

UTILIZATION OF SPENT OIL SHALE IN A FLUIDIZED BED PROCESS

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Abstract

The Center for Applied Energy Research (CAER) is currently developing the KENTORT II oil shale retorting process for eastern U.S. oil shales. This is a fully integrated multi-stage fluidized-bed retorting process, which is designed to maximize extraction and utilization of the organic and inorganic components of the shale. After pyrolysis, the spent shale undergoes gasification for generation of hydrogen sulfide and synthesis gas. Combustion of the previously pyrolyzed and gasified shale generates the heat necessary to drive the process.

Introduction

Testing of the KENTORT II retorting concept was initiated in 1986 in a 3.8-cm diameter fluidized bed reactor,¹ and further evaluation was performed in a fully integrated 7.6-cm diameter unit.^{2,3} The KENTORT II process is currently being scaled up to a 15.2-cm diameter 23-kg/hr process demonstration unit (PDU). Recent cold flow studies in a full scale model and information from the successful 7.2-cm diameter system provided design data for the PDU.^{4,5}

A detailed discussion of the rationale behind the KENTORT II design has been published previously.⁶ The primary motivation behind the design was the complete utilization of the spent shale from the pyrolysis step. This is currently not the case for two of the world's largest processors of oil shale, however. The Petrosix process in Brazil currently discards pyrolyzed shale, and this accounts for nearly 50% of the energy losses from the system.⁷ The Estonian oil shale industry also discards pyrolyzed shale, and because of the nature of the shale and the process, this results in environmental problems at the shale disposal site.⁸ So it is important for process efficiency and sound environmental practices that the pyrolyzed shale be sufficiently utilized within the retorting process. In addition to in-process utilization of spent shale, it may be possible for spent shale to be employed as feedstock for the production of construction materials. Raw Michigan Antrim oil shale is currently in use for the production of portland cement, but it has been suggested that spent shale would be suitable also.⁹

While fluidized bed pyrolysis of oil shale is an efficient method of quickly generating relatively large yields of crude shale oil, substantial amounts of residual carbon and sulfur remain in the spent shale. Traditionally, direct combustion of the char from pyrolysis has been reserved as the method for utilizing the residual carbon. This technique presents two problems when applied to Eastern shales. First, char from fluidized bed pyrolysis contains more carbon than required to provide heat for the retort. It would be necessary to remove substantial amounts of energy from the reactor in order to deplete all the carbon in this manner. Second, the sulfur to carbon weight ratio of pyrolyzed shale is large, which if combusted could produce prohibitive amounts of SO₂.

Steam gasification of the excess carbon from the char represents an alternative to direct combustion. Tests at the CAER have shown that fluidized bed pyrolysis char gasifies readily at 800

°C and 1 atmosphere steam partial pressure.¹ Under these conditions over 40% of the carbon in the pyrolyzed shale was gasified following 30 minutes mean char residence time. Steam fluidization enables also steam/ FeS_x reactions to go nearly to completion. Studies have shown that 90% sulfur removal can be achieved at residence times greater than 30 minutes and temperatures less than 600 °C.¹⁰ Therefore, introduction of an intermediate gasification step between pyrolysis and combustion provides means for attaining total carbon utilization as well as removing substantial amounts of sulfur prior to combustion.

Process Description

The heart of the KENTORT II process (Figure 1) consists of four fluidized bed vessels. The four zones are configured in cascade, where the shale undergoes pyrolysis, gasification/desulfurization, combustion and cooling. The pyrolysis, gasification and cooling sections are aligned vertically and share a common fluidizing gas. Combustion takes place in the fourth bed which is placed adjacent to the other three, and the fluidizing gas is supplied separately. The main body of the KENTORT II unit is constructed from 316 stainless steel. Because of the combination of extreme temperature and corrosive environment in the gasification and combustion section, these sections have been aluminized to prevent scaling and spalling of the reactor material.⁵ Aluminizing is a process where aluminum diffuses at high temperature onto the surface of a base metal for a minimum dept of 100 microns, producing an aluminum-rich alloy on the surface. The different sections of the unit are separated by gas distributors which are sandwiched between flanges. The total height of the unit is about 6 meters.

Shale Handling Systems

A screwfeeder is used to meter the shale into the pyrolysis section at a rate of 23 kg/hr. The screwfeeder is supplied by a 140-kg capacity sealed feed hopper. Additional shale can be loaded into the hopper during operation, so truly continuous operation can be achieved. Processed shale at about 400 °C leaves the unit trough an overflow port in the cooling zone. The spent shale is collected in a sealed bin, which may be emptied out during a run to permit lengthy periods of operation. Fines recovered from the pyrolysis cyclone are feed to the combustor by an air lift.

Shale Conveying System

J-valves with corresponding liftpipes provide a conveying system for shale recirculation from the gasification section to the pyrolysis and combustion sections. Solids are transported in a lean phase through the liftpipes, using nitrogen as the carrier gas in the pyrolyzer liftpipe and air as carrier gas in the combustor liftpipe. Nitrogen is used to meter the flow of solids through the J-valves and into the liftpipes. Recirculation rates of up to 90-kg/hr to the pyrolysis section and 225-kg/hr to the combustion section can be achieved simultaneously.

Start-Up System

A propane burner (Figure 2) is used to heat the fluidizing air for the combustor during start-up. By circulating solids among the zones, most of the heat required for preheating is provided by the burner. A superheater upstream of the cooling zone provides the rest of the energy needed to preheat the system. Air, rather than steam, is used during most of the preheating period so that the amount of steam condensate is kept as small as possible. Once steady state conditions are approached, the energy provided by the burner and superheater is reduced or eliminated completely.

Pyrolysis Section

Raw shale is fed over-bed to the pyrolysis section, and a mixture of steam and product gases from the gasification stage below serves as the fluidizing medium. Heat is provided to the pyrolysis section by a combination of fluidizing gas and recirculating solids from the hotter gasification section. The pyrolysis zone has a vertical baffle which splits the section into two equally sized beds. The purpose of the baffle is to narrow the particle residence time distribution by creating two beds in series. By narrowing the particle residence time distribution, greater chemical conversion can occur per unit reactor volume. The operational conditions for the pyrolyzer are: temperature, 500-550 °C; mean shale residence time, 3 minutes; bed depth, 30.5 cm.

Gasification Section

Shale from the pyrolysis section is transferred to the gasification/desulfurization zone by a gravity feed downcomer. The bed depth is designed to be adjustable between 38-76 cm so that solid residence time may be adjusted from 30-60 minutes. Like the pyrolyzer, the gasifier is baffled to narrow the particle residence time distribution. The gasification section is heated by hot solids from the combustion section entering the lower part of the bed, and the operational temperature is from 750 to 850 °C. Steam from the cooling zone below is used as the fluidizing medium.

Cooling Section

A downcomer transfers shale from the gasifier to the cooling section which also serves to preheat the steam that fluidizes the gasification bed. The cooling zone is the primary exit point for solids from the reactor. An overflow outlet in the wall of the vessel creates a 38-cm deep bed.

Combustion Section

The combustor provides the heat required for the pyrolysis and gasification sections of the KENTORT II retort. The gasification and the combustion zones are closely aligned to facilitate the transfer of solids. To minimize mixing of the gas streams, however, the pressure between the two vessels is balanced. The bed depth is 30.5 cm, although this is adjustable by regulating the height of the standpipe. Carbon-containing shale recycled from the gasification section via a pneumatic lift pipe, is the primary fuel for the combustor. Fines recovered from the pyrolysis cyclone are also fed into the combustor to provide additional fuel. Air is used for fluidization in the combustor.

Oil Collection System

Gases and vapors from the pyrolyzer enter a cyclone for fines removal. A combination convection/liquid-injection heat exchanger then cools the vapor stream to 150 °C which causes an oil aerosol to develop. This aerosol is trapped by an electrostatic precipitator (ESP) which contains approximately 10 m² of collection surface area and includes two, two-stage Penney-type collection cells in series to ensure high collection efficiency. Downstream of the ESP, a shell-and-tube condenser is then used to condense steam and light oil that remain. Light oil and water from the condenser are separated, and the water is sufficiently treated to be fed back into the steam generator. Mist collection, further cooling and more mist collection are performed before the gas stream is sampled by an on-line gas chromatograph and mass spectrometer.

Combustion Flue Gas System

Fines are removed from the combustion gas stream by a cyclone before the gas is cooled to approximately 250 °C and released to the ventilation system.

Fines and water are removed from a small portion of the gas stream for analysis by on-line combustion gas analyzers which provide a continuous measure of all major flue gas components.

Discussion

The KENTORT II process utilizes pyrolyzed shale to generate valuable by-products such as elemental sulfur and synthesis gas. The shale is also used to facilitate the operation of the retort by providing the energy to drive the process and the means to transfer this energy throughout the process by recirculating the shale itself. The pyrolysis step of the process actually represents a small fraction of the whole system. It is the additional processing of the shale to extract process heat and by-products that occupies much of the unit. Since fluidized bed pyrolysis is so efficient, the combustion and gasification zones do not make the process any larger than current commercial units which only pyrolyze the shale.^{7,8} There is, of course, a point of diminishing returns relating to the carbon utilization of the shale. An objective of the testing with the 23-kg/hr PDU is to evaluate carbon burn-off as a function of gasification and combustion conditions. Once this is complete, an economically-based determination of the optimal carbon burn-off can be made.

It is important from an environmental point of view that the pyrolyzed oil shale be sufficiently processed so that its acid leaching potential upon disposal is not high. The iron disulfide (pyrite and marcasite) content of eastern U.S. shale is high which can lead to acid drainage if these minerals are not converted to FeS (pyrrhotite).¹¹ Fluidized bed pyrolysis only results in partial conversion of the disulfide to the monosulfide so either combustion or gasification or both, as in the case of the KENTORT II process, is needed so that the conversion is enhanced by the oxidation of the iron. The advantage of using gasification rather than combustion to accomplish this is that H₂S is produced which can be readily scrubbed and converted to elemental sulfur, whereas SO₂ control technology is relatively expensive and inefficient.

The use of the processed shale to transfer heat increases process efficiency in two ways. First, the volumetric heat capacity of shale is high compared to gases which means that large volumes of gas are not needed to heat the system. Second, by using the shale, which is present in the system anyway, rather than an added heat-transfer material, the need for a step to separate the shale from the heat carrier is eliminated. The properties of the shale will dictate the extent to which pyrolyzed shale can be used as the heat carrier. The shales of the eastern U.S. are fairly refractory and can be processed at high temperatures with relatively little decrepitation. The Western shales on the other hand lose their strength when subjected to normal combustion or gasification temperatures because of their high carbonate content; therefore, processes which have been designed for Western shale that combust the spent shale utilize combustion temperatures of less than 700°C.¹²

Summary

A 23-kg/hr integrated fluidized bed Process Demonstration Unit (PDU) called the KENTORT II, has been built at the Center for Applied Energy Research. The PDU effectively utilizes the organic and inorganic components of eastern U.S. oil shales through pyrolysis, gasification/desulfurization and combustion. Autothermal operation is achieved by combustion of the residual carbon following pyrolysis and gasification. Heat is transferred among the different sections of the unit by recirculation of hot combusted solids. The main product from the KENTORT II is a high yield of liquid hydrocarbons from the pyrolyzer, and important by-products include elemental sulfur (from hydrogen sulfide gas) and synthesis gas.

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References

1. Rubel, A.M and Davis, E., "Evaluation of the Gasification Potential of Kentucky Oil Shale Char Produced Under High Yield Fluid Bed Conditions," 1987 Eastern Oil Shale Symposium Proceedings, Univ. of Kentucky, Lexington, Ky.
2. Carter, S.D., Robl, T.L., Rubel, A.M., and Taulbee, D.N., "Processing of Eastern U.S. Oil Shale in a Multistaged Fluidized Bed System," Fuel, 1990, 69, 1124.
3. Carter, S.D., Robl, T.L., Taulbee, D.N., and Rubel, A.M., "Testing of an Irati Oil Shale in a Multistaged Fluidized Bed System," Fuel, 1991, 70, 1347.
4. Vego, A., Carter, S.D., Stehn, J.L. and Neathery, J.K., "Scaleup of the KENTORT II Process, Cold Flow Modeling of the 50-lb/hr. retort", 1991 Eastern Oil Shale Symposium Proceedings, University of Kentucky, Lexington, KY.
5. Carter, S.D., Rubel, A.M., Robl, T.L., and Taulbee, D.N., "The development of the KENTORT II Process for Eastern U.S. Oil Shale", Final Report for U.S. Department of Energy, Cooperative Agreement NO: DE-FC21-86LC-11086.
6. Carter, S.D., "The KENTORT II Concept: A Process Description," 1987 Eastern Oil Shale Symposium Proceedings, Univ. of Kentucky, Lexington, Ky.
7. Lisboa, A.C., Novicki, R.E., and Piper, E., "Petrobras Boosts Oil Shale Fines Processing," 1989 Eastern Oil Shale Symposium Proceedings, University of Kentucky, Lexington, Ky.
8. Urov, K., 6th Australian Workshop on Oil Shale, 1991, Univ. of Queensland, St. Lucia, Brisbane, pp. 25-31.
9. Schultz, C.W., Lamont, W.E., and Daniel, J., "The Use of Devonian Oil Shales in the Production of Portland Cement," 1991 Eastern Oil Shale Symposium Proceedings, Univ. of Kentucky, Lexington, Ky.
10. Carter, S.D. and Taulbee, D.N., "Fluidized Bed Steam Retorting of Kentucky Oil Shale," Fuel Processing Technology, 1985, 11, 285.
11. Robl, T.L., Barron, L.S., Schram, W., and Thomas, G., 1988 Eastern Oil Shale Symposium Proceedings, IMMR88/101, University of Kentucky, Lexington, Ky.
12. Lewis, A.E., Braun, R.L., and Diaz, J.C., 17th Oil Shale Symposium Proceedings, 1984, Colorado School of Mines, pp. 1-16.

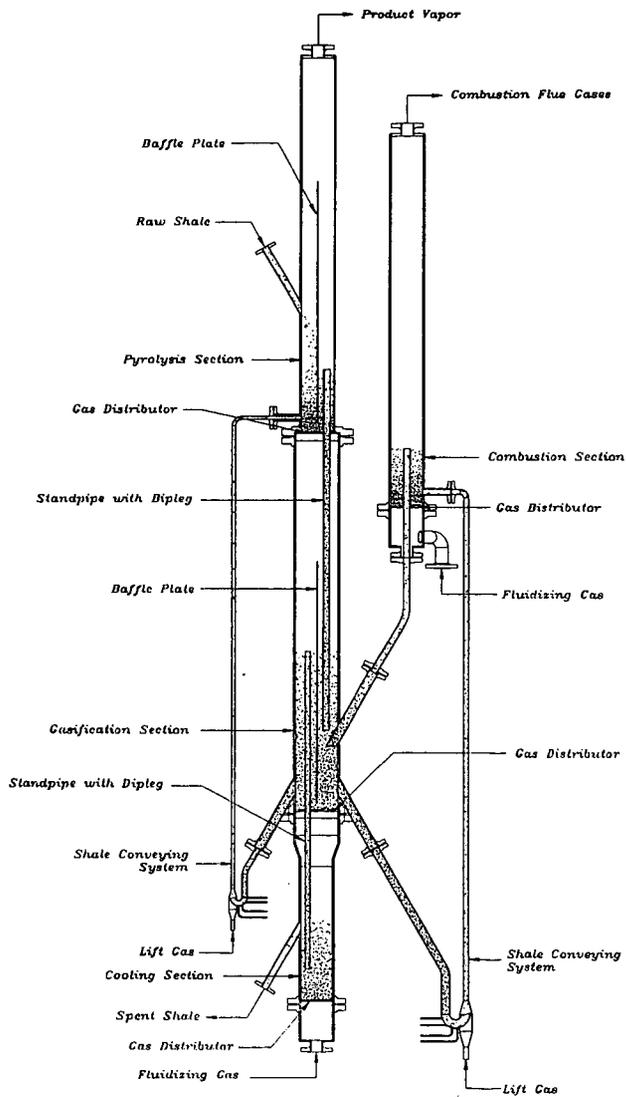


Figure 1. KENTORT II Reactor with Internals

