Evolution on Development of Daqing Oil Shale In China

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Abstract

Dwindling supplies of crude oil as well as fluctuation in energy markets of the world have revived the interest in the utilization of oil shale. In 2006, Petrochina Company Limited located 62.94 million tons of oil shale in Liushuhe basin and Ningan basin, Daqing oilfield. Physical and chemical property tests of the oil shale show high oil yield, high water content, very small grain size, and poor heat stability. The shale contains the saprohumolith type of kerogen.

On the basis of investigative research on the oil shale pyrolysis process, we found that the Daqing oil shale was more suitable to a Galoter process to retort. The material and heat balance of Daqing oil shale processing in a solid heat carrier installation (UTT-3000) was simulated using a computer simulation program created by TTU Ltd. This simulation showed that it could improve oil shale utilization in both economic efficiency and product type.

Keywords: oil shale; Galoter process; oil yield; Daqing

Introduction

The fossil fuels - coal, petroleum and natural gas - have been the primary suppliers of reliable, low-cost energy in the world for many years. The decreasing availability of these conventional energy sources, combined with the development of heavy industry, has placed great pressure on the world's energy supplies. In response, facilities for the technical development of diverse, clean energy generation have become available.

Oil shale, a fine-grained sedimentary material with organic matter called kerogen, is rich and widespread in the world. Statistics show that the natural resources of oil shale around the world are about 10×10^{12} tonnes (t), which is 40% more than coal. The potential shale oil is about $4{,}750\times10^{8}$ t (50% more than traditional petroleum). China also has enormous potential resources of oil shale, the proven reserves (about 315 $\times10^{8}$t) being the fourth in the world (Li and Tang, 2006). In order to reasonably develop and utilize these resources, it is necessary to strengthen research in geology and resource distribution, and use advanced foreign experiences for reference. The gradual decrease in the reserves of conventional energy resources has motivated China to investigate efficient means to use oil shale as an alternative energy source as soon as possible. For example, burning oil shale to generate electricity (Jiang et al., 2001; Loosaar et al., 2005) and retorting oil shale to produce shale oil (Rubens, 1985; Silva et al., 1985), are parts of a multi-purpose process strategy for oil shale exploitation.

As the country's largest oil and gas producer, Petrochina Company Limited plans to invest 10 billion yuan by 2020 to develop alternative energy including oil shale. In 2006, the reserves of 62.94 million tons of oil shale in Liushuhe basin and Ningan basin of Daqing Oilfield, in comparison with reserves of 6.32 million tons of shale oil, are proven. This provides assured resources for large oil shale refineries. In addition, the proven resources rate is less than 10%, enhancing prospects.

In this paper, the physicochemical properties of Daqing oil shale are analyzed. On the basis of analytical data, the Galoter process for oil shale is simulated and analyzed for economics.

Experimental procedure

Oil shale was obtained from Liushuhe and Ningan basin, in Daqing oilfield. The oil shale samples were ground into particles <8 mm in diameter. Proximate analysis, ultimate analysis, Fischer Assay shale oil yield, and solid calorific value are the basic data that reflect the characteristics and composition of the oil shale, and are the indexes used to appraise the quality of oil shale.

Kerogen, the organic matter of oil shale, is present as a complex combination of carbon, hydrogen, sulfur and oxygen that cannot be extracted with organic solvents. Upon heating, the kerogen is initially converted to bitumen and then to the final products, such as shale oil and hydrocarbon gases. The optimum pyrolysis temperature for maximizing shale oil yield is in the region of 500-530 °C (Dogan and Uysal, 1996; Williams and Chisti, 2000). The results, in which shale oil prepared by pyrolysis of Daqing oil shale was characterized and compared to petroleum, showed that shale oil may be used as a substitute for gas oil or heavy fuel oil (Akash and Jaber, 2003).

The proximate analysis was carried out using standard GB212-91 method and the ultimate analysis was carried out using standard GB/T 476-2001 method. Fischer Assays were carried out on 100 g samples of the 3-6mm shale. The oil shale was heated from 25 °C to 520 °C very nearly linearly over a 50 min period while being purged with nitrogen. The heating rate was, therefore, approximately 10 °C /min. Following heating, the sample was held at 500 °C for 30 minutes and the oil and gas collected were measured. The shale oil was distilled into individual gasoline, diesel oil and heavy oil fractions and the fractions were tested using standard ASTM methods, including quality differential distillation.

Properties of Daqing oil shale

Oil shale consists of inorganic and organic constituents. The inorganic portion is dependent on input from the environment in which the debris was buried, which certainly had an effect on the evolutionary path of the organic structure. Also, presence of inorganic constituents may play an important role in processing of the oil shale. The proximate analysis of oil shale yields the ratio of organic and inorganic constituents. A typical proximate analysis for Daqing oil shale is given in Table 1.

The organic portion of oil shale may also be classified in two general classes: bitumen and kerogen. The bitumen is the portion soluble in petroleum based solvents and kerogen is the complex matrix which is converted into tar, gas and residue (semi-coke) when heated in an oxygen free-lean environment. The elemental analysis of Daqing oil shale is given in Table 1.

A set of 13 oil shale samples was used for Fischer Assay analysis with a heating rate of 10°C/min, and a final temperature of 510°C. Physicochemical properties of Daqing oil shale are shown in Figure 1. Figure 1a shows that the reserves of Daqing oilfield have a high oil yield, 12.49%, compared to Fushun oil shale, 8.73%. Experimental results show that the oil yield of Daqing oil shale is high and of industrial value. Figure 1b shows the Daqing oil shale has high moisture content, 27.14%, compared to Fushun oil shale, 21.05%, because the moisture content increases with increasing groundwater. The higher the moisture

Table 1: Proximate and Ultimate Analysis of Daqing oil shale

Proximate analysis		Ultimate analysis (wt %)	
Shale oil	9.55	C	55.09
Water	33.42	H	4.18
Gas	9.80	O	20.93
Semicoke + loss	47.23	N	0.83
Caloric value (kJ/kg)	32,773	S	0.23

content, the more energy is needed in cooling pyrolysis products, an inconvenience to the commercial plant. As was shown in Table 1, the dominant composition of oil shale is inorganic material, often called mineral matter. In all practical senses, the inorganic matter of oil shale is represented by the content of ash. The minerals in the oil shale include quartz, kaolin, clay, biotite, carbonate and pyrite, and so on, but mainly clay. Figure 1c shows the Daqing oil shale has low ash content, 35.85%, compared to Fushun oil shale, 71.44%. Ash evaluation is an important indicator of oil shale. The low ash content means the remaining residue is low, reducing the operation load of a commercial plant. Figure 1d shows the Daqing oil shale has a high calorific value, 13.86MJ/kg, compared to Fushun oil shale, 3.51MJ/kg. The calorific value is an important quality indicator of oil shale's comprehensive utilization. It is the calculated basis of heat balance, consumption, and thermal efficiency of the process of combustion.

Table 2 shows different properties of domestic oil shale. It is concluded that Daqing oil shale is high in oil yield, water content, and volatile content, and is low in sulfur content and ash content. The Daqing oil shale is suitable to retort to produce shale oil.

Organic matter type

Organic matter (kerogen) in source rocks generally can be divided into three categories: sapropelinite type (Type I), mixed type (Type II) and humus type (Type III). The mixed type can be divided into humosapropelic type (Type II_1) and saprohumolith type (Type II_2) (Zhang et al., 1999).

Analysis (Figure 2) shows H/C ranging from 0.8 to 1.1, and O/C from 0.25 to 0.4, indicating the kerogen of the oil shale belongs to the saprohumolith type, which has a high content of organic matter and a strong source capacity.

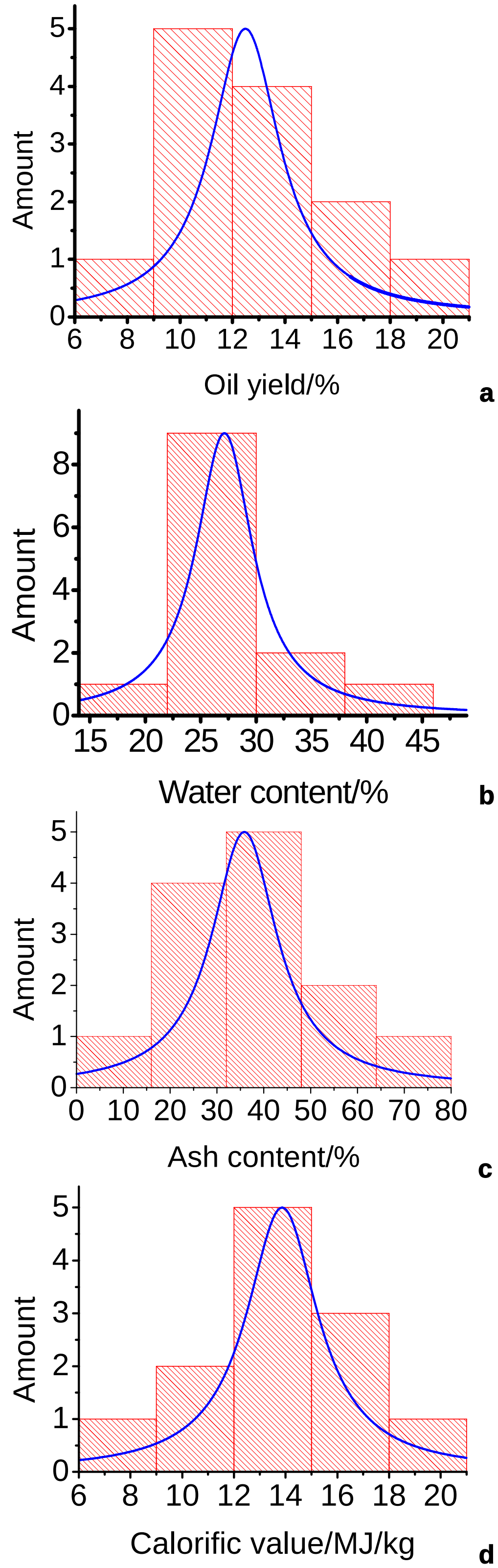

Figure 1: The physicochemical property of Daqing oil shale

Table 2. Comparison of domestic oil shale's property

Type of oil shale	Oil yield (wt %)	Calorific value (MJ/kg)	Ash (wt %)	Volatile matter (wt %)	Moisture (wt %)	Sulfur (wt %)
Fushun	8.73	3.51	71.44	21.05	3.04	2.54
Maoming	7.27	5.02	65.00	20.12	17.00	5.78
Huadian	12.00	9.63	64.40	81.93	2.90	1.00
Longkou	14.00	12.20	49.92	35.66	15.20	1.20
Liushuhe	12.49	13.86	35.85	65.04	36.77	0.22
Ningan	7.54	10.60	48.65	66.34	33.47	0.25

Organic carbon and organic hydrogen

The organic matter of sedimentary deposits must undergo a transformation with accumulation of carbon, hydrogen and constant reduction of oxygen in the conversion to oil (Zhang et al., 1999).

The organic carbon content of Daqing oil shale is high, from 20% to 60%. On the basis of current price of crude oil, the mining of oil shale whose oil yield is >3.5%, can have economic value. The correlation study between oil yield and the amount of organic carbon shows a significant linear correlation between the two factors (Figure 3a). With the increase in organic carbon content, the oil yield of oil shale gradually increases.

The organic hydrogen content of Daqing oil shale is high, from 2.5% to 4.5%. The correlation study between oil yield and organic hydrogen shows a significant linear correlation between the two factors (Figure 3b). With the increase in organic hydrogen content, the oil yield of oil shale gradually increases. Organic hydrogen content of oil shale is one of the geochemical factors that affect oil yield.

The main sedimentary organic matter of oil shale is kerogen, the main chemical components of which are elemental C and H. The carbon content of oil shale is up to 76.4%, whereas the hydrogen content is up to 6.3% (Zhang et al., 1999).

From the above analysis, we find that a linear correlation between oil yield and the C

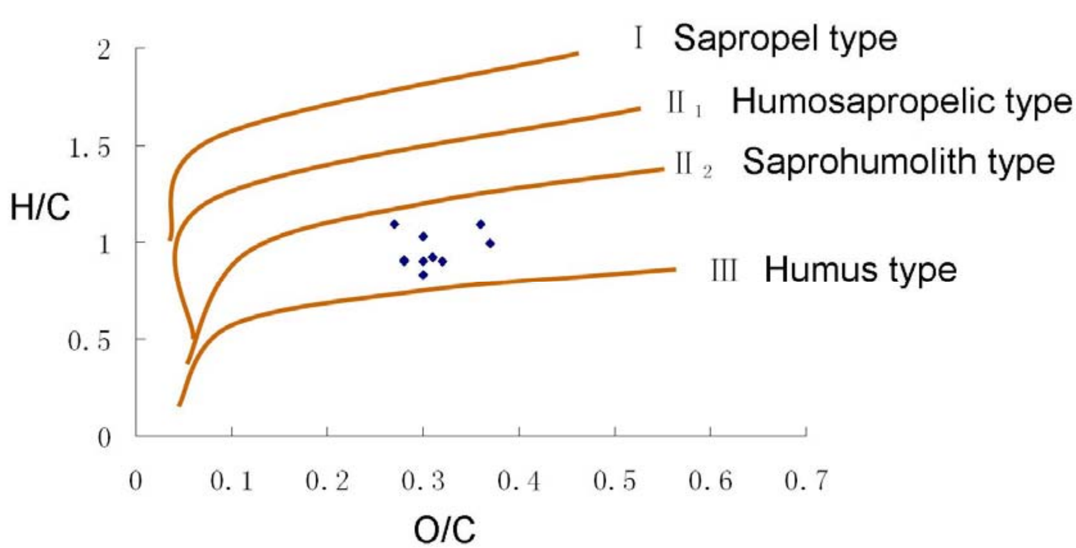

Figure 2: Kerogen types

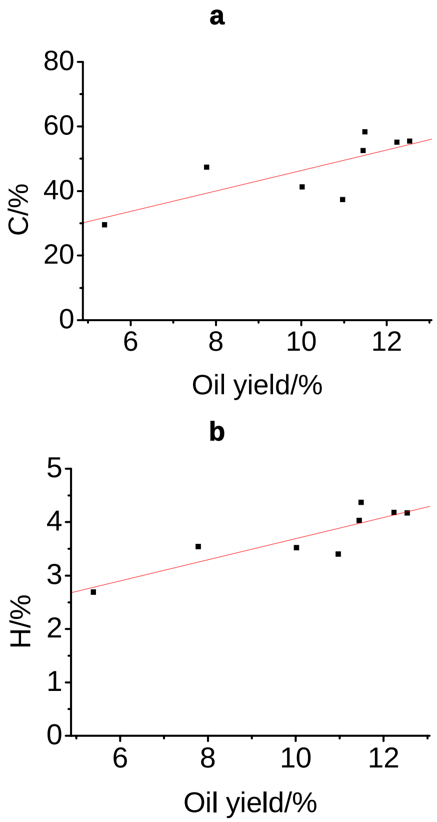

Figure 3: The relation between oil yield, organic carbon and hydrogen

and H content exists, and the genesis of oil shale is similar to that of source rocks. Therefore, on the basis of the affecting factor of the type of organic matter and the abundance of oil shale, we identified the factors influencing oil yield.

Physicochemical properties

The density of kerogen is generally about 1.08-1.16g/m^3. The density of minerals is generally about 2.3-2.7g/m^3 (Jiang, 2006). When the mineral content is high, the density of oil shale is also high, but the calorific value is low. Because of low kerogen content, the oil content is also low. It is feasible to approximately determine the grade of oil shale through the ash content, mineral content, calorific value, and ASG (apparent specific gravity) (Figure 4).

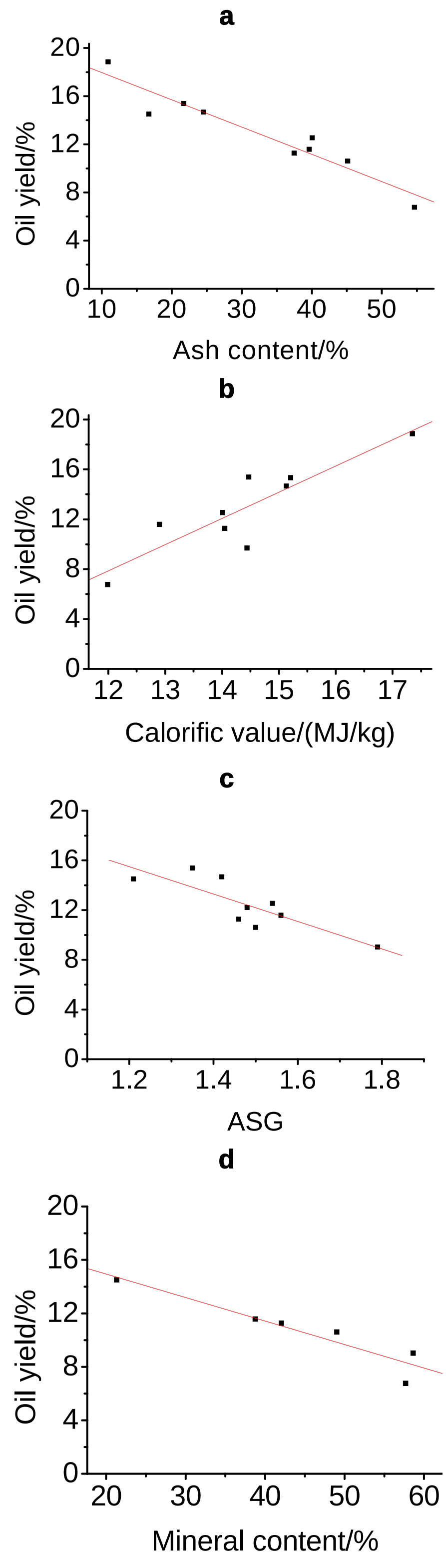

Figure 4: The relationships between chemistry parameters and oil yield (a) ash content (b) calorific value (c) ASG and (d) mineral content

Characterization of shale oil

Table 3 shows that Daqing shale oil is high grade compared to Daqing crude oil and Fushun shale oil with initial boiling point 101 °C and end point 509 °C. The Diesel oil fraction of Liushuhe shale oil occupies 55%, highest among the three samples, making it suitable to process for diesel oil which has high industrial value. The heavy oil fraction can be used as a feedstock for petrochemical refining, and the gasoline fraction as a fuel oil.

Comparison of world oil shale commercial retorting technologies

There are several processes for the conversion of the solid insoluble organic matter (kerogen) in the host rock to oil and gas by pyrolysis (retorting). The world's current oil shale commercial retorting technologies are listed and compared in Table 4.

1. Chinese, Russian and Estonian Generator type lump shale retort is of small capacity with low oil yield on Fisher Assay, is not advanced, but suitable for small plant due to its low investment.
2. Estonian Kiviter lump shale retort is of middle capacity, with middle oil yield, its investment is relatively not high, and it is suitable for medium scale plant.
3. Estonian Galoter particulate shale retort is of large capacity, with high oil yield on Fisher Assay, and producing high calorific gas, but its construction is rather complex, and maintenance is expensive. It is suitable for large scale plant.
4. Brazilian Petrosix lump shale retort is of large and very large capacity, with high oil yield and producing high calorific gas. Its investment is costly, and it is suitable for medium and large scale plant.
5. Australian SPP-Alberta Taciuk particulate shale retort is of very large capacity, with high oil yield on Fisher Assay, and

Table 3: Comparison of different region's oil fraction

Type of oil	Gasoline (wt %)	Diesel oil (wt %)	Heavy oil (wt %)
Daqing shale oil	9	50	41
Daqing crude oil	12	20	68
Fushun shale oil	0	45	55

Table 4: Comparison of World's Commercial Oil Shale Retort Technologies

Retort	Chinese Generator	Kiviter	Galoter	Petrosix	Alberta Taciuk
Company	Fushun Shale Oil	Viru Keemia Grupp	Narva Power	Petrobras	SPP
Country	China	Estonia	Estonia	Brazil	Australia
Oil Shale T/d	100	1000	3000; 1600	6200	6000
Size, Mm	10-75	10-125	0-25	6-50	0-25
Configuration	Vertical Cylindrical	Vertical Cylindrical	Horizontal Cylindriical	Vertical Cylindrical	Horizontal Cylindriical
Process	Shale Pyro. Coke Gasi	Shale Pyro. Coke Cool	Shale Pyro. Coke Comb	Shale Pyro. Coke Cool	Shale Pyro. Coke Comb
Heat Carrier	Gas	Gas	Ash	Gas	Ash
Fisher Assay Oil yield ,%	65	75-80	85-90	90	85-90
Products	Fuel Oil Low Cal. Gas Ash	Fuel Oil Chemicals Low Cal. Gas Ash	Fuel Oil Chemicals High Cal. Gas Ash	Fuel Oil Naphtha Sulfur High Cal. Gas Coke	Low S Naphtha Light Fuel Oil High Cal. Gas Ash

producing high calorific gas. The light naphtha is upgraded to produce ultra low sulfur gasoline fraction, but its investment is costly. It is going to normal operation and is suitable for large and medium scale plant.

Rough economic evaluation of one UTT-3000 installation on Daqing oil shale

On the basis of the above utilization program, a comprehensive utilization system with handling capacity of 3000 t/day Daqing oil shale has been designed. The final products mainly involve shale oil, fuel gas, and electricity. A major portion of electricity generated in the self-supply power plant is supplied to the comprehensive utilization system, and the surplus will be sold.

For obtaining a high economic efficiency, this comprehensive utilization system was optimized, and the total investment and the economic efficiency were estimated, based on these simplifying assumptions:

(a) oil shale compositions do not greatly vary;

(b) every part of the comprehensive utilization system can operate steadily;

(c) the waste from one process will entirely be introduced into another;

(d) the market price is close to that in 2007 and can keep constant for many years.

The detailed distribution data of the estimated investment are shown in Table 5, which indicates the total investment for the system is $40,032 per day. Based on the data of Table 5, the comprehensive utilization system can achieve a high economic efficiency. With increased petroleum price and demand, regulation is required to maintain the economic efficiency of the entire system.

Capital costs for the plant consisting of one UTT-3000 (USD 40 million per one train) with considerations of Power Plant (turbine house with specific capital cost USD 500 per 1 kW of installed capacity for 70 MW) will make USD 74,775,000, including infrastructure. Calculations for daily operations of one UTT-3000 with considerations of Power Plant are given below. Table 5 shows the project is viable and the investments will be paid back in 1.14 years.

Conclusion

In summary, this paper presents a preliminary characterization of Daqing oil shale and

Table 5: Rough economic evaluation of UTT-3000 on Daqing oil shale

	Quantity (tons/day)	Rating ($per ton)	Amount ($/day)
Total Expenses			*40,032*
oil shale mining	3,336	10	33,360.00
oil shale processing	3,336	2	6,672.00
Total Income			*292,820.69*
shale oil	318.58	325	103,539.96
gas	326.72	200	65,344.34
electricity (kWh/day)	1,549,205	0.08	123,936.39
Operational Profit			252,788.69
Amortization of UTT			8,194.53
Profit after taxation (-30%)			244,594.15
Net profit after taxation (-30%)			171,215.91
Cash flow			*179,410.44*
Payback period (days)			416.78
Payback period (years)			*1.14*

its economical analysis and a simulated Galoter process. The results presented in this paper indicate that the Daqing oil shale is high in oil yield, water content, and volatile content, and is low in sulfur content, and ash content. The data also show a linear relationship between ash content, mineral content, calorific value and oil yield. Based on the analysis of oil shale, the Galoter process was chosen to process the Daqing oil shale and was simulated and economically evaluated, the results of which were favorable.

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