Investigation on Properties of Gas Evolution from Oil Shale Retorting Coupling with Methane Dry Reforming

Lizhi Song [a], Sha Wang [b], Mingjie Wang [c]

Shanghai University of Engineering Science, Shanghai, 201620, China

[a]18245128247@163.com, [b]wangsha_84@163.com, [c]jacky97@126.com

Abstract

An integrated process of oil shale retorting with dry reforming of methane was developed to improve the shale oil yield of oil shale retorting. This paper utilized HSC Chemistry software to study the characteristics of gas products evolution from three kinds of integrated processes of oil shale retorting with methane dry reforming for shale oil production, which refer to the gas product obtained from methane dry reforming used as the reaction atmosphere for oil shale pyrolysis, the gas product derived from methane-catalyzed dry reforming used as the reaction atmosphere for oil shale pyrolysis, and the gas product of dry reforming of methane used as the reaction atmosphere for catalytic pyrolysis of oil shale, respectively. The results show that the reaction effect is optimal under the second integrated process.

Keywords

Methane dry reforming; oil shale retorting; integrated process; gas products.

1. Introduction

Oil shale, a fine-grained sedimentary rock containing relatively large amount of orgnic matter known as kerogen [1], is widely distributed throughout the world. The estimated total global resources of oil shale correspond to around 3 trillion barrels of crude oil [2, 3], and there are about 720 billion tonnes oil shale reserves in China [4]. Therefore, oil shale is a potential alternative to crude oil when the scarcity of light crude becomes a worldwide problem [3]. Kerogen in the oil shale is a complex heterogeneous mixture of organic compounds which could be pyrolyzed into shale oil, gases and char in different proportions as a result of several physical and chemical reactions occurring simultaneously in series and parallel, depending on the operation conditions [5, 6]. Therefore, it is difficult to determine the oil shale conversion pathways and fully understood the mechanism of pyrolysis. For maximising the output and conversion efficiency of oil shale retorting, it is necessary to study the characteristics of oil shale pyrolysis referred as a theoretical basis for investigation the combustion and gasification process [7]. However, some problems have been reported about the traditional oil shale pyrolysis technologies, such as low shale oil yield and utilization rate of oil shale reserves, and the limitations of hydrocracking and catalytic hydrocracking of oil shale, so it is necessary to utilize suitable alternative hydrogen source.

The reaction of carbon dioxide reforming of methane to synthesis gas has attracted great interest from both environmental and industrial perspectives. The conversions of these two gases into a valuable synthesis gas would not only converts both greenhouse gases of CO2 and CH4, but also produces syngas with low H2/CO molar ratio which is a preferable feedstock for the synthesis of liquid hydrocarbons or oxygenates [8-11] Therefore, the hydrogen product obtained by dry reforming of methane can be used as the alternative hydrogen source of oil shale pyrolysis.

The pyrolysis of oil shale is a very complex process involving the parallel and consequent rupture of different chemical bonds with different energies. However, an experimental study of the influence of all the variables in depth would be time-consuming and not cost-effective for the present research team [12]. ASPEN flowsheeting package has been used for the oil shale conversion process in different reactors (such as fischer assay retort, simple fluidized-bed and a two-vessel fluidized-bed) based on a minimization of Gibbs free energy at equilibrium [13-15]. In addition, thermodynamic simulation using Outokumpu HSC Chemistry version 4.1 was conducted to predict the thermodynamically predominant gas species at different temperatures[16].

In this paper, HSC Chemistry software was utilized to study three kinds of integrated processes of oil shale retorting with methane dry reforming for shale oil production, i.e., the gas products obtained from methane dry reforming were used as the reaction atmosphere for oil shale pyrolysis (S-1), the gas products derived from methane-catalyzed dry reforming were used as the reaction atmosphere for oil shale pyrolysis (S-2), and the gas products of dry reforming of methane were used as the reaction atmosphere for catalytic pyrolysis of oil shale (S-3), respectively. The characteristics of gas products obtained by the integrated processes were determined, aiming to utilize efficiently oil shale resources.

2. Methodology

Outokumpu HSC Chemistry 6.0 was used for predicting the characteristics of products obtained from Huadian oil shale pyrolysis integrated with dry reforming of methane[17]. This program is designed for various kinds of chemical reactions and equilibria calculations based on the thermochemical database which contains enthalpy (H), entropy (S) and heat capacity (C) data for more than 17000 chemical compounds. In this paper, the Equilibrium Composition module is used for calculation based on the minimization of the Gibbs free energy of the system, subject to the usual constraint of mass conservation for each chemical element. The main elements C, H, O, N, and S and ash composition in the oil shale sample were taken into account. In addition, the following species were considered [18-22]: H, H_2, C, O, O_2, OH, S, H_2S, COS, CS_2, SO_2, SO_3, H_2O, CO, CO_2, CH_4, C_2H_2, C_2H_6, C_3H_8, C_4H_{10}, C_2H_4, C_3H_6, C_4H_8, CH_3SH, C_2H_5SH, C_4H_4S, N, N_2, NO, NO_2, CN, NH_3, HCN, CH_3CN, C_3H_3N, C_4H_7N, CH_4O, C_3H_6O, C_6H_6, C_7H_8, C_8H_{10}.

The HSC Chemistry performs the thermodynamic simulation of oil shale pyrolysis using the properties described in Table 1 and Table 2. The thermodynamic calculation considered the Molar content of element and ash component of 50g oil shale showed in Table 3. Meanwhile, a temperature of 900oC and a pressure of 1 bar were considered. All gaseous products were assumed to behave ideally, and all condensed products were treated as pure phases with carbon in the form of graphite considered as the only solid species.

Table 1 Characteristics of Huadian oil shale

Ultimate analysis /(wt.%,ad)		Proximate analysis	
C	31.63	M/(wt.%,ad)	2.9
H	4.37	A/(wt.%,ad)	51.61
O	7.764	V/(wt.%,ad)	41.89
N	0.726	FC/(wt.%,ad)	3.6
S	1	Qad,net/(kJ/kg)	8374

Table 2 Characteristics of shale ash from Huadian oil shale

Composition	Mass content/(wt.%)	Composition	Mass content/(wt.%)
SiO2	52.9	MgO	2.99
Al2O3	17.74	K2O	1.27
CaO	14.78	Na2O	0.89
Fe2O3	6.56	TiO2	0.55

Table 3 Molar content of element and ash component of oil shale

Element	C	H	O	N	S
Molar content/mol	1.32	2.19	0.238	0.026	0.013
Ash composition	SiO2	Al2O3	Fe2O3	CaO	MgO
Molar content /mol	0.228	0.045	0.011	0.068	0.019

The organic carbon conversion rate is defined as follows:

$$X_C = \left[\left(F_{C,in} - F_{C,out}\right) / F_{C,in}\right] \times 100\% \quad (1)$$

Where: $F_{C,in}$ and $F_{C,out}$ mean molar content of carbon before and after reactions respectively.

3. Results and discussion

3.1 Organic carbon conversion rate

Figure 1 shows the organic carbon conversion rate obtained from three integrated processes at 0.1MPa and 900°C. The selected catalyst in both S-2 and S-3 processes is 5% Ni/95% SiO_2. It can be seen that all the organic carbon conversion rates are 18.367% under the three different coupling modes, which means the coupling modes have no effect on the organic carbon conversion rate.

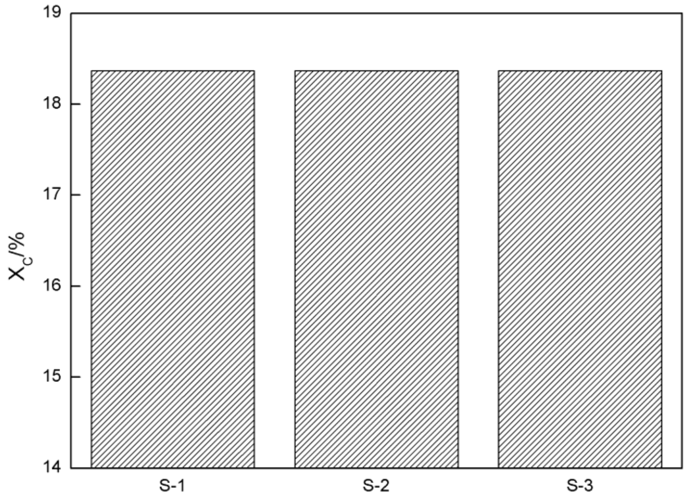

Figure 1 Organic carbon conversion rate obtained under different coupling modes

3.2 Gas Products Analysis

3.2.1 Non-hydrocarbon gases

Figure 2 shows the non-hydrocarbon gas products yield obtained from three integrated processes at 0.1MPa and 900°C. The selected catalyst in both S-2 and S-3 processes is 5% Ni/95% SiO_2. It can be seen from Figure 2 that the hydrogen yield is the highest among all the non-hydrocarbon gas products under three coupling modes, which is 1050kmol. And the carbon monoxide yield is second only to hydrogen. The water yield obtained from the third integrated process increases by 0.24kmol than the other two integrated processes. The methane and CO_2 yields obtained from both the first and second integrated processes are 12.5kmol and 1.48kmol respectively, but those derived in the third integrated process reduce by 0.3kmol and 0.03kmol respectively. There are little differences in the non-hydrocarbon gas yields under different coupling modes.

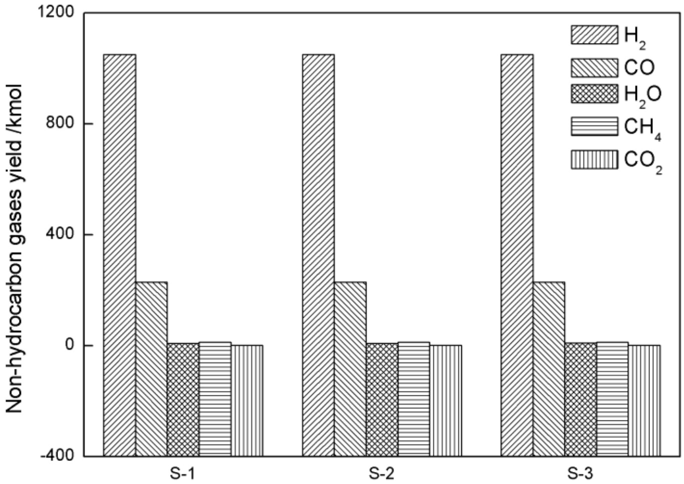

Figure 2 Yield of non-hydrocarbon gases obtained under different coupling modes

3.2.2 Gases containing nitrogen/sulfur

Figure 3 shows the yield of gases containing nitrogen/sulfur obtained from three integrated processes at 0.1MPa and 900°C. The selected catalyst in both S-2 and S-3 processes is 5% Ni/95% SiO_2. It can be seen from Figure 3 that the same yields of N_2, H_2S and COS are obtained under the three different coupling modes, and they are 13.0kmol, 12.9kmol and 0.0878kmol respectively. But there are some slight changes in NH_3 and HCN yield. Under the third integrated process, NH_3 increases by 10^{-4}kmol, while HCN decreased by 1.3×10^{-4}kmol.

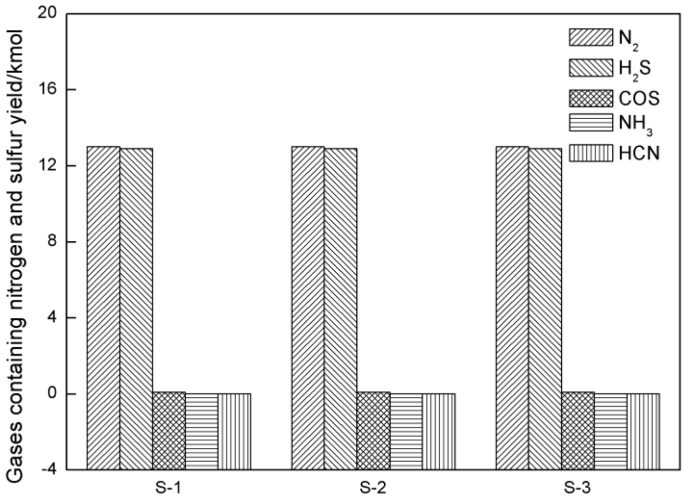

Figure 3 Yield of gases containing nitrogen/sulfur obtained under different coupling modes

3.2.3 Hydrocarbon gases

Figure 4 shows the hydrocarbon gases yield obtained from three integrated processes at 0.1MPa and 900°C. The added catalyst in both S-2 and S-3 processes is 5% Ni/95% SiO_2. It can be seen from Figure 4 that the yields of C_2H_4 and C_2H_6 obtained from the three integrated processes are small, and the third integrated process generates the lowest amounts of C_2H_4 and C_2H_6 among the three integrated processes.

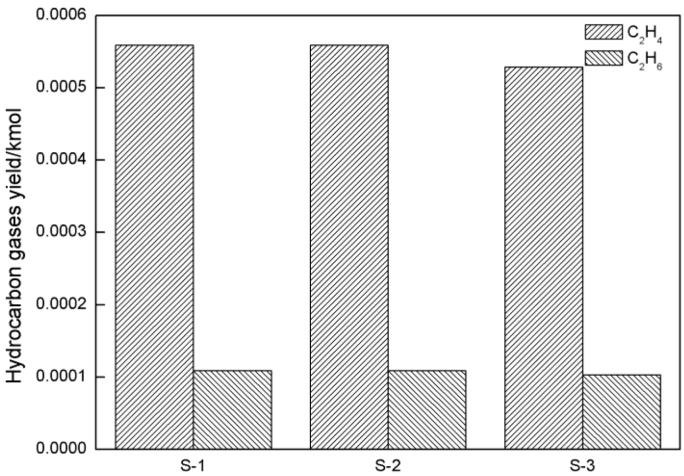

Figure 4 Yield of hydrocarbon gases obtained under different coupling modes

4. Conclusion

Oil shale is a kind of unconventional energy source with abundant reserves and wide distribution. It can be used to produce shale oil with carbon to hydrogen ratio similar to natural petroleum and combustible gas. It is one of the most potential alternative energy sources. However, traditional oil shale retorting technology has many problems, such as low shale oil yield and quality. Therefore, in order to improve the yield and quality of shale oil derived from oil shale retorting, this paper utilized HSC Chemistry software to study the characteristics of gas evolution from three kinds of integrated processes of oil shale retorting with methane dry reforming, which refer to the gas product obtained from methane dry reforming used as the reaction atmosphere for oil shale pyrolysis, the gas product derived from methane-catalyzed dry reforming used as the reaction atmosphere for oil shale pyrolysis, and the gas product of dry reforming of methane used as the reaction atmosphere for catalytic pyrolysis of oil shale, respectively. The results show that the reaction effect is optimal under the second integrated process.

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