Zero CO₂ Emission Oil Shale Process

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Abstract
Due to the peak production of conventional crude oil and the higher oil price in the last couple of years, shale oil is a possible alternative source of oil in the future. The global shale oil resources could be trillions of barrels but must first be extracted by retorting the oil shale. Current retorting technologies generate and emit CO₂ similar to coal-fired power plants. New shale oil projects may need to consider reducing CO₂ emissions to meet future government environmental regulations.

This paper proposes a novel Zero Emission Oil Shale Process (ZEOSP). The concept is to produce shale oil, energy (electricity, steam) and high purity CO₂ from oil shale with near zero emission of CO₂ and other atmospheric pollutants. A mixture of high purity oxygen and CO₂ from flue gas is used in the spent shale combustion instead of air and thus achieves a concentrated CO₂ flue gas which can be captured and stored.

Current existing solid heat carrier oil shale processes and vertical gas heat carrier processes can be upgraded with the ZEOSP concept. The conceptual process design and operation performance are evaluated by using an oil shale process simulation package on the energy efficiency improvement and sequestration of CO₂ without affecting shale oil yield. Shale oil production cost is analyzed to provide an insight on the economic performance of the technology.

Introduction
The increase of green house gas (GHG) concentration in the atmosphere is considered to be the major cause of global warming over the last 50 years (Intergovernmental Panel 2001). Governments are expected to make laws to reduce current CO₂ emission level to stabilize the atmospheric CO₂ concentration in complying with the Kyoto protocol (which states, for example, that the GHG emission of the EU-15 until 2010 should fall by 8% compared to the emissions during the base year 1990). The Australian government is planning to introduce the National Carbon Trading Scheme to combat global warming. This will affect design and development of oil shale processes in Australia and worldwide due to the large amount of carbon emission in oil shale retorting.

Carbon sequestration technology, called carbon capture and storage (CCS), is shown as a potential option to reduce carbon emission after being studied in coal-fired power plants, the dominant source of global CO₂ emission. A cryogenic air separation unit is integrated with a conventional coal-fired power plant. The O₂ is separated from air at temperatures of about -180°C and used in coal combustion. Economic analysis of CO₂ sequestration technology for combustion in O₂ instead of air has been recently studied for a coal fired power plant, which shows a significant penalty in the power plant performance (≈ 8.5%) (Kakaras et al, 2007). The decrease of power output resulting from the CO₂ sequestration technology is expected and is a negative factor for wide application of CO₂ sequestration technology. However, the development of low cost O₂ ceramic membrane separation technology is reported to be near the commercialization stage. The cost of oxygen can be reduced by 35% compared with a conventional air separation unit (ASU). The development of low cost oxygen separation technology will help the wide application of CO₂ sequestration technology in coal-fired power plants (Fassbender 2007; Technical and Economic Feasibility, 2007) and make carbon sequestration technology economic.
The study of carbon sequestration technology has been limited in oil shale process development literature. Oil shale processes generally can be classified as above ground surface retorting and in-situ underground retorting processes. Above-ground retorting technology is the most utilized commercially, such as Petrosix, Kiviter, Galoter and Fushun retort or under research and development such as ATP, Paraho process etc. (Qian and Wang, 2006; Schmidt, 2003; Schmidt 2006; Trikkal and Kuusik, 2006). All these oil shale process technologies have the potential to integrate with air separation units in order to apply to carbon sequestration technology.

Due to the significant oil price increase in the last couple of years, more and more oil shale projects are under construction or under developmental study in the US, Australia, China, Estonia and Jordan using above ground retorting technology. All conventional retorting technologies cause significant CO₂ emission to the atmosphere. Even though the exact amount of CO₂ emission for oil shale processing and its effect on climate change has not been specifically studied (Bartis, 2005), additional oil shale projects could further increase global warming if improvements in CO₂ emission are not achieved. With increasing concerns about greenhouse gas emission, the application of CO₂ sequestration technology in oil shale processes could assist compliance with stricter environmental laws in the future. The study of carbon sequestration technology is necessary for oil shale processes to meet the potential strict environmental emission regulations.

This paper investigates the potential to upgrade conventional vertical gas heat carrier and solid heat carrier oil shale processes using an oil shale process simulation package developed by PROCOM.

Previous studies in O₂/CO₂ combustion power technology showed that a significant reduction of the efficiency and net power output occurred due to the costly ASU and CCS technology [2]. This indicates that O₂/CO₂ separation in oil shale processing will result in increased investment cost and decreased plant performance. However, the performance penalties can be significantly reduced if the huge amount of heat produced from the process could be recovered and integrated throughout the process. The potential of commercial development of O₂/CO₂ combustion technology will be of interest to the oil shale industry and governments.

For all commercial oil shale retorting processes, the coke and toxic organic compounds in spent shale cannot be burnt completely due to technology limitations and trapping inside the ash. Thus huge amounts of heat (or energy) remaining in the ash in the form of coke or organic compounds are lost (or unrecovered) for all currently operated oil shale technology. The toxic organic compounds remaining within the ash from oil shale plants are a source of environmental pollution. ZEOSP process uses O₂/CO₂ to burn more coke and organics within the spent shale and improves the energy recovery efficiency using the appropriate oxygen concentration which can be controlled from 20%-35%. The cost of the shale oil can be increased due the costly ASU and CCS technology; however the cost of ASU and CCS technology could be recovered with the integration of heat recovery in flue gas condensation, flue gas compression, and maximum combustion of organics inside the spent shale in the ZEOSP process. Low GHG emissions and higher energy recovery efficiency are advantages of the ZEOSP design assessed in this paper.

This work is conducted to simulate a potential application of O₂/CO₂ combustion and CO₂ sequestration technology in oil shale processing, including economic performance analysis to provide an insight for future oil shale development.

**ZEOSP Process Review**

In this paper, the ZEOSP process is developed and simulated based on the integration of existing solid heat carrier retorting
processes such as ATP and Galoter (Opik et al., 2001), vertical gas heat carrier oil shale processes such as Petrosix, Kiviter and Fushun retort, with air separation and CO₂ capture units. In the ZEOSP process, the O₂/CO₂ combustion technology is used instead of air combustion technology in conventional oil shale process.

The process flow diagram of the ZEOSP application in solid heat carrier process is shown in Figure 1. This process concept design used the existing Galoter (or UTT 3000) process (Volkov and Stelmakh, 1999) and the Australian ATP plant (Schmidt 2003) as references. The air separation unit is referenced to conventional cryogenic air separation processes and the CO₂ capture unit is referenced to a conventional liquefied CO₂ carbon capture (CCS) process. The process flow diagram of the ZEOSP application in a vertical gas heat carrier is also illustrated in Figure 2. Mass and heat balance throughout the process streams were calculated using a flexible oil shale process simulator developed by PROCOM.

Comparison of ZEOSP Process and Conventional Oil Shale Process

The reference oil shale retort process was based on the reported solid heat carrier retort process (Volkov and Potapov, 2000; Volkov and Stelmakh, 1999) because its flexibility makes it easily adapted with other unit operations and the large amount of published process data available.

The original retort process includes:
1. fluidized bed feed oil shale dryer
2. rotary drum retort
3. oil vapor and spent shale separation chamber
4. fluidized coke combustion furnace
5. heat recovery boilers
6. electrostatic precipitator
7. air feed blower.

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Figure 1: ZEOSP application in Solid Heat carrier oil shale process.
The new ZEOSP process integrates an air separation unit (ASU) and carbon capture unit into the original reference retort process. The ASU provides oxygen with purity of 95% to the fluidized combustion furnace instead of air. The flue gas from the spent shale furnace is mainly composed of CO₂ and H₂O (vapor). About two thirds of the flue gas is recycled back to the furnace after passing through the shale dryer and mixed with oxygen from the ASU. Therefore most of the odorous organic compounds from the shale dryer are also removed by combustion inside the furnace. The rest of the flue gas exiting the unit is cooled down and captured in the CCS unit. The coke and potential toxic organic compounds remaining inside the spent shale can be nearly completely combusted and leave the ash as an environmentally friendly landfill material. The maximum of heat can be recovered from the furnace to generate steam or electricity. The ZEOSP process includes:

1. fluidized bed feed oil shale dryer
2. rotary drum retort
3. oil vapor & spent shale separation chamber
4. fluidized coke combustion furnace

5. heat recovery boilers (larger than reference original retort process)
6. electrostatic precipitator
7. recycle flue gas compressor
8. carbon capture & storage (CCS) unit
9. air separation unit (ASU).

The main differences from the existing reference retort process is that the ZEOSP includes ASU and CCS units and it provides improved heat and mass flow control throughout the process.

**Air Separation Unit design**

A conventional cryogenic air separation unit was used in the ZEOSP process because of its reliability and cost-effectiveness. Cryogenic, ITM (ion transportation membrane) and PSA are the available commercial technologies. Among these technologies, the oxygen cost from cryogenic technology is the most economical at US$20~30/ton O₂ for large scale oxygen plants, according to previous studies (Figure 3) (Kobayashi and Hassel, 2005). The cost of ASU for the ZEOSP process will increase the cost of the shale oil. The integration of heat recovery from the air compression and utilization of liquid oxygen vaporizer to cool the CO₂-enriched flue gas
is essential to maximum the economic performance of the process. Generally, the cryogenic air separation process includes:

1. air compression
2. liquefaction of air at about –180 °C
3. oxygen and nitrogen separation.

A maximum oxygen production rate of 28t/h is required. An oxygen purity of 95% is selected as the most favorable because of the zero N₂ in product gas but 5% impurity of argon.

**CO₂ Capture and Storage (CCS) Unit Design**

Carbon dioxide (CO₂) capture and storage (CCS) is a process consisting of the separation of CO₂ from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere. CCS has the potential to reduce overall mitigation costs and increase flexibility in achieving greenhouse gas emission reductions. The widespread application of CCS would depend on technical maturity, cost, overall potential, diffusion and transfer of the technology to developing countries and their capacity to apply the technology, regulatory aspects, environmental issues and public perception.

Due the CO₂ rich flue gas in ZEOSP process, the cost of CO₂ capture can be minimized with gas compression, cooler and transportation pipe without de-sulfurization. Ocean storage is considered as a potential way of CO₂ storage due to the low cost as shown in figure 4. Ocean storage could be done in two ways: by injecting and dissolving CO₂ into the water column (typically below 1,000 meters) via a fixed pipeline or a moving ship, or by depositing it via a fixed pipeline or an offshore platform onto the sea floor at depths below 3,000 m, where CO₂ is denser than water and is expected to form a “lake” that would delay dissolution of CO₂ into the surrounding environment (Metz, 2006).

**Process Simulation**

**Reference original oil shale process**

The exiting solid heat carrier retort plant, UTT3000 and Australia ATP stage 1, is used as the base for the comparison of efficiency of a modified ZEOSP process. An Excel™ workbook model is developed which includes the collective thermal properties of oil shale components, process flow diagram and the mass and energy balance calculations for various streams. The process model is designed with the capability of simulating oil shale processes with variable shale feed rate and sensible effect on the oil shale properties.

The properties of average Estonian oil shale used as feed shale in this study are shown in Table 1. In this design, the feed shale is dried and preheated in a fluidized bed by the hot flue gas and then mixed with hot recycled spent shale and pyrolyzed in a rolling bed within a rotary drum. This technology is facing strict EU and Australian environmental emission regulations due to its large amount of GHG emission, huge amount of water consumption...
and potential environment pollution caused by the remaining toxic organic compounds in the ash. The simulation results for the original oil shale process are shown in Table 2. The shale feed rate of 250 t/h remained the same in all the simulation cases.

**ZEOSP process**

In this ZEOSP process simulation, the O₂/CO₂ combustion technology and CCS technology have been integrated into the reference original oil shale process. O₂ with purity of 95% mixed with recycling CO₂ is used in the spent shale combustion furnace and thus the flue gas is composed mainly of CO₂ and water vapor. About two thirds of the CO₂-rich flue gas is recycled and mixed with high purity oxygen (95%) and the rest of the flue gas is cooled, captured and stored to prevent emission to the at-

<table>
<thead>
<tr>
<th>Oil shale Grade</th>
<th>98.00</th>
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<tbody>
<tr>
<td>Bulk Density kg/m³</td>
<td>771.40</td>
<td>771.40</td>
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<tr>
<td>In-situ Density kg/m³</td>
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<td>1700.00</td>
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<td>Void fraction v/v</td>
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<td>Kerogen wt% db</td>
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<tr>
<td>Carbonate as CO₂ wt% db</td>
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<tr>
<td>Hydrates as H₂O wt% db</td>
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<tr>
<td>Ash wt% db</td>
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<tr>
<td>Free Water Content in Raw Oil Shale wt% db</td>
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Table 2: Comparison of cost and operation for original and ZEOSP process.

<table>
<thead>
<tr>
<th>Plant performance and costs</th>
<th>Original plant</th>
<th>ZEOSP Plant</th>
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<tr>
<td>Oil Shale Grade (LT0M)</td>
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<td>Shale feed rate (t/h)(max)</td>
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<td>Gross oil product (t/h)(max)</td>
<td>32.5</td>
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<td>Gross gas product (t/h)(max)</td>
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<tr>
<td>Boiler Power (MW)</td>
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<td>144.76 (max)</td>
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<td>Plant Power consumption (MW)</td>
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<td>Operating hours</td>
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<tr>
<td>Shale plant</td>
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<td>250.00</td>
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<tr>
<td>ASU</td>
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<td>Flue Gas Scrubber</td>
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<td>Oil shale cost (US$/M/year)</td>
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<tr>
<td>Mining Cost US$/t</td>
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<td>5.00</td>
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<tr>
<td>Crushing Cost US$/t</td>
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<tr>
<td>Total Annualized Cost (US$/M/year)</td>
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<td>65.10</td>
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<tr>
<td>Shale oil cost price (US$/bbl)</td>
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<td>41.19</td>
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<tr>
<td>Emitted CO₂ t/bbl</td>
<td>0.21</td>
<td>0.00</td>
</tr>
<tr>
<td>CCS Avoidance Cost (US$/bbl oil)</td>
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<td>5.46</td>
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mosphere. A centrifugal flue gas compressor is designed to support the recycle and capture the flue gas. Three waste heat boilers are designed to recover the heat from flue gas and ash. Heat from flue gas and ash are recovered in boilers. This design will help to improve process control on mass and heat balance throughout the process, which includes feed shale temperature, oxygen flow rate, flue gas recycle and heat recovery from flue gas and hot ash. High content of hydrocarbons (mainly measured as CH₄) was found in reference plant stack gas as a result of overheating of the finest oil shale particles in the oil shale drier or incomplete combustion (Opik et al., 2001).

In the ZEOSP process, the hydrocarbons and odorous substances in the stack gas will be recycled and burned off within the spent shale combustion furnace. CO₂ and SO₂ were both compressed and captured and stored in the ocean. The carbon emission to the atmosphere can be minimized. This will result in a cost saving in flue gas treatment processes. The ASU is the main extra cost in the ZEOSP plant and will result in higher capital operation and maintenance costs. But the higher heat recovery efficiency will benefit the process economically by improving combustion efficiency and generating power. The simulation results of mass and heat balance summary for the ZEOSP process are shown in Table 2.

**Economic Evaluation**

**Assumptions for economical analysis**

To evaluate the cost and performance of ZEOSP process, a comparison of cost and performance between the reference original oil shale process and ZEOSP process has been conducted based on the following assumptions:

1) The capacity of processing oil shale remains the same for the two processes;
2) The size and major retort equipment are the same for the two processes;
3) The cost of the reference original plant is assumed to be $250M according to the estimation of existing oil shale plant.

The major cause of increase in costs for the ZEOSP is investment cost and operation cost of the ASU which alone requires an estimated $110M of investment (Table 2). Costs for accessory equipment such as recycle flue gas compressor are estimated and illustrated in Table 2. Some equipment such as recycle flue gas compressor, extra gas splitter and pipe lines will also require more capital cost, but can be ignored compared with the cost of the ASU.

**Plant performance and cost analysis**

The oil shale feed rate, shale oil production rate and gas production rate can be calculated from the oil shale process simulator for the reference oil shale process and the ZEOSP process. The calculated results can be compared with the existing plant and used to optimize the performance of the existing plant. With more test data available from the existing plant, the oil shale process simulator could be further improved to provide more accurate information.

The capital cost, operation cost and the shale oil production cost for the reference and ZEOSP process were analyzed and are illustrated in Table 2. The operating life for the plants is designed for 20 years assuming that the EPC and construction are completed in the first year. A cost analysis for each process (oil shale plant, ASU) was conducted to obtain the shale oil production cost and the avoidance cost was obtained from an oxygen/CO₂ power plant (Andersson and Johnsson, 2006). The shale oil production cost is the total annualized cost divided by the annual shale oil production. The shale oil production cost varies with interest rates and oil shale costs (Figures 3, 4).

Figure 3 shows the shale oil production cost increased with the interest rate increase if the oil shale cost remains the same US$7/t on the basis of 20 years operation life for both reference and ZEOSP plant. The oil shale cost normally includes
the mining, crushing and processing cost. Oil shale price is also dependent on its grade (LT0M). In this calculation, we assume the oil shale grade remains the same and the oil shale cost is dependent on mining and processing. The analysis shows the existing solid heat carrier process can be upgraded to a low emission oil shale process with shale oil production cost at $20-40/bbl, which means a reasonable profit at the current world crude oil price at about $80/bbl.

Figure 4 shows the shale oil production cost versus the oil shale cost with constant interest rate of 10%. The results indicate that the shale oil production cost is within $21-41/bbl if the shale costs $5-14/t respectively.

Both Figures 3 and 4 indicate the shale oil from ZEOSP will cost more than conventional oil shale process. However, a reasonable profit for the shale oil is obvious for the ZEOSP even without considering...
the gain of higher heat efficiency and government GHG emission credit.

**Conclusion**

The zero CO₂ emission oil shale process (ZEOSP) can be developed through application of O₂/CO₂ combustion technology in both a conventional solid heat carrier oil shale process and a vertical gas heat carrier oil shale process. Although the accuracy of economic data is dependent on assumptions, the study does provide insight into the economic performance of the concept-designed low CO₂ emission oil shale process. The results from this study propose an O₂/CO₂ combustion oil shale process and show that:

1) The oil shale process simulation package developed by PROCOM demonstrates the capability in simulation of conventional and new concept oil shale processes. Mass and heat balance throughout process streams have been calculated. The steady state operation performance in various condition can be well simulated and provides essential information for process optimization or scale up.

2) The oxygen combustion technology can be applied to conventional oil shale processes to establish a new Zero CO₂ emission oil shale process (ZEOSP).

3) The shale oil production cost in the ZEOSP is expected to be higher than that in conventional oil shale processes with the same feed rate.

4) The simulation results showed that the heat efficiency is increased significantly in ZEOSP compared to conventional oil shale processes which may contribute to more power generation.

5) Shale oil production costs versus varied interest rate were analyzed and showed that the shale oil production cost in ZEOSP commercial operation is within the range of $19/bbl-$39/bbl for 250t/h feed rate with the varied shale cost at $5-$14/t.

6) Shale oil production cost versus varied oil shale mining cost were analyzed and showed that the shale oil production cost in ZEOSP commercial operation is within the range of $21/bbl-$41/bbl for 250t/h feed rate with the varied shale cost at $5-$14/t.

7) The ZEOSP commercial operation is quite profitable with the current crude oil price in world oil market for the current interest rate and oil shale cost even without considering the gains of higher heat efficiency and government GHG credit.

**Acknowledgement**

PROCOM Consultants P/L is a small dedicated Australian company set up to provide specialist services to a range of process industries. The directors, employees and associates of PROCOM have significant knowledge and experience in all aspects of executing an oil shale development project. www.procom-consultants.com.

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