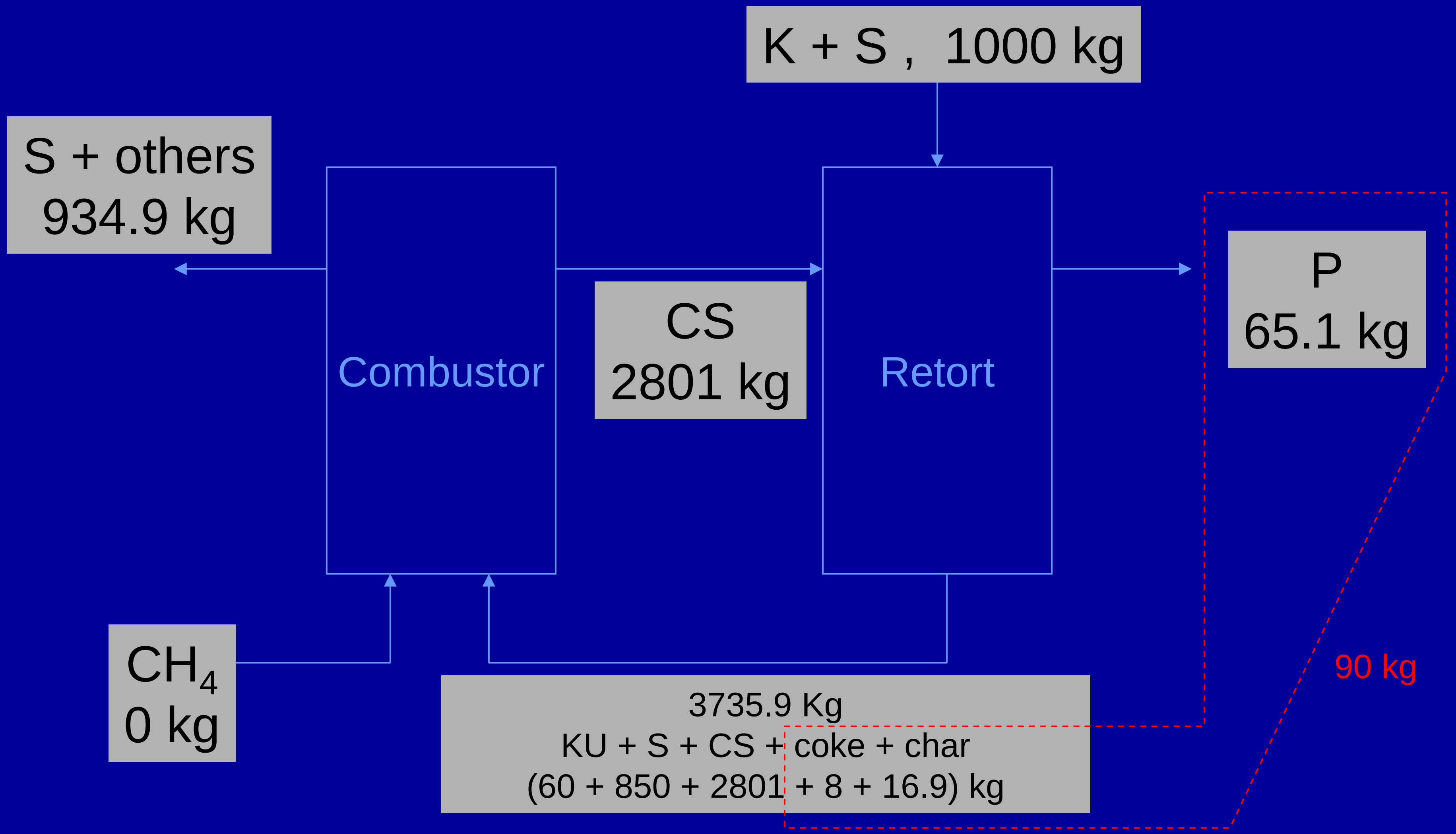
CS	2801
S+other	934.9

Out

In

[Unit: kg]

Overall Mass Balance, x=0.6 @ Retort



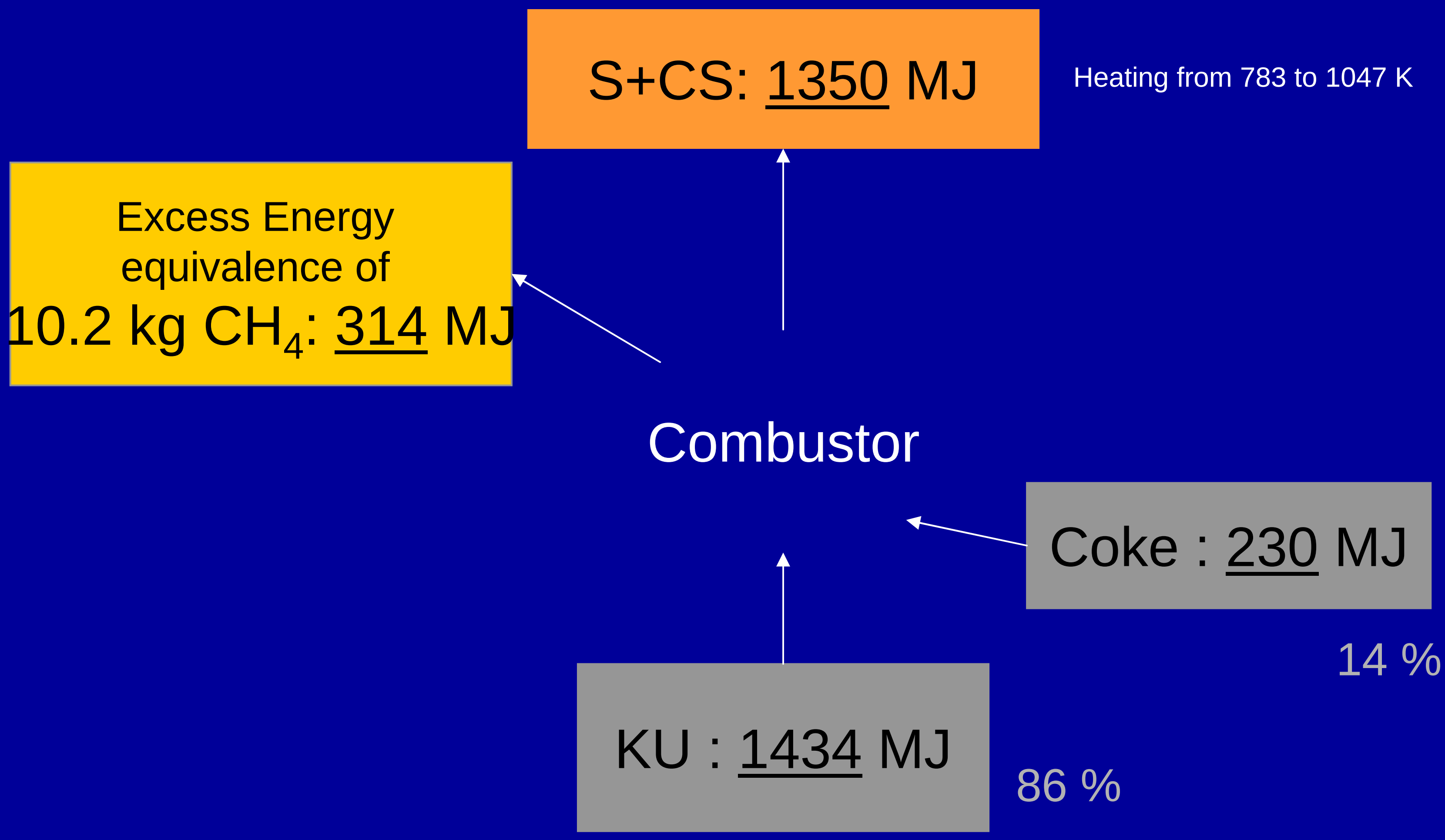
Energy Balance in Retort, x=0.6

[MJ]

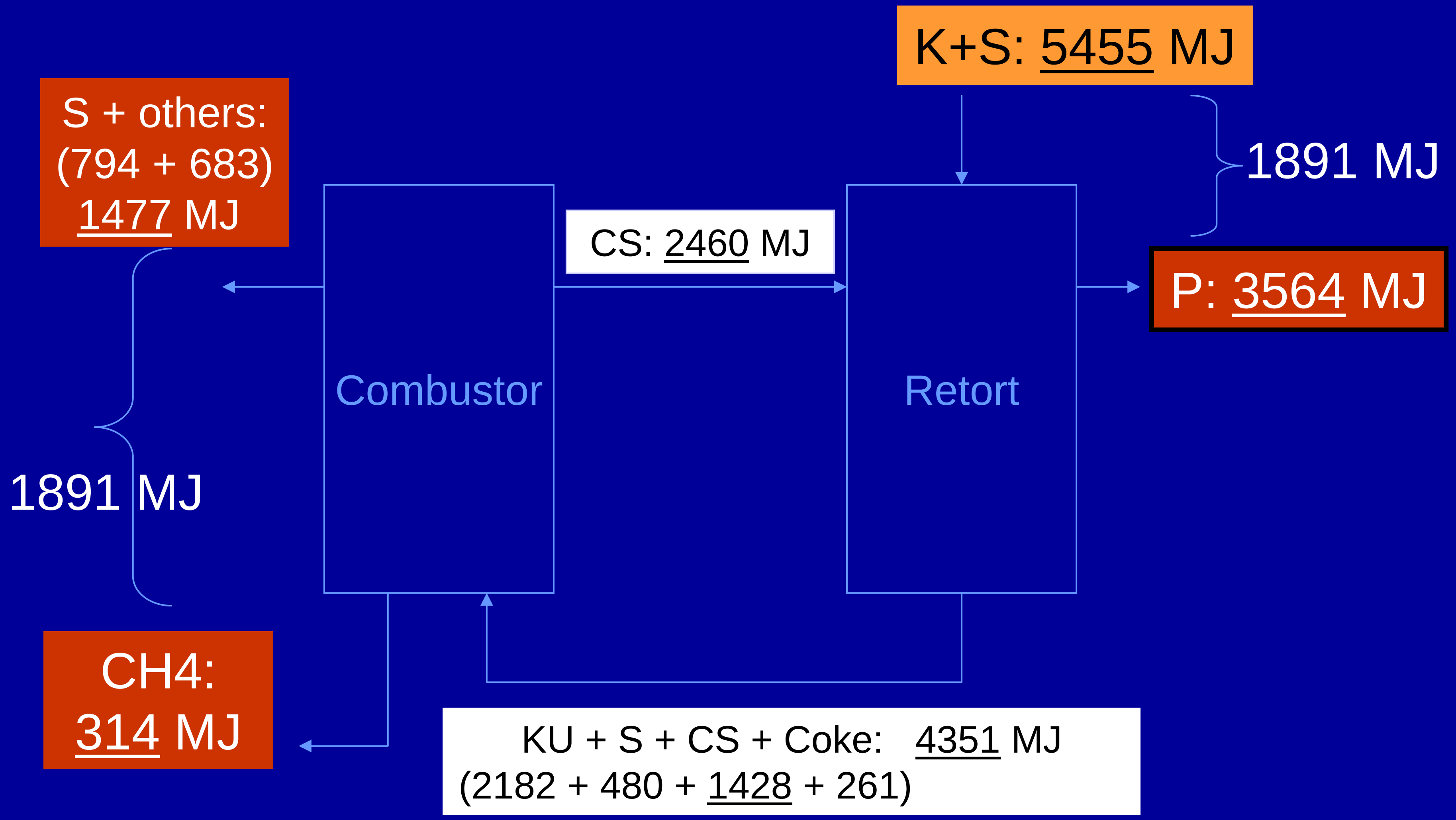
Retort In	Energy consumption of CS	1032
	Initial heating value of Kerogen	5455
	Sub total	6487

Retort Out	Heating value of Product	3564
	Heating value of coke	261
	Energy gain for shale	480
	Energy in unreacted Kerogen	2182
	Sub total	6487

Energy Balance in Combustor feed=1000 kg, x=0.6 @ Retort



Overall Energy Balance: x=0.6



Overall Mass Balance, x=0.8

Retort

Combustor

Retort – Out

P	86.8
coke	10.6
char	22.6
CS	3046
KU	30
S	850

Retort – In

CS	3046
K	150
S	850

Combustor – Out

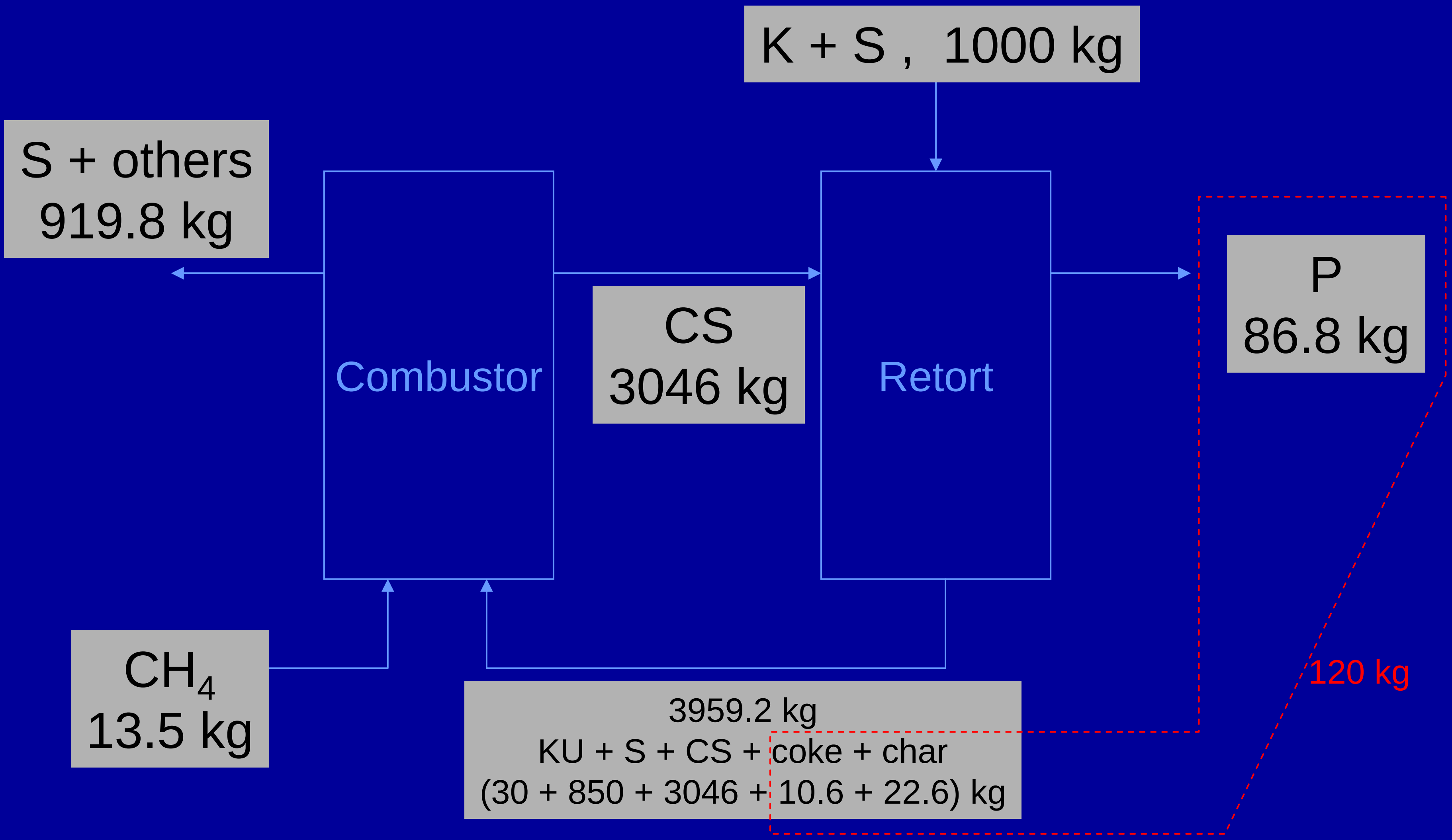
CS	3046
S+other	919.8

Combustor – In

coke	10.6
char	22.6
CS	3046
KU	30
S	850
CH4	6.6

[Unit: kg]

Overall Mass Balance, x=0.8 @ Retort



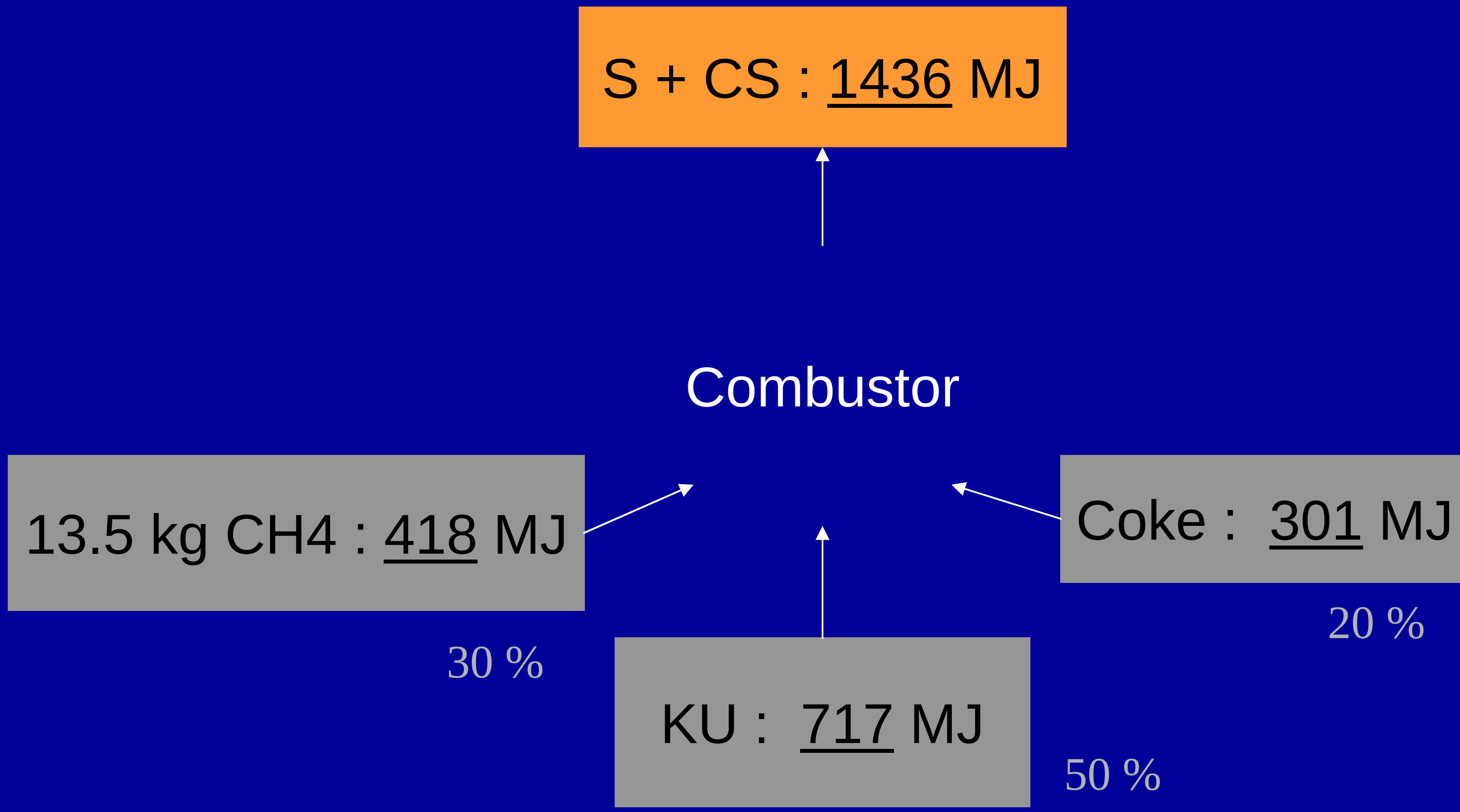
Energy Balance in Retort, x=0.8

[MJ]

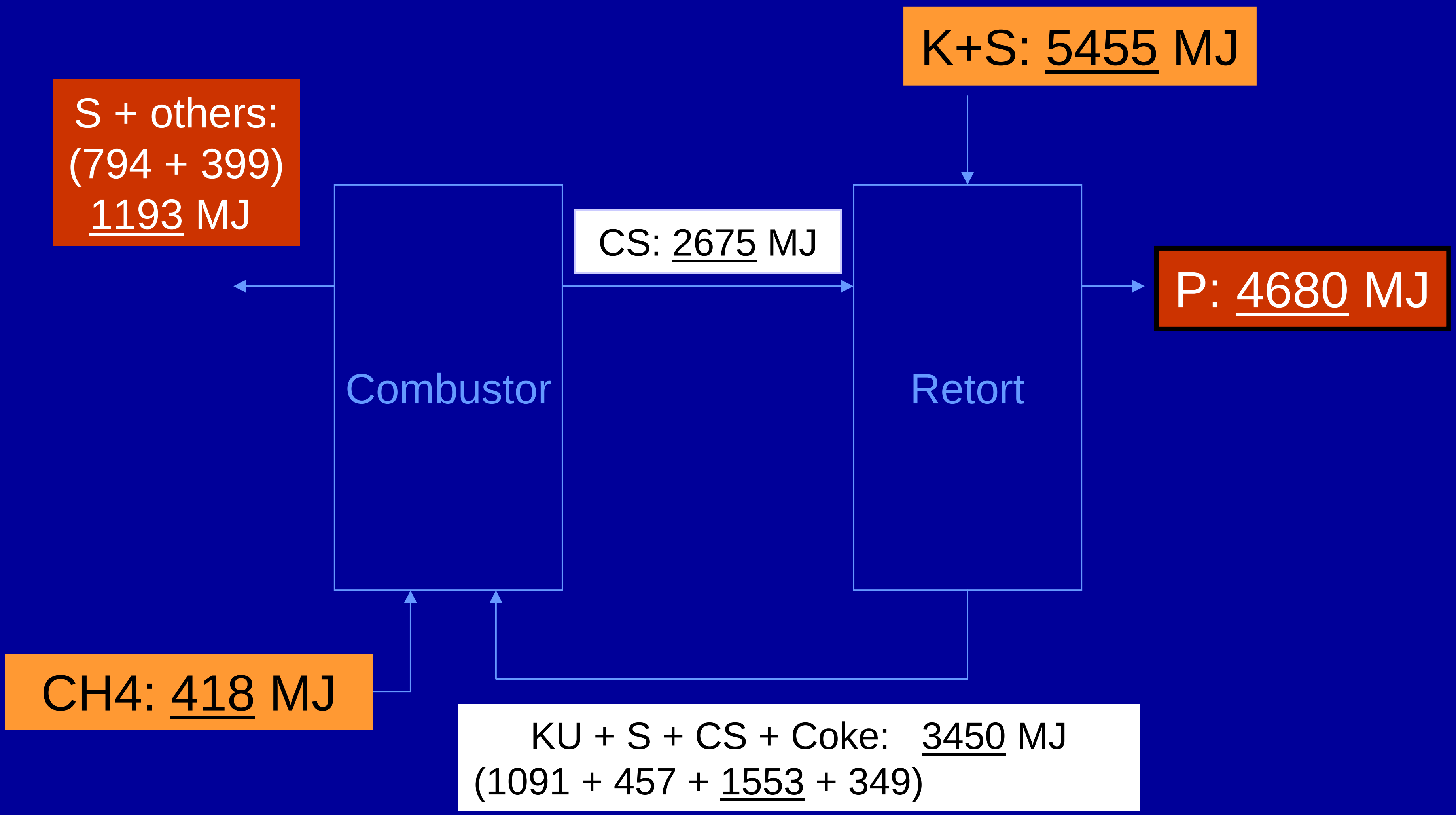
Retort In	Energy consumption of CS	1122
	Initial heating value of Kerogen	5455
	Sub total	6577

Retort Out	Heating value of Product	4680
	Heating value of coke	349
	Energy gain for shale	457
	Energy in unreacted Kerogen	1091
	Sub total	6577

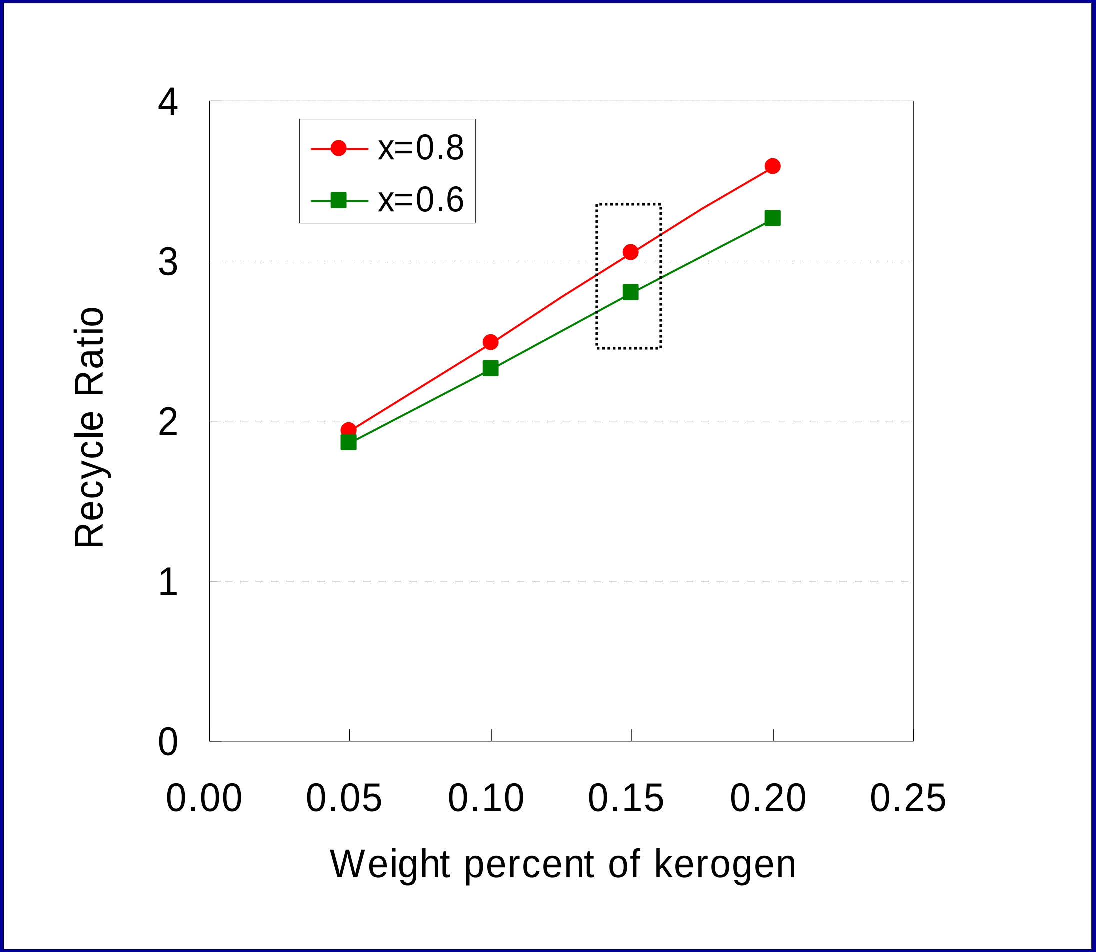
Energy Balance in Combustor
feed=1000 kg, x=0.8 @ Retort



Overall Energy balance: x=0.8 @ Retort



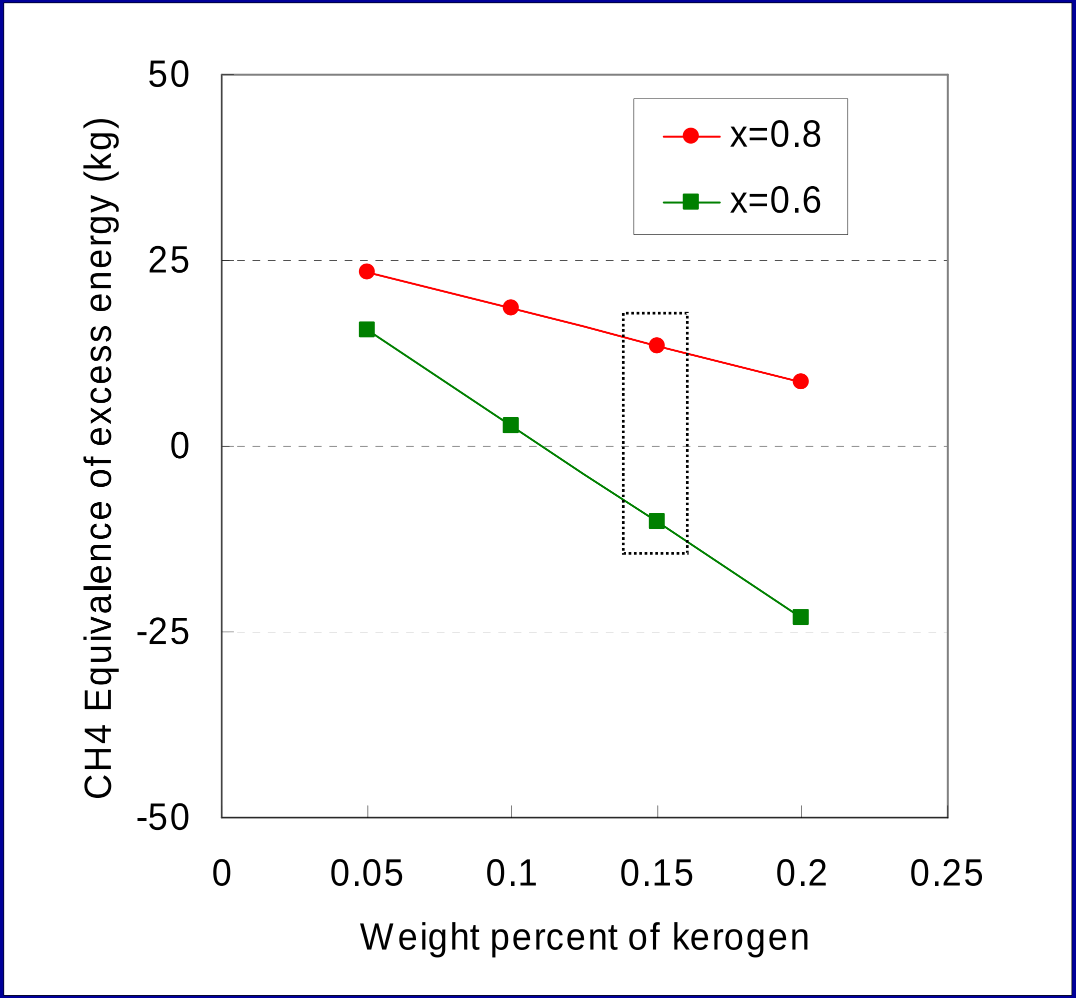
Recycle ratio vs. Wt% Kerogen in Shale



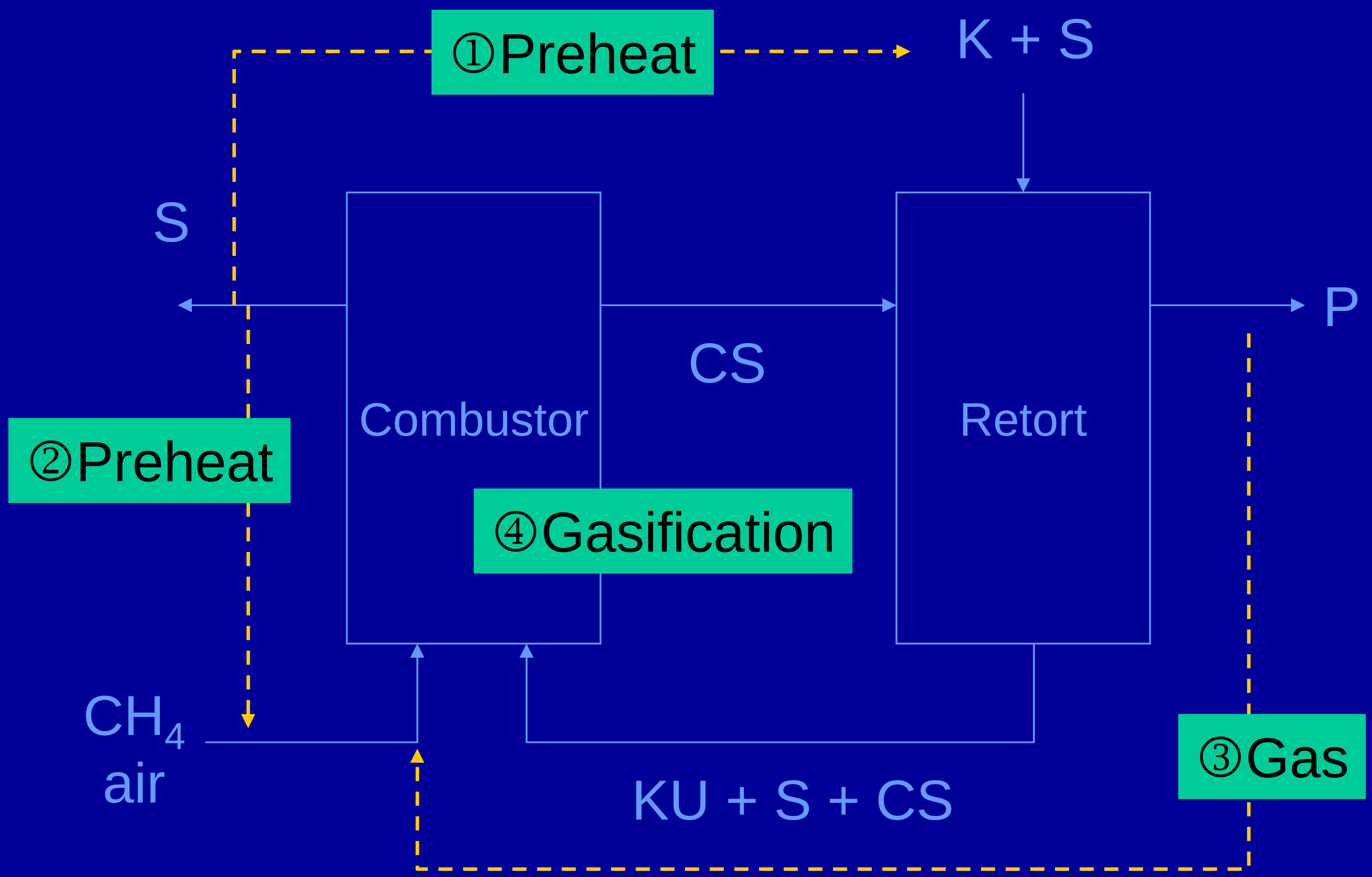
x=0.6	x= 0.8
1.86	1.94
2.33	2.49
2.80	3.05
3.26	3.59

$$\text{*Recycle ratio} = \frac{\text{Mass of recycle shale}}{\text{Mass of raw shale}}$$

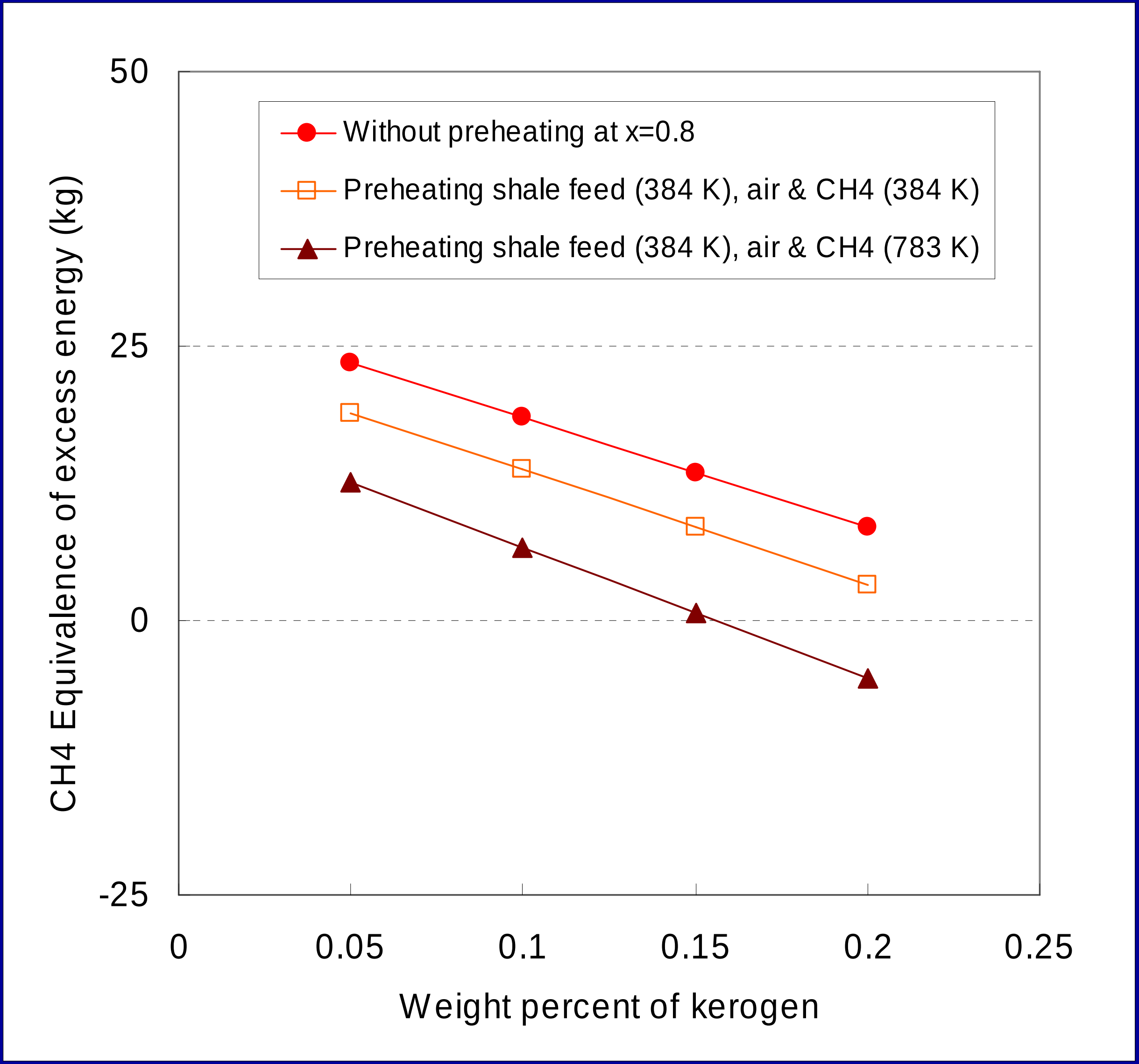
CH_4 Requirement vs. Wt% Kerogen in Shale



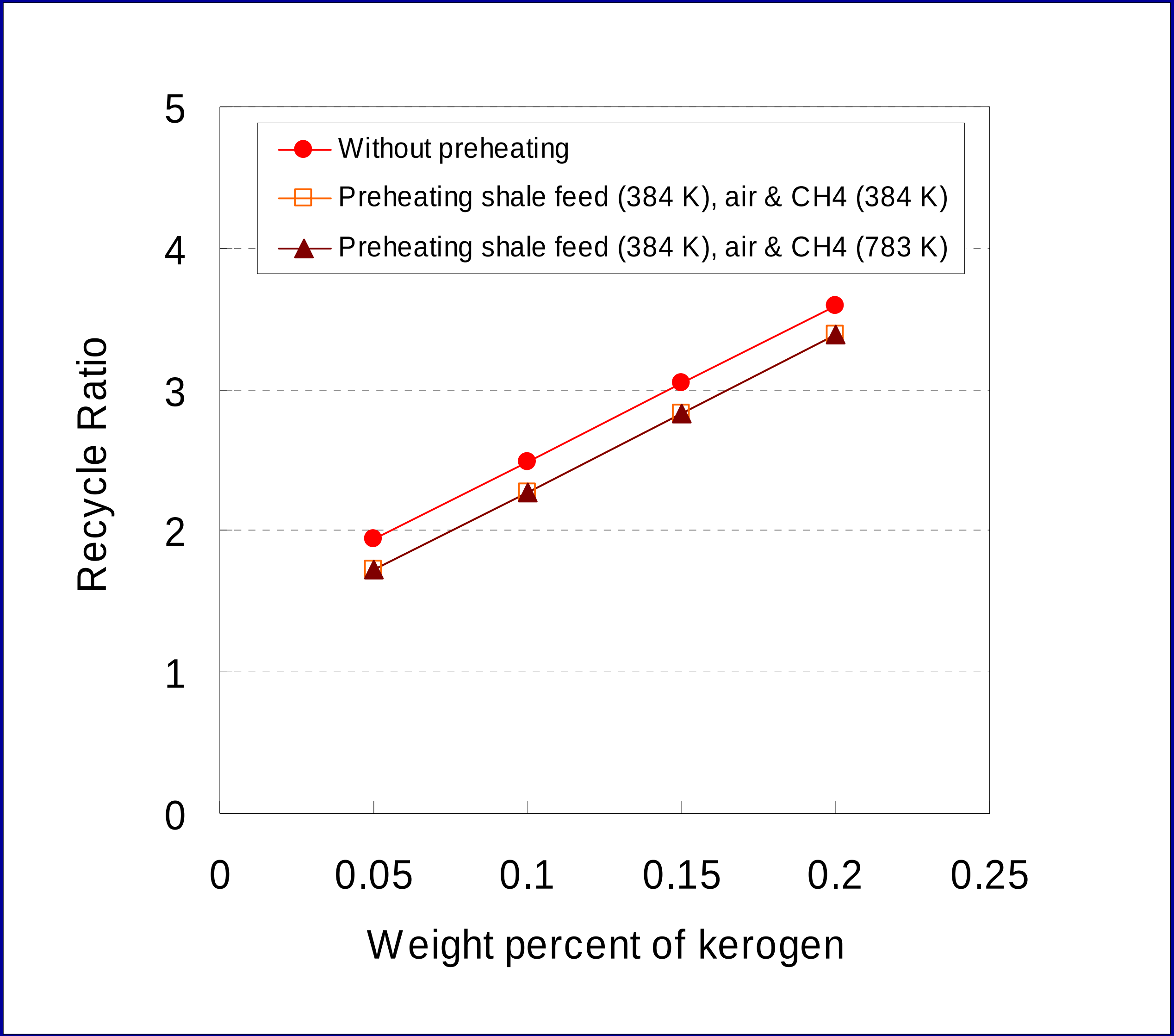
Other Heating and Process Options



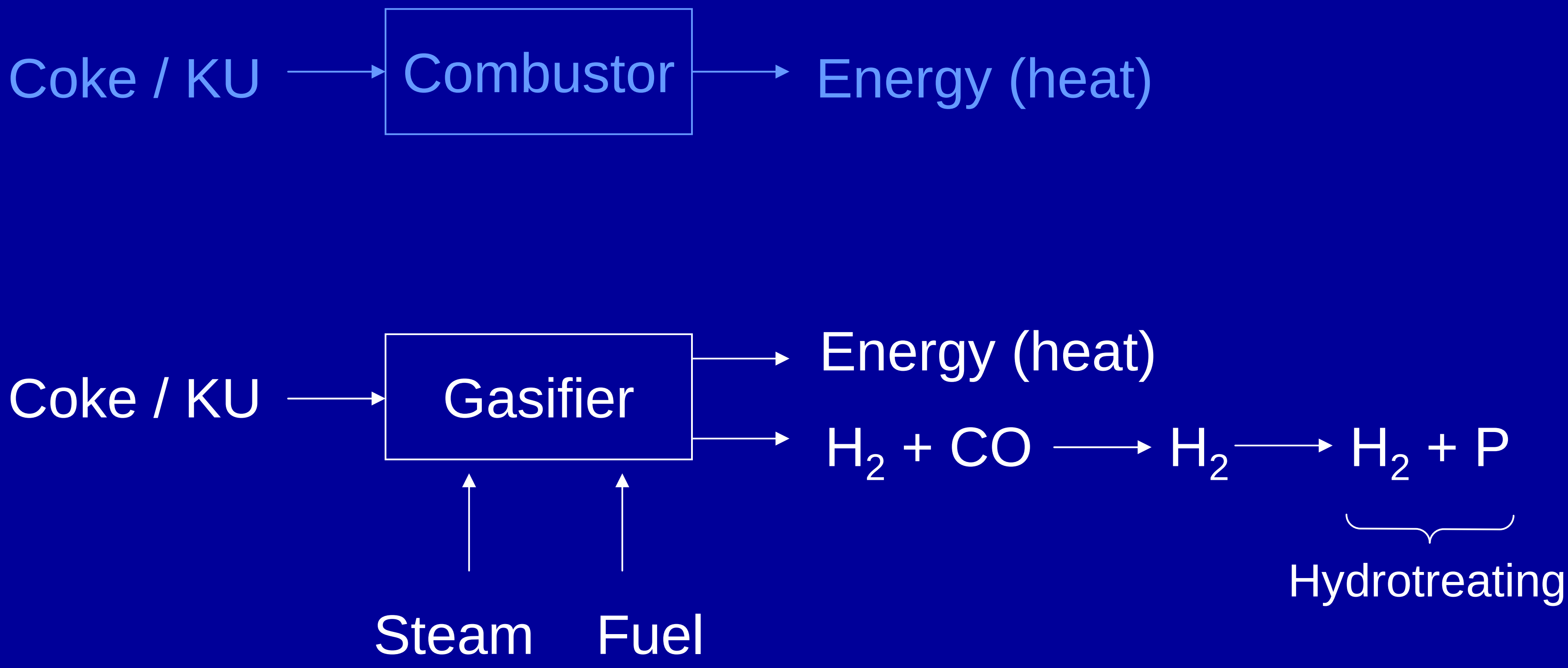
Example of Preheating Effect, x=0.8



Example of Preheating Effect, x=0.8



Gasification option



Summary

- At lower conversions, excess energy with a retort-combustor combination
- At higher conversions, energy needs to be supplied
- Higher recycle ratio of combusted shale(CS) required at higher kerogen contents in raw shale
- Heat loss will increase with increasing excess air
- Better, more definitive stoichiometric and kinetics models needed for future work

Acknowledgements

UHOC (Univ. of Utah Heavy Oil Center)

www.uhoc.utah.edu

PERC (Petroleum Research Center)

www.perc.utah.edu