

Integration of Large-Scale Retorting Operations with Laboratory Testing and Analyses

Mark T. Atwood

atwoodmark@aol.com

303-460-0347

Stages of Development

- *Idea*
- *Laboratory Testing*
- *Bench Scale Testing*
- *Patent Application*
- *Semi-Works*
- *Commercial Scale*

Oil Shale Properties

Oil shales from Colorado, Utah,
and Wyoming
(Emphasis on Piceance Creek
Basin of Colorado)

- Oil shale kerogen is a 3-dimensional polymer binding a fine-grained sedimentary rock.
- Kerogen analysis (J.W. Smith, 1961)
- Elemental analysis (10 samples, Colo. & Utah)
 - Carbon 80.52 wt %
 - Hydrogen 10.30
 - Nitrogen 2.39
 - Sulphur 1.04
 - Oxygen 5.75
 - 100.00 wt %
 - Organic carbon/0.8052 = wt % of kerogen

Kerogen Structure

Kerogen is primarily aliphatic (70%) rather than aromatic in composition. Aliphatic structures pyrolyze to give volatile hydrocarbons. Aromatic structures would give large yields of coke.

Kerogen contains 25% of carboxylic acid salts.

(S.Dorrance, WRI , 1985)

RESERVE ESTIMATES

Fisher assays were done over a number of years by the U.S. Bureau of Mines at Laramie.

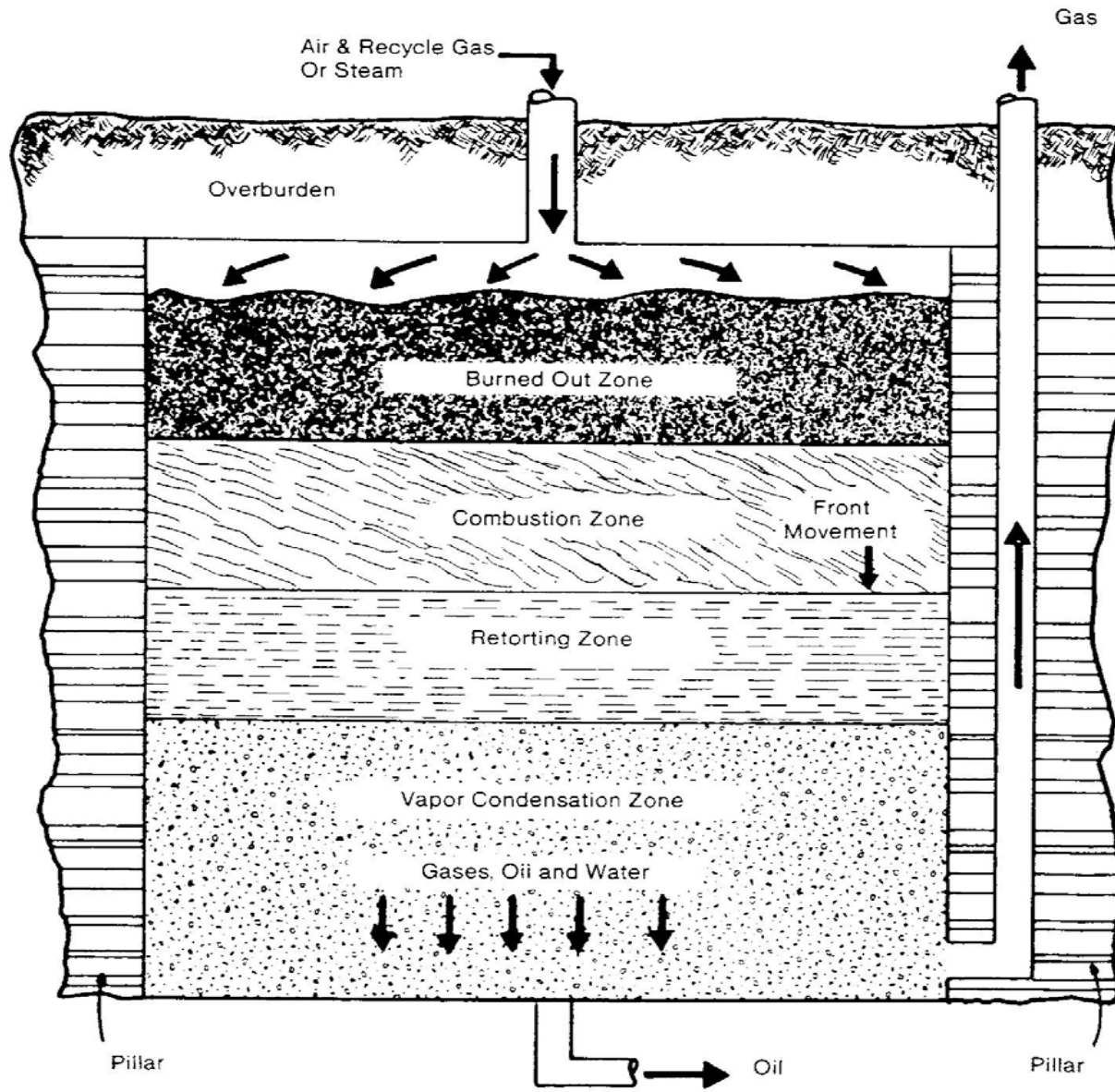
Fischer assay involves heating to 500 degrees C. in a laboratory retort with capture and measurement of oil vaporized and condensed in a cold trap. (Stanfield, 1949 and Hubbard, 1965)

ADVANCED MODES OF SURFACE RETORTING

	<u>Retorting Vessel</u>	<u>Heating Medium</u>	<u>Largest Scale</u>
a. Tosco II	Rotary kiln	Ceramic balls	1,000 tons/day
b. Union B	Vertical	Hot gas	Goal 11,000 t/d
c. Petrosix	Vertical kiln	Hot gas	Commercial
d. Lurgi	Screw mixer	Hot solids	1 ton/day
e. Paraho	Vertical kiln	Direct/indirect	1.1 tons/hr

ADVANCED IN SITU PROCESSES

NAME	FLOW	HEAT SOURCE	SCALE
Geokinetics	Horizontal	Rubblized Shale Combustion	26 Retorts
IITRI	Vertical	Radio frequency	Utah Field Tests
Shell	Horizontal	Electric ?	Long Term Field T
EGL	Vertical	Hot liquids	Colo. Field Test
VMIS	Downward Sump	Rubblized Shale Combustion	10 ton, 150 t



—VMIS oil shale retort

DIAGNOSTICS

These techniques permit rapid feedback of analytical information, obtained on site, to field operating personnel in order to control operating conditions. Since, in many cases, liquid hydrocarbons and spent shales are not readily available for sampling from operating in situ retorts diagnostic procedures are usually based on chemical properties of gas and vapor products which must issue rapidly and continuously from the retorting operation.

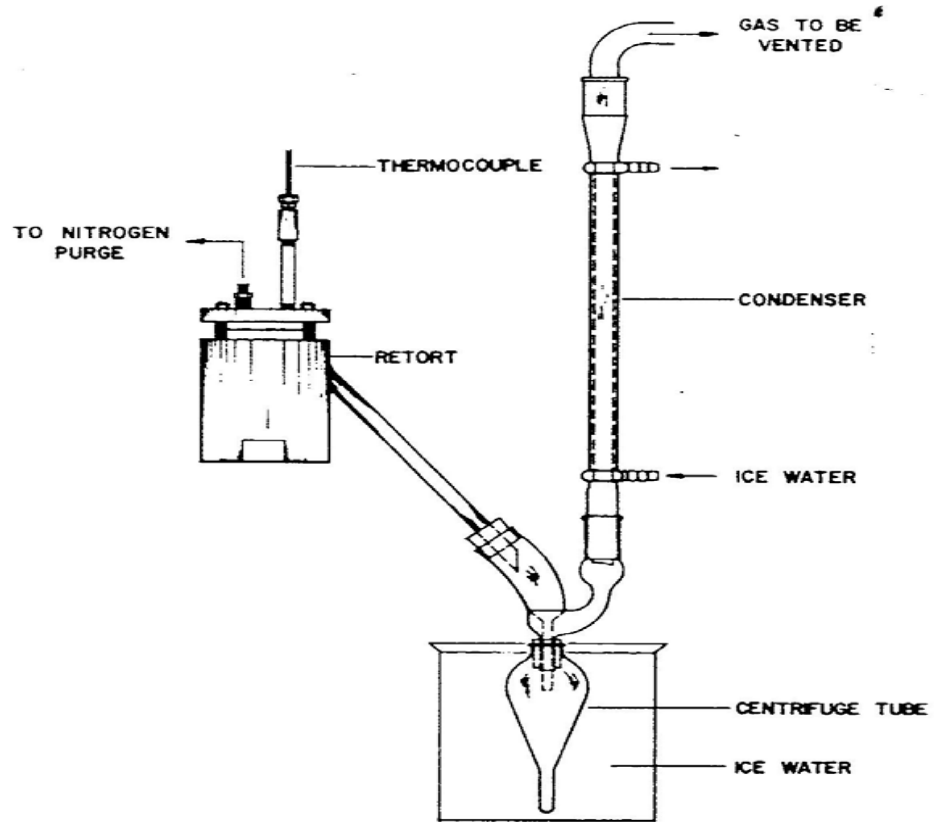
DIAGNOSTICS (CONT'D)

Factors limiting product yields and quality, including cracking, coking and burning and general interference with smooth operations will be addressed.

- A. Base sediment and water (BS@W).*
- B. Ethylene/ethane ratio (Retorting Index).*
- C. Higher molecular weight alkenes/alkanes ratios.*
- D. Naphthalene ratio to C11 and C12 hydrocarbons.*
- E. Toluene ratio to C7 and C8 paraffinic hydrocarbons.*

EXPRESSIONS OF PRODUCT YIELDS

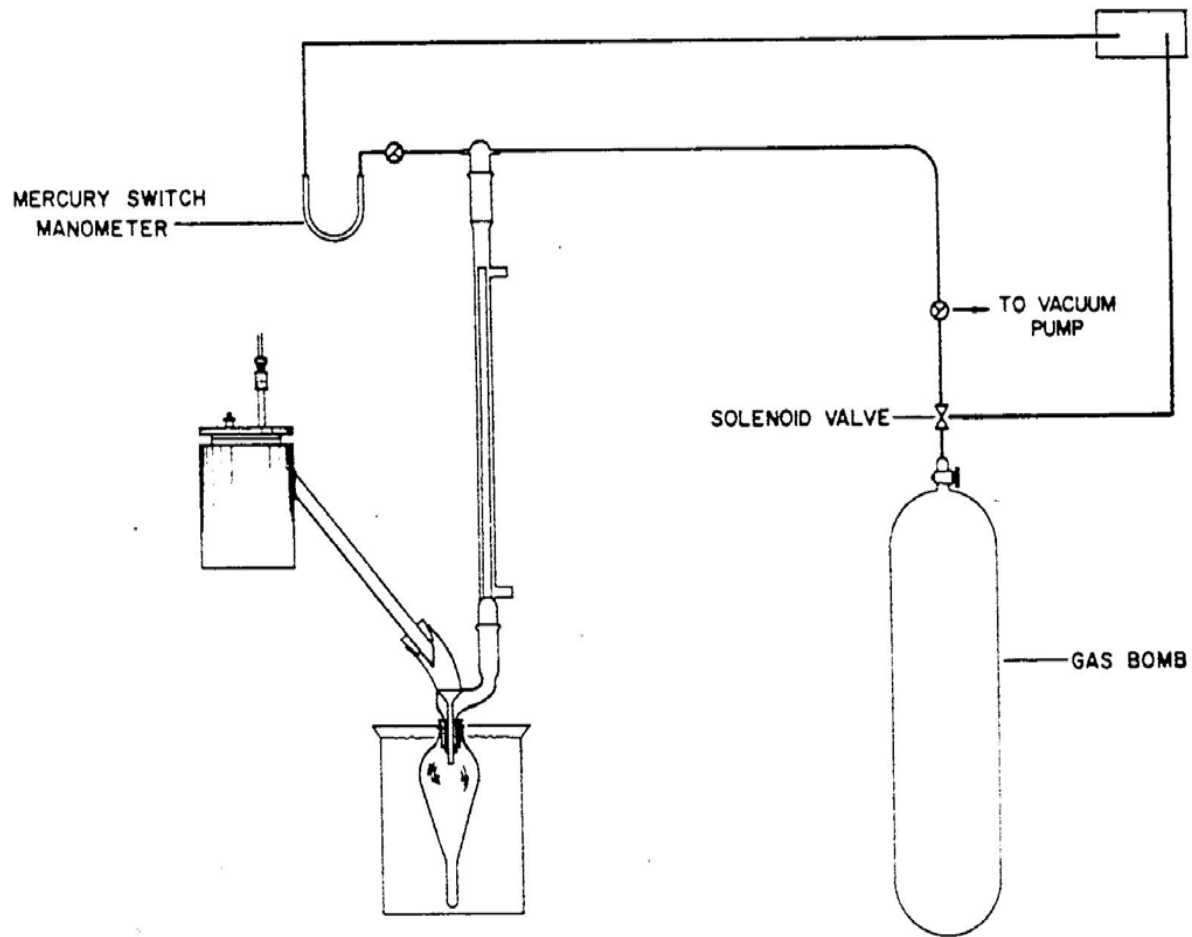
- A. Fischer assay*
- B. Tosco Material Balance Assay*
- C. Energy efficiency index*
- D. Organic carbon efficiency index*



—PRODUCT COLLECTION ASSEMBLY - BASIC

TMBA

Tosco Corporation developed and perfected a material balance assay procedure (Tosco Material Balance Assay) where Fischer assays were run and, all of the products, including gas and vapor, were collected and measured. (Goodfellow, 7th Oil Shale Symposium). This then permitted material balances and organic carbon, mineral carbon, nitrogen, sulfur and BTU balances to be done.



—PRODUCT COLLECTION ASSEMBLY—TOSCO MATERIAL BALANCE ASSAY (TMBA)

THE TOSCO II SYSTEM- 1,000 TON/DAY SEMI-WORKS

Lbs. Yield/100 Lbs FA-OIL

Semi-Works

TMBA

C3 & lighter	10.8	11.7
C4 & heavier	<u>105.8</u>	<u>104.1</u>
Subtotal	116.6	115.8
Acid Gases	<u>9.9</u>	<u>10.3</u>
Total	126.5	126.1

Also good organic carbon, sulfur and nitrogen balance comparisons.

ENERGY EFFICIENCY INDEX

EEI =

$$\frac{\text{Combustion Energy of Oil \& Gas}}{\text{Combustion Energy of Acid
Leached Raw Shale}} \times 100\%$$

FREE PROCESS

Treatment of Green River Oil Shale with Methanol/Water

(Based on Sam Dorrance, WRI , 1985)

1. Treat oil shale at 400 degrees C, 1 hour with Methanol/Water at supercritical conditions.
2. Kerogen becomes 90% liquid (130% of FA)
3. Add methylene chloride to dissolve liquids.
5. Settle or centrifuge to remove spent shale.
6. Send liquid product to coker. Refine coker liquids.
7. Send product coke to fuel.