

Chapter I

INTRODUCTION

A constant increase in the consumption of liquid fuels is evident throughout the world. In certain countries this tends to move up at a great rate and introduce the question of how to cover the ever-increasing demand for oil. Although there is no indication that the world's natural petroleum resources will be exhausted in the foreseeable future, its cost of exploring and drilling new petroleum wells, are steadily increasing. Attention is therefore directed towards raw materials which are suitable for use as base materials in the production of synthetic crude oil, of which coal, tar sand and oil shale are of primary importance. In Thailand, oil shale is the only unexploited source for synthetic crude oil. There are a number of oil shale deposits in Thailand and their properties are claimed to be the best in the world. The oil shale reserve as estimated may reach 3,000 million metric tons, with an average of 42 U.S. gal/ton, would yield about 3,000 million barrels of crude shale oil.

The only way to recover the organic matter from oil shale is by applying heat, in the absence of air to it. The organic solid or semisolid obtained is called shale oil.

niques, this oil can be converted to products similar to those from petroleum (3).

2.2 Oil Shale Retorting

The retorting of oil shale is a simple operation. The major steps involve the heating of the oil shale and the recovery of the vapour evolved. Nevertheless, for a commercially feasible process it is necessary to consider and properly choose one of the many possible methods.

Although hundreds of retorts have been designed and patented, they may be divided into four major classes based on the method by which heat is applied to produce oil (1), as follows :

| Class | Method of Heat Application | Examples |
|-------|--|---|
| I | Heat is transferred to the shale through a wall. | Pumpherson; Hayes; Berg. |
| II | Heat is transferred to the shale from the combustion occurring in the retort by burning product gases and the residual carbon in the retorted shale. | N-T-U; Union Oil Co.; Pintsch, Bureau of Mines Gas-Combustion. |
| III | Heat is transferred to the shale by passing previously heated | Swedish Industrial; Bureau |

| Class | Method of Heat Application | Examples |
|-------|--|--|
| | gases or liquids through the shale bed. | of Mines Gas-Flow; Royster. |
| IV | Heat is transferred to the shale by introduction of hot solids into the retorting bed. | Standard Oil Co. Fluid-Flow; Bureau of Mines Hot-Solids-Contact. |

2.3 Enthalpy Requirement for Oil Shale Retorting.

Retorting of oil shale involves heating to about 482°C. Heat of retorting is accounted for by , sensible heat of kerogen and inorganic components, and heat of decomposition of mineral carbonates and kerogen (4). The best experimental work on heat of oil shale retorting was reported on various oil shale grades (5) which were examined by multiple regression analysis to give the following equation :

$$\Delta H_s = -28.985 + 0.5586 T' - (2.088 \times 10^{-3} - 7.404 \times 10^{-6} G) T'^2 + 5.443 \times 10^{-6} T'^3 - 47.55 \times 10^{-10} T'^4 \dots\dots\dots (2.1)$$

Where ΔH_s = Enthalpy above 25°C. in cal/gm.

$$T' = (T^{\circ}\text{C} + 17.78).$$

$$G = \text{Modified Fischer assay, gal/ton.}$$

The enthalpy requirement for 35 gallon per ton oil shale at 477°C was of about 167 cal/gm. The components of retorting heat requirement from 25°C to 477°C were as follows: sensible heat of organic material 29% and of inorganic material 55%, and decomposition heat of organic material 7% and of inorganic material 9% (4).

2.4 Specific Heat of Oil Shale

The specific heat of oil shale can be calculated by an equation proposed by Shaw of the Bureau of Mines (6).

The equation is :

$$C_s = 0.1720 + (0.1206 + 0.0029 G) \times 10^{-3} T'' \dots\dots\dots (2.2)$$

Where C_s = Mean specific heat of raw shale above 25 °C
in cal/gm °C.

$$T'' = (273 + T^{\circ}\text{C}), \text{ absolute temperature in } ^{\circ}\text{K}$$

$$G = \text{Modified Fischer assay, gal/ton.}$$

2.5 Effect of Retorting Temperature on Oil Yield

European oil shale was retorted in a rotary kiln to test the effect of temperature on shale oil. The tests were carried out using retorting temperatures between 400° and 608°C at atmos-

spheric pressure. The dependence of oil yield on various temperatures (Fig. 2.1) is of special interest. Temperatures which are too low result in an incomplete conversion of kero- gen and an incomplete evaporation of oil. A too high tempera- ture causes partial cracking of the oil vapours. The yield drops as the temperature increases. If the process is con- trolled with a maximum yield of oil at the optimum temperature around 530°C, the yield of oil determined in individual test ranges up to 93% of that indicated by the Fischer assay, which is certainly not the maximum yield attainable (7).

2.6 Effect of Oil Shale Particle Size on Oil Yield

Sampling and sample size reduction of raw shale are very important. The Fischer assay and other tests on raw shale sam- ples are the bases of material balances for each experimental retort run.

Several steps of size reduction take place from the tons of raw shale mined to the 100.00 gm of raw shale charged to the laboratory retort for Fischer assay. However, the minus eight mesh shale fed to the laboratory retort must be representative of the sample of interest. When raw shale is crushed, the leaner, more brittle material concentrates in the finer parti- cles, while the richer, tougher material resists crushing and concentrates in the larger particles (8).

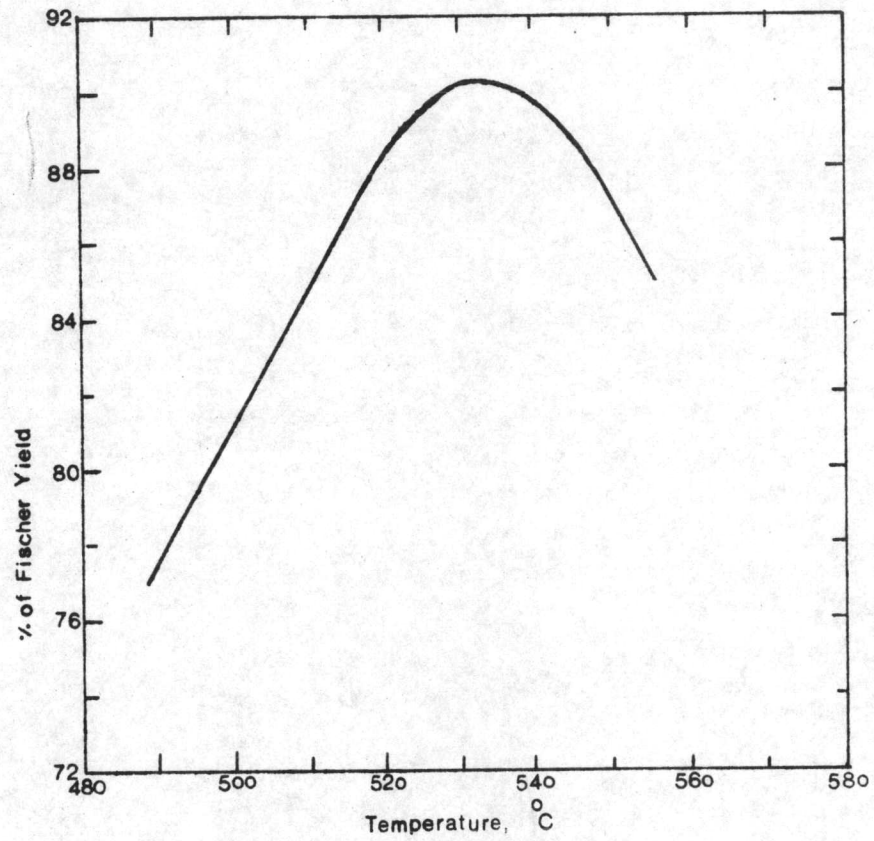


FIG. 2.1- YIELD OF OIL AT VARIOUS TEMPERATURES

Matzick (9) presented a curve showing the reaction time required at various temperatures to achieve 90 percent decomposition of kerogen in "finely-ground" oil shale at various temperatures. The result is presented in Fig. 2.2. The reaction time of large particle size retorting, presumably, must be longer than is shown on the curve (10).

2.7 Oil Shale in Thailand

The major oil shale deposit in Thailand is located in the North-Western part of the country along the border line of Burma and covers the area of West to East 15 kilometers, North to South 30 kilometers with Mae Sot town in its center. According to the geological surface exploration by the Thai Government, total amount of oil shale rock reserve is estimated to be as much as 2.5 billion metric tons. Mae Sot oil shale is tough, chocolate brown, massive and in place contains finely laminated beds with fossil fish. The high grade oil shale will yield 26.1 percent (11).

Recently oil shale has been found in close association with lignite in the minor basin of Ban Pa Kha, about 14 kilometers Southeast of Li district, Lamphun province, Northern Thailand. The Li oil shale deposit is estimated to have a total reserve of about 15 million metric tons. Li oil shale is dense and tough, with a colour varying from light gray to dark brown. It yields about 17.7 percent in average (12). Li and Mae Sot oil shale lie in the same tertiary basin of Northern

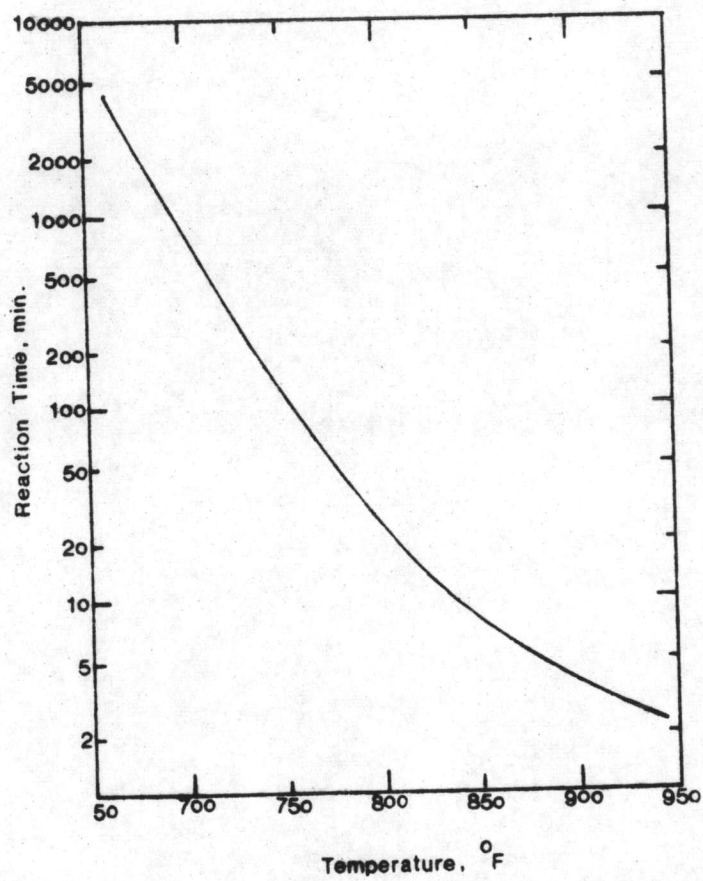


FIG. 2. 2 -REACTION TIME FOR 90 % DECOMPOSITION
OF FINELY-GROUND OIL SHALE.

Thailand.

When the Mae Sot oil shale was pyrolysed in a Gray King furnace, decomposition started at about 300°C. The evolution of shale oil was substantially complete at 500°C and there were some evidence that some of the shale oil cracked when pyrolysis was carried out at 600°C (13).

2.8 Fluidization

Fluidization is the operation by which fine solids are transformed into a fluidlike state through contaction with a gas or liquid. This method of contacting has a number of unusual characteristics, and fluidization application is concerned with efforts to take advantage of this behavior and put it in good use.

2.8.1 The phenomena of fluidization

A fluidized bed is considered a layer of solid particles, displayed in a vertical column, the bottom of which is closed by a porous plate (distributor) which supports the solids. If a rising fluid flow is established through the bed of particles, different phenomena may happen : -

1. For low fluid flows, the bed of particles remains fixed. This is a fixed bed.
2. With an increment of flow rate, particles move apart and a few are seen to vibrate and move about in restricted regions. This is the expanded bed.

3. At a still higher velocity, a point is reached when the particles are all just suspended in the upward flowing gas or liquid. At this point the frictional force between a particle and fluid counterbalances the weight of the particle, the vertical component of the compressive force between adjacent particles disappears, and the pressure drop through any section of the bed about equals the weight of fluid and particles in that section. The bed is considered to be just fluidized and is referred to as an incipiently fluidized bed or a bed at minimum fluidization.

4. For an increment of flow rate above minimum fluidization, both gas and liquid fluidized beds are considered to be dense phase fluidized beds. However, at a sufficiently high fluid flow rate the terminal velocity of the solids is reached, the upper surface of the bed disappears. It is the phenomena of pneumatic or hydraulic transport at the higher fluid flow rate.

2.8.2 Minimum fluidization

The onset of fluidization (14) occurs when

~~drag force~~ by upward moving gas = weight of particles ... (2.3)

$$\text{or } \left[\begin{array}{l} \text{Pressure drop} \\ \text{across bed} \end{array} \right] \cdot \left[\begin{array}{l} \text{Cross sectional} \\ \text{area of column} \end{array} \right] =$$

$$\left[\begin{array}{l} \text{Volume} \\ \text{of bed} \end{array} \right] \cdot \left[\begin{array}{l} \text{Fraction} \\ \text{of solids} \end{array} \right] \cdot \left[\begin{array}{l} \text{Specific weight} \\ \text{of solids} \end{array} \right] \dots\dots\dots (2.4)$$

and for the case of minimum fluidizing condition, that

$$\Delta P.S = W = (S.L_{mf}) (1-\epsilon_{mf}) (\rho_s - \rho_g) \frac{g}{g_c} \dots\dots(2.5)$$

by rearranging,

$$\frac{\Delta P}{L_{mf}} \cdot g_c = (1-\epsilon_{mf}) (\rho_s - \rho_g) g \dots\dots\dots(2.6-A)$$

Minimum fluidizing velocity of a fluidizing gas is obtained from the correlation of momentum balance concerning the gas and solid particles at minimum fluidizing condition which can be represented by a fixed bed. The correlation giving the value of $\Delta P \cdot g_c / L_{mf}$ in Eq. 2.6-A is similar in fixed bed. Geldart (15) suggested combination of Kozeny-Carman's and Burke-Plummer's correlation, as shown in Eq. 2.6-B.

$$\begin{aligned} \frac{\Delta P}{L_{mf}} \cdot g_c = & \frac{180 U_{mf} \cdot \mu}{d^2} \cdot \frac{(1-\epsilon_{mf})^2}{\epsilon_{mf}^3} \\ & + 1.75 \frac{1-\epsilon_{mf}}{\epsilon_{mf}^3} \cdot \frac{\rho_g U_{mf}^2}{d} \dots\dots\dots(2.6-B) \end{aligned}$$

In a bed at onset of fluidization the voidage is a little larger than in a packed bed, and it actually corresponds to the loosest state of a packed bed of hardly any weight. Thus ϵ_{mf} can be estimated from random packing data, by pouring a known weight of particles very gently into a measuring cylinder (15).

Then : $\epsilon_{mf} = 1 - \frac{\text{weight of particles}}{\rho_s \cdot \text{Volume occupied by solids}} \dots\dots(2.7)$

Then U_{mf} , minimum fluidizing velocity, is found by combining Eq.2.6-B with Eq. 2.6-A. Geldart (15) recommended the following equations in designing a fluidized bed : -

1. For value of $Re_{mf} > 0.2$ use :

$$1.75 \rho_g U_{mf}^2 + \frac{180(1 - \epsilon_{mf}) \cdot \mu}{d} \cdot U_{mf} - \epsilon_{mf}^3 d(\rho_s - \rho_g) \cdot g = 0 \dots\dots\dots(2.8)$$

For particles of density less than 3 gm/cm^3 and $250 < d < 500$ microns the first term can often be ignored. The full expression should be used for particles larger than 500 microns.

2. For value of $Re_{mf} < 0.2$ use :

$$U_{mf} = \frac{0.0008 (\rho_s - \rho_g) g d^2}{\mu} \dots\dots\dots(2.9)$$

Most particles are less than about 250 microns in size and having particle densities less than about 3 gm/cm^3 .

2.9 Heat Transfer in Fluidized Bed

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2.9.1 Heat transfer between fluidized bed and surface.

One of the remarkable features of the fluidized bed is its temperature uniformity, with effective thermal conductivities up to one hundred times that of silver. In practice,

this uniformity exists in both radial and axial direction, even in beds ten meters in diameter.

To maintain a given temperature level in the bed a definite amount of heat needs to be removed by contact with an appropriate heat exchange surface. Consequently, quantitative information on the heat transfer coefficient between surface and bed is needed for the rational design of fluidized bed reactors.

The bed-wall heat transfer coefficient, h_w , is defined by

$$q = A_w h_w \Delta T \dots\dots\dots (2.10)$$

Various authors have developed empirical correlations to relate heat transfer coefficients to various parameters, which can be listed as being of importance, the following factors :

1. Properties of the materials :

Fluidizing fluid : thermal conductivity, density, viscosity, specific heat.

Fluidizing particles : thermal conductivity, shape factor, size, size distribution, density, specific heat.

2. Design of fluidization chamber : location and geometry of heat transfer surface.

3. Operating conditions : flow rate of fluids, feed or

recycling rate of solids, bed height, concentration of solids in bed, etc.

In selecting the kind of correlation care should be exercised in comparing the actual operating conditions with those corresponding with the experiments which have led to the correlation. The correlation which is based upon the data with closest similarity in operating conditions and fluidizing properties should be selected. A correlation, if applicable, can be used to explore the safety factor for the design.

Wender and Cooper's (16) correlation is the best one for the wall to bed heat transfer, as follow :

$$\frac{h_w d}{k_g} \cdot \frac{1}{(1 - \epsilon_{mf})} \cdot \frac{C_g \rho_g}{C_s \rho_s} \cdot \frac{1}{1 + 7.5 \exp(-0.44 \frac{L_m C_g}{D C_s})} = \text{fn} (Re_p)$$

.....(2.11)

The correlation was shown in Fig. 2.3.

2.9.2 Heat transfer between gas and solids

The most characteristic property of a fluidized bed is the uniformity of temperature throughout the fluidized layer. The turbulent motion of solid particles gives to the bed a very important heat conductivity. In deed heat is absorbed by rapidly moving particles at some hot spots in the bed and released to cold spots. Thus the temperature everywhere is kept at a constant level.

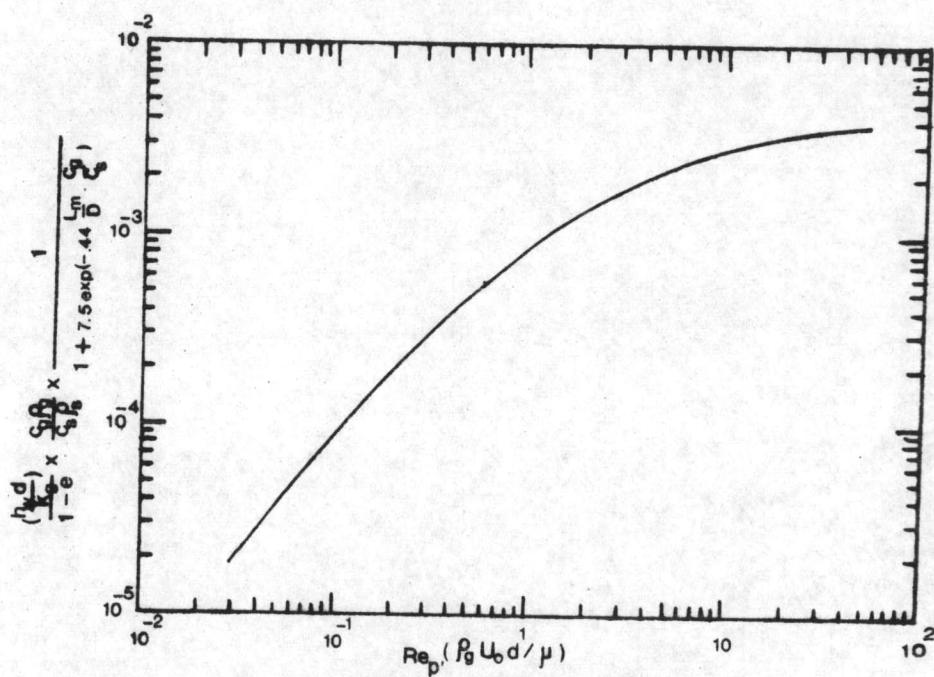


FIG. 2.3 - CORRELATION FOR WALL TO BED HEAT TRANSFER.

If a batch of solids originally at temperature T_{so} is fluidized with gas entering at temperature T_{gi} . Assuming a uniform temperature for the solid in the bed and plug flow for the gas stream, the temperature of the leaving gas T_{ge} can be determined by using Eq. 2.12 (14).

$$\frac{T_{ge} - T_s}{T_{gi} - T_s} = \exp \left\{ \frac{h_p}{\rho_g \dot{U}_o C_g} \cdot \frac{6(1-\epsilon)L_m}{\phi \bar{d}_p} \right\} \dots\dots (2.12)$$

For the bed more than 1.28 cm high the temperature of exiting gas will certainly approach within 5% of the temperature of the bed solids. This shows that for ordinary fluidizing conditions, the exiting gas can be reasonably taken to be at the temperature of the solids or

$$T_{ge} \approx T_s \dots\dots\dots (2.13)$$

Heat balance to find the change of bed temperature with time,
(heat lost by gas) = (heat gained by solids)

$$S \rho_g \dot{U}_o C_g (T_{gi} - T_s) dt = S \rho_s (1-\epsilon) L_m C_s dT_s \dots\dots (2.14)$$

Solving the heat balance with the initial conditions

$$T_s = T_{so} \quad \text{at} \quad t = 0$$

$$\text{gives, } \frac{T_{gi} - T_s}{T_{gi} - T_{so}} = \exp \left\{ - \frac{\rho_g C_g}{\rho_s C_s} \cdot \frac{\dot{U}_o}{(1-\epsilon)L_m} \cdot t \right\} \dots\dots (2.15)$$

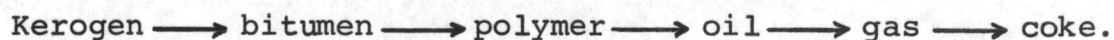
Eq. 2.15 is used to calculate the preheating time of the solids in the fluidized bed at the required temperature.

2.10 Mass Transfer in Fluidized Bed

Various kinds of mass transfer processes may occur in fluidized beds. They can be classified in three :

1. Physical transfer processes, for example dissolution. These transfers are only diffusional ones.
2. Transfers with chemical reaction, for example reaction between zinc and hydrochloric acid. These processes are more complex and can be decomposed into two steps; a diffusional step and a reaction step.
3. Transfers with catalytic chemical reactions. These processes are the most complex.

For oil shale retorting, several kinetics of kerogen decomposition were suggested. One suggestion is that at high temperatures (450° to 620°C) bitumen and oil are produced more rapidly than they can escape from the pores in which they are located (17). During the time the initial products are confined in the pores, polymerization occurs and subsequent decomposition of the polymer yields on the average higher molecular weight products than the primary oil. The following mechanism was proposed for high temperature pyrolysis :



From a gas-liquid-chromatography trace for experiment of oil shale (2), the products were swept to the flame ioniza-

tion detector while temperature was increased at the rate of 4°C per minute. In contrast with the isothermal experiments, the rate of kerogen decomposition was steadily increasing and passed through a maximum at about 440°C, after that a sharp drop in rate was observed, as shown in Fig. 2.4.

It can be concluded from the mentioned studies on the decomposition of oil shale that kerogen decomposition depends on temperature. Therefore, fluidized-bed retorting of oil shale may be carried out at various temperatures to find the change of products mass with time.

By assuming that the organic matter vapourized from oil shale pores behaves like water vapourized from solid, mass transfer in oil shale retorting process is similar to drying. Therefore, by taking heat balance in the process, as follow : heat lost by entering gas equals to heat transferred to solids to decompose the kerogen, and if ΔH_s is the heat requirement for retorting of oil shale (14), this becomes

$$S \rho_g U_o C_g (T_{gi} - T_{ge}) dt = - S \rho_s L_m (1-\epsilon) \Delta H_s dQ \dots\dots (2.16)$$

integration of Eq. 2.16, from $t = 0$ to $t = t$ and from

$$Q = Q_o \text{ to } Q = Q, \text{ gives}$$

$$Q_o - Q = \frac{\rho_g}{\rho_s} \cdot \frac{C_g (T_{gi} - T_{ge})}{\Delta H_s} \cdot \frac{t}{(1-\epsilon) L_m / U_o} \dots\dots (2.17)$$

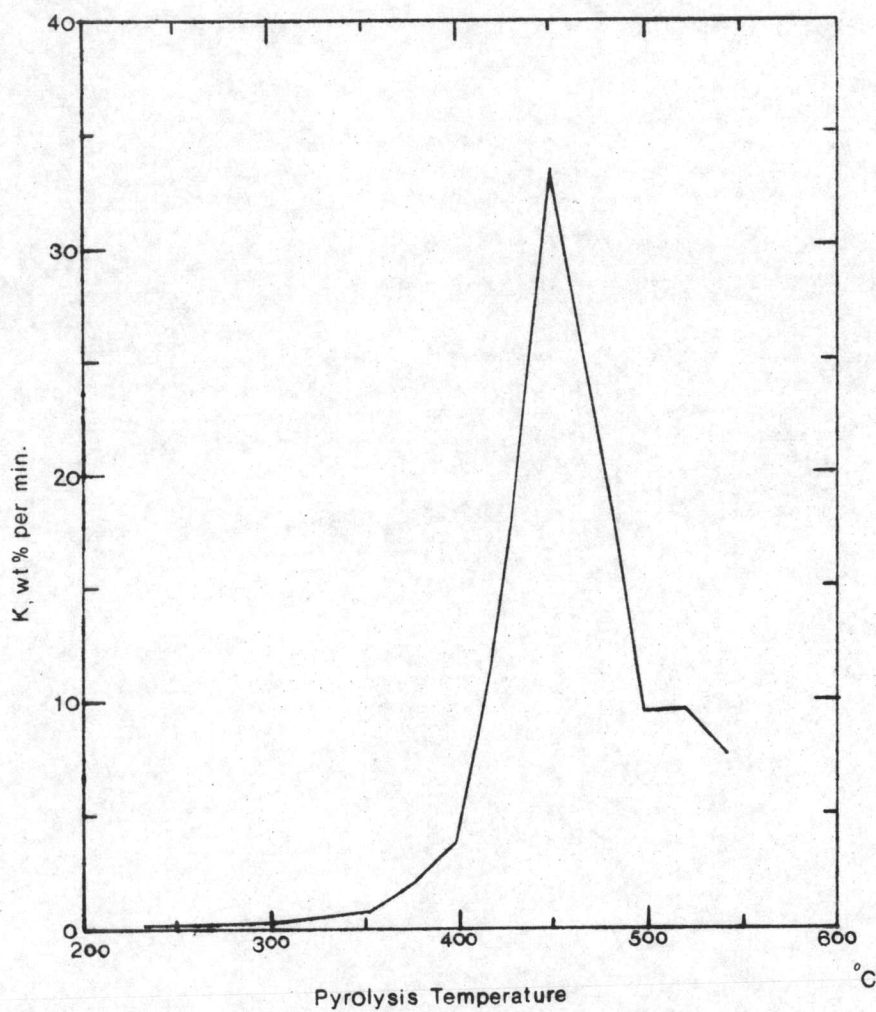


FIG. 2.4 - RATE CONSTANTS FOR KEROGEN DECOMPOSITION.

with $Q_o - Q =$ the products weight fraction
 $\Delta H_s =$ heat requirement of oil shale retorting was
obtained from Eq. 2.1, cal/gm.

2.11 Application of Fluidization to Oil Shale Retorting

Hemminger (18) reported that when oil shale was contacted with hydrogen in a fluidized system under the pressure of 300 to 800 psig. at 510°C, it would result in increment of products.

Hoffert (19) suggested that hydrocarbons were distilled from oil shale by fluidization technique. Lump shale was passed downwardly through a contacting zone concurrently with super-heated shale fines, where by the hydrocarbons were distilled from the shale. The products are removed from the upper portion of the contact zone and distilled lump shale and shale fines are removed separately from the lower portion of the contact zone.

Reyburn (20) advised that volatile material could be recovered from oil shale, by introducing the oil shale into a retorting zone and fluidizing the oil shale within the retorting zone. Volatile material was retorted and withdrawn from the retorting zone. The spent shale was withdrawn and transferred to a burnoff zone. The spent shale was fluidized in the burnoff zone and carbon residue was combusted. The burned spent shale and combustion products were withdrawn

from the burnoff zone. The experimental work was done using the fluidizing gas of 90 volume % natural gas and 10 volume % CO₂ and gave higher oil yield than when only natural gas was used.

2.12 Selection of Experimental Study

From the literature survey, the fluidization technique may be advantageously applied to oil shale retorting. A batch process of laboratory fluidized-bed retort was selected to be the experimental equipment, because it is simple to operate and there are no various variables to interfere the system such as feed rate of raw shale, spent shale outlet, and others. The nitrogen gas was selected to be the fluidizing gas to prevent combustion and reaction with products. Oil shale retorting requires a temperature of 420° to 650 °C to produce products such as shale oil and gas, therefore, electrical heating was chosen to provide heat to the retort indirectly.

For the process concerning fluidization of oil shale retorting, there are two important variables, as follows : the retorting temperature and the particle size of oil shale. Therefore, these variables were planned to be studied about their effects on oil yield. The detailed description of the experiment is described in Chapter III.