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# THE EFFECT OF ATMOSPHERE ON OIL SHALE RETORTING

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**Summary**

*An attempt was made to study the effect of atmosphere on Mae Sot oil shale retorting in a modified Fischer assay retort employing nitrogen, carbon dioxide and hydrogen gases. Mae Sot oil shale of 4-10 mesh size was retorted at 400°, 450° and 500°C, each at various flow rates of 0.010, 0.015 and 0.020 cu ft/min. It was found that the maximum oil yield was 64.0 gallons/ton under carbon dioxide atmosphere retorting at 400°C and 0.010 cu ft/min. This is 18% higher than the Fischer assay oil yield of similar oil shale. The oil quality, judging from the low pour point and the high heating value is best at 34.5°C and 10,545 cal/g obtained under hydrogen atmosphere retorting at 400°C and 0.015 cu ft/min. However, the properties of oil produced under various conditions are only slightly different.*

*The effect of carbon dioxide on higher oil yield at lower temperature can be explained as the result from carbon dioxide suppression of the decomposition of inorganic carbonates in oil shale resulting in higher heat available for kerogen decomposition at lower temperature. Continuous flow of gas during retorting also assists the diffusion of oil vapors from oil shale pores which is the rate determining step, hence increasing the oil yield.*

## Introduction

Oil shale, a promising future fuel in Thailand, is found in commercial quantity in Mae Sot, Tak Province. Oil shale contains appreciable quantities (5%–65%) of an organic polymerized material called kerogen which is insoluble in organic solvents and which, on pyrolysis, yields oil, gas and residual carbon. Robinson[1] reported that when Green River kerogen is pyrolyzed it yields approximately 66% of its weight as oil, 9% gas, 5% water and 20% carbon residue. When pyrolysis takes place in a furnace or kiln, it is called retorting. The application of heat to oil shale effects the mineral carbonates thus reducing the heat available for kerogen and lower the retort gas heatin value[2,3]. Oil yield depends on various parameters such as particle size, rate and duration of heating, and pressure and atmosphere.

Bae[4] has reported results of batch type retorting experiments at 510°C investigating the effect of pressure and atmosphere of $N_2$, $CO_2$, $H_2O$, $NH_3$ and $H_2$ on the retorting of oil shale. Test results indicated that:–

1. The higher the pressure the lower the oil yield but the larger the volume of light hydrocarbon gases.

2. The crude shale oil produced at high pressure has high aromaticity and a lower pour point than the low pressure shale oil.

3. hydrogen atmosphere favors the kerogen decomposition.

Esso Research and Engineering Company[5] claims that retorting oil shale under pressure with hydrogen and nitrogen improved the oil product quality but the type of gas had no measurable effect.

Preliminary investigation on Mae Sot oil shale reveals its high quality by having high heating value and low sulfur content[13]. Detailed studies on various effects upon retorting should give further insight into the commercial value of this oil shale.

## Materials and Methods

*Oil shale.* Mae Sot oil shale, collected from outcrops was used*.

*Gases.* Nitrogen, carbon dioxide and hydrogen (manufactured by the Army Science Division, Ministry of Defence) were used without further purifications.

*Reagents.* Laboratory grade chemicals and distilled water were used.

The apparatus employed was a modified Fischer assay retort[6,7] with slight modification to accommodate the gas inlet tube. The retort is shown in Fig. 1. Heating was done electrically and the temperature controlled by an automatic temperature controller. The retort, complete with other accessories is shown in Fig. 2.

In all runs the procedure is as follows. Exactly 100.0 grams of 4–10 mesh oil shale sample was introduced one third at a time into the retort, each portion separated by a perforated aluminum disc with two short vertical tubes placed at the centre, one for gas inlet and the other for the vapors. The setup was completed and heating was commenced with gradual temperature increase so that it reached the required temperature in 30 minutes and was kept constant for 45 minutes. The condenser was circulated with cold water at 3°C. At the end of each run the receiver was removed and the condenser was washed with n-hexane. The oil in the receiver was combined with the oil collected after n-hexane evaporation and centrifuged to separate the water.

The experiments were divided into 3 parts, each employed different gas retorting at 400, 450 and 500°C and at various flow rates of 0.010, 0.015 and 0.020 cu ft/min. Four runs were required at each condition so that sufficient amount of oil was collected. The volume of oil yield retorted repeatedly at each condition did not vary to greater than 2.50 ml, and in most cases was closer than ± 1.0 ml.

The shale oil samples were then analysed for their pour points, densities and heating values employing standard methods[8-10].

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## Results

Mae Sot oil shale, having a Fischer assay oil yield of 54.3 US gallons/ton, 4–10 mesh size, was employed throughout the experiment.

Tables I, II and III show the effects of gas flow rates on oil yields at 400, 450 and 500°C, retorting under nitrogen, carbon dioxide and hydrogen atmosphere respectively. These data are presented in graphical forms in Fig. 3-8.

The analyses of shale oil products are shown in Table IV.

## Discussion

*Retorting under nitrogen atmosphere*

From Table I and Fig. 3, the maximum retorting oil yield was 63.3 US gallon/ton at 500°C and gas flow rate 0.015 cu ft/min. Under the nitrogen atmosphere, the higher the retorting temperature, the higher the oil yield. This is in agreement with the Fischer assay retorting of Colorado oil shale (retorting at 500°C, with no gas flowing through the retort) reported earlier[11]. This confirms that nitrogen is inert to kerogen pyrolysis. On increasing the gas flow rates, the oil yield was lowered. The gas flow through the retort promotes the diffusion of the oil and vapors (products of decomposition) from the pores, which is the rate controlling step, the oil yield was then higher than that obtained with no gas flow. However, as the flow rate was further increased, the gas might carry away some of the uncondensed vapors from the condenser, causing some losses of the oil yield. As should be anticipated, the gas flow has smaller effect on oil yield than temperature, as is seen from the closeness of the flow rate curves shown in Fig. 3 compared with the temperature curves shown in Fig. 4.

**TABLE I:** EFFECT OF TEMPERATURE AND GAS FLOW RATE ON OIL YIELD UNDER NITROGEN ATMOSPHERE.

| Retorting temperature °C | Gas flow rate cu ft/min | Average volume of product ml | Oil yield U.S. gallons/ton |
|---|---|---|---|
| 400 | 0.010 | 19.1 | 45.7 |
| | 0.015 | 17.8 | 42.8 |
| | 0.020 | 16.1 | 38.6 |
| 450 | 0.010 | 24.6 | 59.3 |
| | 0.015 | 22.5 | 53.9 |
| | 0.020 | 19.7 | 47.2 |
| 500 | 0.010 | 25.8 | 61.7 |
| | 0.015 | 26.4 | 63.3 |
| | 0.020 | 21.9 | 52.4 |

*Retorting under carbon dioxide atmosphere*

From Table II and Fig. 5, the maximum yield was 64.0 US gal/ton at 401°C and 0.010 cu ft/min. This shows an enormous effect of carbon dioxide on oil shale retorting. Under this atmosphere, the oil yield was not directly related to temperature and flow rate. Fig. 6 shows that optimum flow rate at all three temperatures is 0.010 cu ft/min, which is the lowest flow rate. However, when the flow rate was increased, the oil yield obtained shows optimum dependence on temperature at 450° and 500°C but continued to decreased almost linearly at 400°C.

**TABLE II:** EFFECT OF TEMPERATURE AND GAS FLOW RATE ON OIL YEILD UNDER CARBON DIOXIDE ATMOSPHERE.

| Retorting temperature °C | Gas flow rate cu ft/min | Average volume of product ml | Oil yield U.S. gallons/ton |
|---|---|---|---|
| 400 | 0.010 | 26.7 | 64.0 |
| | 0.015 | 23.8 | 57.0 |
| | 0.020 | 20.5 | 49.1 |
| 450 | 0.010 | 25.0 | 59.9 |
| | 0.015 | 23.1 | 55.5 |
| | 0.020 | 24.3 | 58.2 |
| 500 | 0.010 | 23.6 | 61.6 |
| | 0.015 | 17.6 | 42.2 |
| | 0.020 | 23.6 | 56.6 |

Matzick[12] studied the mineral carbonate decomposition problem and reported that in Colorado oil shale the dolomite ($CaCO_3 . MgCO_3$) begins to dissociate at 566°C, and calcite ($CaCO_3$) at 621°C, yielding $CO_2$. These temperatures are somewhat lower than those observed for the corresponding pure carbonate minerals. This is an endothermic reaction, which consumes part of the heat input into the system, therefore reducing the thermal efficiency in retorting. By introducing carbon dioxide into the atmosphere, its partial pressure was increased, the equilibrium was upset, resulting in lower rate of decomposition. Higher heat is then available for kerogen pyrolysis, resulting in higher oil yield obtained at lower temperature.

Mae Sot oil shale has high carbonate content, as shown by its high yield of carbon dioxide in the retort gas[13]. The same effect described above was then observed, i.e. high oil yield at low temperature. When the temperature was increased, the available heat might become excessive, causing partial cracking of the oil vapors and bitumen into smaller hydrocarbon molecules of low boiling points which escaped from the condenser with other gas products, hence lower the oil yield.

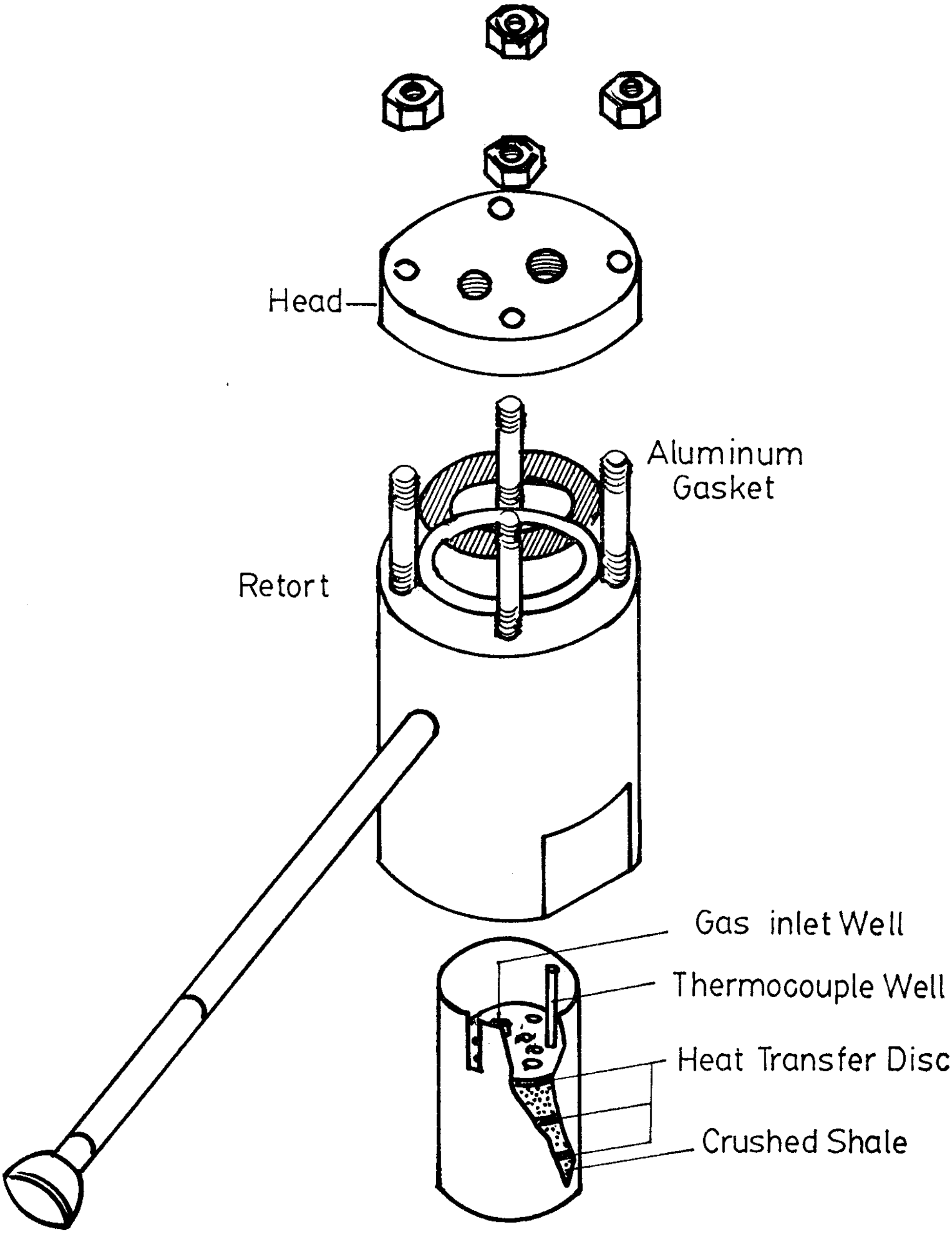


**Fig. 1.** A Fischer assay retort

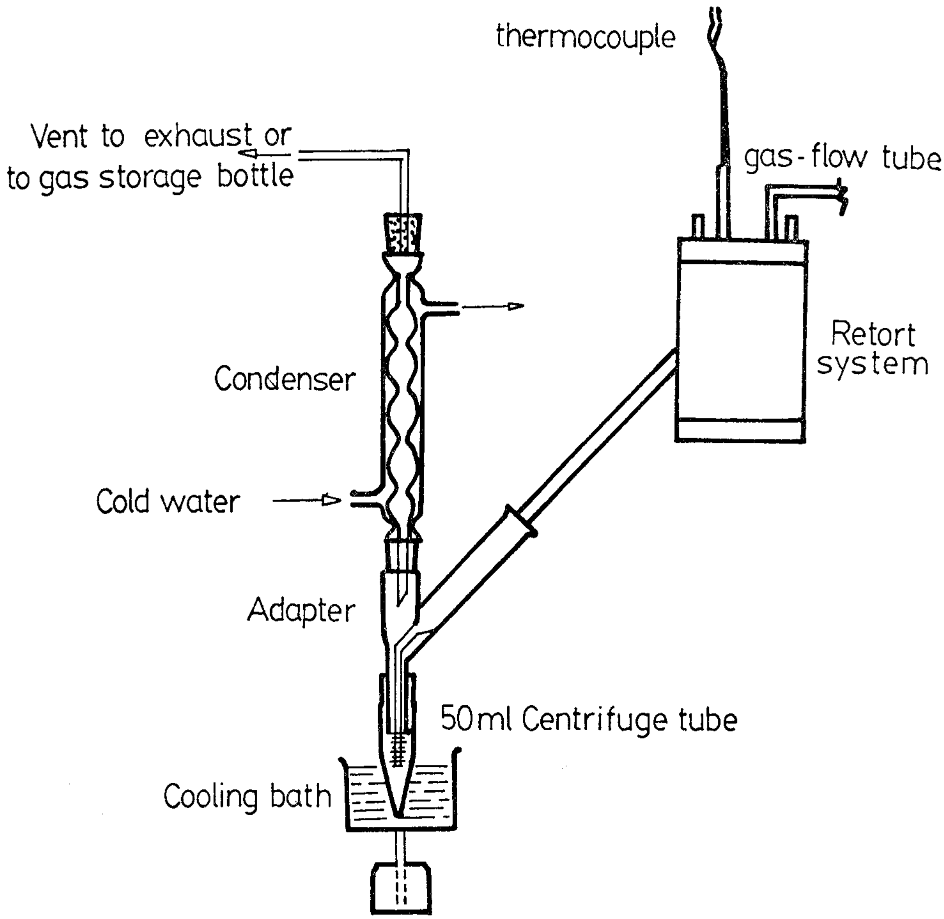


**Fig. 2.** The experimental set-up

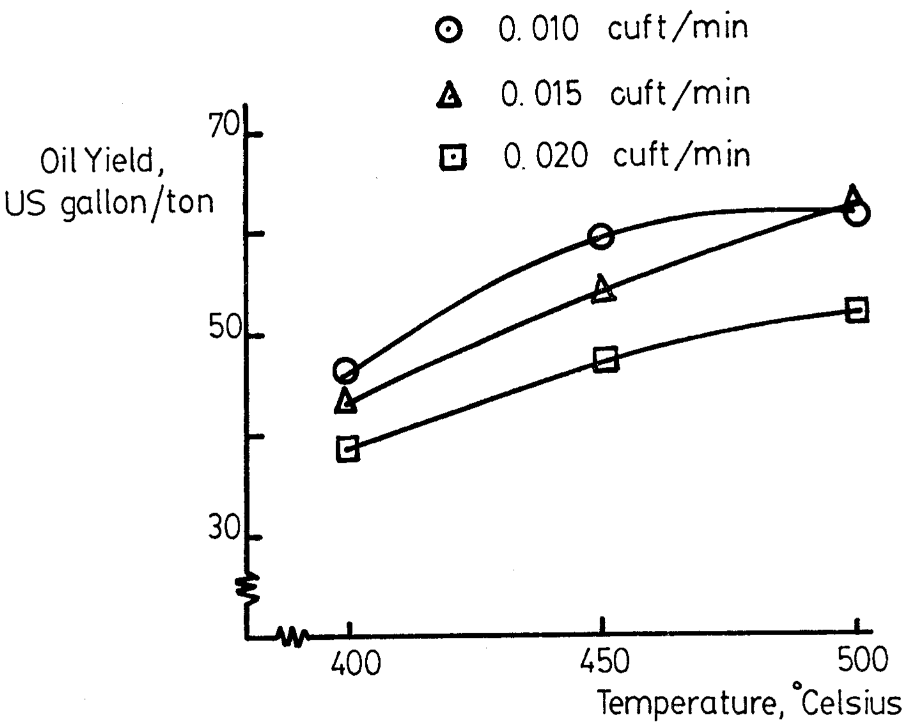


**Fig. 3.** Effect of temperature on oil yield under nitrogen atmosphere

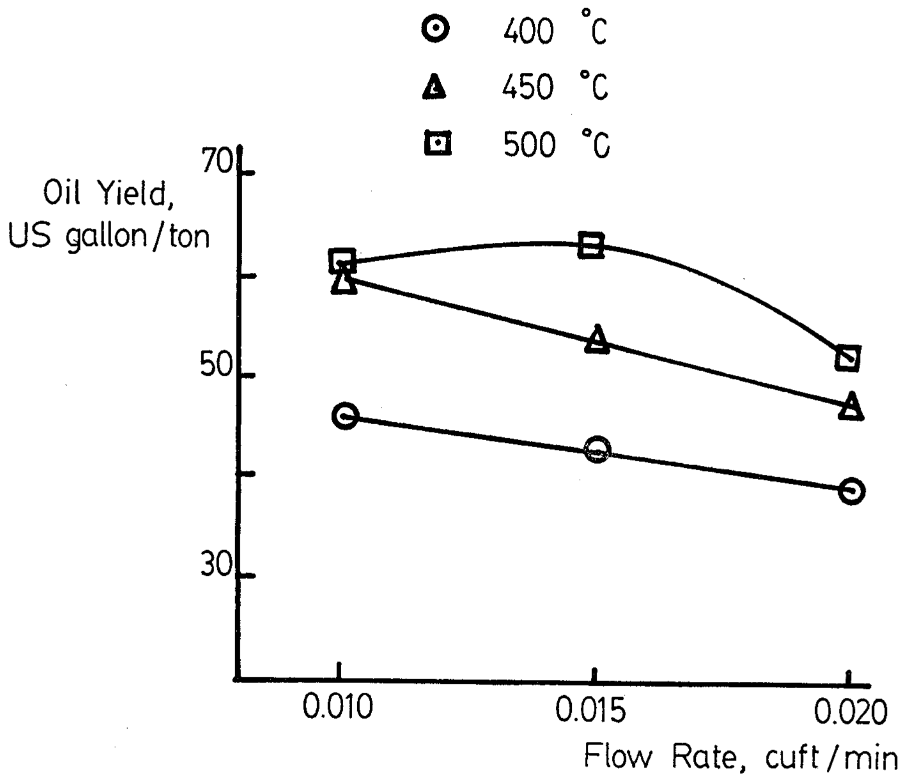


**Fig. 4.** Effect of gas flow rate on oil yield under nitrogen atmosphere

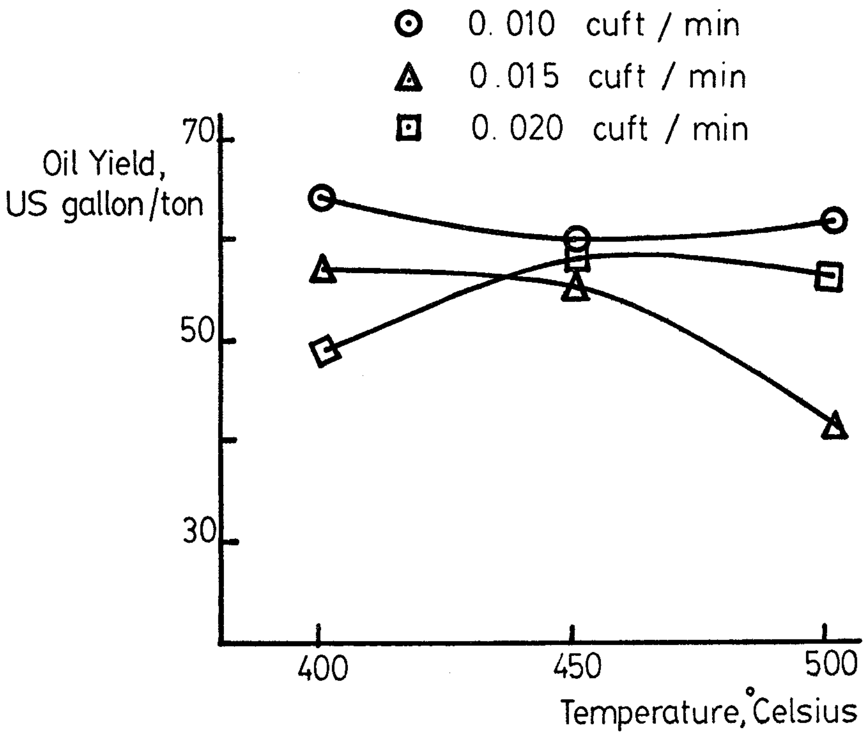


**Fig. 5.** Effect of temperature on oil yield under carbon dioxide atmosphere

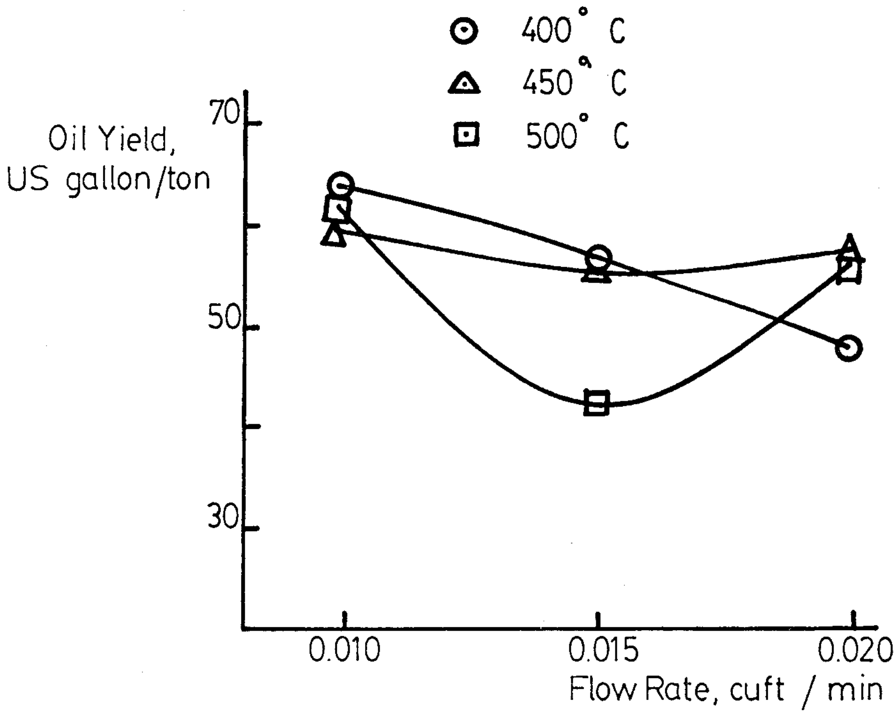


**Fig. 6.** Effect of gas flow rate on oil yield under carbon dioxide atmosphere

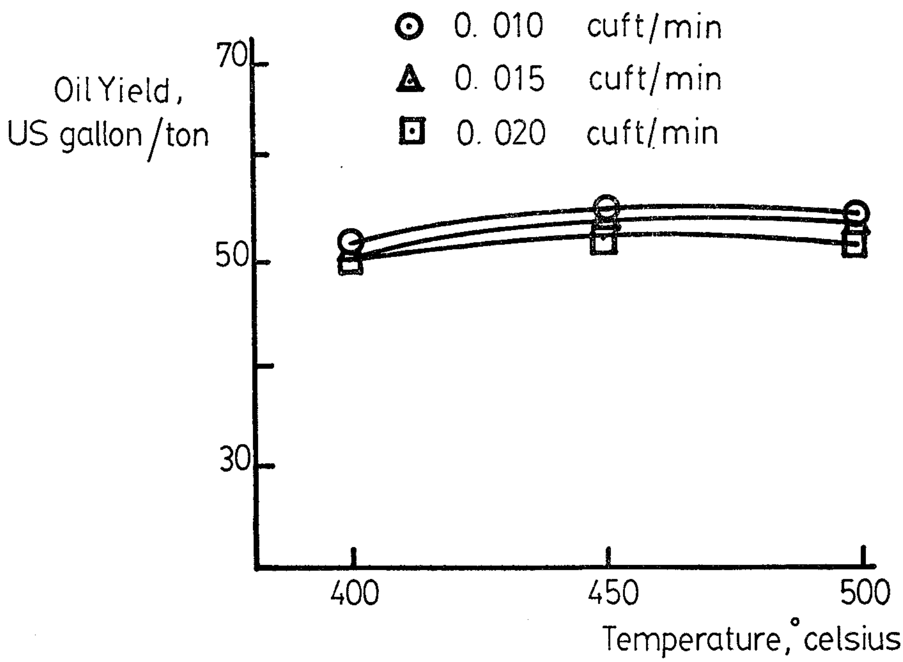


**Fig. 7.** Effect of temperature on oil yeld under hydrogen atmosphere

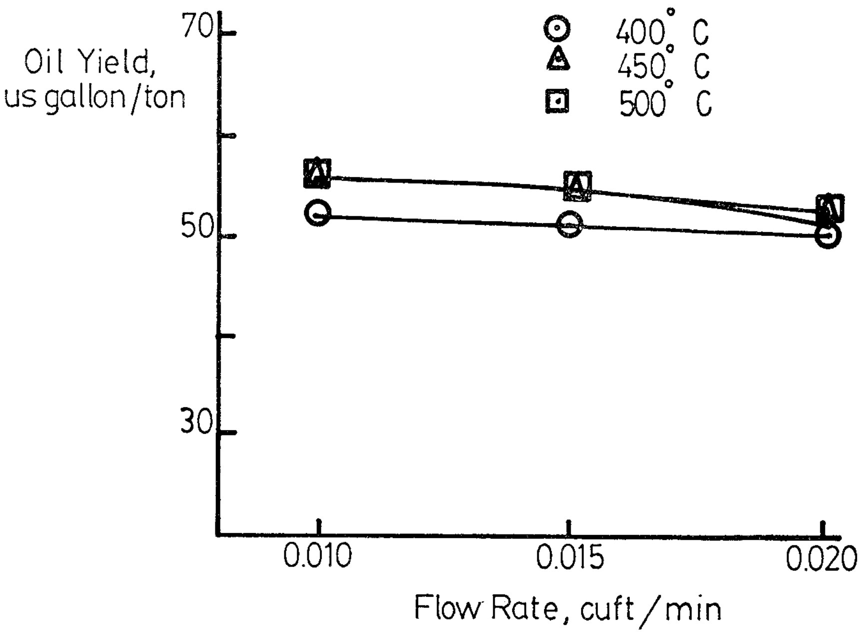


**Fig. 8.** Effect of gas flow rate on oil yield under hydrogen atmosphere

On the other hand, the peculiar increase of oil yield at 450 and 500°C and 0.020 cu ft/min might be explained as follows: at high flow rate the larger volume of carbon dioxide gas flowing through the oil shale bed became sufficient to take up the excessive heat available for kerogen in the form of sensible heat (carbon dioxide has larger heat capacity than that of nitrogen or hydrogen), the pyrolysis of kerogen was then taking place at optimum conditions, resulting in an increase in oil yield again. This, combined with the suppression of carbonates decomposition result in highest oil yield obtained at lowest temperature and flow rate under investigation.

*Retorting under hydrogen atmosphere*

Temperature and gas flow rate had small effect on oil yields. As seen from Table III and Fig. 7, the effect of temperature is similar to that under nitrogen atmosphere, i.e., the higher the temperature, the higher the oil yield. Fig. 8 also shows that the higher the gas flow rate, the lower the oil yield. The similar effect of nitrogen and hydrogen on oil yield has been reported earlier[5].

**TABLE III:** EFFECT OF TEMPERATURE AND GAS FLOW RATE ON OIL YIELD UNDER HYDROGEN ATMOSPHERE.

| Retorting temperature °C | Gas flow rate cu ft/min | Average volume of product ml | Oil yield U.S. gallons/ton |
|---|---|---|---|
| 400 | 0.010 | 21.9 | 52.5 |
| | 0.015 | 21.6 | 51.8 |
| | 0.020 | 21.3 | 51.1 |
| 450 | 0.010 | 23.4 | 56.1 |
| | 0.015 | 22.8 | 54.7 |
| | 0.020 | 21.8 | 52.3 |
| 500 | 0.010 | 23.4 | 56.1 |
| | 0.015 | 22.9 | 54.9 |
| | 0.020 | 22.2 | 53.2 |

*Effect of atmosphere and other conditions on oil quality*

Table IV reveals that the oil quality obtained under various operating conditions vary only slightly. However, it is quite apparent that the oil obtained under hydrogen atmosphere retorting is slightly better, having the lowest pour point (34.5°C) and highest heating value (10,545 cal/g) at 400°C and 0.015 cuft/min. It is probable that hydrogen, even at atmospheric pressure, does have some influence on the kerogen breakdown (cleavage of bonds), causing slight improvement in oil quality.

TABLE IV: ANALYSES OF SHALE OIL

| Temp., °C | Flow rate cu ft/min | Density, g/ml 40 °C | Density, g/ml 15.6 °C | Pour point, °C | Heat of combustion cal/g |
|---|---|---|---|---|---|
| *Nitrogen atmosphere* | | | | | |
| 400 | 0.010 | 0.8541 | 0.8631 | 41.7 | 10,340 |
| | 0.015 | 0.8626 | 0.8716 | 39.5 | 10,355 |
| | 0.020 | 0.8539 | 0.8629 | 40.0 | 10,255 |
| 450 | 0.010 | 0.8549 | 0.8639 | 37.7 | 10,475 |
| | 0.015 | 0.8574 | 0.8664 | 36.5 | 10,280 |
| | 0.020 | 0.8591 | 0.8681 | 35.0 | 10,275 |
| 500 | 0.010 | 0.8551 | 0.8641 | 36.6 | 10,595 |
| | 0.015 | 0.8519 | 0.8609 | 35.0 | 10,454 |
| | 0.020 | 0.8599 | 0.8689 | 37.0 | 10,310 |
| *Carbon dioxide atmosphere* | | | | | |
| 400 | 0.010 | 0.8585 | 0.8675 | 37.0 | 10,420 |
| | 0.015 | 0.8537 | 0.8627 | 37.0 | 10,300 |
| | 0.020 | 0.8554 | 0.8644 | 39.0 | 10,325 |
| 450 | 0.010 | 0.8563 | 0.8653 | 36.0 | 10,655 |
| | 0.015 | 0.8575 | 0.8665 | 37.0 | 10,300 |
| | 0.020 | 0.8587 | 0.8677 | 35.5 | 10,380 |
| 500 | 0.010 | 0.8628 | 0.8718 | 38.5 | 10,350 |
| | 0.015 | 0.8535 | 0.8625 | 39.0 | 10,345 |
| | 0.020 | 0.8622 | 0.8712 | 40.0 | 10,225 |
| *Hydrogen atmosphere* | | | | | |
| 400 | 0.010 | 0.8501 | 0.8591 | 35.0 | 10,570 |
| | 0.015 | 0.8546 | 0.8636 | 34.5 | 10,545 |
| | 0.020 | 0.8665 | 0.8755 | 40.0 | 10,410 |
| 450 | 0.010 | 0.8636 | 0.8726 | 37.0 | 10,165 |
| | 0.015 | 0.8657 | 0.8747 | 38.0 | 10,355 |
| | 0.020 | 0.8526 | 0.8616 | 37.0 | 10,235 |
| 500 | 0.010 | 0.8695 | 0.8785 | 35.5 | 10,523 |
| | 0.015 | 0.8641 | 0.8731 | 36.0 | 10,335 |
| | 0.020 | 0.8674 | | 38.5 | 10,280 |
| Fischer assay shale oil | | 0.8591 | 0.8681 | 36.3 | 10,450 |

The above discussion and the consideration of the accuracy of the determination, which varies to within ± 3.0 U.S. gal/ton leads to the conclusion that:

1) Oil shale retorting at 400°C, 0.010 cuft/min under carbon dioxide atmosphere gave maximum oil yield at 64.0 U.S. gal/ton, which is comparable to 63.3 U.S. gal/

ton, oil yield obtained under nitrogen atmosphere at 500°C, 0.015 cu ft/min. This is 17.9 and 16.6% higher than the Fischer assay oil yield of similar shale.

2) Hydrogen and nitrogen atmosphere retorting is effected by temperature and flow rate in the same way, i.e., the oil yield increases with increasing temperature but decreases with increasing flow rate, although their effects are smaller under hydrogen atmosphere. The quality of oil obtained under hydrogen atmosphere is slightly better.

3) Retorting under carbon dioxide atmosphere is strongly influenced by both temperature and gas flow rate. Their fluctuating effects are explained as being due to three factors, carbonates decomposition suppression, diffusion aid to oil vapors and the high heat capacity of high molecular weight carbon dioxide.

## Acknowledgements

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## บทคัดย่อ

ได้ทำการศึกษาอิทธิพลของบรรยากาศของกาซไนโตรเจน คาร์บอนไดออกไซด์และไฮโดรเจน ที่มีต่อการกลั่นสลายตัวของหินน้ำมันในรีทอร์ทแบบ Fischer โดยใช้หินน้ำมันแม่สอด ขนาด 4–10 เมช ที่

อุณหภูมิ 400, 450 และ 500 องศาเซลเซียส และอัตราเร็วของกาซต่าง ๆ กันคือ 0.010, 0.015 และ 0.020 ลูกบาศก์ฟุต/นาที พบว่าปริมาณน้ำมันหินที่ได้สูงสุด คือ 64.0 แกลลอน/ตัน จากการกลั่นภายใต้บรรยากาศของกาซคาร์บอนไดออกไซด์ที่อุณหภูมิ 400 องศาเซลเซียส และอัตราเร็วของกาซ 0.010 ลูกบาศก์ฟุต/นาที ซึ่งสูงกว่าการกลั่นมาตรฐานแบบ Fischer ถึงร้อยละ 18 สำหรับคุณภาพของน้ำมันหินพบว่าดีที่สุด เมื่อกลั่นหินน้ำมันภายใต้บรรยากาศของกาซไฮโดรเจนที่อุณหภูมิ 400 องศาเซลเซียส และอัตราเร็วของกาซ 0.015 ลูกบาศก์ฟุต/นาที โดยมีจุดเทตัวต่ำสุด 34.5 องศาเซลเซียส และค่าความร้อน 10,545 แคลอรี/กรัม อย่างไรก็ดีคุณภาพของน้ำมันหินที่ได้จากการกลั่นภายใต้สภาวะต่าง ๆ ไม่แตกต่างกันมากนัก

การที่กาซคาร์บอนไดออกไซด์สามารถเพิ่มปริมาณน้ำมันหินที่ได้ โดยทำการกลั่นที่อุณหภูมิต่ำนั้นเกิดขึ้นเนื่องจากกาซนี้ไปกดดันการสลายตัวของสารอนินทรีย์คาร์บอเนตที่มีในหินน้ำมัน ทำให้คีโรเจนได้รับปริมาณความร้อนเพิ่มขึ้น นอกจากนี้การที่มีกาซไหลภายในรีทอร์ทตลอดเวลา จะช่วยพาไอน้ำมันออกจากรูพรุนของหินน้ำมันซึ่งเป็นขั้นตอนที่ช้า ดังนั้นปริมาณน้ำมันที่ได้จึงสูงขึ้น