

EVALUATION OF VARIOUS SHALE PROCESSING OPTIONS

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The organic matter in geological oil shale formation converts into valuable hydrocarbons in the form of gas and vapor products by thermal process known as retorting. Oil production option from oil shale resources has been revived recently since the shortage concerns of oil resources became a global issue critically. Various processes have been proposed in the surface retorting as well as in-situ retorting. This study evaluates the energy efficiency during oil production from oil shale in surface retorting options. In fact, a number of process options are available for producing oil from mined shale, such as fluidized bed, fixed bed, rotary kiln retorting. The economic merit of a process option will depend on conversion of organic matter to oil and on energy integration of the process. Options available for energy integration include appropriate preheating, gasification of carbon residue on spent shale, recycling gas. This study helps streamline a protocol for evaluating different processing possibilities for mined oil shale. Once process data are available, this protocol could be used for plant design, cost evaluation and upscaling.

Symbols

A, B, C, D	– heat capacity constant, J/(kg·K)
C_0	– heat capacity
$\left\langle C_P \right\rangle_H$	– mean heat capacity
exc	– stoichiometric excess, 0.2
f_k	– fraction of pyrolyzed kerogen
i	– component
n	– mole number
R	– gas constant
T	– final temperatures
T_0	– initial temperature
w	– kerogen fraction in oil shale feed
ΔH_R	– heat of reaction
ΔH_{298}	– standard enthalpy of formation at 298.15 K
ΔH_P	– enthalpy change of product
τ	– $\tau \equiv T/T_0$

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Introduction

Oil shale is commonly defined as a sedimentary rock bound with organic matter that is mostly insoluble in organic solvents. The organic matter, broadly used as kerogen, exists as inextricably combined formation with inorganic rocks but converts into fuels by thermal process known as retorting. Kerogen decomposition begins at relatively low temperature ($< 300\text{ }^{\circ}\text{C}$), but proceeds more rapidly and more completely at higher temperature. The rate of kerogen decomposition is the highest at retort temperature of $480\text{--}520\text{ }^{\circ}\text{C}$ on which the kerogen converts into organic fractions: gas, oil and residual carbon. Thermal process varies with many operational parameters, such as time-temperature history, pressure, heat carrier, etc. [1–5].

In the surface retorting, the product was to send directly to primary upgrading plants of catalytic and hydrogen treating to remove nitrogen and metals. Thereafter this upgraded shale oil would be an appropriate feedstock for oil refining facilities and comparable to that of light, sweet crude oil. Although various retort processes resulted in different yield and properties, the following trends were generally observed [1–6].

- Oil yield decreases but gas product increases in higher temperature retorting
- Oil product became more aromatic as retort temperature increased
- Spent shale contains carbonaceous residue
- Water and gases are eliminated in preheating option

Heat is indispensable to kerogen decomposition in a retort unit. Various surface retorting processes can be categorized by heating options. In indirect retorting, thermal process is driven by heat carriers, such as combusted spent shale, solid ceramic balls (TOSCO II), and recycling gas. These heat carriers are heated separately from the oil shale feed and recirculated. Meanwhile, in direct retorting, the combustion of residual hydrocarbon in the spent shale is carried out in the same pyrolysis vessel by injecting air and recycled gas, or by the combustion of shale gas with air. Shale gas is partially recycled into the process vessel, where the direct countercurrent contact between the gas and oil shale generate the heat and promote internal heat exchange through different zones of oil shale moving bed [1–6].

There are controversies in evaluating energy requirement and energy balance for oil recovery from oil shale. More energy requirement than the oil recovery may impede the oil industries to decide oil shale development and exploration. The evaluation of energy balance in oil shale process would provide the insight for further application and process development. In this study we laid out the combustor-retort combined system so that spent shale circulates between retort unit and combustor unit playing a role of a heat carrier. Evaluation includes the degree of kerogen conversion in the retort unit, the supplemental energy supply in the combustor unit, and the pre-heating options.

Procedures

Figure 1 shows the schematic diagram of the combustor-retort combined system to be evaluated in this study. Steady state and CSTR assumption are employed in both retort unit and combustor unit. Isothermal condition was set at 783 K and 1047 K for retort unit and combustor unit, respectively. In Fig. 1, the fresh oil shale feed is represented by kerogen (K) and shale (S) and supplied to the retort unit at ambient temperature (298 K). In retort unit, the fresh oil shale is mixed with heat-carrying combusted shale (CS) at 1047 K supplied from the combustor unit and converts to gas and vapor products (P), char, coke and unreacted kerogen (KU). The product composition is dependent on the kerogen conversion. The list of products (P) is used as shown in literature [7] and P does not include either char or coke. KU, S, CS, char and coke generated from the retort unit at 783 K are conveyed to the combustor unit. In combustor unit, KU, char and coke at 783 K are combusted in 20% excess air supply. If more heat is required for the potential heat carrier (CS at 1047 K), methane is supplied into the combustor as a supplemental combustion fuel. When the methane is used, adiabatic temperature calculation is used in the combustion. Rejection from the combustor unit is shown as S + others. This study used two different kerogen conversions (60% and 80%). The mass and energy balance in retort unit was calculated first followed by the decision of the amount of requiring recycle CS. Then the mass and the energy balances in combustor unit result in the decision of the methane options.

Heat capacities of shale, spent shale and kerogen are used from the Eq. (1) below [8].

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

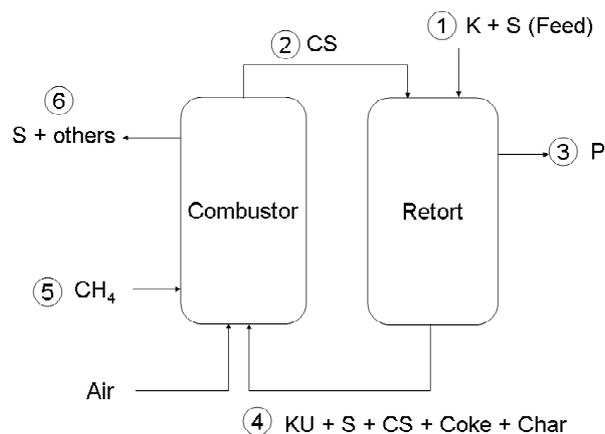


Fig. 1. Conceptual diagram of combustor-retort combined process.

Here, f_k represents the fraction of pyrolyzed kerogen and w represents kerogen fraction in oil shale feed [8].

Products are listed in Table 1. The products were obtained from the primary and secondary kerogen decomposition. Naphtha, distillate, gas oil and bottoms, which are primary decomposed products, decompose consequently to produce secondary decomposed products. Heat capacities of P are used from reference value [9]. Energy was calculated by enthalpy changes by equations (2–4) of mean heat capacities shown below.

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

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

$$\begin{aligned} \langle C_P^0 \rangle_H &= \sum_i n_i \langle C_{P_i}^0 \rangle_H \\ &= R \left(\sum_i n_i A_i + \frac{\sum_i n_i B_i}{2} T_0 (\tau + 1) + \frac{\sum_i n_i C_i}{3} T_0^2 (\tau^2 + \tau + 1) + \frac{\sum_i n_i D_i}{\tau T_0^2} \right) \quad (4) \end{aligned}$$

$$\Delta H = \Delta H_R + \Delta H_{298} + \Delta H_P. \quad (5)$$

Here, T_0 , T represent initial and final temperatures. ($\tau \equiv T/T_0$). A , B , C and D in Eq. (2)–(4) are heat capacity constants [9] and shown in Table 2.

Table 1. Stoichiometry for kerogen pyrolysis and oil cracking (weight fraction)

Product	Primary	Secondary				Product Wt. fraction
	Kerogen	Naphtha	Distillate	Gas Oil	Bottoms	
Naphtha	0.099	–	0.66	0.4	0.28	0.285
Distillate	0.191	–	–	0.4	0.28	0.159
Gas Oil	0.353	–	–	–	0.28	0.018
Bottoms	0.064	–	–	–	–	0.000
CO ₂	0.031	–	–	–	–	0.031
CO	0.005	0.018	0.015	0.014	0.04	0.017
H ₂ O	0.022	–	–	–	–	0.022
H ₂	0.002	0.004	0.008	0.0003	–	0.004
H ₂ S	0.001	0.004	0.004	0.004	0.005	0.004
CH ₄	0.013	0.040	0.014	0.007	–	0.022
C ₂ H ₄	0.003	0.057	0.015	0.010	0.005	0.015
C ₂ H ₆	0.008	0.142	0.037	0.026	0.018	0.040
C ₃ H ₆	0.003	0.056	0.015	0.010	0.005	0.015
C ₃ H ₈	0.008	0.140	0.036	0.025	0.013	0.038
C ₄ H ₈	0.003	0.047	0.012	0.008	0.004	0.013
C ₄ H ₁₀	0.006	0.117	0.03	0.021	0.011	0.031
NH ₃	–	0.022	0.01	0.009	0.013	0.008
Char	0.188	–	–	–	–	0.188
Coke	–	0.354	0.145	0.064	0.051	0.089

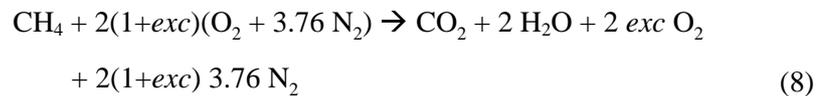
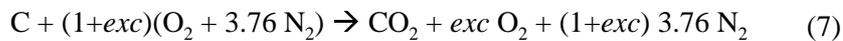
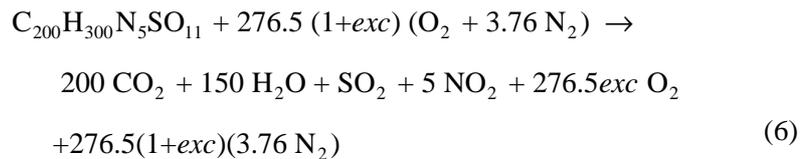
Table 2. Heat capacities of gases in the ideal state, $C_p(ig)/R$, J/(mol·K)Constants in equation $C_p(ig)/R = A + BT + CT^2 + DT^2$, T (Kelvin) from 298 K to T_{max}

Component	A	B	C	D
CO ₂	5.457	1.045E-03	0	-1.157E+05
CO	3.376	0.557E-03	0	-0.031E+05
H ₂ O	3.470	1.450E-03	0	0.121E+05
H ₂	3.249	0.422E-03	0	0.083E+05
H ₂ S	3.931	1.490E-03	0	-0.232E+05
CH ₄	1.702	9.081E-03	-2.164E-06	0
C ₂ H ₄	1.424	14.394E-03	-4.392E-06	0
C ₂ H ₆	1.131	19.225E-03	-5.561E-06	0
C ₃ H ₆	1.637	22.706E-03	-6.915E-06	0
C ₃ H ₈	1.213	28.785E-03	-8.824E-06	0
C ₄ H ₈	1.967	31.630E-03	-9.873E-06	0
C ₄ H ₁₀	1.677	37.853E-03	-11.945E-06	0
NH ₃	3.578	3.020E-03	0	-0.186E+05

$\langle C_p^0 \rangle_H$ represents the mean heat capacity. The heat capacity constant values were used after converting to J/(kg·K). Heat capacities of naphtha, distillate and gas oil are used as constant values; 2000, 2500 and 3000 J/(kg·K) for naphtha, distillate and gas oil respectively.

Model kerogen was used in the molecular formula of C₂₀₀H₃₀₀N₅SO₁₁ for combustion model [10]. Standard heat of kerogen formation was taken as -6 MJ/kg. This value was arbitrarily chosen by appropriate recycle ratio. All combustions were carried out in 20% excess of stoichiometric air. And it is assumed that char has negligible heating value in combustion. Some part of shale will be disposed from combustor. Heat in the disposed spent shale can be used for preheating the shale feed in retort and for preheating air, KU, coke and methane in combustor unit.

Combustion models of KU, coke and methane are presented in Eq. (6–8).



Here, *exc* represents stoichiometric excess air supply (*exc* is 0.2).

Results and discussion

The study was performed with basis of 1000 kg oil shale feed. Kerogen content in oil shale feed was fixed to 15 wt. %. The mass and energy balances of 60% kerogen conversion are presented in Fig. 2, and the result of mass and energy balances in both 60% and 80% kerogen conversion is listed in Table 3.

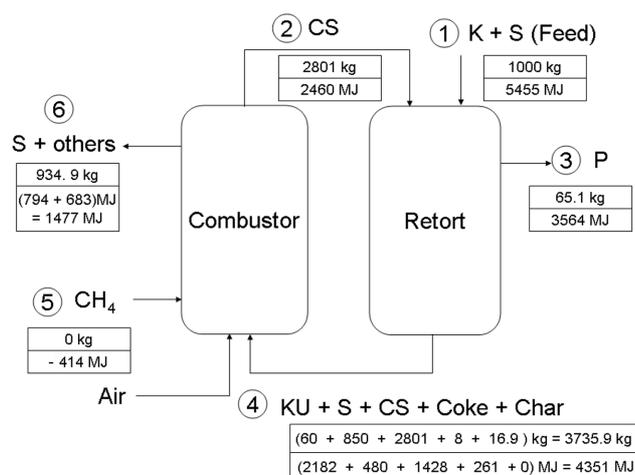


Fig. 2. Mass and energy balances in combustor-retort combined option based on 1000 kg of shale feed.

Table 3. Mass and energy balance in both 60% and 80% kerogen decomposition in retort unit

Stream	Species	60% Conversion		80% Conversion	
		Mass balance (kg)	Energy balance (MJ)	Mass balance (kg)	Energy balance (MJ)
①	K	150	5455	150	5455
	S	850	–	850	–
②	CS	2801	2460	3046	2675
③	P	65.1	3564	86.8	4680
④	KU	60	2182	30	1091
	S	850	480	850	457
	CS	2801	1428	3046	1553
	Coke	8	261	10.6	349
	Char	16.9	–	22.6	–
⑤	CH ₄	–	–314 ^a	13.5	418
⑥	S + others	934.9	1477	919.8	1193

^a Negative value represents imaginary excess energy, which is excess energy equivalent to methane amount and can be compared to 80% case.

In case of 60% kerogen conversion, 90 kg of kerogen (initial kerogen amount is 150 kg in 1000 kg feed) decomposes to produce 65.1 kg of gas and vapor product (P), 8 kg of coke and 16.9 kg of char. Unreacted kerogen (KU, 60 kg) and coke (8 kg) are supplied as fuels in combustor unit. In retort unit, 2801 kg of CS at 1048 K provides heat energy and comes out from retort unit at 783 K without mass changes by circulating between retort unit and combustor unit. In this case, the enthalpy, 1032 MJ, from CS contributes to the thermal cracking process in retort unit. Overall energy balance is obtained before (retort-in) and after (retort-out) the retorting process. Energy summation of retort-in (6487 MJ) is composed of energy consumption of CS in the form of temperature decrease from 1047 K to 783 K (1032 MJ) and kerogen heating value (5455 MJ). Energy summation of retort-out (6487 MJ) is composed of heating value of P (3564 MJ), coke (261 MJ), KU (2182 MJ) and energy gain of S in the form of temperature increase from 783 K to 1047 K (480 MJ). In combustor, energy from KU combustion (1434 MJ) and coke combustion (230 MJ) contributes the energy transfer in the form of temperature increase of S and CS from 783 K to 1047 K (1350 MJ). Excess energy is obtained (314 MJ) and expressed by negative value of methane supply in Fig. 2. Energy differences for KU between 2182 MJ in retort-out and 1434 MJ in combustor for KU are caused by retort-out temperature (783 K). Heating values in retort-out are obtained by 298 K basis. Less value as mentioned here is also resulted from the heat loss by supplied air in the form of temperature increase for unreacted excess air.

In case of 80% kerogen conversion, 120 kg of kerogen (150 kg in feed) decomposes to produce 86.8 kg of P, 10.6 kg of coke and 22.6 kg of char. 30 kg of KU and coke are supplied as fuels in combustor. 2046 kg of CS at 1048 K provides the heat energy in retort and comes out from retort at 783 K without mass changes. In this case, 1122 MJ of energy is provided from CS in retort. In retort-in, energy summation (6577 MJ) is composed of energy consumption of CS in the form of temperature decrease from 1047 K to 783 K (1122 MJ) and kerogen heating value (5455 MJ). Energy summation of retort-out (6577 MJ) is composed of heating value of P (4680 MJ), coke (349 MJ), KU (1091 MJ) and energy gain of S in the form of temperature increase from 783 K to 1047 K (457 MJ). In combustor, energy from KU combustion (717 MJ) and coke combustion (301 MJ) contributes the energy transfer in the form of temperature increase of S and CS from 783 K to 1047 K (1436 MJ). Energy deficiency requires methane supply (13.5 kg, 418 MJ) in this case.

Recycle ratio is defined by the ratio of the mass of recycle shale to mass of feed shale. Figure 3 shows the effect of recycle ratio changes with respect to the kerogen fraction at the range of 0.05 to 0.2. Linear increase was observed in both 60% and 80% kerogen conversions. The result shows that extra energy is required in combustor unit in case of 80% kerogen conversion.

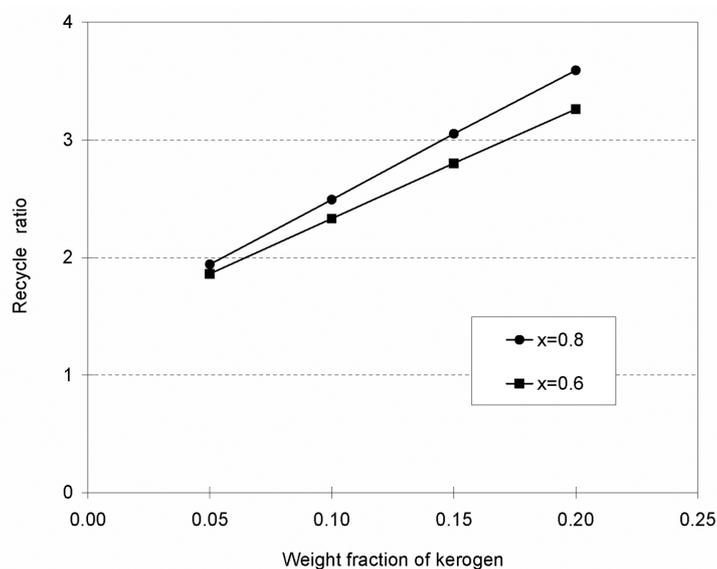


Fig. 3. Effect of recycle ratio on kerogen weight fraction.

Figure 4 shows the effect of preheating on CH_4 and air supply in case of 80% kerogen conversion. Preheating effect was examined by two scenarios; one is preheating to 384 K for shale feed, air and methane, and the other is preheating to 384 K for shale feed and 783 K for air and methane. Preheating lowered the methane requirement in both cases and specifically more in

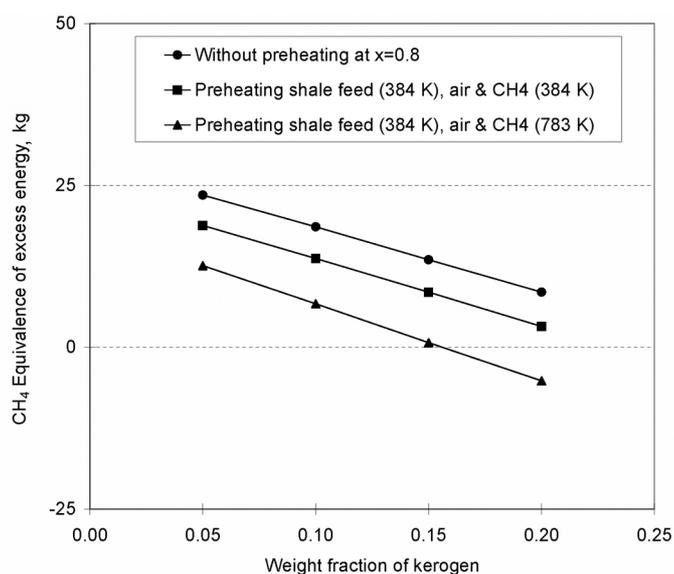


Fig. 4. Effect of preheating gases, CH_4 and air, on kerogen weight fraction.

the latter case. From this result, preheating options suggested that the 80% kerogen conversion case could be an energy self-sustaining process without external fuel supply in case of 15 wt.% or more kerogen content.

Relations between preheating options and recycle ratios are shown in Fig. 5. Preheating options reduce external energy requirement. However, recycle ratio is only affected by preheating shale feed not by preheating air and methane.

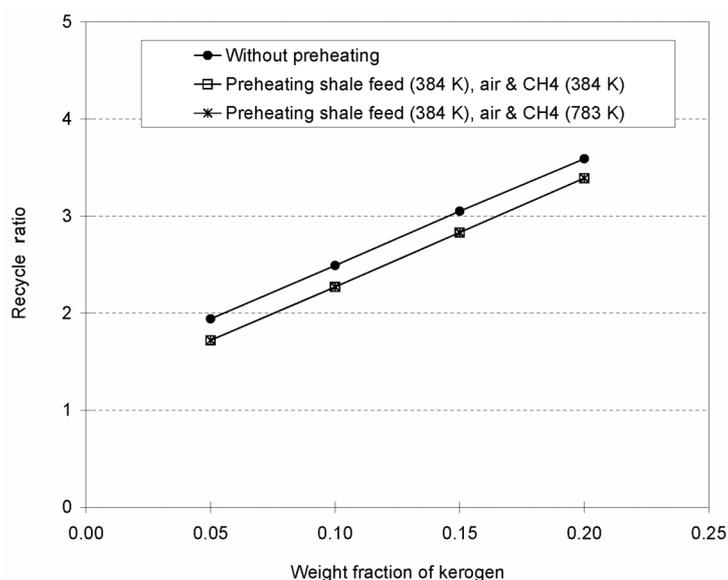


Fig. 5. Effect of preheating options: relation between recycle ratio and weight fraction of kerogen.

Summary

Energy evaluation was examined in the process of retort-combustor combination. Results were compared at two different kerogen conversions. Excess energy was obtained in case of 60% kerogen conversion in retort unit. Combustion of unreacted kerogen (KU) and coke produce energy surplus in combustor unit. However, extra energy was required in case of 80% kerogen conversion. Linear increase of CS recycle ratio was found at the range of 5 to 20 wt.% kerogen content in both cases. Higher kerogen conversion requires higher CS recycle ratio. Heat loss was observed larger with increasing air supply in combustor unit.

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