PYROLYSIS OF OIL SHALE IN A SPOUTED BED PYROLYSER

by

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B.A.Sc., The University of Toronto, 1978

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

THE FACULTY OF GRADUATE STUDIES

DEPARTMENT OF CHEMICAL ENGINEERING

We accept this thesis as conforming

to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

July 1987

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Date July, 1987

DE-6(3/81)

ABSTRACT

Pyrolysis of a New Brunswick oil shale has been studied in a 12.8cm diameter spouted bed reactor. The aim of the project was to study the effect of pyrolysis temperature, shale particle size , feed rate and bed material on oil yield. Gas and spent shale yields were also determined. Shale of different particle size ranging from 0.5mm to 4mm was studied using an electrically heated reactor containing sand or spent shale which was spouted with nitrogen or nitrogen/carbon dioxide mixtures.

For a given particle size and feed rate, there is a maximum in oil yield with temperature. For particles of 1-2mm at a feed rate of about 1.4kg/hr, the optimum temperature is at 475°C with an oil yield of 7.1% which represents 89.3% of the modified Fischer Assay yield. For the 2-4mm and the same feed rate, the optimum temperature is 505°C with an oil yield equal to 7.4% which is 94.3% of the modified Fischer Assay value. At a fixed temperature of about 500°C, the oil yield increases with increasing particle size. This trend is in agreement with the Fischer Assay values which showed oil yields increasing from 5.2% to about 8% as the particle size was increased. In the spouted bed, the oil yield decreases as the oil shale feed rate increases at a given temperature. The use of spent shales as the spouting solids in the bed also has a negative effect on oil yield. The gas yields which were low (less than 2.1%) and difficult to measure do not seem to be affected by

particle sizes, feed rate and bed material. Hydrogen, methane and other hydrocarbons are produced in very small amountS. CO_2 and CO are not released in measurable yield in the experiments. The trend of the spent shale yield has not been successfully understood due to the unreliability of the particle collection results. Attrition of the spent shale appears to be a serious problem.

Results of the experiments are rationalized with the aid of a kinetic model in which the kerogen in the oil shale decomposes to yield a bitumen and other by products and the bitumen undergoes further decomposition into oil. The spouted bed is treated as a backmixed reactor with respect to the solids. A heat transfer model is used to predict the temperature rise of the shale entering the pyrolyzer.

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ACKNOWLEDGEMENT

I wish to thank Dr. A.P. Watkinson and Dr. J. Lim, under whose supervision and guidance this research work was conducted, for their advice and encouragement in all stages of this work.

I am also grateful to Dr. B. Bowen for his advice on the mathematical modelling; to Dr. G.K. Khoe for his assistance in the modifications to the apparatus and the carry out of some of the experimental runs; and to Dr. K.C. Teo for his help in doing the gas samples analysis.

In addition, I wish to thank Mr. Michael Standbrook for his assistance in operating the experimental apparatus.

Finally, my appreciation to the staffs of the Chemical Engineering Department workshop and stores for their continuing assistance through this work.

1. INTRODUCTION

Oil shales are widely distributed throughout the world with known deposits in every continent. The vast majority of known oil shale resources are found in United States (75% of the estimated world recoverable oil reserves), with other major deposits in China (about 11% of the estimated world reserves) and Canada (about 7% of estimated world reserves)[1]. After the discovery of crude oil and petroleum, the oil shale industry which had previously become established could not compete. At present, oil shale is exploited in only two countries - the USSR and China.

Synthetic crude oil can be obtained from oil shale. The organic matter in oil shale is composed of about 10% bitumen, and about 90% kerogen. Both are thermally unstable, and with the application of heat (250°C or greater), thermally decompose to form gaseous and liquid products that can be refined to synthetic crude. Therefore, many studies have been made of oil shale retorting. For the Western US shales, a high level of conversion can be achieved by a simple thermal retorting procedure, whereas for the Eastern US shales, rapid retorting or the use of hydrogen as a retorting gas is employed to achieve comparable organic matter recovery.

By contrast, little attention has been paid to oil shales in Canada. Only a few research studies have been done on the shales from New Brunswick, Ontario, Quebec, Newfoundland and Nova Scotia. Since oil shale is one of the

promising alternate energy resources in parts of Canada, given the level of reserves, it is essential to investigate those parameters that will influence the overall yield of products derived from oil shale retorting, and which affect the distribution of products among gases, light oils and heavy oils. In this research, a spouted bed reactor that was constructed for coal pyrolysis[2] was used to study the pyrolysis of New Brunswick oil shale.

1.1 Objective of the Thesis

The object of the study is to investigate the effect of pyrolysis temperature, shale particle size, shale feed rate and bed composition on oil,gas and spent shale yield from Albert Formation New Brunswick oil shale in a spouted bed pyrolyser. The shale is pyrolysed in either N_2-CO_2 mixtures or N_2, and in beds of either inert silica (Ottawa sand) or spent shale. Results are compared with predictions of the Fischer Assay, which is a standardized test for potential oil yield. *

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* The Fischer Assay method is used for determining the quantity of recoverable liquid oil and other products from oil shale . A 100 gm sample of finely crushed oil shale is heated at a rate of 12°C. per min to a final temperature of 500°C and held for an additional 70 minutes at 500°C in a sealed aluminum retort under controlled conditions. As kerogen is pyrolysed, the gaseous and liquid products evolved are collected and measured using standardized equipment.

2. BACKGROUND

2.1 The Properties of Oil Shale

Oil shales are geologically classified as marlstones because of their large percentage of carbonates. Average shales are composed of about 86% mineral and 14% organic matter. Table 1 shows the inorganic minerals present in a typical medium grade oil shale and Table 2 shows the chemical composition of the inorganic portions of oil shale.

The organic matter is present in the oil shale as a resinous solid, not as an oily liquid. It is composed of about 10% bitumen and 90% kerogen. The bitumen is a heteroatomic polymer soluble in many organic solvents, whereas the kerogen is a heteroatomic polymer having a molecular weight of greater than 3000 and is insoluble in most organic solvents. To the unaided eye, kerogen appears black in colour. Under the microscope, thin sections of kerogen appear yellow in colour with a minor portion appearing brown or black. It has no well designated structure, appearing as stringers, masses and irregular granules all intermixed with the inorganic materials in the rock. The kerogen subunits are cross-linked to one another by oxygen and sulfur. Upon application of heat, both kerogen and bitumen decompose to form gaseous and liquid products. Table 3 shows a modified Fischer assay for typical oil shale samples. Table 4 shows the conversion of kerogen by Fischer assay.

TABLE 1: Inorganic Minerals Present in Typical Medium Grade Colorado Oil Shale

Mineral	Formula	Wt %
Dolomite	$(CaMg)CO_3$	33
Calcite	$CaCO_3$	20
Plagioclase	$NaAlSi_3O_8$ and $CaAl_2Si_2O_8$	12
Illite	$K_2O.3Al_2O_3.6SiO_2.2H_2O$	11
Quartz	SiO_2	10
Analcite	$NaAlSi_2O_6.H_2O$	7
Orthoclase	$KAlSi_3O_8$	4
Iron	Fe	2
Pyrite (or marcasite)	FeS_2	1
Total		100

TABLE 2: Chemical Composition of the Inorganic Portion of Colorado Oil Shale

Chemical Constituent	Very Low Grade Shale	Medium Grade Shale	High Grade Shale	Very High Grade Shale
SiO_2, percent	40.9	26.1	25.5	26.4
Fe_2O_3	4.3	2.6	2.9	3.1
Al_2O_3	9.4	6.5	6.3	7.0
CaO	11.0	17.5	14.2	8.3
MgO	5.4	5.3	5.6	4.5
SO_3	0.1	0.6	1.2	1.4
Na_2O	1.8	2.6	2.7	1.9
K_2O	3.4	1.0	1.9	1.0

TABLE 3: Modified Fischer Assay for Typical Colorado Oil Shale Samples

	For Very Low Grade Shale	For Medium Grade Shale	For High Grade Shale	For Very High Grade Shale
Oil, gal/ton	10.5	26.7	36.3	61.8
Oil, wt %	4.0	10.4	13.8	23.6
Water, wt %	0.5	1.4	1.5	1.1
Spent Shale, wt %	94.4	85.7	82.1	70.4
Gas, wt %	1.1	2.0	2.2	4.2
Loss, wt %	-	0.5	0.4	0.7

TABLE 4: Conversion of Kerogen by the Fischer Assay

Grade of Shale, gal/ton	10.5	26.7	36.3	57.1	61.8	75.0
Conversion of Kerogen by the Fischer Assay to						
Oil, wt %	51	65	69	66	69	71
Gas, wt %	14	12	11	12	12	11
Organic Residue, wt %	35	23	20	22	19	18
Water	(Excluded from calculations)					
	100	100	100	100	100	100

2.2 The Basic Principle of Oil Shale Pyrolysis

Oil shale pyrolysis involves the heating of oil shales in an inert atmosphere to cause decomposition. Over a long period of time, complete devolatilization can be achieved at temperatures of around 400-425°C. The mechanism usually given for oil shale decomposition is as follows:

$$\text{Kerogen} \longrightarrow \text{Bitumen} + \text{Gas}_1 + \text{Carbon Residue}_1$$

$$\text{Bitumen} \longrightarrow \text{Oil} + \text{Gas}_2 + \text{Carbon Residue}_2$$

Typically at temperatures below 470°C the decomposition of kerogen into soluble bitumen is a fairly rapid step compared to the decomposition of bitumen to oil. However, at temperatures above 470°C, the decomposition of bitumen appears to be rapid[4]. The kinetics of oil shale pyrolysis will be dicussed in Section 3.1.

2.3 The Oil Shale Pyrolysis Process

There are many types of retorting processes described in the literature. Only the most developed ones are discussed in the thesis.

Retorting processes can be classified into two types: the direct-heating processes and the indirect-heating processes. The direct-heating processes rely on internal combustion of fuel with air or oxygen within the bed of shale to provide all necessary process heat requirements.

The indirect-heating processes rely on the heat provided by the injection of heated solid or gaseous heat-carrier media into the retort.

Among the direct-heating processes are the Gas Combustion retorting process and the Union Oil retorting process[1][5]. The Gas Combustion retorting process features the continuous pyrolysis of coarsly crushed oil shale in a vertical kiln retort. The heat is provided by an internal combustion of the process-derived fuel with air within a downward-moving bed of shale. The kerogen in the shale is pyrolyzed or decomposed by heat in the retorting zone. The necessary heat is provided by the hot gases rising from the combustion zone. As the kerogen pyrolyzes, it yields oil (as vapour), gas, and a residual carbonaceous product which adheres to the solid retorted shale. All vapours and gases are swept upward, and the solids descend into the combustion zone where oxidation of the carbon occurs to produce the hot flue gases. The oil recovery of the Gas Combustion process is in the range of 80 to 90 percent of the Fischer Assay.

The Union Oil retorting process features a 'rock pump' shale feeding device which pushes oil shale upward into an inverted-cone-shaped vessel which is open to the atmosphere at the top. The shale solids, after having been pyrolyzed, overflow the vessel walls at the top. Air enters the bed of shale at the top and supports combustion within the bed of shale. The flow of air, combustion product gases and pyrolysis product vapors is downward, countercurrent to the

upward flow of solids.

The TOSCO II, the Petrosix, and the Lurgi-Ruhrgas processes use indirect heating[1][5]. The TOSCO II oil shale retorting process[6] features the use of a circulating load of heated ceramic balls as a heat carrying medium for transferring the necessary process heat to finely crushed oil shale for pyrolysis of the shale's kerogen in a rotating drum type of vessel. The vessel is kept under an internal pressure of about 135.8kPa to prevent admittance of air. No combustion occurs in the retort. The ceramic balls and the finely ground spent shale are first separated from each other by a trommel. Then the ceramic balls are reheated in a separate gas-fired furnace. Some of the balls break from repeated thermal shock of alternate heating and cooling. The TOSCO II retorting technology is well advanced and has been demonstrated at a semi-works scale.

The Lurgi-Ruhrgas process requires finely crushed oil shale. It features the use of heat carrier solids of small particle size such as sand grains, coke particles, or spent shale solids derived from the shale retorting process. The hot heat-carrier solids are mixed with the oil shale in a sealed screw-type conveyor and pyrolysis occurs during the mixing operation.

In the Petrosix retorting process[1][5] heated recycle gas rather than combustion air is injected into the bed of shale to provide the necessary heat for pyrolysis. The retort unit is 5.48m in diameter and is capable of

processing about 2500 tons of oil shale feed/day. This scale of operation is much greater than any other modern retorting process. This process utilises a vertical kiln retort very similar in design to the Gas Combustion retort. However, in this case, recycle gas heated in a separate furnace is used instead of combustion gas.

Most of the processes described above are slow retorting processes in which large particles are slowly heated to reaction temperature. In theory, rapid pyrolysis processes tend to produce higher liquid yields than slow retorting processes due to the minimization of secondary cracking of the liquid to solids and gases. Typically, slow retorting processes have a particle heating rate around 12°C/min whereas the rapid retorting processes have a heating rate of upto 33,000°C/min.

For liquid yield reasons, fluid bed technology has been suggested as a basis for an oil shale retort. Marshall J. Margolis[7] investigated the pyrolysis of Eastern U.S. Oil shales in a fluidized bed system. The fluid bed reactor provides a rapid heat-up of the oil shale particle because of its excellent heat transfer characteristics; and its short vapour residence time helps to mininize coking and oil decomposition. The basic unit consisted of a quartz reactor vertically mounted within an electrically heated tube furnace and was capable of operating at temperatures up to to 1200°C. The fluid bed capacity was approximately 15 grams of shale. Raw shale was fed into the fluidized bed through a

variable speed screw feeder which was mounted at the top of the reactor. Nitrogen gas was used to maintain fluidization. During operation, the spent shale was continuously displaced as raw shale was added to the reactor bed. Volatile products were swept from the reactor into a series of two cooled traps. The amount of oil produced was determined by weighing the amount of material collected in the traps and correcting for water and particulate matter content. The experimental results showed that there is an improvement over the carbon removal achieved under Fischer Assay conditions. Also, evaluation of spent shale carbon analyses and product collection data suggest that oil yield equivalent to 120-140 % of the Fischer Assay may be achieved.

Salib, Barua and Furimsky[8] have studied the retorting of New Brunswick oil shales in direct and indirect modes in a pilot scale moving bed retort. The retort had a square cross-sectional area of 0.053m^2 and a height of 2.4m. The crushed shale was fed by gravity through a rotary valve at the top of the reactor. The descending shale was heated by the ascending hot gas (air + recycle retorting gas). Oil was recovered from the off gases by hot cyclone, condenser, packed column and electrostatic precipitator. Spent shale was discharged by an extraction screw. The effect of shale grade, bed height, retort temperature profile, recycle gas and its distribution, and air feed rate on oil recovery were studied. The maximum oil recoveries are 81% and 89% of the Fischer Assay for direct and indirect mode retorting

respectively.

Levy et al[43] have investigated the vapour phase thermal behaviour of shale oil samples derived from the Condor, Nagoorin carbonaceous and Stuart deposits of Australia. The oil vapours released during retorting were passed through packed beds of sand, or the spent shale ash corresponding to the particular oil at temperatures between 500 and 600°C over a range of residence times. The results showed that there was minimal oil cracking over the sand. Oil degradation was attributed to thermal cracking. When the oil vapours were passed through the spent shale, their behaviour was quite different from that over the sand. The spent shale ash catalysed oil degradation greatly and resulted in major oil losses due to coking even at 500°C the lower range of the temperature studied.

Dung et al[44] report the pyrolysis behaviour of Condor and Stuart Shales in a 150mm diameter fluidized bed process development unit. The process used the hot shale ash as a heat carrier. The aim of the project was to determine if the recycle of the shale ash from this oil shale would adversely affect the oil yield. When the ash to shale recycle ratio was two, the results show an oil yield of loss of 28% compared to retorting in the absence of hot shale ash. The loss oils were mainly heavy fractions which adsorbed onto the shale ash. The loss seriously affect the economic feasibility of oil shale processing. Dung[45] has studied a new concept for retorting oil shales. The principle of the

proposed method was the transfer of heat through walls separating the heat source and the shales. The heat was supplied by combusting spent shale. The oil shale particles were conveyed by gas through heat exchange tubes, the heated shales then being retorted in the absence of ash. Calculations based on data and correlations in the literature demonstrated that shale particles can be heated effectively while being conveyed, in dilute phase, in heat exchanger tubes immersed in a fluidized bed of combusting spent shale. Experimental information about the performance and operation of the reactor is required to confirm the proposed advantages.

One of the main disadvantages of the fluidized bed is the difficulties in handling relatively large particle sizes (>1 mm) which may lead to unstable fluidized bed operation. The employment of a spouted bed reactor could solve this problem. Spouted bed technology was developed in the 1950's in Canada to dry wheat with air prior to storage. The properties and applications of spouted beds are described in a book by Mathur and Epstein[9] and other literature[10]-[15].

Leite et al[16] have studied oil shale pyrolysis in a 8cm diameter spouted bed reactor. The oil shale of 1.11mm particle size is pyrolyzed at 600°C at a feed rate of 2.7 to 9.0kg/hr with nitrogen, steam and air mixture as spouting gas.

Jarallah[2] has studied coal pyrolysis in a 12.8cm diameter continuous spouted bed reactor. The effects of coal feed rate, particle size, reactor temperature and bed height on yields from two British Columbia bituminous coals and one Alberta sub-bituminuous coal were investigated. The spouting gases used were either nitrogen or a nitrogen-carbon dioxide mixture. Coal sizes between 0.6 and 3.36mm were fed at atmospheric pressure to the electrically heated reactor containing sand as spouting media. The tar yield was determined by sampling the outlet gas through a series of cooled impingers. In this thesis, the spouted bed developed by Jarallah[2] was used to study the pyrolysis of New Brunswick oil shale.

2.4 Parameters Affecting Oil Shale Pyrolysis

Studies show that the oil shale pyrolysis is affected by many parameters, such as pressure, temperature & heating rate, particle size and shale feed rate.

Bae[17] has investigated the effect of pressure and surrounding atmosphere on the retorting of oil shale. He conducted batch experiments at 510°C using different retort gases such as N_2, CO_2, H_2O, NH_3, and H_2 at pressures ranging from atmospheric to 2500 psig. Test results in Figure 1 indicate that high pressure reduces the oil yield significantly, but produces a larger volume of light hydrocarbon gases. High pressure favours the secondary reaction of the primary volatiles. Oil yields were generally

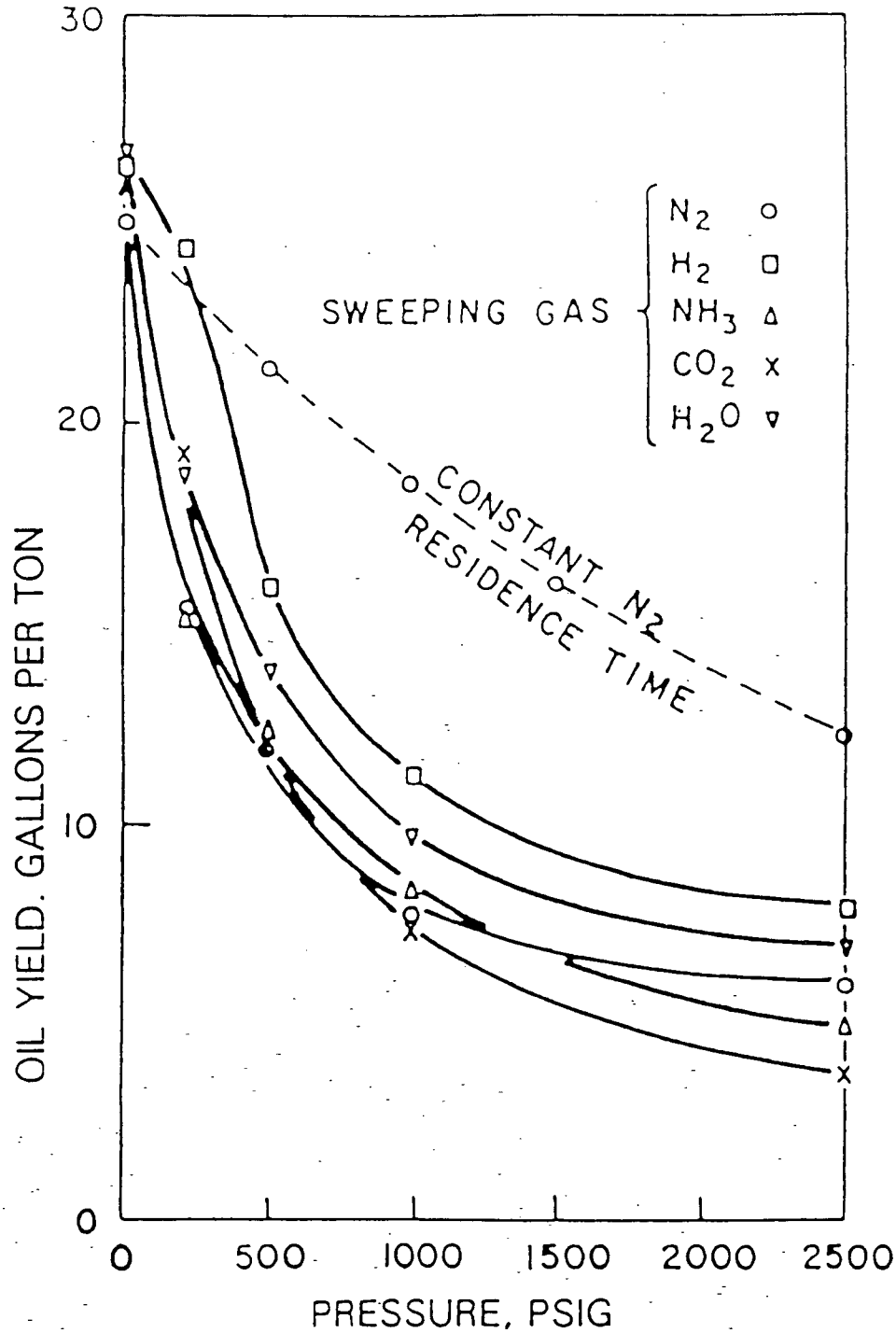


Fig 1: Effect of Pressure on Oil Yield

(Adapted from Reference No. 17)

similar in nitrogen than carbon dioxide atmospheres. As the aim of the present project is to find conditions for high oil yield, experiments have been conducted under atmospheric pressure.

Furimsky et al[18] have studied the retorting of thirty oil shales samples form Eastern Canada by Fischer assay retort and pyrochem retort. The oil yield increased significantly with hydrogen as the retorting gas. This is due to the stablization of reactive radical intermediates by hydrogen which would otherwise polymerize to higher molecular weight species.

The effect of temperature on oil shale pyrolysis, especially the oil yield, is very significant. Studies show that the kerogen in oil shale will begin to decompose at 250°C. and will even pyrolyse completely at temperatures around 400°C. Table 5 lists the results of a temperature study on Colorado oil shale by Hill[19]. It can be seen that for lower temperatures, a longer retorting period is required. From a practical standpoint, therefore a higher temperature is preferred to shorten the retorting period.

The temperature affects both the decomposition of oil shale and the secondary reactions of the primary volatiles. In the absence of secondary reactions, the oil yield will increase gradually with temperature. In the presence of substantial secondary reactions, an increase in temperature will enhance the cracking of the oil into lighter volatiles. Therefore, typically there is a maximum oil yield at an

TABLE 5: Effect of Temperature on Oil Yield

Test	Temperature (°C)	Duration (hr)	Oil Wt%	Yield %Fischer Assay
D-4	331	550	4.0	33.6
D-5	347	425	4.8	40.4
D-19	353	159	4.3	39.1
D-7	364	312	6.0	52.6
D-22	395	71	7.6	71.6
D-16	399	86.5	8.0	72.8
D-17	420	38.0	8.8	80.0
D-10	427	37.5	8.9	78.1
D-1	500	13.5	7.6	92.6

Tests were performed at the University of Utah
All experiments were carried out at atmospheric pressure

optimum temperature. This is in agreement with the findings of Liu et al[20]. They have studied the pyrolysis of 20-40 mesh Colorado oil shale in a twin fluidized bed reactor. A mixture of nitrogen and steam was used as the fluidizing gas. The feed rate of oil shale was 7.2Kg/hr. Figure 2 shows the test results. It indicates that oil yield increases from 60% Fischer Assay at 427°C to 67% Fischer Assay at 491°C. Beyond 491°C, oil yield decreases to 42% Fischer Assay at 548°C. The optimum retorting temperature for this condition is estimated to be approximately 477°C.

The study of the effect of particle size on oil yield is necessary because the operational requirements of a retorting process frequently require the shale to be of a specific particle size range. For example, the TOSCO II process requires feed shale to be smaller than 1.27cm , so that the spent shale can be separated from the 1.27cm diameter heat-carrier ceramic balls by screening. Gas combustion and Petrosix processes require discrete particle larger than 0.64cm size. A series of Fischer Assays was made on 100 gram of a Colorado oil shale crushed to various sizes range from 2 to 65 mesh and pyrolysed according to the standard retorting rate. The results are listed in Table 6 and it can be seen that the effect seems to be very small. Jarallah[2] has also studied the particle size effect on coal pyrolysis and found that there is a higher oil yield with decreasing particle size. Figure 3 shows the plot of coal particle size versus tar yield. His explanation is that

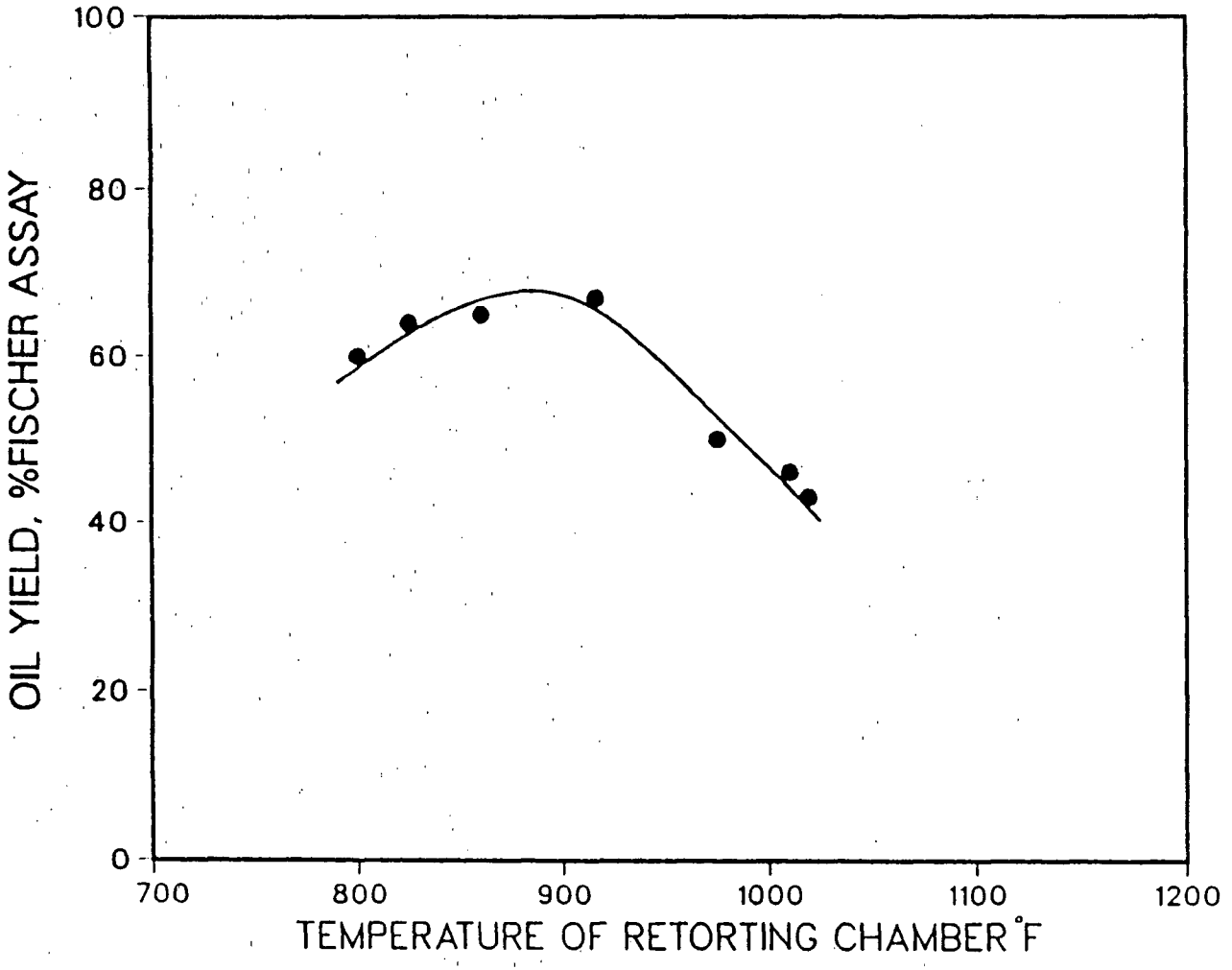


Fig 2: Effect of Retorting Temperature on **Oil Yield**

(Adapted from Reference No. 20)

TABLE 6: Effect of Particle Size On Oil Yield

Particle Size (mesh)	Number of determinations	Oil Wt%
Minus 2	2	14.22
Minus 4	2	14.78
Minus 8	5	14.37
Minus 20	2	14.45
Minus 65	2	13.47

100.0gm samples of Colorado oil shale No. 44L-69 were heated from room temperature to 500°C in 50 minutes and then maintained at 500°C for an additional 70 minutes.

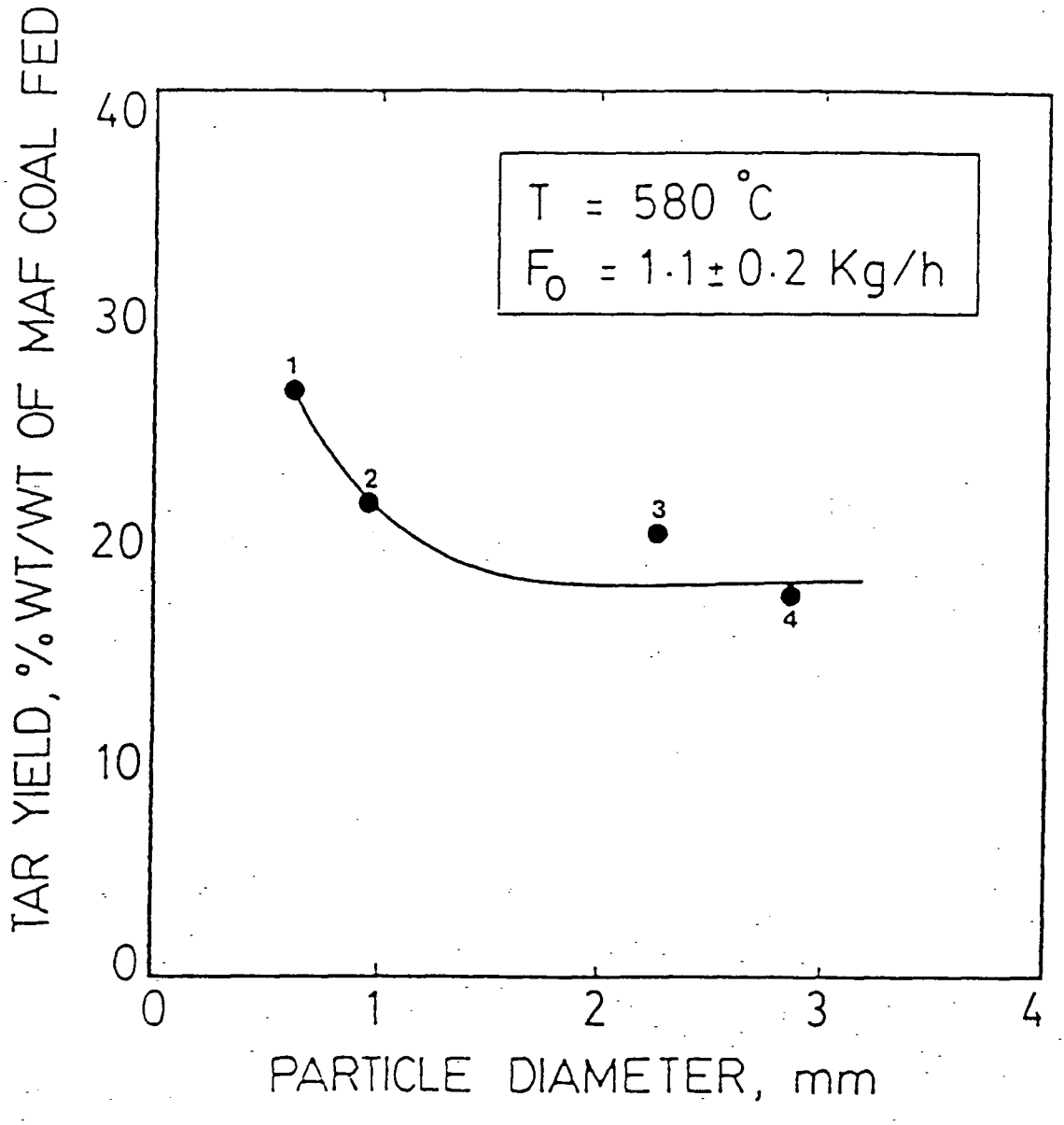


Fig 3: Effect of Particle Size on Tar Yield

(Adapted from Reference No. 2)

for smaller particles, the pyrolysis is more rapid and the opportunity for polymerization and deposition within the particle is reduced. However, the Fischer Assay values for the New Brunswick oil (Table 12) shale A indicate that the smaller oil shales particles have a smaller potential oil yield, and therefore comparisons of particle size effects should not be based on the magnitude of the oil yield alone.

The study of shale feed rate on oil yield is of special interest in this case. Jarallah[2] found that increasing coal feed rate has negative effect on oil yield. The char accumulated in the reactor apparently enchanced the secondary cracking of tar to volatiles. Therefore, it is necessary to observe if the spent shale accumulated in the reactor over the time of the experiment would have a similar effect on oil yield.

2.5 Heat Transfer in Spouted Beds

Because retorting is an endothermic process, it is very important to understand the heat transfer in a spouted bed. In our experiment, the oil shale is fed at room temperature to the apex of the spouted bed. It is necessary to find out the time required for the oil shale particle to reach the bed temperature, and whether a significant intraparticle temperature gradient exists. In other words, knowledge of the temperature history of the oil shale particle helps in understanding the pyrolysis kinetics.

Work on spouted beds to 1974 can be found in the book by Mather and Epstein[9]. The spouted bed consists of two distinct regions: the spout and the annulus. Figure 4 shows a schematic diagram of a spouted bed. In the spout, the average gas velocity is often one or two orders of magnitude higher than the annulus, whereas the volume fraction of particles, $(1-\epsilon)$, is at most one-fifth of that in the dense phase annulus. An equation[9] for estimating the heat transfer coefficient in the spout for the particle Reynolds number higher than 1000 is,

$$Nu = A + BPr^{1/3} + Re^{0.55} \qquad (2.1)$$

where $A = 2/[1-(1-\epsilon)^{1/3}]$ and $B = 2/3\epsilon$

For the annulus region, the packed bed correlation[9] for estimating the heat transfer coefficient where Re for the particle is generally smaller than 100 is,

$$Nu = 0.42 + 0.35\ Re^{0.8} \qquad (2.2)$$

It should be noted that the above correlation is based on experimental data using air near room temperature. In this research, the reactor temperature is at least 450°C, therefore equation 2.2 may only give an estimate of the heat transfer coefficient.

It can be shown that the heat transfer coefficient in the spout is much higher than in the annulus region.

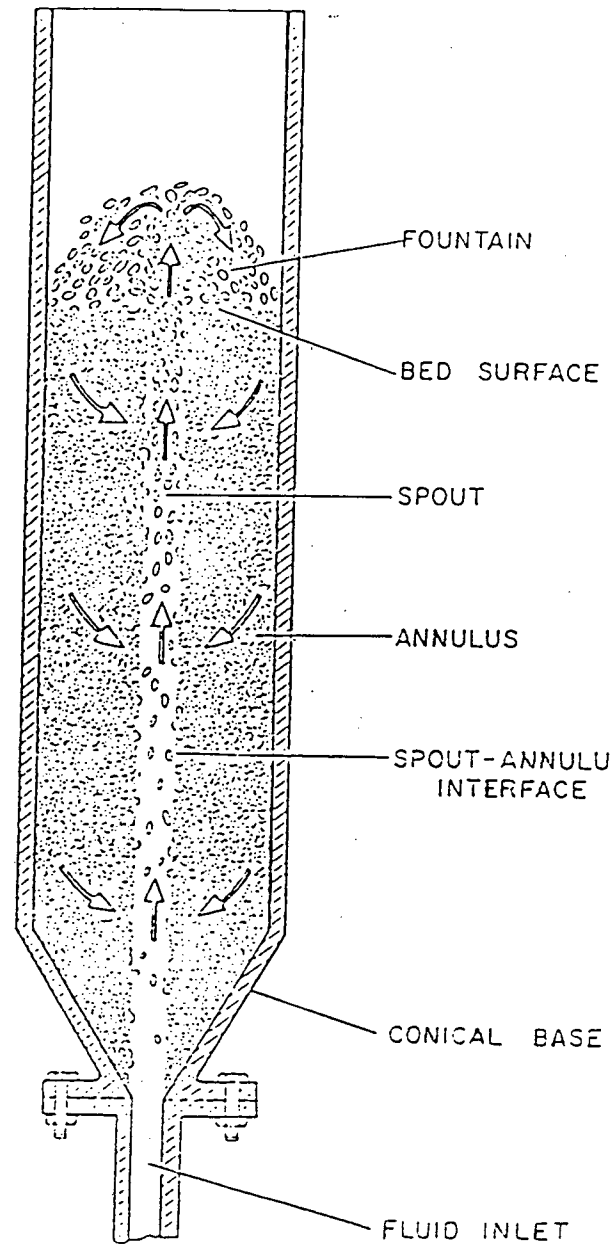


Fig 4: Schematic Diagram for Spouted Bed

However, the time which a particle spends in the spout is very small compared to that in the annulus. Therefore, the total heat transferred in the spout will be less than that in the annulus. The time required to bring a feed particle close to the bulk solids temperature is given by the following unsteady state equation,

$$\frac{T_p - T_{po}}{T_b - T_{po}} = 1 - \exp\left[\frac{h_p A_p' t}{M_p C_{pp}}\right] \qquad (2.3)$$

From this equation, the time required to heat up a typical size oil shale particle, say 2 mm diameter from room temperature to a bed temperature of 500°C was estimated to be of the order of 20 seconds. Since the practical mean residence time in the annulus is at least several minutes, the steady state concentration of bed particles reaching the bed temperature is high. Therefore, the overall heat transfer rate would not normally be limited by the external heat transfer. For equation 2.3, the temperature within the particle is assumed uniform. However, in the case of the spouted bed where large sized particles may be used, the intraparticle temperature gradient could not be ignored. The magnitude of the intraparticle temperature difference relative to the temperature difference between the particle surface and fluid is determined by Biot number, $Bi_H = h_p r_p / k_p$, provided that the Fourier number $Fo_H = \alpha t / r_p^2$, which is a dimensionless time variable, exceeds a minimum value of 0.2. The relative magnitude of intraparticle temperature

difference decreases with decreasing Bi_H, the maximum value becoming less than 5% of the temperature difference between the fluid and particle surface at Bi_H=0.1.

For the oil shale particles used in our experiment, assuming that an intraparticle temperature gradient exists, the particle temperature profile can be predicted by the unsteady state conduction equation,

$$\frac{\partial T}{\partial t} = \frac{a}{r^2} \frac{\partial (r^2 \partial T/\partial r)}{\partial r} \qquad (2.4)$$

and can be calculated as a function of time for the variable conditions along the 4 different regions of the spouted bed: spout, fountain (upward), fountain (downward) and annulus region, by a numerical solution of this equation as the longitudinal profiles of gas and particle velocities, gas temperature and spout voidage are known. The boundary condition in this case is,

$$K_p(\partial T/\partial r)_{r=rp} = h_p(T_b - T_{r=rp}) \qquad (2.5)$$

The details of the computer program are given in Appendix A. Table 7 and 8 list the particle temperature history for oil shale of 3mm, 1.5mm and 0.75mm diameter after one and two passes in the reactor respectively. The temperature history is estimated at a function of time along the spout, fountain (upward), fountain (downward) and annulus regions. The reactor temperatures chosen are 723,

773 and 823K. The velocity of the oil shale particle at the apex of the spout is assumed to be zero.

From the typical results shown in Table 7, it can be seen that for the 3mm particle size oil shale, there is a considerable temperature gradient in the spout, fountain (upward) and fountain (downward) regions. But during the slow travel down in the annulus section, the temperature gradient is effectively relaxed. It should be noted that after the first pass through the four regions, the particle has not yet reached the reactor temperature. In fact, the temperature of the particle is only at 568.0 - 606.2K which is not even high enough for pyrolysis to start. The particle has to travel the cycle the second time in order to effectively reach the reactor temperature, and pyrolysis is expected to take place in the annulus.

For the 1.5mm diameter size oil shale, a temperature gradient still exists in the particle but is less significant than for the 3mm particle size. For reactor temperature 773 and 823K, the particle reaches to 732.1 and 767.6K respectively in the annulus region, which is high enough for pyrolysis to begin. Again, pyrolysis is expected to take place in the annulus.

For the 0.75mm particle size oil shale, intraparticle temperature gradient greater than 10K hardly exist. At the top of the spout, the particle has not reached the reactor temperature but the temperature is sufficient for pyrolysis to take place. As the 0.75mm oil shale is smaller than the

Table 7: Particle Temperature History for 3.0, 1.5 and 0.75mm Oil Shale (After One Pass)

Reactor Temperature (K)	Particle Size (mm)	Particle	Spout (K)	Fountain (Upward) (K)	Fountain (downward) (K)	Annulus (K)
723.0	3.0	centre	361.8	367.4	372.9	567.1
		surface	431.4	422.3	418.1	568.0
	1.5	centre	533.8	543.6	550.0	690.0
		surface	566.2	559.3	557.9	690.1
	0.75	centre	693.2	696.1	696.8	722.2
		surface	697.8	696.8	697.1	722.2
773.0	3.0	centre	359.8	366.7	373.5	591.1
		surface	439.1	428.1	423.4	592.2
	1.5	centre	545.0	557.8	565.6	731.9
		surface	584.3	575.6	574.2	732.1
	0.75	centre	732.3	736.4	737.3	771.9
		surface	738.7	737.3	737.7	771.9
823.0	3.0	centre	347.2	356.4	365.6	604.9
		surface	438.1	423.9	419.0	606.2
	1.5	centre	533.4	552.8	562.7	767.3
		surface	584.4	572.8	572.2	767.6
	0.75	centre	757.5	764.5	766.0	821.0
		surface	767.9	765.8	766.9	821.0

* Inlet temperature of the particle is assummed to be at 298K
* The temperatures are calculated as particle leaving different regions of the spouted bed reactor

Table 8: Particle Temperature History for 3.0, 1.5 and 0.75mm Oil Shale (After Two Passes)

Reactor Temperature (K)	Particle Size (mm)	Particle	Entrance (K)	Spout (K)	Fountain (Upward) (K)	Fountain (downward) (K)	Annulus (K)
723.0	3.0	centre	567.1	590.9	593.0	595.0	666.3
		surface	568.0	616.4	613.1	611.5	666.3
	1.5	centre	690.0	708.3	709.1	709.6	720.4
		surface	690.1	710.9	710.3	710.2	720.5
	0.75	centre	722.2	722.9	722.9	723.0	723.0
		surface	722.2	723.0	723.0	723.0	723.0
773.0	3.0	centre	591.1	615.3	617.9	620.5	703.6
		surface	592.2	645.6	641.4	639.6	704.0
	1.5	centre	731.9	753.3	754.4	755.1	769.5
		surface	732.1	756.7	756.0	755.9	769.5
	0.75	centre	771.9	772.9	772.9	772.9	773.0
		surface	771.9	772.9	772.9	772.9	773.0
823.0	3.0	centre	604.9	625.9	629.8	633.6	732.7
		surface	606.2	663.7	657.8	655.8	733.2
	1.5	centre	767.3	792.4	794.4	795.5	817.1
		surface	767.6	797.8	796.5	796.5	817.1
	0.75	centre	821.0	822.8	822.8	822.8	823.0
		surface	821.0	822.8	822.8	822.8	823.0

* The temperatures are calculated as particle leaving different regions of the spouted bed reactor

spouting sand, 1.11mm , it is expected that some of the oil shale will actually escape from the fountain (upward) region and be entrained to the cyclone. Even in this case, these particles will still undergo pyrolysis.

In the actual experimental case, there is a 17.8cm long section between the feed point and the apex of the spouted bed. A supplementary program (in Appendix A) was written to calculate the particle temperature profile for this section. It was found that the oil shale particles are still essentially at room temperature as they leave this section. This indicated that the above assumption that the particle at the apex of the spouted bed is at room temperature is correct.

3. KINETICS

3.1 Literature Review of the Kinetics of Oil Shale Pyrolysis

Several investigations[22]-[34][39]-[41] have been carried out on the kinetics of the decomposition of kerogen in oil shale. The first comprehensive experimental study of the process was reported by Hubbard and Robinson[22]. They studied the decomposition of kerogen in Colorado oil shale at temperatures from 400 to 525°C by heating the shale sample in the absence of oxygen at atmospheric pressure and measuring the decomposition products. The first decomposition products to form were gas and bitumen. On further heating, the bitumen decomposed to form the final products: gas (the non-condensable vapors), oil (the condensable vapors) and carbonaceous residue. Hubbard and Robinson interpreted their data by assuming that the total amount of kerogen that decomposed was equal to the total amount of gas, oil and bitumen.

Braun and Rothman[24] studied the Hubbard and Robinson data and proposed to include a thermal induction period in the data analysis, and represented the kinetics of oil production by a simple mechanism involving two consecutive first order reactions. The thermal induction period was required to account for the non-isothermal heating effects in the Hubbard and Robinson experiments.

The pyrolysis of kerogen can be expressed as:

$$K \xrightarrow{k_1} B + G_1 + C_1 \qquad (3.1)$$

and

$$B \xrightarrow{k_2} A + G_2 + C_2 \qquad (3.2)$$

The rate of kerogen decomposition is given by,

$$\frac{\partial K}{\partial t} = -k_1 K \qquad (3.3)$$

The net rate of bitumen formation and decomposition is,

$$\frac{\partial B}{\partial t} = k_1 f_1 K - k_2 B \qquad (3.4)$$

The rate of oil production is given by,

$$\frac{\partial A}{\partial t} = k_2 f_2 B \qquad (3.5)$$

The rate of gas production is

$$\frac{\partial G}{\partial t} = k_1 f_3 K + k_2 f_4 B \qquad (3.6)$$

Integrating equation (3.3) for $K=K_o$ at $t=t_o$ gives:

$$K = K_o e^{-k_1 (t-t_o)} \qquad (3.7)$$

By combining (3.4) and (3.7), and integrating for B=0 at

$t=t_o$, then the amount of B, bitumen at any time is:

$$B = \frac{k_1 f_1 K_o}{(k_2-k_1)}[\, e^{-k_1(t-t_o)} - e^{-k_2(t-t_o)}\,] \qquad (3.8)$$

Combining equations (3.5) and (3.8), and integrating for A=0 at $t=t_o$, then the fraction of initial kerogen A/K_o that is converted to oil at any time t is:

$$\frac{A}{K_o} = \frac{f_A}{(k_2-k_1)}\{k_2[1- e^{-k_1(t-t_o)}] - k_1[1- e^{-k_2(t-t_o)}]\} \qquad (3.9)$$

Combining equations (3.6) and (3.8), and integrating for G=0 at $t=t_o$, the fraction of initial kerogen G/K_o that is converted to gas at any time t is:

$$\frac{G}{K_o} = f_3[1-e^{-k_1(t-t_o)}] + \frac{f_1 f_a}{(k_1-k_2)}\{k_2[1-e^{-k_1(t-t_o)}] - k_1[1-e^{-k_2(t-t_o)}]\} \qquad (3.10)$$

Braun et al[24] used equation (3.9) to analyse the data of Hubbard and Robinson[22] for production of oil from a Colorado oil shale having a Fischer Assay of 26.7 gal/ton. The measured and calculated values of A/K_o are found to be in agreement with each other.

Johnson et al[25] used thermogravimetric analysis (TGA) to study the pyrolysis of oil shale spheres. The sample weight was measured while the temperature was increased with heating time. They developed a complex kinetic model which incorporated both heat transfer and chemical kinetics, but the kinetic scheme required a series of ten coupled chemical reaction steps.

Campbell et al[27] obtained kinetic data on Colorado oil shale pyrolysis by both the isothermal and the non-isothermal technique. The non-isothermal results show that the oil evolution process can be quite accurately represented as a first order reaction.

Granoff and Nuttal[28] investigated the pyrolysis kinetics for large single particle (12.7mm diameter cylinder and sphere). The experiment was carried out at 384 to 520°C with nitrogen as pyrolyzing gas. The weight loss of the oil shale particle was continuously measured with a Cahn recording thermobalance. They also obtained the centreline temperature histories for the oil shale with a microthermocouple. The non-isothermal shrinking-core model and non-isothermal homogeneous model were developed in order to describe the pyrolysis process.

For the non-isothermal shrinking-core model, it is assumed that the reaction always occurs at the interface between the unreacted core and the surrounding spent shale layer. The model consists of the dynamic distributed energy balance, convective and radiant surface boundary condition,

and a first order kinetic controlled shrinking core material balance. The resulting equations must be solved simultaneously, since the rate of core shrinkage is strongly temperature dependent as indicated by the Arrhenius expression.

The partial differential equation describing the dynamic temperature profile within a sphere is,

$$\rho_s C_{ps} \frac{\partial T_s}{\partial t} = k_s\left[\frac{1}{r^2}\frac{\partial}{\partial r} r^2\left(\frac{\partial T_s}{\partial r}\right)\right] + C\left(\frac{\partial a}{\partial t}\right) \Delta H_{rxn} \qquad (3.11)$$

$$a = \frac{(w_o - w_t)}{(w_o - w_\infty)}$$

where the initial condition is,

$T_s = T_{initial}$ at t=0

T_g = constant steady-state value at t=0

and the boundary condition is,

$$Q_{rp} = hA_p(T_{rp} - T_g) + \delta \epsilon A_p(T_{rp}^4 - T_w^4) \qquad (3.12)$$

The shrinking-core material balance equations are,

$$\frac{\partial r_c}{\partial t} = -k_i \exp\left(-\frac{\Delta E}{RT_c}\right) \qquad (3.13)$$

$$\frac{\partial a}{\partial t} = \frac{4\pi r_c^2 k_i \exp[(-\Delta E/RT_c)/C]}{0.75\pi r_p^3 C} \qquad (3.14)$$

therefore the appearance rate of individual species is given as:

$$\frac{\partial a}{\partial t} = \frac{4\pi r_c^2 k_i \exp[(-\Delta E/RT_c)/C_i]}{0.75\pi r_p^3 C_i} \qquad (3.15)$$

The model fits very well at high temperature (520°C), but is not so good at the lowest temperature.

The second model developed was the non-isothermal homogeneous model in which it is assumed that there are no temperature gradients within the particle. The particle temperature is given by:

$$\rho_s V_p C_{ps} \frac{\partial T_s}{\partial t} = hA_p (T_g - T_s) + \delta \epsilon_p A_p (T_w^4 - T_s^4) + k(1-a)V_p \qquad (3.16)$$

The model was able to match both the high and low temperature conversion for small and moderate oil-sized spherical particles where the particle temperature is assumed to be uniform.

Wang and Noble[31] carried out oil shale pyrolysis under non-isothermal conditions between 350 and 500°C. and at different pressures (78 and 765 kPa). They used a comprehensive analytical procedure to separate the oil shale into five individual components: polar, weak polar,

saturates, aromatics and olefins. They proposed a simplified kinetic scheme that include the distribution of products as follows:

$$\frac{\partial C_i}{\partial t} = \frac{k_i}{C} \exp\left[\frac{-E_i}{RT} - \left(\frac{fK_o}{C}\right)\left(\frac{RT^2}{E_o}\right) \exp\left(\frac{-E_o}{RT}\right)\right] \quad (3.17)$$

Yang and Sohn[33] studied a Chinese oil shale, and found that the mechanism of kerogen decomposition can be represented by an overall first-order kinetics.

In view of the above survey, it appears that from an engineering standpoint, the rate of oil generation can be adequately described by an overall first order kinetics.

3.2 Development of the Kinetic Model

A model was derived to predict the change of kerogen, bitumen and oil content of the oil shale with time. The basic idea is that upon the application of heat, kerogen in the shale particles is first decomposed to bitumen and gas. The bitumen is defined as the benzene-soluble organic material that does not vaporize but remains in the shale sample. Then the bitumen is heated to decompose to form oil and gas, and carbonaceous product adheaved to the shale mineral matrix. Oil is defined as the condensable hydrocarbons and other compounds escaping from the shale sample, whereas gas is defined as the non-condensable vapours escaping from the shale sample. The carbonaceous residue is the benzene-insoluble portion of the kerogen

remaining in the spent shale. On further heating, oil is decomposed to gas and carbonaceous products.

The pyrolysis of kerogen is expressed as

Kerogen ——————→ Bitumen + Gas + Carbonaceous residue

Bitumen ——————→ Oil + Gas + Carbonaceous residue

Oil ——————→ Gas

The first two reactions take place in the solid phase and the time of reaction can be taken as the residence time of the solids. Whereas the oil decomposition occurs in the gas phase, and the time for reaction is very short i.e. the mean residence time of the gas (Vol of the gas phase/Flow rate of gas).

The kinetic equations used to describe the reactions are taken from Braun and Rothman[13] and were presented in the beginning of Section 3.1. In the present research, the amount of oil produced is measured by sampling of the off-gas. Neither kerogen nor bitumen were measured.

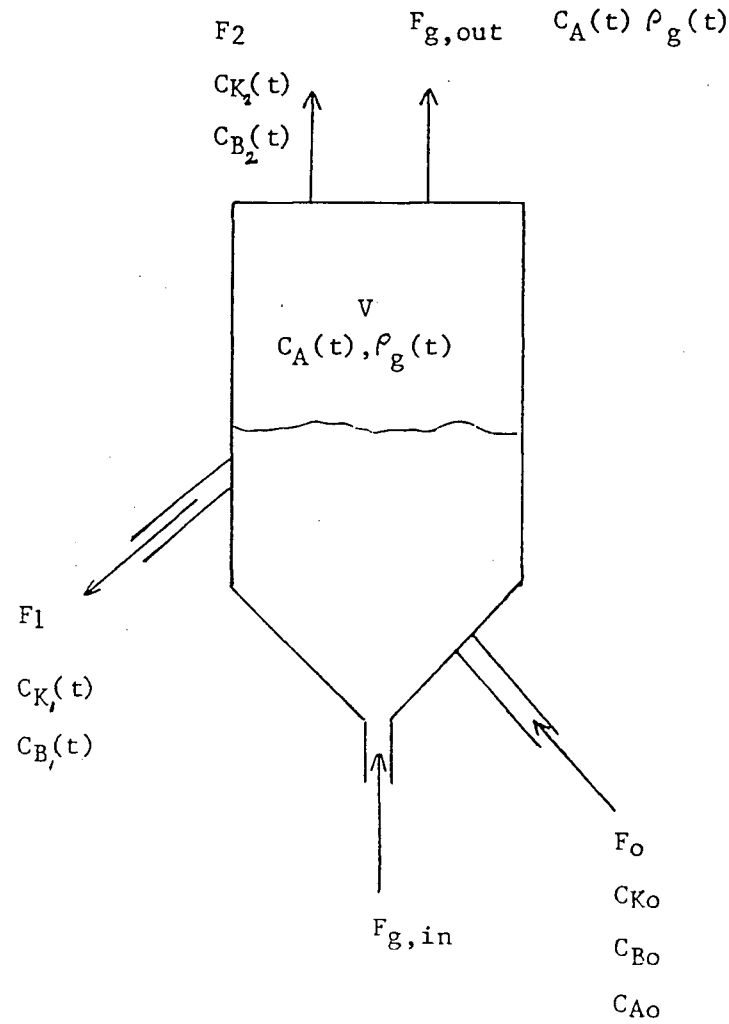
The structure of the spouted bed is not taken into account. However, a few assumptions are made based on the charactistics of the spouted bed.

1) F_o, C_{k0}, $F_{g,in}$, F_1, F_2, V are all constant.

2) Bed solids and gases within the reactor are well mixed.

3) The intraparticle temperature gradient of the oil shale is ignored because the time required to heat up the particles (in the range of 20 seconds, Section 2.6) is insignificant compared to the average holding time of the particle in the reactor (in the range of 30 minutes).

The configuration of the model is shown as below:



Unsteady State Material Balance

weight of solid fed in	+	weight of gas inflow	-	weight of solid withdrawn & entrained	-	weight of gas outflow	=	weight Accumulated

$$F_o + F_{(g,in)}\rho_{(g,in)} - (F_1 + F_2) - F_{(g,out)}\rho_{(g,out)} = \frac{dW}{dt} \qquad (3.19)$$

Assuming $F_{g,in}\rho_{g,in} = F_{g,out}\rho_{g,out}$ (as spouting gas accounts for 97% of the total gas outflow), then (3.19) becomes,

$$F_o - F_1 - F_2 = \frac{dW}{dt} \qquad (3.20)$$

Kerogen Balance

Kerogen entering with shale	-	Kerogen withdrawn & entrained	-	Kerogen decomposed	=	Kerogen Accumulated

$$F_oC_{Ko} - F_2C_{K2} - F_1C_{K1} - r_K = \frac{dC_KW}{dt} \qquad (3.21)$$

Bitumen Balance

Bitumen produced by kerogen	-	Bitumen decomposed	-	Bitumen withdrawn & entrained	=	Bitumen Accumulated

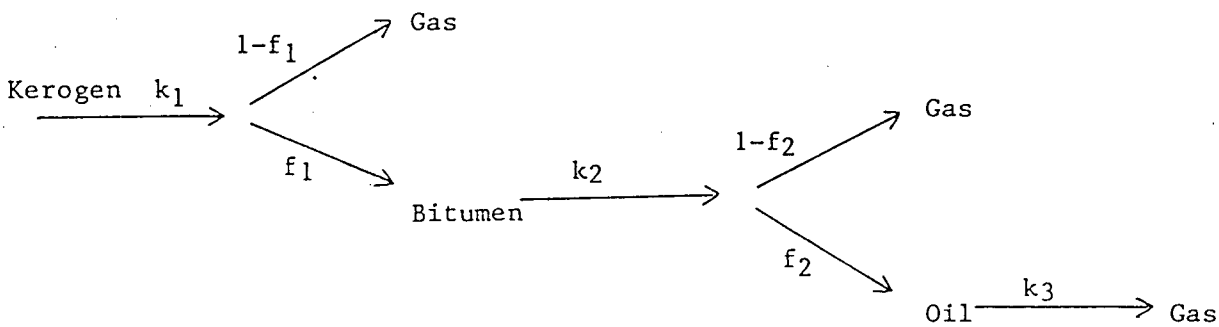
$$r_B - F_2C_{B2} - F_1C_{B1} = \frac{dC_BW}{dt} \qquad (3.22)$$

Oil Balance

Oil produced by bitumen	-	Oil decomposed	-	Oil entrained	=	Oil Accumulated

$$r_A - F_gC_A = \frac{dC_AV}{dt} \qquad (3.23)$$

Reaction Kinetics



$$r_K = -k_1C_KW \qquad (3.24)$$

$$r_B = f_1k_1C_KW - k_2C_BW \qquad (3.25)$$

$$r_A = f_2k_2C_BW - k_3C_AV \qquad (3.26)$$

From the experiment, F_0, F_1, F_2, V, C_{K0} are known, and from the literature, k_1°, k_2°, E_1, E_2 f_1, f_2 are known, then W(t), $C_K(t)$,$C_B(t)$, $C_A(t)$ can be solved from equations (3.20), (3.21), (3.22) and (3.23).

A simplified model with one less equation to solve was based on further assumption that W was constant at the average of the initial weight and final weight of the bed. This model can be used to work out k_3°, E_3 and then solve for $C_K(t)$, $C_B(t)$ and $C_A(t)$.

For Kerogen

Recall equation (3.21),

$$F_0C_{K0} - F_2C_{K2} - F_1C_{K1} - r_K = \frac{dC_KW}{dt} \qquad (3.21)$$

By assumption $C_{K1} = C_{K2} = C_K$ because of backmixing, and W=constant then equation (3.21) becomes,

$$F_0C_{K0} - F_2C_K - F_1C_K - r_K = W\frac{dC_K}{dt} \qquad (3.27)$$

Substitute (3.24) into (3.27),

$$F_0C_{K0} - F_2C_K - F_1C_K - k_1C_KW = W\frac{dC_K}{dt} \qquad (3.28)$$

Rearranging (3.28) gives,

$$\frac{F_0C_{K0}}{W} - (k_1 + \frac{F_1}{W} + \frac{F_2}{W})C_K = \frac{dC_K}{dt} \qquad (3.29)$$

and

$$A = \frac{F_O K_O}{W} \qquad B = (k_1 + \frac{F_1}{W} + \frac{F_2}{W})$$

$$\frac{dC_K}{dt} = A - BC_K \tag{3.30}$$

For Bitumen

Recall equation (3.22),

$$r_B - F_2 C_{B2} - F_1 C_{B1} = \frac{dC_B W}{dt} \tag{3.22}$$

For $C_{B1} = C_{B2} = C_B$, and taking W constant, and substituting (3.25) into (3.22), gives

$$f_1 k_1 C_K W - k_2 C_B W - (F_1 + F_2) C_B = W \frac{dC_B}{dt} \tag{3.31}$$

Rearranging (3.31) gives,

$$f_1 k_1 C_K - (\frac{F_1}{W} + \frac{F_2}{W} + k_2) C_B = \frac{dC_B}{dt} \tag{3.32}$$

Let $C = f_1 k_1$

$$D = \frac{F_1}{W} + \frac{F_2}{W} + k_2$$

To solve for C_B, equation (3.30) and (3.32) have to be taken together. Using Laplace transformation, these become,

$$C_K = \frac{A}{B}(1 - e^{-Bt}) \tag{3.33}$$

$$C_B = CA(C_{11} + C_{12}e^{-Dt} + C_{13}e^{-Bt}) \tag{3.34}$$

where $C_{11} = \frac{1}{BD}$

$$C_{12} = \frac{1}{(D^2 - BD)}$$

$$C_{13} = \frac{1}{(B^2 - BD)}$$

Then

$$\underset{\text{(mass)}}{\text{Kerogen}} = K_B W \tag{3.35}$$

$$\underset{\text{(mass)}}{\text{Bitumen}} = C_B W \tag{3.36}$$

For Oil

Recall equation (3.23),

$$r_A - F_g C_A = \frac{dC_A V}{dt} \tag{3.23}$$

Substitute (3.26) into (3.23),

$$f_2 k_2 C_B W - k_3 C_A V - F_g C_A = \frac{dC_A V}{dt} \qquad (3.37)$$

$$\frac{f_2 k_2 C_B W}{V} - C_A\left(\frac{F_g}{V} + k_3\right) = \frac{dC_A}{dt} \qquad (3.38)$$

Let

$$P = \frac{f_2 k_2 C_B W}{V} \qquad Q = \frac{F_g}{V} + k_3$$

therefore,

$$C_A = \frac{P}{Q}(1 - e^{-Qt}) \qquad (3.39)$$

Total oil accumulated over time, t=0 and t=t

$$\underset{\text{Yield}}{\text{Oil}} = \int_0^t C_A F_g dt \qquad (3.40)$$

Predictions of equation 3.40 will be compared with the accumulated oil yield determined by sampling the outlet vapour.

4. EXPERIMENTAL EQUIPMENT AND PROCEDURE*

4.1 Pyrolysis Apparatus

The apparatus used in this thesis was originally designed and built by A. Jarallah[2] for coal pyrolysis. A number of modifications were made to improve the operation and reliability of the apparatus. The design characteristics of the major units are listed in Table 9. A schematic diagram of the experimental apparatus is shown in Figure 5.

A new feed system was installed to replace the original vibratory feeder which was difficult to control and was not designed to handle particles below 1mm diameter. The new system includes a plexi-glass hopper, a rotary feeder and a inclined glass section.

The feed hopper was 305mm high x 165mm diameter. It had a conical bottom which was fitted with a 12.5mm diameter ball valve. A plastic tube connected the feed hopper and the inclined inlet pipe section to balance the pressure in the feed hopper with that in the reactor in order to get a constant feed rate. A syntron magnetic vibrator (Model V-2-B) was mounted on the bottom of the hopper which aided the flow of the oil shale out of the rotary valve. The valve rotation speed was controlled by the G K Heller motor controller. Because of the low feed rate required, a 30:1 gear reductor was installed. The controller was always set

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* The author is indebted to Dr. G.K. Khoe who assisted with the modifications to the apparatus, and made many of the improvement in techniques and helped carry out some of the experimental runs.

TABLE 9: Design Characteristics of Spouted Bed Pyrolyzer System

Reactor:	Material - 317 Stainless Steel Inside diameter - 128mm Wall Thickness - 6.6mm Cone Angle - 70° Disengaging Section Diameter - 255mm Height (includes cone and disengagement section) - 1.22m
Spent Shale Receiver:	Material - Mild Steel Outside Diameter - 305mm Height - 0.91m
Oil Shale Hopper:	Material Steel - Plexi-glass Outside Diameter - 165mm Height - 305mm
Spouted Bed Furnace:	Electrical Rating - 6.9kW Maximum Temperature - 1200°C Heaters: 6 1/4-Round 304mm high x 178mm I.D. Heated Length - 0.69m
Spouted Gas Preheater:	Electrical Rating - 8.45kW Maximum Temperature - 1200°C Heaters: 4 semi-cylinderical 69.85mm x 44.45mm I.D. Flexible electrical heating tape Heated Length - 0.69m
Oil Shale Feeder:	Rotary Feeder

Gas-Solid Cyclone:	Material - Stainless Steel Diameter - 150mm Cylinder Height - 500mm Cone Height - 300mm
Condenser:	Shell - 316 Stainless Steel Inside Diameter - 128mm Wall Thickness - 6.6mm Tubes - 6 U-tubes 0.86m long Diameter - 12.7mm Area - 4130 cm^2
Oil Receiver:	Material - Glass and Stainless steel Inside Diameter - 229mm Height - 305mm
Oil Filter:	Material - Stainless steel Diameter of orifice - 19.1m
Piping:	Material - 316 Stainless steel

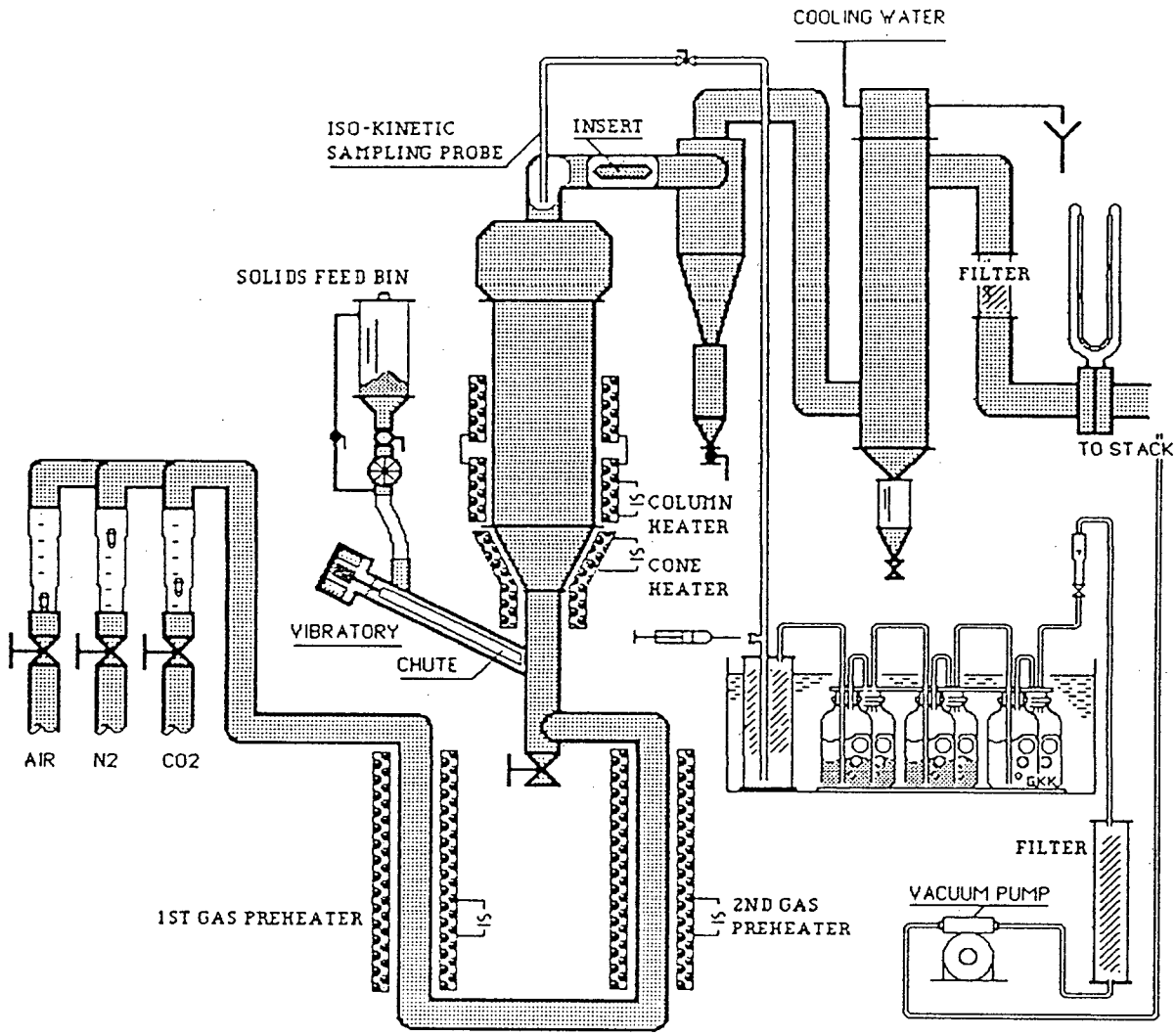

Fig 5: A Schematic Diagram for the Experimental Apparatus

below 10% of the maximum speed rate and slight fluctuations were recorded. For this reason, a higher gear ratio reducer is recommended.

The oil shale dropped from the rotary valve through the rubber tubing onto the copper pipe that was fitted inside a 25.4mm x 150mm QVF glass tube. A second syntron vibrator was attached to the end of the copper pipe to promote transfer of the oil shale directly to the inlet pipe of the reactor. Trials had been done in which the oil shale dropped directly onto the glass tubing itself, i.e. in the absence of the copper pipe, but accumulation of the solids and eventual blockage at the entrance of the inlet occurred.

The off-gas sampling train from which the oil yields were to be determined was completely rebuilt from Jarallah's design[2]. Instead of stainless steel impingers, glass impingers were used. These were easier to handle and provided a clear view during the experiment. The impinger train was immersed in a tank filled with cracked ice and water. The whole system rested on a trolley which could be carried to a fume hood for oil recovery. The position of the off-gas sampling point was also relocated. Previously, it was at the outlet pipe of the drying column that was placed after the last impinger. However, some of the methylene chloride solution had evaporated with the gas and therefore affected the gas chromatograph results. The off-gas sampling point was therefore located at the upstream of the first impinger (refer to Figure 5).

The heating system was also modified. The preheater had to be rebuilt because the original semi-cylindrical heaters were burnt out and as the heaters were touching the surface of the stainless steel pipe, a hole had been made in the pipe as well. An electric forced air duct heater element enclosed in a fluidized sand bed was then tried. The sand was used to improve the heat transfer and avoid hot spots in the heater box. This system failed as the electrical element overheated and melted. Finally, the Lindberg half circle heating unit was used. These consisted of 4 semicylindrical heaters of 44.5mm ID which were clamped around the 3.8cm diameter pipe to give a heated length of 698.5mm. The total electrical rating of these heaters was 7.2kW. To avoid a short circuiting of these heaters as occurred in the previous case, an air gap of 1.5mm was left between the heating element and the pipe section. To increase the rate of heat transfer, the pipe section was filled with ceramic Raschig rings. A thermocouple was inserted in the air gap, and the temperature was controlled by an Omega controller. As it was the temperature in the air gap that was measured, the control was a bit difficult.

In the original design, the main heater on the spouted bed reactor consisted of 16 quarter-cylindrical electrical elements each of 178mm ID and 152mm height. These were mounted around the main cylindrical section of the reactor to form a shell. An air gap of 18mm existed between inside of the heaters and the outside surface of the reactor. This

reduced the efficiency of heat transfer and the time for heating up was lengthy. After rearrangement, 6 quarter-cylindrical electrical elements were used. The heated section was 609.6mm high and the total electrical ratings for these heaters was 6.9kW. The air gap was reduced to 1.5mm, therefore the rate of heat transfer was improved and the heating up time was halved. The temperature was controlled by an Omega controller mounted on the control panel.

There was a serious heat loss between the preheaters and the main heater, therefore a flexible electrical heating tape (Heavily insulated Samox) was wrapped around the conical section of the reactor. The total electrical rating was 1.25 kW, and the power applied was adjusted by a variac.

Both the reactor and the downstream pipe were insulated by 5-7.5cm ceramic blanket to prevent heat loss to the surroundings.

Other modifications included provision of new gaskets in all joints; and the installation of an insert in the horizontal pipe upstream of the cyclone to reduce the cross-sectional area available for flow, so as to avoid the settling of solids in this region.

The temperature throughout the appartus was measured by by chromel-alumel thermocouples with 316 stainless steel sheath of 1.6mm diameter. In the reactor, and the preheaters, more rugged K-type thermocouples of 6.3 mm diameter were used.

4.2 Properties of the Oil Shale

The oil shales studied in this project were supplied by the Research Productivity Council of New Brunswick. The original coarse oil shale, as received was reduced in size using a jaw crusher. It was then screened to 3 different sizes: 2-4mm, 1-2mm and 0.5-1mm which were stored in separate plastic buckets. Representative samples of the oil shales were sent to the General Testing Laboratories of Vancouver for proximate and ultimate analyses. The results are listed in Table 10. Table 11 gives the analysis of oil shale ash and carbon. It can be seem that there is slight variation among the different sizes. Table 12 lists the modified Fischer Assay results for the different sizes of oil shale A and reports that larger size fractions have better oil yields. These analyses were carried out at the Research and Productivity Council of New Brunswick.

4.3 General Procedure

The basic mode of operation with this pyrolysis unit is to fill the reactor with inert solids (sand or spent shale), heat to the required temperature with air, then switch the gas to N_2/CO_2 or N_2. The velocity of gas is set at 10% above the minimum spouting velocity. (The calculation for mimumum spouting velocity is included in the computer program - Profile.) The oil shale is fed into the reactor over a period of 1 1/2 hour. In this case, the height of the bed will graduately rise with time. The oil is recovered from

TABLE 10: Proximate and Ultimate Analysis of Blend of Oil Shale A

Proximate Analysis	
% Moisture	1.69
% Ash	72.53
% Volatiles	25.17
% Fixed Carbon	0.61
	100.00

Ultimate Analysis (Dry Basis)	
% C	15.91
% H	2.05
% N	0.51
% S	0.92
% Cl	0.01
% Ash	73.78
% Oxygen (diff)	6.82
	100.00

TABLE 11: Analysis of Oil Shale Ash and Carbon

Size Fraction (mm)	0.5-1.0	1-2	2-4
Total Organic Carbon (%)	10.2	10.6	12.4
Total Carbon (%)	12.3	13.3	14.7
SiO_2 (wt%)	43.4	41.9	41.6
Al_2O_3	10.6	10.4	10.3
Fe_2O_3	4.56	4.38	4.36
CaO	8.32	9.03	8.10
MgO	3.38	3.57	3.20
Na_2O	0.95	1.05	1.05
K_2O	1.63	1.60	1.57
SO_3	1.70	1.87	2.22
Loss on Ignition	24.1	25.1	26.1
Ba (ppm)	310	306	283
Mn	602	568	508
Sr	309	333	302
Ti	2910	2560	2890

* Digested samples in mixture of acids, analyzed solution by inductively coupled Argon Plasma Spectrograph
Carbon and Sulphur by Leco Induction Furnace
Analyses by Can-Test Ltd.

TABLE 12: Modified Fischer Assay of Oil Shales

	Shale Sample A					Shale Sample B	
Size Fraction (mm)	0.5	0.5-1.0	1-2	2-4	4	0.5-1.0	1.0-2.0
Oil Yield (wt%)	5.2	5.5	7.8 8.1 7.95	8.1 7.6 7.85	7.6	2.9	4.5
Water Yield (wt%)	2.1	2.0	2.2 2.3 2.25	2.2 1.8 2.0	1.6	3.2	2.4
Gas Lost (wt%)	1.2	5.5	3.0 1.6 2.3	1.7 3.6 2.7	4.8	1.4	3.1
Char Yield (diff.)	91.5	87.0	87.0 88.0	87.0 88.0	86.0	92.5	90.0
Oil Yield (I.gal/ton)	12.1	12.7	18.0 18.6	18.9 17.4	17.4	6.7	10.4
Oil Density (g/ml at 15.5°C)	0.8562	0.8670	0.8670 0.8678	0.8563 0.8763	0.8752	0.8573	0.8634

Analysed at Research and Productivity Council, Fredericton

the off-gas sampling train which is activated 5 minutes after the oil shale feeding begins. The gas samples are obtained by syringe during the experiment.

Other sets of experiments were carried out in which the height of the bed material was kept constant. This was achieved by releasing part of the overflow material through a side pipe at the concial section of the spouted bed at specific time intervals (5 or 10 minutes). The overflow material dropped through a ball valve into a stainless steel pipe section with an end-cap. After closing the ball valve, the end-cap was unscrewed to release the overflow material. Then the end-cap was put on again, and the ball valve was opened to allow more material to be removed. In this way the reactor operated in a quasi-steady state, rather than having the solids holdup steadily increasing.

4.4 Detailed Operating Procedure

The screened oil shale (about 2 kg) was loaded into the feed hopper. The required amount of inerts (Ottawa sand -14 +20 mesh, 5.9kg) was charged into the reactor from the top. This give a static bed height of 33cm. During charging, the air was turned on at a low rate to prevent the sand from dropping into the spouting gas inlet pipe and creating a blockage. To conserve nitrogen and carbon dioxide, air was first used for spouting to heat up the sand to the desired temperature. The tube section of the off-gas sampling line was installed and the ball valve closed. Then the air flow

was adjusted to the operating flow, and the main reactor heater, spouting gas preheater, tape heater and the cooling water for the condenser were all turned on.

During the heating up period, the assembly of the remaining parts including the impinger train was carried out. The impingers were prepared as explained in Section 4.5. Soon after the required temperature of about 500°C was reached, the air was replaced by a mixed gas stream of CO_2 and N_2 (volume ratio 15:85), and a period of 15 minutes was allowed to purge the air before oil shale feeding was started. It was recognised that when the temperature reached above 500°C. the air stream should be replaced with inert gas, as there was some oil which had been deposited in previous experiments along the pipe, which could be ignited if the temperature became too high. Before the oil shale feeding was begun, a zero feed rate gas sample was obtained. This was done by opening the ball valve of the impinger train, followed by extracting a blank gas sample using a syringe. The ball valve was then closed. The sample was injected into the gas chromatograph.

The oil shale feeder controller was set at the desired point and the feeder turned on. The time at which oil shale feeding started was recorded. After 5 minutes, the ball valve of the impinger train was opened and the gas sample pump was then turned on and oil collection started. The five minutes delay was designed to exclude the non-steady state effects during the initial minutes of feeding. Gas sample

flow rate was adjusted to the desired value and the gas sample rotameter reading was recorded. Gas samples were extracted at respectively 15, 30, 45, 60, 75 and 80 minutes. After the last extraction, the feeder, gas pump and heaters were turned off. Oil collection lasted for 75 minutes (5 to 80 minutes). All temperatures and pressures throughout the system were recorded, and the spouting gas rotameter reading was taken. The nitrogen inlet gas stream was used to cool the system. The feed hopper was emptied of unused oil shale to determine the oil shale feed rate.

4.5 Oil Collection

The oil vapour is collected by isokinetic sampling of the off-gas. The velocities of the gases in the main pipe and the sampling tube are set equal. The first impinger was a 9.5mm x 30mm QVF glass tube filled with glass wool to provide a large contacting surface for condensation and filtering effects. This also helped to retain heavier oil fraction.

The second to the fifth impingers were filled with a mixture of methlylene chloride and water (2:1 volume ratio). The sixth impinger contained methanol to trap the remaining oil-mist and entrained methlyene chloride. The last impinger contained water to trap any entrained methanol. The containers were interconnected in the last minute before the sampling line was activated inorder to prevent a backspill of methlyene chloride from the second impinger into the

first one. This could contaminate the gas samples that were extracted through a septum at the upstream of the first impinger. For this reason, a slight vacuum was always maintained during an interruption, and the ice was added to the water bath just before the start of the oil collection.

The day after the experiment, the impingers, interconnecting pipes and the tube sections of the sampling lines which connected to the main off-gas line were thoroughly rinsed with solvents (methlyene chloride and methanol), and then cleansed and dried before the next experiment.

The solution in the impingers and the washing solution would then be filtered to remove all fine particles. The water was separated from the methyl chloride and methanol - oil solution by using separation funnel. Any remaining trace of water was removed by adding sodium sulphate to the solution. The solution was then filtered and evaporated in a rotrary evaporator (at 55°C, 20mmHg) to recover the oil. The recovered oil was weighed and the weight was recorded.

4.6 Gas Analysis

The gas analysis was performed on a Hewett-packard 5710A gas chromatograph with a 3388A automatic integraton system. The column separates hydrogen, oxygen, nitrogen, methane, carbon dioxide and carbon monoxide. Because of the limitation of this gas chromatograph, the hydrocarbons with molecular weight higher than methane cannot be detected. For

a few experiments , the gas analysis was done by using a another chromatograph by K.C. Teo[35] which was able to resolve upto C_6 hydrocarbons. The gas sample was extracted by a syringe through a septum at the upstream of the first impinger. The gas samples were analyzed and the values reported for each run.

4.7 Spent Shale Determination and Analysis

After the experiment, the reactor and the cyclone receiver were emptied and the contents of each one were separatly weighed. The weight of the spent shale produced was obtained by subtracting the weight of original Ottawa sand from the total weight of above. Although some solids have passed through the cyclone and were not recovered, the weight of the material from the dust receiver was taken to represent the solid entrained.

5. RESULTS AND DISCUSSIONS

5.1 General considerations

There were 26 successful experiments done on the New Brunswick oil shale A. The experimental conditions for each run are listed in Table 13.

The oil yield is calculated from the weight of oil collected from the sampled gas, multiplied with the ratio of the mass flow rate of the sampled gas streams to the total gas output from the reactor, and then divided by the oil shale feed rate. Care was especially required in washing the impinger train and sampling lines to recover oil from the sampled gas because the final oil product weighed about 1-4 gm.

The gas yield by species is calculated from the individual gas analysis, the total gas output from the reactor and the oil shale feed rate. Because of the limitation of the gas chromatograph, hydrocarbon gases of molecular weight higher than methane and gaseous sulphur, and nitrogen compounds are not detected. However, it is expected that the quantities of these gases are very small.

The spent shale yield is calculated from the weight of shale remaining in the reactor and cyclone receiver vessel after the run and the oil shale feed rate. Data indicated that about 2/3 of the oil shale feed remained in the reactor and cyclone receiver , and 1/3 had passed through the cyclone as entrained fines. Because the cyclone is oversized, the collection efficiency is not high. Since a

TABLE 13: Experimental Conditions for Each Run

Expt. No	Particle Size mm	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Initial Bed Sand/Spent Shale (kg)	Pyrolyzing Gas N_2/CO_2 (vol%)
2	0.5-1	509	509	1.49	5.9/0.0	85/15
3	0.5-1	505	505	1.37	5.9/0.0	85/15
4	1-2	503	503	1.65	5.9/0.0	85/15
5	1-2	501	501	1.33	5.9/0.0	85/15
6A	2-4	507	518	1.25	5.9/0.0	85/15
6B	1-2	540	528	1.29	5.9/0.0	85/15
7	1-2	554	554	1.33	5.9/0.0	85/15
8	1-2	454	450	1.39	5.9/0.0	85/15
9	1-2	530	530	1.39	5.9/0.0	85/15
10	2-4	506	505	1.21	5.9/0.0	85/15
11	1-2	477	470	1.52	5.9/0.0	85/15
12	2-4	506	502	2.71	5.9/0.0	85/15
12A	2-4	506	502	1.94	5.9/0.0	85/15
14	1-2	500	491	1.35	5.9/0.0	100/0
15	1-2	480	470	1.37	0.0/5.0	85/15
16	1-2	470	470	1.26	0.0/5.0	85/15
17	1-2	500	500	1.27	5.9/0.0	100/0
18	0.5-1	501	498	1.27	5.9/0.0	85/15
19	1-2	470	480	3.39	0.0/5.0	85/15
20	1-2	472	476	4.45	0.0/5.0	85/15
21	2-4	518	518	1.3	5.9/0.0	85/15
22	1-2	470	480	1.63	2.4/3.0	85/15
23	1-2	474	474	1.13	4.1/1.5	85/15
24	1-2	500	500	1.89	5.9/0.0	85/15
25	1-2	505	506	3.32	5.9/0.0	85/15
26	2-4	471	476	1.35	5.9/0.0	85/15

significant amount of fines passed through the cyclone, therefore an overall mass balance could not be closed. It was found that a small fraction of the fines were stuck onto the wall of the cyclone, and mechancial brushing was employed in Runs 16 to 26 to recover as much of the fines as possible to obtain a more reliable spent shale yield.

5.2 Effect of Temperature on Oil Yield and Composition

The study of the temperature effect was done on two feed sizes: 1-2mm and 2-4mm, at a constant feed rate of 1.40 and 1.28kg/h respectively. All of these experiments were done in a bed of silica sand, with pyrolyzing gas of 15% CO_2 and 85% N_2. The height of the bed increased gradually as the feed shale accumulated in the reactor during the experiment. There are two temperatures of potential importance in the oil shale pyrolysis experiments; the inlet temperature and the bed temperature. The inlet temperature refers to the temperature of the preheated gas where it meets the shale at the bed inlet, and the bed temperature refers to the average temperature in the annulus of the spouted bed itself. If the heating rate in the inlet region is low, the particle will reach pyrolysis temperature only after passing into the bed. Then the bed temperature will govern the oil yield. If the heating rate in the inlet region is high and the particle begins to pyrolyze before reaching the bed, the inlet temperature will be important. In all experiments, the inlet temperature and the bed temperature were kept to the same

value within experimental error except for Run 6B. The calculated temperature history for the oil shale particles was presented in Section 2.5. It was shown that the particles are still near room temperature at the entrance of the spouted bed. In other words, pyrolysis of the shale particles does not start before the particles are in the bed, thus the inlet temperature is less important in this case.

Table 14 lists the results. Figure 6 and 7 are plots of oil yield versus temperature. It can be seen that a maximum oil yield exists at some optimum temperature. For particles of 1-2mm, the optimum temperature is around 470-490°C. The oil yield is 7.1% which represents 89.3% of the modified Fischer Assay yield. It can be seen that the result for Run 6B in Figure 6 is slightly above the smooth curve through the other results. If the oil yield is plotted against the inlet temperature the curve will seem to be smoother, so it was thought that the temperature difference of 12°C between the inlet temperature and the bed temperature has produced this result. However, the temperature history calculation suggested little effect of inlet temperature. Experiment 6B should be repeated to verify the reliability of this data point.

For the 2-4mm particle size, the small number of data points preclude the determination of an optimum temperature. The few results in Figure 6 suggest an optimum somewhere between 490 and 510°C. At 505°C the oil yield was 7.4% which

TABLE 14: Effect of Temperature on Oil Yield

Expt No.	Particle Size (mm)	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Oil wt%	Yield %Fischer Assay
8	1-2	454	450	1.39	4.3	54.1
11	1-2	477	470	1.52	7.1	89.3
5	1-2	501	501	1.33	6.3	79.2
4	1-2	503	503	1.65	5.8	73.0
9	1-2	530	530	1.39	3.3	41.5
6B	1-2	540	528	1.29	5.3	66.6
7	1-2	554	554	1.33	2.4	30.2
26	2-4	471	476	1.35	4.2	53.3
10	2-4	506	505	1.21	7.2	91.7
6A	2-4	507	518	1.25	7.4	94.3
21	2-4	518	518	1.30	3.3	42.0

Initial Bed Compostion: Ottawa sand -14 +20 mesh
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

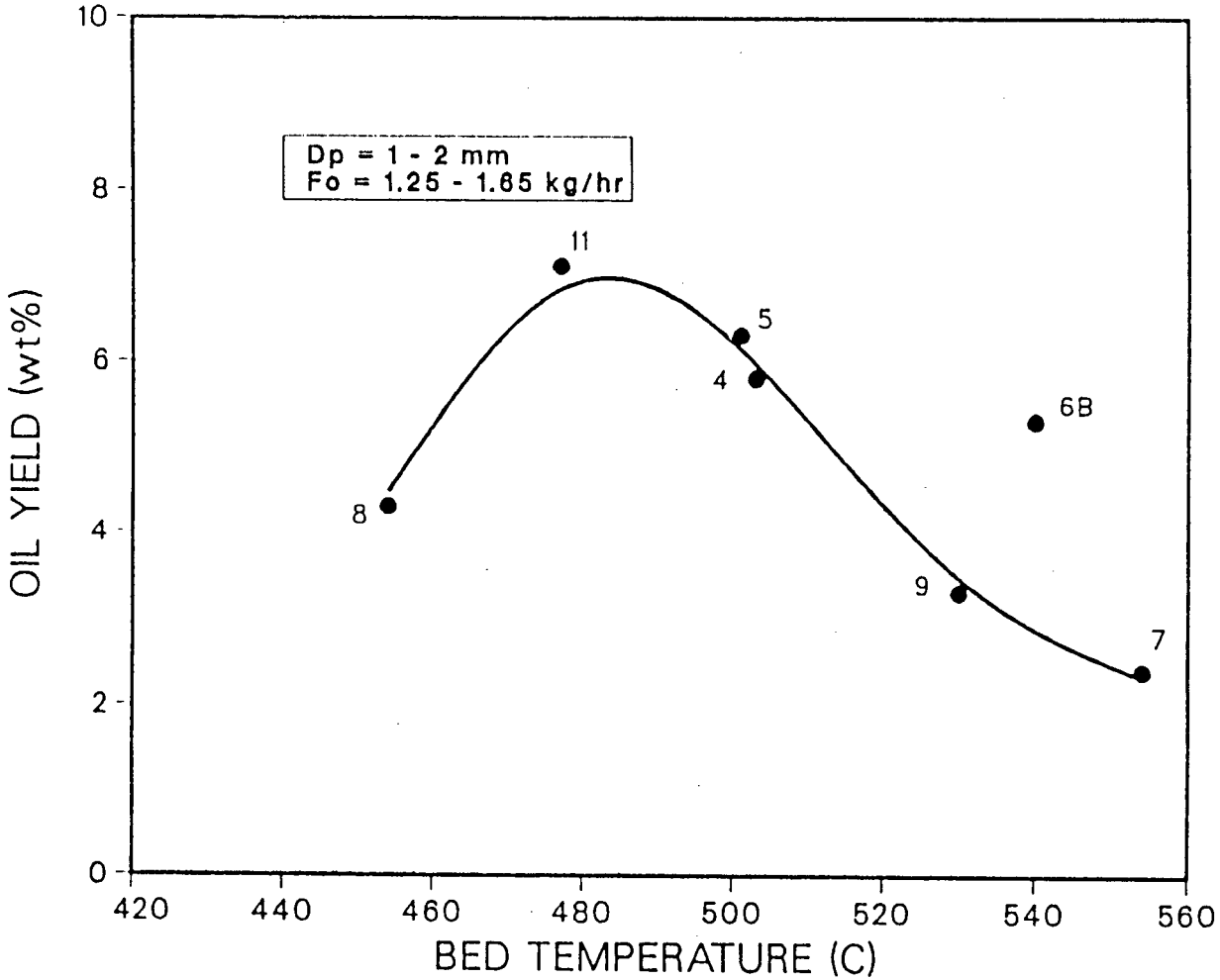

Fig 6: Oil Yield Versus Temperature Plot

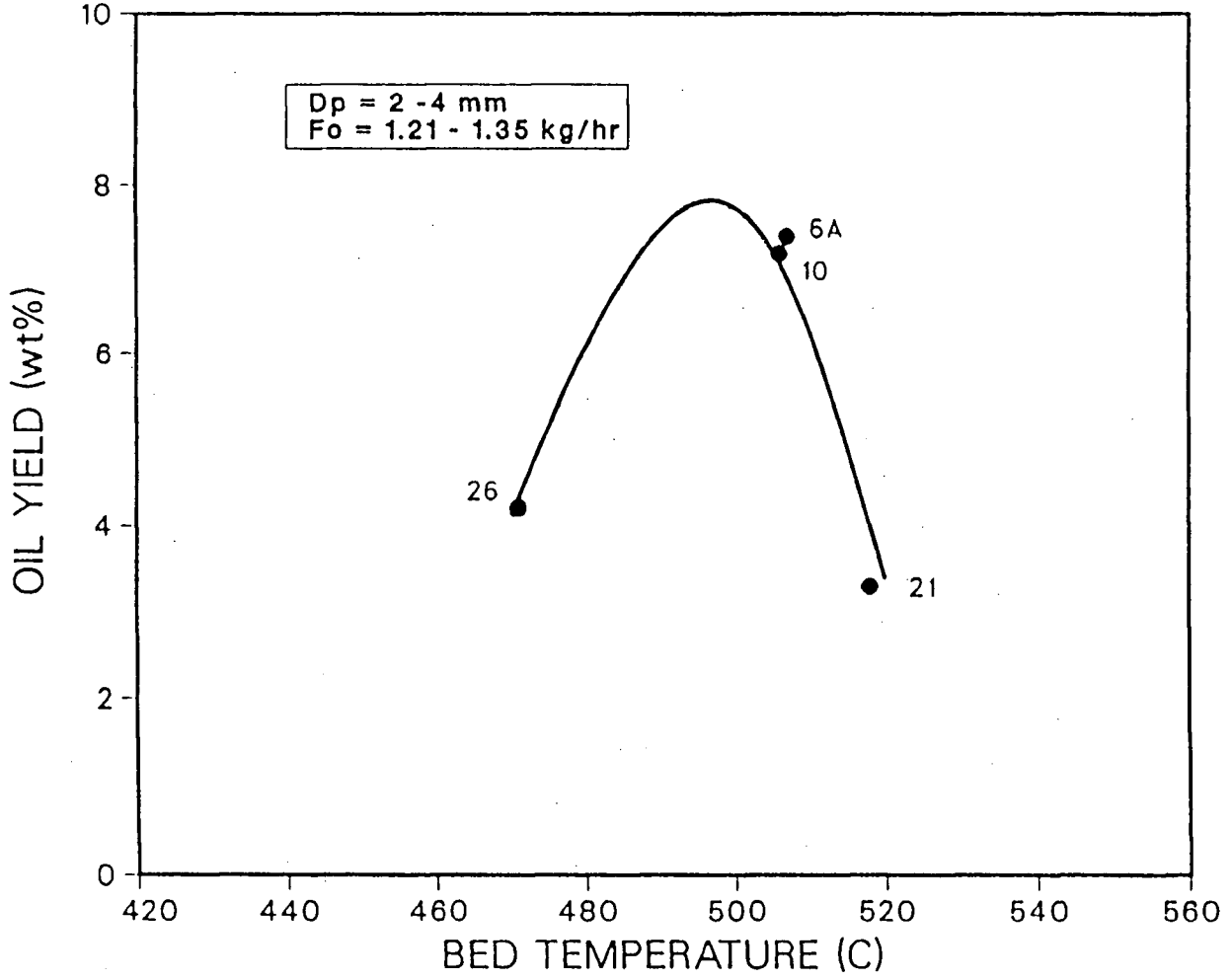

Fig 7: Oil Yield Versus Temperature Plot

represents 94.3% of the modified Fischer Assay yield. However, more experiments are required to quantify the temperature optimum.

Figure 8 shows a plot of the percentage of the Fischer Assay oil yield versus temperature plots for both 1-2mm and 2-4mm particle sizes. It can be seen that the curve for the 2-4mm is shifted slightly to the right, reflecting a higher optimum temperature for maximum oil yield compared to the 1-2mm size. This might arise because the 2-4mm particle is larger and will have larger internal temperature gradients, and will require a longer heating period or higher temperature to heat up the entire particle for complete pyrolysis. As mentioned earlier, more experiments are required to be done for 2-4mm sizes at 500-550°C. However, the trend of the Fischer Assay oil yield - Temperature curve in Figure 8 is in agreement with those observed by Liu et al[20] (refer to Figure 2). They have also concluded that that there is an optimum temperature corresponding to a maximum oil yield.

Table 15 lists the composition of the oils produced at different temperatures for particles of diameter 1-2mm. Typical oils contain 81.5-83.0% C, 10.6-10.9% H, 1% N and 5-6.8% is not accounted for. It was first thought that the unaccounted species present in the oils was either methanol or methylene chloride from the solvent train. An investigation was carried out by dissolving the oil in ethylbenzene and injecting into a 50m long DB5 capillary

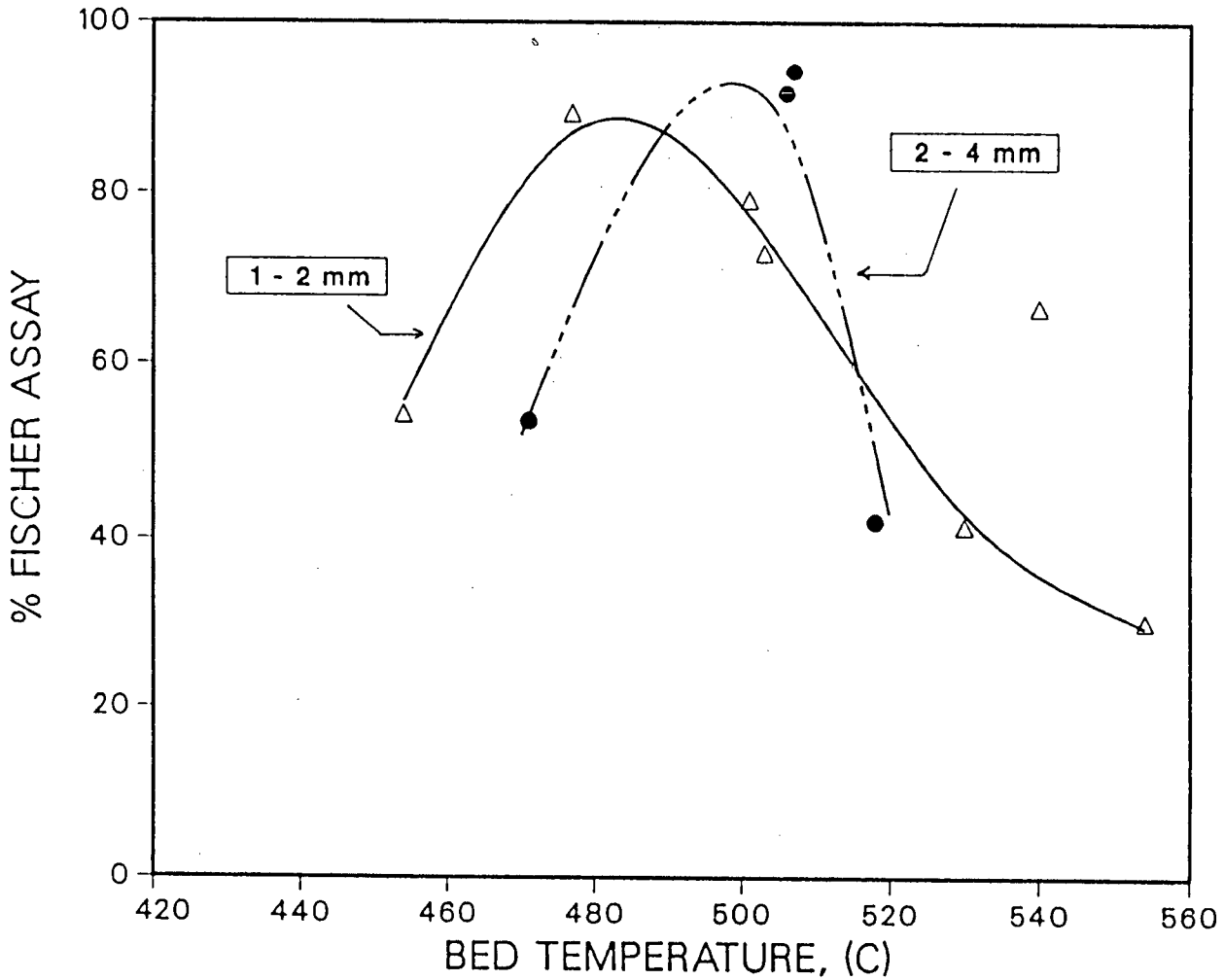

Fig 8: % Fischer Assay VS Temperature Plot

TABLE 15: Effect of Temperature on Oil Yield and Composition

Expt No.	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Oil wt%	Yield %Fischer Assay	Oil Analysis* (wt%) C	H	N	S	**	Atomic Ratio H/C
8	454	450	1.39	4.3	54.1	83.03	10.55	1.25		5.17	1.51
11	477	470	1.52	7.2	90.6						
5	501	501	1.33	6.3	79.2	82.46	10.66	1.13	0.63	5.12	1.54
4	503	503	1.65	5.8	73.0	81.47	10.70	1.02		6.81	1.57
6B	540	528	1.29	5.3	66.6	81.92	10.91	0.88		6.29	1.59
7	554	554	1.33	2.4	30.2	81.77	10.92	0.81		6.50	1.59

Oil Shale Particle Size: 1-2mm
Initial Bed Composition: Ottawa Sand -14 +20 mesh
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

* Microanalytical Analysis
** Unaccounted

column in a chromotograph. Results indicated that neither methanol nor methylene chloride was present. The unaccounted species are as yet unidentified. As the pyrolysis temperature increases, the atomic H/C ratio increases. At the optimum temperature, H/C is 1.54, which seems to be in agreement with the expected values for shale oils produced by pyrolysis.

5.3 Effect of Oil Shale Particle Size on Oil Yield and Composition

The study of the particle size effect on oil yield and composition was carried out for 2-4, 1-2, and 0.5-1mm sizes. All of these experiments were done at about 506°C with 15% CO_2 and 85% N_2 as pyrolyzing gas. The bed was initially filled with silica sand, and the bed height increased gradually with time as the feed shale accumulated during the experiment.

Table 16 lists the results. Figure 9 shows the oil yield versus mean particle sizes. It can be seen that oil yield increases with increasing particle size. This is exactly opposite to the observation made by Jarallah[2] on coal pyrolysis. He found that the tar yield decreases with increasing particle size, and his explanation is that there is an increased extent of secondary reactions which consume tar for larger particles. The extent of secondary reactions may be less significant in oil shale pyrolysis. If the experimental temperature is higher than the optimum

TABLE 16: Effect of Particle Size on Oil Yield

Expt No.	Particle Size (mm)	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Spent Shale In Bed (gm)	Oil wt%	Yield %Fischer Assay
18	0.5-1	501	498	1.26	681.0	2.4	43.6
3	0.5-1	505	505	1.37	454.0	4.2	76.4
2	0.5-1	509	509	1.49	510.8	2.4	43.6
5	1.0-2	501	501	1.33	681.0	6.3	79.2
4	1.0-2	503	503	1.65	539.1	5.8	73.0
10	2.0-4	506	505	1.21	652.6	7.2	91.7
6A	2.0-4	507	518	1.25	908.0	7.4	94.3

Initial Bed Composition: Ottawa Sand -14 +20 mesh
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

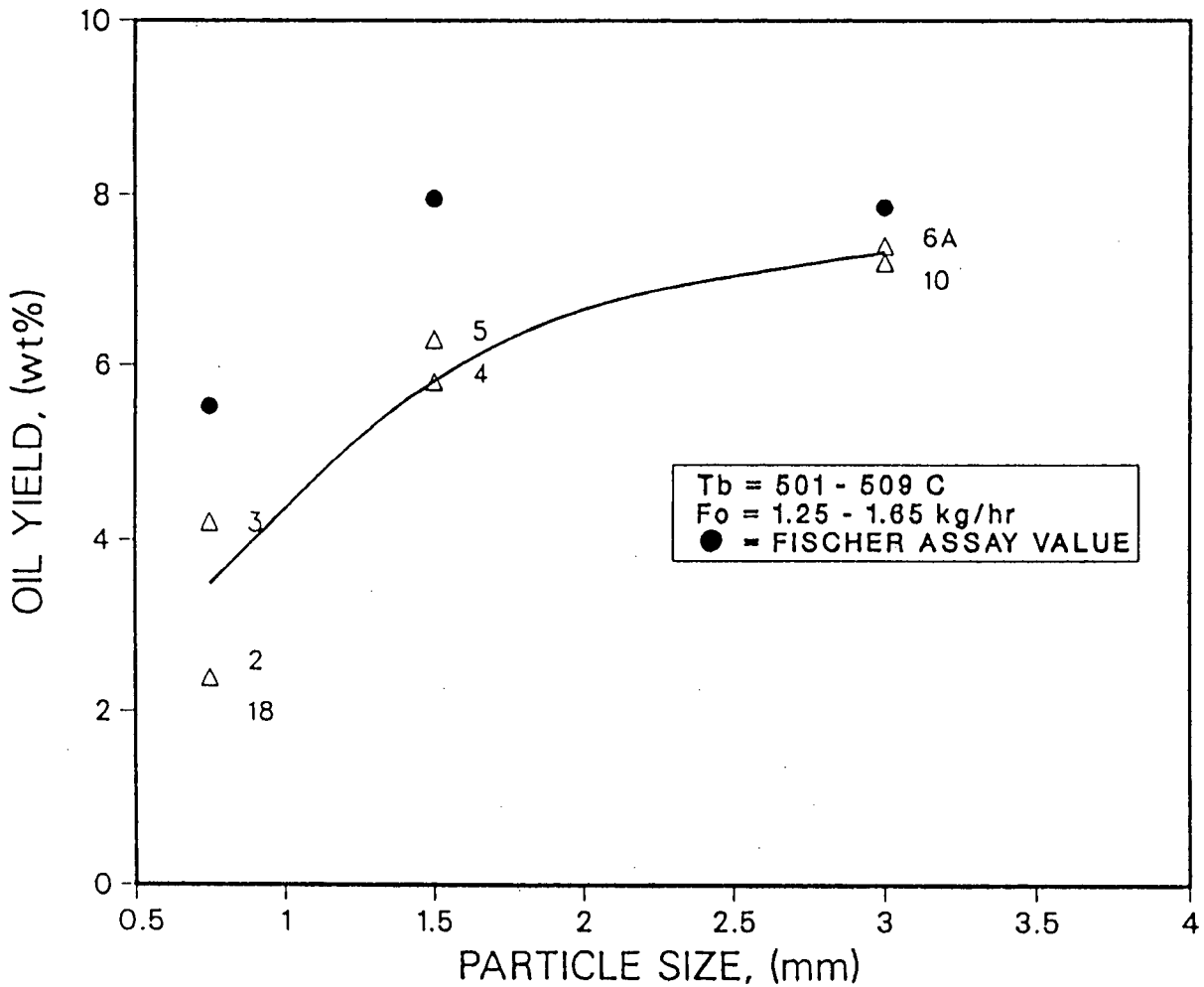

Fig 9: Oil Yield VS Particle Size Plot

temperature, the chance is greater that the oil is further decomposed to secondary volatiles. In the present case, the optimum temperature for 1-2mm particle size is around 475°C which is about 31°C lower than the experimental temperature in Figure 7. The extra temperature has enhanced secondary reaction, and therefore the oil yield obtained at 6.3% is lower than the maximum of 7.1%. Whereas for the 2-4mm size, the optimum temperature is around 505°C which is approximately the same as the temperature in Figure 6. For the 0.5-1mm particle size, although the optimum temperature was not studied, it is expected to be lower than 475°C. With the same argument, therefore the greater difference between the experimental and optimum temperature results in an even lower oil yield for the smallest particles.

Based on these observations, the dependance of oil yield on particle size will be different if the comparision is made at say 475°C. In this case, the 2-4mm particles will produce a lower oil yield as the optimum temperature has not been attained, whereas for the 0.5-1mm particle, the gap between the optimum and experimental temperature is reduced, so a higher oil yield is expected. Certainly, more tests at lower temperature should be carried out to provide a more complete picture.

Table 17 lists the elemental composition of the oils produced. There is no consistent trend among the three samples analyzed. The 2-4mm sized shale has the highest atomic H/C ratio and lowest unaccounted for species.

TABLE 17: Effect of Particle Size on Oil Yield and Composition

Expt No.	Particle Size (mm)	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Oil wt%	Yield %Fischer Assay	C	Oil Analysis* (wt%) H	N	S	**	Atomic Ratio H/C
2	0.5-1	509	509	1.49	2.4	43.6	81.58	11.02	0.7		6.70	1.61
3		505	505	1.37	4.2	76.4	82.18	10.73	1.05		6.04	1.56
4	1-2	503	503	1.65	5.8	73.0	81.47	10.70	1.02		6.81	1.57
5		501	501	1.33	6.3	79.3	82.46	10.66	1.13	0.63	5.12	1.54
6A	2-4	507	518	1.25	7.4	94.3	82.73	10.66	1.14		5.47	1.54
10		506	505	1.21	7.2	91.7	82.64	11.35	1.12		4.89	1.64

Initial Bed Composition: Ottawa Sand -14 +20 mesh
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

* Microanalytical Analysis
** Unaccounted

5.4 Effect of Oil Shale Feed Rate on Oil Yield and Composition

The feed rate study was carried out for 2 sizes: 2-4mm and 1-2mm. All of these experiments were done at 500-506°C, using 15% CO_2 and 85% N_2 as pyrolyzing gas. The bed initially consisted of silica sand and the bed height increased gradually as the feed shale accumulated during the experiment.

Tables 18 and 19 list the results. Figures 10 and 11 show the plots of oil yield versus shale feed rate. Both curves indicate that there is a marked decrease of oil yield with increasing feed rate. For 1-2mm shale, the oil yield has dropped from 6.3% to 2.9% as the feed rate was increased from 1.33 to 3.32kg/h, which is a drop of 79.2 to 36.5% of modified Fischer Assay values. Similar results were observed for the 2-4mm sized shale where feed rate increases from 1.53 to 2.71kg/h resulted an oil drop from 7.4 to 2.0%, which is a drop of 94.3 to 25.5% of modified Fischer Assay values. It can be seen in Figure 10 that the first three points are in a straight line, indicating a linear decreasing effect and then the line approaches an asymptotic value. The reason for the decrease is presumably that the hot spent shale accumulated in the reactor has acted as a surface on which the secondary oil-consuming reactions occur, or perhaps as a catalyst for oil decomposition. This effect will be demonstrated further below. The trends in Figure 10 and 11 are in the same direction as those observed

TABLE 18: Effect of Feedrate on Oil Yield (Unsteady Height Expt.)

Expt No.	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Spent Shale In Bed (kg)	Oil Yield wt %	% Fischer Assay
5	501	501	1.33	0.68	6.3	79.2
4	503	503	1.65	0.54	5.8	73.0
24	506	506	1.90	1.31	3.4	42.8
25	505	506	3.32	1.46	2.9	36.5

Oil Shale Particle Size: 1-2mm
Initial Bed Composition: Ottawa Sand -14 +20 mesh
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

TABLE 19: Effect of Feedrate on Oil Yield (Unsteady Height Expt.)

Expt No.	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Spent Shale In Bed (kg)	Oil wt%	Yield % Fischer Assay
10	506	505	1.21	0.65	7.2	91.7
6A	507	518	1.25	0.91	7.4	94.3
12A	506	502	1.94	1.02	4.5	57.3
12	506	502	2.71	1.28	2.0	25.5

Oil Shale Particle Size: 2-4mm
Initial Bed Composition: Ottawa Sand -14 +20 mesh
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

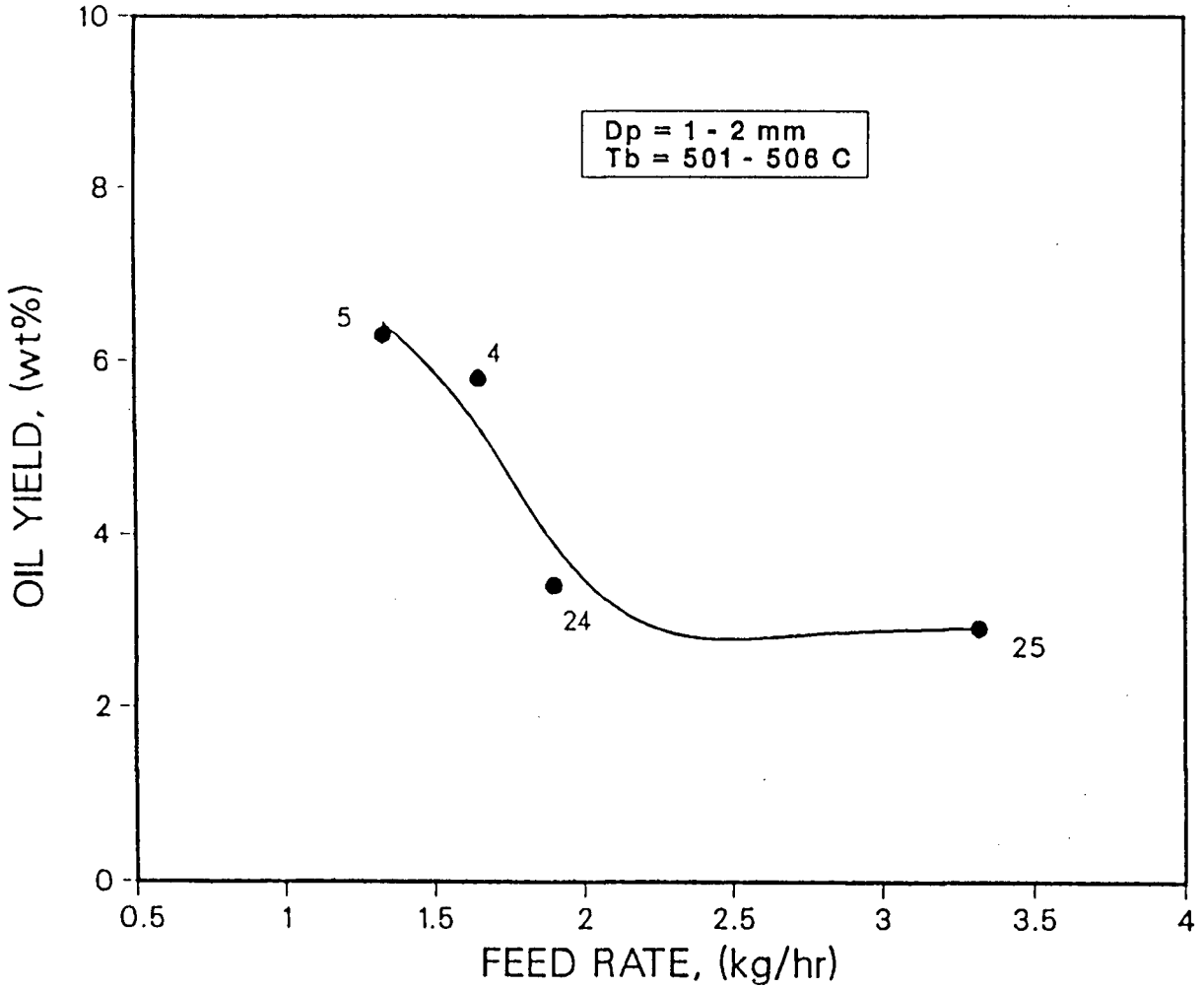

Fig 10: Oil Yield VS Feed Rate Plot

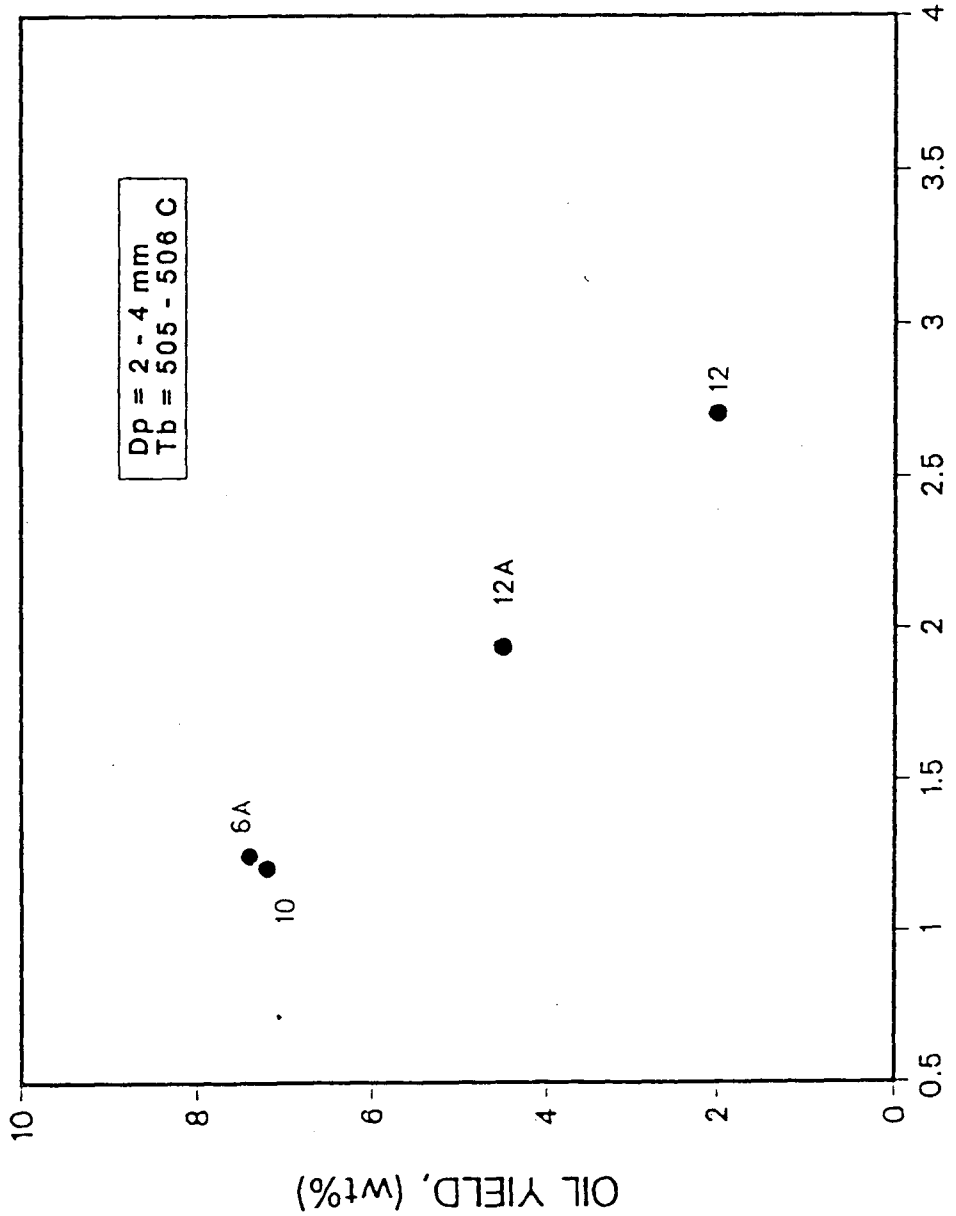

Fig 11: Oil Yield VS Feed Rate Plot

by Jarallah[2] on coal pyrolysis.

Another series of feed rate experiments was carried out in a bed consisting initially of spent shale with the bed height kept constant by releasing the accumulated spent shale periodically through the bed overflow line. Table 20 lists the results. Figure 12 shows the oil yield versus feed rate plot. Results indicate that the oil yield has remained quite steady at 2.4-2.6% regardless of the feed rate. This value is very close to the lowest yield in previous Figure 10. This implies that the presence of spent shale has indeed enhanced secondary rections of the oil (such as cracking), therefore dropping the oil yield significantly. A careful study of the two figures leads to the conclusion that with increasing feed rate in a sand bed, the oil yield will drop linearly in the beginning, and then gradually approach an asymptotic value of around 2.4%.

Table 21 lists the composition of the oil produced for the 2-4mm size. The hydrogen content decreases, but the hydrogen/carbon atomic ratio seems to increase from 1.46 to 1.56 as the oil yield falls off with increasing feed rate in the sand bed experiments.

5.5 Effect of Bed Material on Oil Yield

The study of the bed material effect on oil yield was carried out on shale of 1-2mm size at 470-477°C with 15% CO_2 and 85% N_2 as the pyrolyzing gas. For all experiments, the volume of the initial bed was kept the same (vol=3735cm^3,

TABLE 20: Effect of Feedrate on Oil Yield (Steady Height Expt.)

Expt No.	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Oil wt%	Yield % Fischer Assay
16	470	470	1.26	2.4	30.2
19	470	480	3.39	2.6	32.7
20	472	476	4.45	2.5	31.4

Oil Shale Particle Size: 1-2mm
Initial Bed Composition: Spent Shale
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

* Periodic release of spent shale from the reactor to keep bed height steady

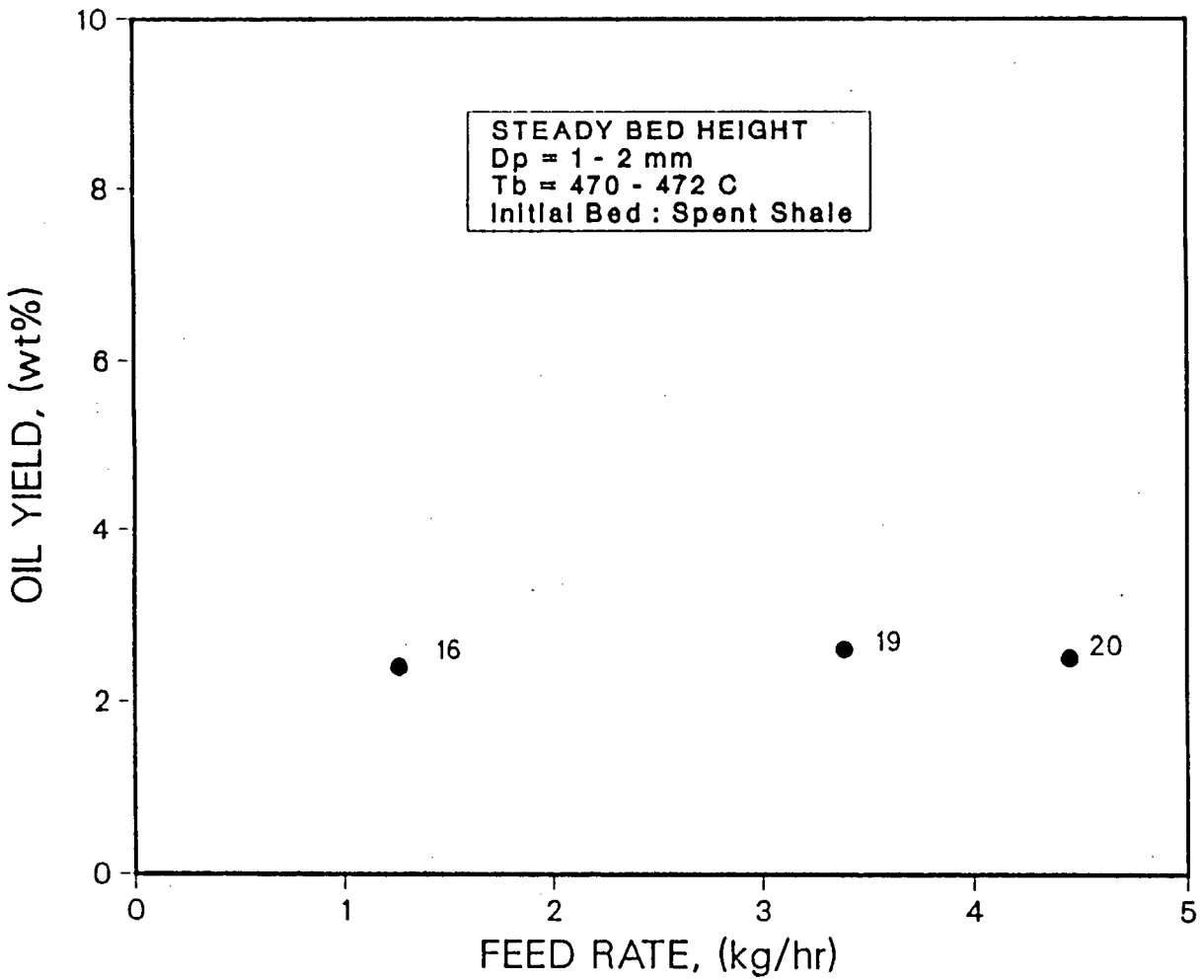

Fig 12: Oil Yield VS Feed Rate Plot

TABLE 21: Effect of Feedrate on Oil Yield and Composition

Expt No.	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	oil wt%	Yield %Fischer Assay	Oil Analysis* (wt%) C	H	N	**	Atomic Ratio H/C
10	506	505	1.2	7.2	91.7	82.64	11.35	1.12	4.89	1.46
12A	506	502	1.94	4.5	57.3	83.65	10.77	1.23	4.35	1.53
12	506	502	2.71	2.0	25.5	83.42	10.89	1.29	4.40	1.56

Oil Shale Particle Size: 2-4mm
Initial Bed Composition: Ottawa Sand -14 +20 mesh
Initial Weight: 5.9 kg
Spouting Gas: 85% N_2 - 15% CO_2

* Microanalytical Analysis
** Unaccounted

initial bed depth=33cm), but the amount of spent shale in the bed ranges from 1 to 6.9kg. The remainder of the bed was silica sand. As the experiment proceeded, the bed height increased gradually as spent shale accumulated in the reactor.

Table 22 lists the results. Figure 13 shows the plot of the oil yield versus the final spent shale mass in the reactor after the run. The final mass represents the spent shale accumulated during the experiment. The results show that there is a marked decrease in oil yield with increasing spent shale mass in the bed. These experiments show essentially the same effect as the feed rate experiments. As more and more spent shale becomes available in the bed, the oil yield drops because the hot spent shale has acted as a sorbent for the oil or a catalyst for the secondary reactions. When the initial bed is comprised solely of spent shale, the oil yield drops to 2.4% which is equivalent to the asymptotic value for Figure 12. It can be concluded that the presence of spent shale has a negative effect on the oil yield. This is in agreement with the observation made by Levy et al[43]. In their study, vaporized oil was passed through a packed bed of sand, or spent shale ash at temperatures between 500 and 600°C. In the case of sand bed, cracking was minimal at 500°C and gradually increased at higher temperatures. In the case for spent shale ash bed, coking was prevalent at all temperatures studied, and a major oil losses was resulted even at 500°C. The ash has

TABLE 22: Effect of Bed Material on Oil Yield

Expt. No	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Initial Bed Spent Shale (kg)	Initial Bed Sand	Final Spent Shale (kg)	Oil wt%	Yield %Fischer
11	470	477	1.52	0.0	5.9	1.0	7.1	89.3
23	474	474	1.13	1.5	4.1	2.25	3.9	49.0
22	470	470	1.63	3.0	2.4	3.73	2.7	34.0
16	470	470	1.26	5.0	0.0	6.84	2.4	30.2

Oil shale Particle Size: 1-2mm
Spouting Gas: 85% N_2 - 15% CO_2

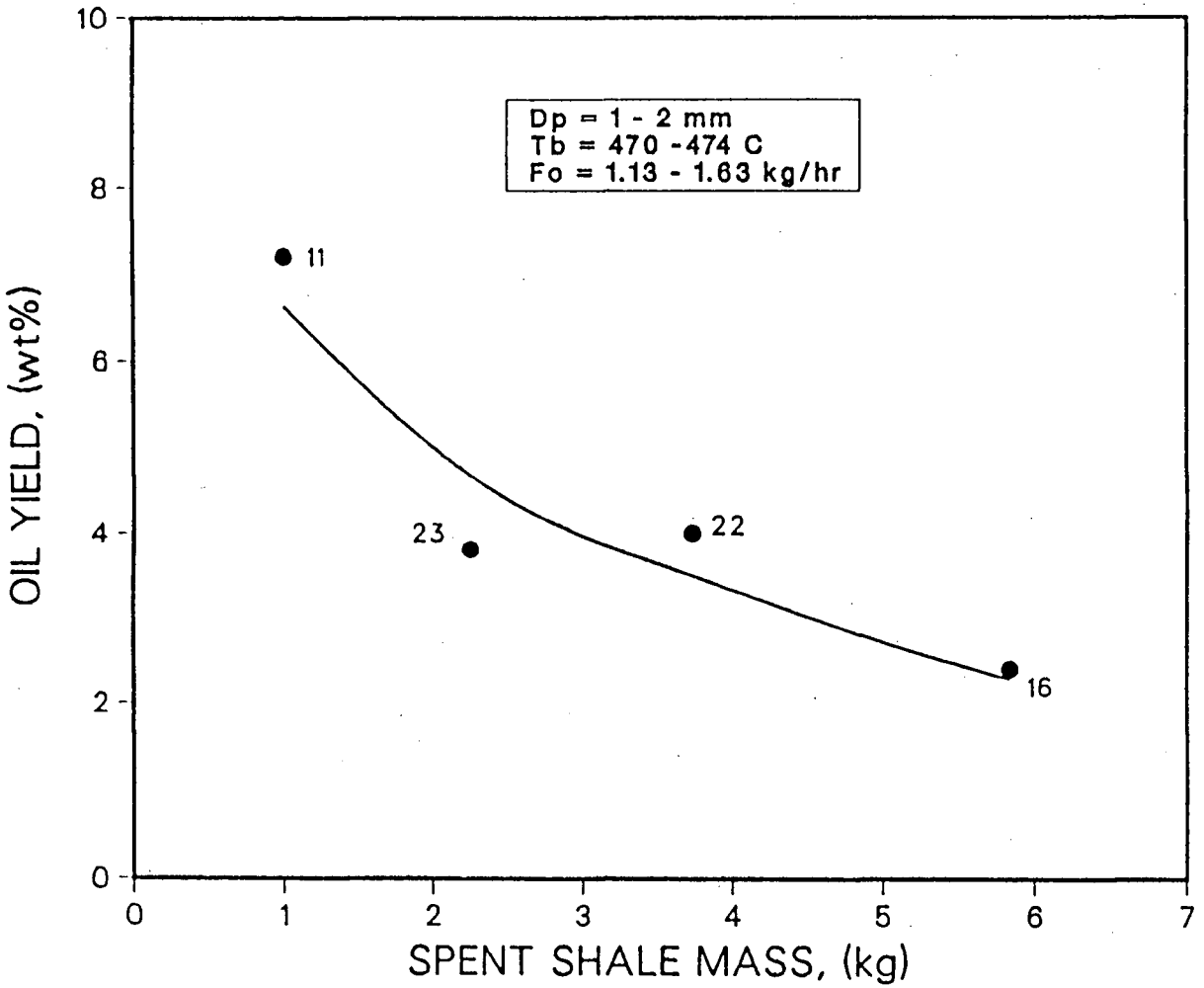

Fig 13: Oil Yield VS Spent Shale In Bed

catalysed the oil degradation greatly. On the other hand, this sorbent effect presumably is specific to the oil shale, as Floess et al.[36] found no difference in oil shale yields in fluidized beds of silica sand and calcined dolomite of surface area 6.3m^2/g.

It should be noted that the feed rate actually fluctuated from 1.13 to 1.63kg/hr. This should not have affected the oil yield result because Figure 10 of Section 5.4 already shows that the oil yield remains around 6% in that feed range.

5.6 Effect of Pyrolyzing Gas on Oil Yield

Two experiments were done in the 1-2mm sized shale at 500°C using N_2 instead of the mixture of 15% CO_2 and 85% N_2 as pyrolyzing gas. Table 23 lists the results. The data are very reproducible, and both reflect a lower oil yield at 3.4% in nitrogen compared to 6.3% when using the N_2 / CO_2 mixture. An explanation of this unexpected result is not available yet. Bae[17] observed that at atmospheric pressure, the oil yield is not affected by the nature of pyrolyzing gas (refer to Figure 1).

5.7 Gas Yields

The spouted bed retorting technique in which a large volume of gas is needed for spouting is not particularly well suited for measurement of gas yields, as concentration of produced gas in the off gas will tend to be very low.

TABLE 23: Effect of Pyrolyzing Gas Composition

Pyrolyzing Gas	85% N_2-15% CO_2		100% N_2	
Expt. No	4	5	14	17
Temperature (Inlet/Bed) °C	503/503	501/501	491/500	500/500
Feed Rate (kg/hr)	1.65	1.33	1.35	1.27
Oil Yield (wt%)	5.8	6.3	3.4	3.4
Oil Yield (%Fischer Assay)	73.0	79.2	42.8	42.8
Oil Analysis (wt%)				
C	81.47	82.46	82.49	
H	10.70	10.66	10.89	
N	1.02	1.13	1.17	
S	-	0.63	0.75	
Unaccounted	6.81	5.12	4.70	
Atomic H/C Ratio	1.57	1.54	1.57	

Oil Shale Particle Size: 1-2mm
Initial Bed Composition: Ottawa Sand -14 +20 mesh
Initial Weight: 5.9 kg

Nevertheless some results were obtained.

As stated in Section 4.6, two chromatographs were used. For most of the runs, the GC used was set for concentration of H_2, CO, CO_2, and CH_4 in the percent range. A few analyses were also done on the second GC, which permitted determination of the above species and addition information on C_2H_2, C_2H_4, C_2H_6,C_3H_8 and C_4H_{10}. Table 24 lists the results.

Hydrogen is produced during pyrolysis of oil shale. The yield ranges from 0.02 to 0.045%, and does not seem to be affected by particle sizes, feed rate and bed material. Figure 14 shows the plot of hydrogen yield versus temperature. The profile seems to be marked by two peaks although the data is scattered. According to Campbell et al[37], the peaks are associated with 'secondary' pyrolysis reaction of the carbon residue remaining after the primary bitumen decomposition.

Methane yields are recorded in a few experiments. Campbell et al [37] observed that methane is released during the oil generation, and higher temperature pyrolysis of the spent shale. The methane released during the secondary pyrolysis (above 500°C) may result primarily from the cleavage of methyl and methoxyl groups bonded to aromatic structures and possibly, from cleavage of methylene bridges between aromatic rings.

The evolution of C_2 and C_3 was determined by the second GC. Campbell et al[37] observed that these gases are evolved

TABLE 24: Gas Yields

Expt No	Particle Size (mm)	% Gas Yield (kg/kg shale) H_2	CH_4	C_2H_4	C_2H_6	C_3H_8	C_4H_{10}	C_6H_{14}	Total
2	0.5-1	0.028							0.028
3	0.5-1								
4	1-2	0.023	0.065	0.059	0.059	0.460			0.666
5	1-2	0.033	0.062	0.042	0.045	0.760			0.942
6A	2-4	0.037	0.098	0.049	0.060	0.820			1.064
6B	1-2	0.027	0.079	0.068	0.075	0.631			0.880
7	1-2	0.021	0.077	0.082	0.052	0.914			1.146
8	1-2	0.032	0.057	0.160	0.095	0.190	0.21		0.744
9	1-2	0.038	0.068	0.028	0.045	0.410	0.220	0.170	0.979
10	2-4	0.036	0.088	0.027	0.064		1.650	0.330	2.195
11	1-2	0.031	0.080	0.038	0.074	0.400	1.220	0.310	2.153
12	2-4	0.042							0.042
12A	2-4	0.024							0.024
14	1-2	0.037							0.037
15	1-2	0.022							0.022
16	1-2	0.034							0.034
17	1-2	0.018							0.018
18	1-2								
19	1-2	0.038							0.038
20	1-2	0.039	0.029						0.068
21	2-4	0.019							0.019
22	1-2	0.015							0.015
23	1-2	0.033							0.033
24	1-2	0.030							0.030
25	1-2	0.038	0.020						0.058
26	2-4	0.030							0.030

* The experimental conditions for each run are listed in Table 12

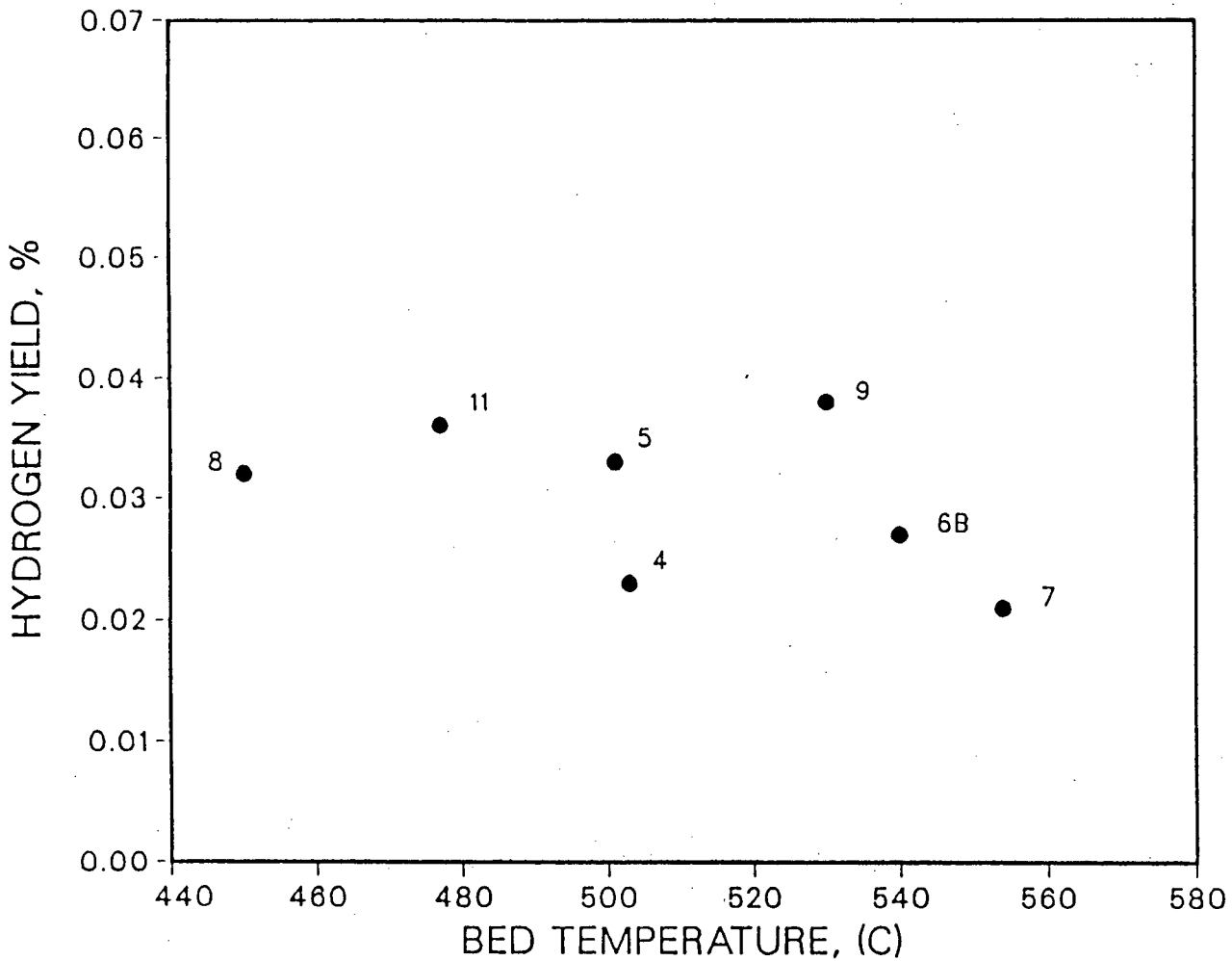

Fig 14: Hydrogen Gas Yield VS Temperature

during the oil generation, i.e. between 350-550°C. The evolution of C_4 and C_6 was determined in a few experiments only, therefore no conclusion can be drawn.

In most experiments, carbon dioxide was included in the pyrolyzing gas at a level of 15%. Because of the fluctuations of the gas inlet flowrate, it was difficult to determine its yield. However, it was noted that for the run done with nitrogen alone as pyrolyzing gas, there was no CO_2 nor CO produced. These results agreed with the findings of Campbell et al[37]. They found that no CO_2 and CO were released during pyrolysis below the temperature of 550°C. The release of CO_2 and CO occurs primarily above 600°C. Carbon dioxide is produced during the decomposition and reaction of carbonate minerals present in the oil shale, and carbon monoxide is then produced by the subsequent reaction of CO_2 with carbon.

5.8 Spent Shale Yields

As mentioned in the beginning of the section, there was a substantial loss of entrained spent shales particles. Some had escaped to the atmosphere due to the inefficiency of the cyclone, and some had stuck onto the wall of the cyclone. From experiment 14 onwards, mechanical brushing had been used to recover the fines from the cyclone, and thus higher percentages of fines were recovered. Table 25 lists the compositions of spent shales found in the bed and recovered from the cyclone catch for three different particle sizes.

TABLE 25: Spent Shale Properties and Yield

Run	3		4		10	
Temperature(°C)	505/505		503/503		506/505	
Particle Size (mm)	0.5-1.0		1-2		2-4	
	Bed Shale	Cyclone Catch	Bed Shale	Cyclone Catch	Bed Shale	Cyclone Catch
Total Carbon (%wt)	4.91	6.84	4.64	6.87	5.33	5.89
Organic Carbon (%)	3.48	4.77	2.37	4.30	2.36	3.20
SiO_2 (%wt)	56.7	61.2	51.6	52.4	50.3	59.8
Al_2O_3	16.6	9.33	14.5	11.2	13.1	8.81
Fe_2O_3	10.1	3.96	5.66	4.80	5.52	3.84
CaO	3.34	6.54	9.30	8.77	10.9	7.42
MgO	2.24	2.50	3.97	3.45	4.28	2.93
Na_2O	1.35	0.95	1.6	1.31	1.38	1.10
K_2O	2.64	1.58	2.23	1.83	2.17	1.55
Ba (ppm)	440	373	390	373	376	300
Mn	790	402	690	570	705	446
Sr	175	290	340	368	385	310
Ti	2960	2440	3430	2970	3180	2340

Mass balances using several species (Sr, Ba, Ti, Fe_2O_3) present in the shale, the bed material and the cyclone catch, all showed that the uncollected material which passed through the cyclone was about one-third of the oil shale feed. Also it can be observed that the cyclone catch contains higher carbon content than does the bed material which indicates that the entrained particles are generally incompletely reacted.

It was intended that the spent shale yield be calculated from the weight of the shale in the shale-sand mixture remaining in the reactor plus the weight of entrained fines in the cyclone after the run. In practice, the actual weight of shale remaining in the reactor cannot be obtained simply by weighing the total solids due to the fact that some of the sand was also entrained to the cyclone. Therefore, the method chosen to obtain the yield is by combining the weight of entrained particles in the cyclone receiver plus the weight of the bed after the run minus the weight of inert material orginally present in the bed. Table 26 lists the results of the spent shale yield. Due to the incomplete recovery, the trends of the spent shale yield with process variable were not meaningful. Attrition is obviously a serious problem for processing these oil shales in a spouted bed.

TABLE 26: Spent Shale Yields

Expt No	Temperature Bed (°C)	Temperature Inlet (°C)	Particle Size (mm)	Shale Feedrate (kg/hr)	Spent Shale Cyclone (gm)	Spent Shale Bed	Total Spent Shale (gm)	Spent Shale Yield (wt%)
2	509	509	0.5-1	1.49	681.0	510.8	1191.8	60.0
3	505	505	0.5-1	1.37	652.6	454.0	1106.6	60.4
4	503	503	1-2	1.65	681.0	539.1	1220.1	55.3
5	501	501	1-2	1.33	397.5	681.0	1078.5	60.8
6A	507	518	2-4	1.25	56.8	908.0	964.8	57.8
6B	540	528	1-2	1.29	397.5	681.0	1078.5	62.6
7	554	554	1-2	1.33	368.9	766.1	1135.0	62.8
8	450	450	1-2	1.38	539.1	595.9	1135.0	61.0
9	530	530	1-2	1.39	567.5	567.5	1135.0	61.0
10	506	505	2-4	1.21	454.0	652.6	1106.6	68.4
11	477	470	1-2	1.52	737.7	681.0	1418.7	70.0
12	506	502	2-4	2.71	1135.0	1276.8	2411.8	66.8
12A	506	502	2-4	1.94	567.5	1021.5	1589.0	61.4
14	500	491	1-2	1.35	835.2	500.0	1335.2	74.2
15	480	472	1-2	1.37	1779.1	(1135.0)*	664.1	66.0
16	470	470	1-2	1.26	948.6	0	948.6	56.5
17	500	500	1-2	1.27	621.0	510.7	1131.7	66.8
18	500	498	0.5-1	1.26	449.3	681.0	1130.3	67
19*	470	480	1-2	3.39	1602.7	1021.5	3298.0	82.1
20*	472	476	1-2	4.45	1906.8	(170.25)*	4823.7	84.3

21	518	518	2-4	1.30	514.0	1078.3	1592.3	91.8
22	470	480	1-2	1.63	803.7	1163.4	1967.1	90.0
23	474	474	1-2	1.13	736.4	595.8	1332.2	88.5
24	500	500	1-2	1.89	824.8	1305.3	2130.1	84.3
25	500	506	1-2	3.32	981.0	1459.2	2740.2	86.9
26	471	476	2-4	1.35	1161.8	170.3	1332.1	73.8

* Discharge for expt 19 is 673.8gm

* Discharge for expt 20 is 2746.6gm

* For experiments 15 and 24, the bed actually had a lost in weight of 1135.0 and 170.25gm respectively

6. Kinetic Model

6.1 General Discussion

From the simplified model developed in Section 3.2, equations (3.33),(3.34), (3.39) and (3.40) have been derived,

$$C_K = \frac{A}{B}(1 - e^{-Bt}) \qquad (3.33)$$

$$C_B = CA(C_{11} + C_{12}e^{-Dt} + C_{13}e^{-Bt}) \qquad (3.34)$$

$$C_A = \frac{P}{Q}(1 - e^{-Qt}) \qquad (3.39)$$

$$\underset{\text{Yield}}{\text{Oil}} = \int_0^t C_A F_g dt \qquad (3.40)$$

with the Arrhenius relationships,

$$k_1 = k_1^{\circ} e^{-E_1/RT} \qquad (6.1)$$

$$k_2 = k_2^{\circ} e^{-E_2/RT} \qquad (6.2)$$

$$k_3 = k_3^{\circ} e^{-E_3/RT} \qquad (6.3)$$

Taking k_1°, k_2°, E_1 and E_2 from the literature[24] and F_o, F_1, F_2, V, C_{K0} and oil yield from the experiments, k_3° and E_3 can be solved for using UBC Library Program NL2SOL. The computer

program is included in Appendix C.

Table 27 lists the experimental data and literature values used for the generation of k_3° and E_3. The predicted oil yield values and the experimental data are plotted in Figure 15. It can be seen that the model predicts a trend similar to the experimental data although the experimental oil yield drops more sharply at low tempartures. The predicted maximum oil yield occurs at a temperature of 440°C, which is some 37°C lower than that found by experiment. No measurements of kerogen and bitumen are available for checking the model.

The values of C_K, C_B, C_A and oil yield as functions of time can be calculated by UBC Library Program Jacobian using the following equations:

$$\frac{dC_K}{dt} = \frac{F_o C_{Ko}}{W} - \left(\frac{F_o}{W} + k_1\right)C_K \qquad (3.44)$$

$$\frac{dC_B}{dt} = f_1 k_1 C_K - \left(\frac{F_o}{W} + k_2\right)C_B \qquad (3.45)$$

$$\frac{dC_A}{dt} = \frac{f_2 k_2 C_B W}{V} - \left(\frac{F_g}{V} + k_3\right)C_A \qquad (3.46)$$

$$\text{Oil} = \int_0^t C_A F_g dt \qquad (3.47)$$

TABLE 27: Effect of Temperature on Oil Yield (Predicted vs Experimental Values)

Expt No.	Particle Size (mm)	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Experimental Oil wt%	Predicted Oil wt%
(Unsteady Height Experiment)						
8	1-2	454	450	1.39	4.3	6.6
11	1-2	477	470	1.52	7.1	6.4
5	1-2	501	501	1.33	6.3	5.7
4	1-2	503	503	1.65	5.8	5.6
9	1-2	530	530	1.39	3.3	3.9
7	1-2	554	554	1.33	2.4	2.2

From Literature(23)

$k_1^{\bullet} = 14.4\ s^{-1}$

$E_1 = 44560\ kJ/mol$

$k_2^{\bullet} = 2.025E10\ s^{-1}$

$E_2 = 177580\ kJ/mol$

From Calculation

$k_3^{\bullet} = 1.7E14\ s^{-1}$

$E_3 = 244319.45\ kJ/mol$

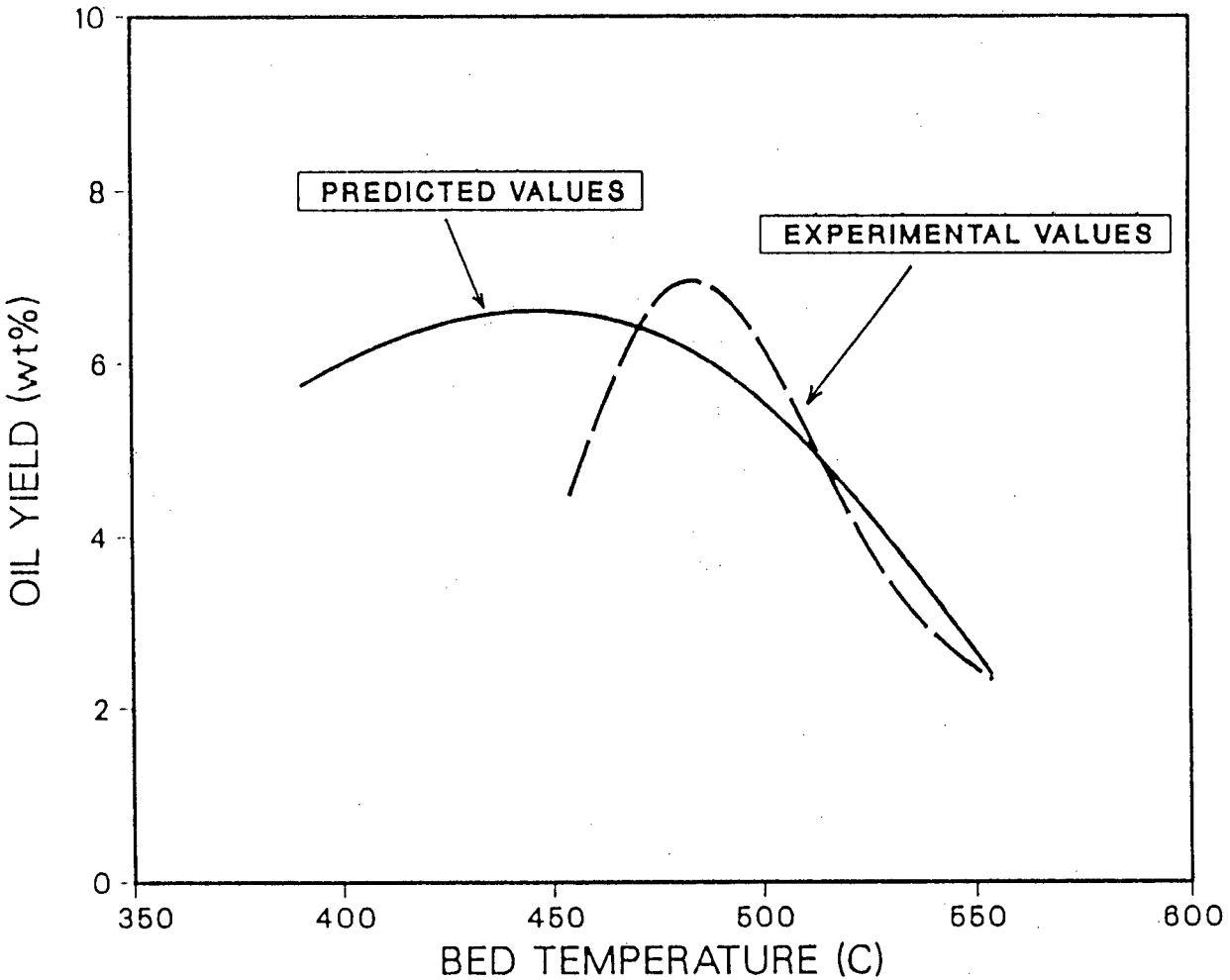

Fig 15: Oil Yield Versus Temperature Plot

Predicted Values VS Experimental Values

The results are plotted in Figure 16 for one experimental run. As expected, C_K, the concentration of kerogen, increases with time and then remains steady as a fraction of the kerogen is decomposed to form bitumen. C_B starts from zero and increases to some value, and then gradually remains constant as the bitumen is decomposed to oil. Oil concentration begins at zero, and gradually increases as it is produced by the decomposition of bitumen. At the same time, the oil degrades to form gas on further heating. The cumulative oil yield increases rapidly at the beginning, and then more slowly as time goes on and gradually approaches a constant value.

6.2 The effect of Rate Constant on Oil Yield

The effect of individual rate constants k_1, k_2 and k_3 on oil yield was studied using the UBC library program Jacobian to solve the model. The k_1, k_2 or k_3 of the Arrhenius relationship (eqn. 6.1-6.3) is multiplied by a factor while holding all other values constant. The computer printout for one experimental run is shown in Appendix C.6. The model gives the same final oil yield results even for different values of k_1 and k_2. As k_1 increases, the time required for the kerogen to decompose to bitumen decreases. The time effect is also true for k_2. As k_2 increases, the time for bitumen to decompose to oil is shorter. Changing k_3, however, will affect the quantity and rate of oil degradation. For this reason, it can be seen that only k_3

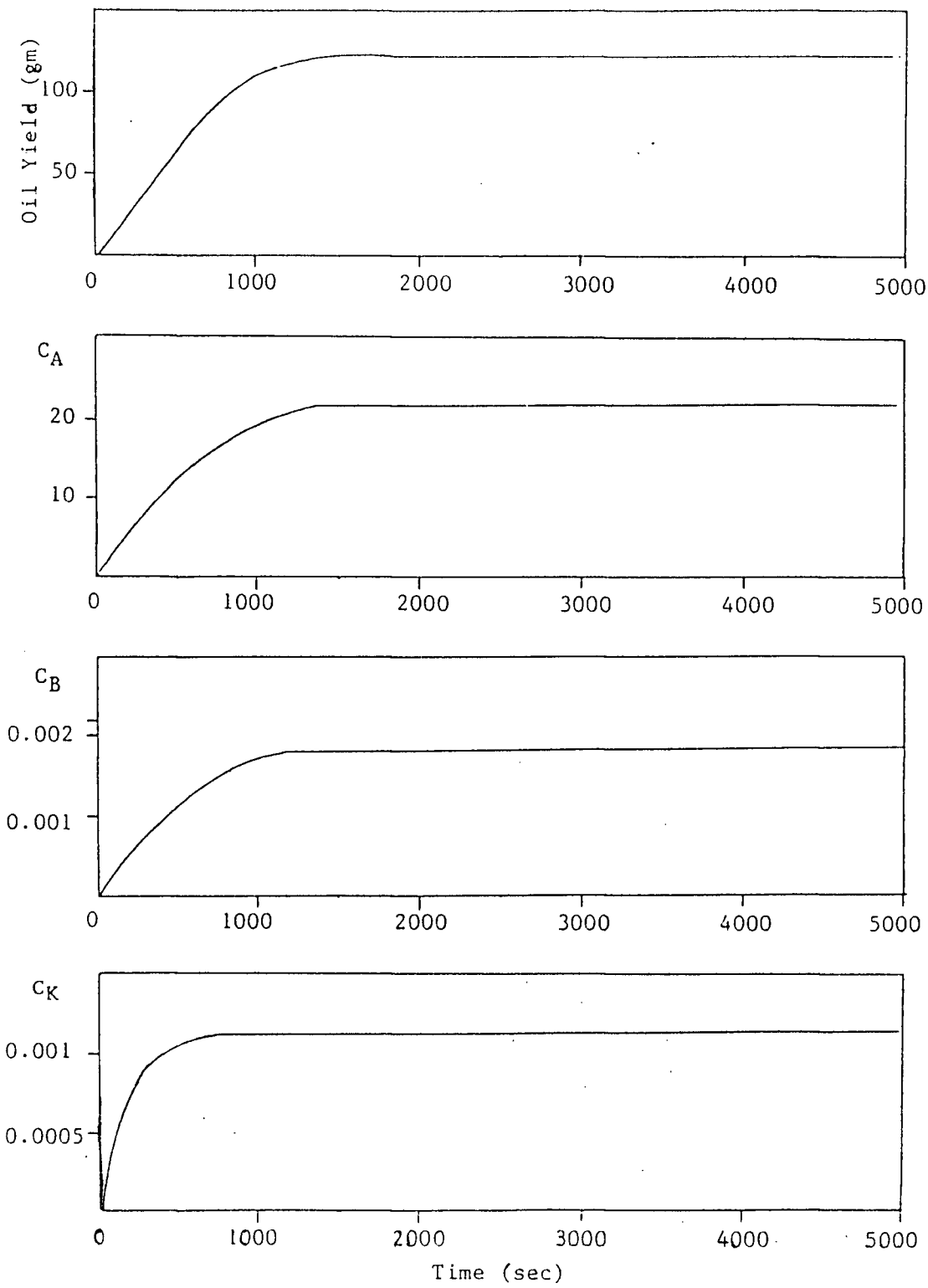

Fig. 16: C_K, C_B, C_A and Oil Yield vs Time Plot

and E_3 have an effect on the maximization of the oil yield. If some data of kerogen and bitumen were taken, a better model could be obtained.

6.3 The effect of Oil Shale Feed Rate on Oil Yield

Using the UBC Library Program Jacobian to solve the model, the effect of oil shale feed rate on oil yield was studied. Table 27 shows the comparison of the predicted oil yield results with the experimental values. Instead of a decreasing trend, the model predicted a constant oil yield value at 5.8 wt% for 2-4mm, and 5.5-6.0 for 1-2mm particle size. For the feed rate experiment carried under the steady height condition, again the model predicted a constant value at 6.6-6.7 wt % oil yield which is higher than the experimental value of 2.4-2.6 wt%. The predicted values indicate that the oil yield should be proportional to the feed rate. However the model does not take into consideration the effect of spent shale that acts as a catalyst for oil degradation. For future development of the model, the effect of spent shale should be included by putting the rate of oil decomposition proportional to the mass of spent shale.

TABLE 27: Effect of Feedrate on Oil Yield (Predicted vs Experimental Values)

Expt No.	Particle Size (mm)	Temperature Bed (°C)	Temperature Inlet (°C)	Shale Feedrate (kg/hr)	Experimental Oil wt%	Predicted Oil wt%
(Unsteady Height Experiment)						
10	2-4	501	501	1.33	7.2	5.8
6A	2-4	503	503	1.65	7.4	5.8
12A	2-4	506	506	1.90	4.5	5.8
12	2-4	505	506	3.32	2.0	5.8
5	1-2	501	501	1.33	6.3	5.7
4	1-2	503	503	1.65	5.8	5.5
24	1-2	506	506	1.90	3.4	6.0
25	1-2	505	506	3.32	2.9	6.0
(Steady Height Experiment)						
16	1-2	470	470	1.26	2.4	6.8
19	1-2	470	480	3.39	2.6	6.7
20	1-2	472	476	4.45	2.5	6.6

7. CONCLUSION

The experimental studies have shown that New Brunswick oil shales can be pyrolyzed in a spouted bed reactor. At optimum pyrolysis temperature, shale particle sizes and feed rate, oil yields up to 94% of the Fischer Assay value were achieved.

The temperature effect was studied using two particle sizes: 1-2mm and 2-4mm. The optimum temperatures are around 457°C and 505°C respectively, and above this temperature the oil yields fall off.

Three particle size range were tested: 2-4mm, 1-2mm and 0.5-1mm. At a given feed rate and temperature, the oil yields increase with increasing mean particle size.

There is a marked decrease of oil yield with increasing shale feed rate in beds of sand. The hot spent shale which accumulates in the reactor appears to act as a sorbent for oil or a surface for the secondary oil-consuming reactions. Results of a series of experiments at fixed feed rate show that as the ratio of spent shale to sand in the initial bed increases, the oil yields decrease. For experiments in which the bed initially consisted only of spent shale, the oil yields remained at a constant low value regardless of the feed rate, over the range tested.

All the experiments were done using 15% CO_2 and 85%N_2 as pyrolyzing gas except for two experiments where N_2 was used alone. For the latter two runs, the oil yields decreased by 50%. No logical explanation for this result is

apparent, and some confirmation of this result is required.

Gas species produced in the pyrolysis are H_2, CH_4, C_2H_4, C_2H_6, C_3H_8 and C_4H_{10}. Carbon dioxide is not produced in the temperature range studied. The yields do not seem to be affected by shale particle sizes, feed rate and bed material. The reported gas yields were generally lower than the Fischer Assay values although for many runs the analytical equipment available did not detect hydrocarbons heavier than methane.

There is a substantial loss of shale which is entrained in the gases and passes through the cyclone. Due to the low percentage recovery, trends of the spent shale yield were not reliable.

A kinetic model which involves release of bitumen from the shale kerogen, and the subsequent decomposition of bitumen into oil accounts for the basic trends of the experimental results.

8. RECOMMENDATIONS FOR FUTURE WORK

As mentioned in the previous Sections 4 and 5, there are a few areas that need further studies. Modifications to the equipment and future work include:

1) An electrostatic precipitator should be installed downstream to enable better collection of oil from the pyrolysis of oil shale.
2) A more efficient cyclone should be used in order to collect all the entrained particles so as to do a better study on the spent shale trend.
3) A higher gear ratio reducer is recommended for the feed system to enable a more constant feeding rate during the experiment.
4) Modifications are recommended to the fountain section of the reactor in order to catch the spent shale ash to enable experiments to be carried out without interference of the spent shale which act as a catalyst for oil degradation.
5) More pyrolysis experiments should be carried out at the lower temperature range, specifically at 380-450°C in order to permit a better comparison with the model developed in Section 3.2.
6) Attempts should be made to collect some data on kerogen and bitumen content so as to obtain a better correlated model as discussed in Section 6.
7) The effect of the spent shale should be included in the future development of the model.

8) A set of oil yield vs temperature experiments should be carried out for the 0.5-1mm oil shale particle size so as to obtain the optimum temperature and compare the optimum oil yield with the Fischer Assay value.

NOMENCLATURE

A	Oil mass, kg
A_p	Surface area of particles, m^2
B	Bitumen mass, kg
Bi_H	Heat transfer Biot number, $h_p r_p / k_p$
C	Concentration of pyrolysable mass, kg/kg
C_i	Carbonaceous mass, kg
C_A	Concentration of oil, kg/kg
C_B	Concentration of bitumen, kg/kg
C_K	Concentration of kerogen, kg/kg
Cp_f	Heat capacity of fluid, KJ/kg·K
Cp_p	Heat capacity of particle, KJ/kg·K
Cp_s	Heat capacity of oil shale, KJ/kg·K
E	Activation energy, KJ/mol
f_1	Weight fraction of kerogen that yields bitumen
f_2	Weight fraction of bitumen that yields oil
f_3	Weight fraction of kerogen that yields gas
f_4	Weight fraction of bitumen that yields gas
F_0	Mass feed rate of oil shale, kg/s
F_1	Mass flow rate of entrained particles, kg/s
F_2	Mass flow rate of oil shale in the side line, kg/s
$F_{g,in}$	Spouting gas flow rate, m^3/s
Fo_H	Fourier number, $\alpha t / r_p^2$
G_i	Gas mass, kg

h_p	Heat transfer coefficient between fluid and particle, $J/m^2 \cdot s \cdot K$
ΔH_{rxn}	Heat of pyrolysis (assumed to be zero)
k_f	Thermal conductivity of fluid, $J/m \cdot s \cdot K$
k_p	Thermal conductivity of solid particle, $J/m \cdot s \cdot K$
K	Kerogen mass, kg
k_1	Frequency factor for kerogen, 1/s
k_2	Frequency factor for bitumen, 1/s
k_3	Frequency factor for oil, 1/s
k_1	Rate constant for kerogen, 1/s
k_2	Rate constant for bitumen, 1/s
k_3	Rate constant for oil, 1/s
M_p	Mass of a particle, kg
Nu	Nusselt number, $h_p d_p / k_f$
Pr	Prantl number, $Cp_f \mu / k_f$
Q_R	Heat transfer rate at particle surface, J/s
r	Radius, m
r_p	Radius of particle, m
r_K	Overall rate of Kerogen production, 1/s
r_B	Overall rate of Bitumen production, 1/s
r_A	Overall rate of Oil production, 1/s
R	Gas rate constant, 8.3143J/mol·K
Re	Reynold number, $d_p u_p \rho_f / \mu$

t	Time, s
t_o	Initial time, s
T	Temperature, K
T_b	Bulk bed solid temperature, K
T_c	Temperature of shrinking core surface, K
T_g	Temperature of gas, K
T_p	Temperature of particle, K
T_R	Temperature of particle surface, K
T_s	Internal particle temperature, K
T_w	Wall or heater temperature, K
V	Volume of the vapor reaction zone, m^3
V_p	Particle volume, m^3
W	Weight of spent shale in bed, kg
w_o	Initial weight of particle, kg
w_t	Weight of particle at time t, kg
w_a	Final weight of particle, kg
a	Thermal diffusivity of particle, $k_p/(\rho_s \cdot Cp_p)$, m^2/s
ϵ_v	Voidage
ϵ	Effective emmissivity (0.9)
μ	Viscosity of fluid, g/cm·s
ρ_s	Average density of oil shale, g/m^3
σ	Stefan-Boltzmann constant, 5.673×10^{-12} $J/cm^2 \cdot s \cdot K^4$

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APPENDIX A

Temperature History Model

The heat transfer in a spouted bed has been discussed in Section 2.6. It is shown that the particle temperature profile is governed by the unsteady state diffusion equation,

$$\frac{\partial T}{\partial t} = \frac{a}{r^2} \frac{\partial (r^2 \partial T/\partial r)}{\partial r} \qquad (2.4)$$

with the boundary condition for r=R,

$$K_p(\partial T/\partial r)_{r=rp} = h_p(T_b - T_{r=rp}) \qquad (2.5)$$

From equation 2.4, the temperature profile of a particle as a function of time can be estimated along the longtitude height of the 4 regions of a spouted bed: the spout, fountain (upward), fountain (downward) and annulus. The sketch of the different regions are shown in Figure 4. The equation can be written as a tridiagonal matrix. The radius of the particle is divided into 10 sections with $r(1)=r_c$, ie. the centre of the particle, and r(10)=R, ie. the surface of the particle, and the longtitude height of the bed is also equally divided into 10 sections, thus forming a matrix of 10 x 10.

To put the equation in a matrix form, equation 2.4 has to be differentiated and put into finite series form,

$$\frac{a}{r^2}\left(2r\frac{\partial T}{\partial r} + r^2\frac{\partial^2 T}{\partial r^2}\right) = \frac{\partial T}{\partial t} \qquad (A.1)$$

$$\frac{2a\partial T}{r\partial r} + a\frac{\partial^2 T}{\partial r^2} = \frac{\partial T}{\partial t} \qquad (A.2)$$

where

$$\frac{\partial T}{\partial r} = \frac{T_{n+1,t} - T_{n-1,t}}{2\Delta r} \qquad (A.3)$$

$$\frac{\partial^2 T}{\partial r^2} = \frac{T_{n+1,t} - 2T_{n,t} + T_{n-1,t}}{\Delta r^2} \qquad (A.4)$$

$$\frac{\partial T}{\partial t} = \frac{T_{n,t} - T_{n,t-1}}{\Delta t} \qquad (A.5)$$

therefore equation (A.2) becomes,

$$\frac{2a}{r}\left(\frac{T_{n+1,t} - T_{n-1,t}}{2\Delta r}\right) + a\left(\frac{T_{n+1,t} - 2T_{n,t} + T_{n-1,t}}{\Delta r^2}\right)$$

$$= \frac{T_{n,t} - T_{n,t-1}}{\Delta t} \qquad (A.6)$$

Rearranging equation (A.6) gives,

$$\left(-\frac{a}{r\Delta r}+\frac{a}{\Delta r^2}\right)T_{n-1,t}+\left(-\frac{2a}{\Delta r^2}-\frac{1}{\Delta t}\right)T_{n,t}+\left(\frac{a}{r\Delta r}+\frac{a}{\Delta r^2}\right)T_{n+1,t}$$

$$=-\frac{T_{n,t-1}}{\Delta t} \qquad (A.7)$$

At the boundary condition when $r=r_c=0$,

then (A.2) becomes,

$$3a\frac{\partial^2 T}{\partial r^2}=\frac{\partial T}{\partial r} \qquad (A.8)$$

$$3a\left(\frac{T_{n+1,t}-2T_{n,t}+T_{n-1,t}}{\Delta r^2}\right)=\frac{T_{n,t}-T_{n,t-1}}{\Delta t} \qquad (A.9)$$

$$\frac{3a}{\Delta r^2}T_{n-1,t}+\left(-\frac{6a}{\Delta r^2}-\frac{1}{\Delta t}\right)T_{n,t}+\frac{3a}{\Delta r^2}T_{n+1,t}$$

$$=-\frac{T_{n,t-1}}{\Delta t} \qquad (A.10)$$

The boundary condition at r=0 is $\frac{\partial T}{\partial r}=0$ (A.11)

$$\left(\frac{T_{n+1,t}-T_{n-1,t}}{2\Delta r}\right)=0 \qquad (A.12)$$

or $T_{n+1,t}=T_{n-1,t}$ (A.13)

Therefore,

$$(-\frac{6a}{\Delta r^2}-\frac{1}{\Delta t})T_{n,t}+\frac{6a}{\Delta r^2}T_{n+1,t}=-\frac{T_{n,t-1}}{\Delta t} \qquad (A.14)$$

The boundary condition at r=R is

$$\frac{\partial T}{\partial r}=\frac{h_p}{k_p}(T_g-T) \qquad (A.15)$$

$$\text{or} \quad \frac{T_{n+1,t}-T_{n-1,t}}{2\Delta r}=\frac{h_p}{k_p}(T_g-T_{n,t}) \qquad (A.16)$$

$$T_{n+1,t}=T_{n-1,t}+2\,r\frac{h_p}{k_p}(T_g-T_{n,t}) \qquad (A.17)$$

Substituting the result into the general form of the (A.7) yields:

$$(-\frac{a}{r\Delta r}+\frac{a}{\Delta r^2})T_{n-1,t}+(-\frac{2a}{\Delta r^2}-\frac{1}{\Delta t})\,T_{n,t}$$

$$+(\frac{a}{r\Delta r}+\frac{a}{\Delta r^2})[T_{n-1,t}+\frac{2\Delta r h_p}{k_p}(T_g-T_{n,t})]=-\frac{T_{n,t-1}}{\Delta t}$$

(A.18)

$$\text{or } \frac{2a}{\Delta r^2}T_{n-1,t} + \left[-\frac{2a}{\Delta r^2} - \frac{1}{\Delta t} - \frac{2\Delta r h_p}{k_p}\left(\frac{a}{r\Delta r} + \frac{a}{\Delta r^2}\right)\right]T_{n,t}$$

$$= -\frac{T_{n,t-1}}{\Delta t} - \frac{2\Delta r h_p}{k_p}\left(\frac{a}{r\Delta r} + \frac{a}{\Delta r^2}\right) T_g \qquad \text{(A.19)}$$

The coordinates of the matrix are listed in table 29.

A library program TRISLV is used to solve the tridiagonal equations. Table 30 lists the correlations used for estimation of the hydrodynamic properties for the spouted bed. There are a few assumptions made:

1) The velocity of the particle at the apex of the spouted bed is assumed to be zero.
2) The particle at the apex of the spouted bed is assumed to be at room temperature, 298°K, ie. the inlet temperature effect on the particle is ignored.
3) The calculation of the hydrodynamic properties of the spouted bed is based on sand as spouting media. The oil shale particle is assumed to follow the flow pattern of the sand.
4) The reactor temperature is assumed to be constant. There is assumed to be no heat loss to the surroundings.

Table 29: Coordinates of the Tridiagonal Matrix of spouted bed

$$b_1 = -\frac{2a}{\Delta r^2} - \frac{1}{\Delta t}$$

$$c_1 = \frac{2a}{\Delta r^2}$$

$$d_1 = -\frac{T_{n,t-1}}{\Delta t}$$

$$a_i = \frac{a}{\Delta r^2} - \frac{a}{r\Delta r}$$

$$b_i = -\frac{2a}{\Delta r^2} - \frac{1}{\Delta t}$$

$$c_i = \frac{a}{r\Delta r} + \frac{a}{\Delta r^2}$$

$$d_i = -\frac{T_{n,t-1}}{\Delta t}$$

$$a_n = \frac{2a}{\Delta r^2}$$

$$b_n = -\frac{2ah_p}{rk_p} - \frac{2ah_p\Delta r}{\Delta r^2 k_p} - \frac{2}{\Delta r^2} - \frac{1}{\Delta t}$$

$$d_n = -\frac{2ah_pT_g}{rk_p} - \frac{2ah_pT_g}{drk_p} - \frac{T_{n,t-1}}{\Delta t}$$

Table 30: Correlations used to estimate the hydrodynamic properties of spouted bed

		Reference
H_m	$0.105(\frac{D_c}{D_p})^{0.75}(\frac{D_c}{D_i})^{0.4}(\frac{D_c}{\rho_p^{1/2}})$	(9)
u_{ms}	$(\frac{D_p}{D_c})(\frac{D_i}{D_c})^{1/3}(\frac{2gHH(\rho_p-\rho_g)}{\rho_g})^{0.5}$	(9)
D_s	$0.118(G)^{0.89}(D_c)^{0.68}$	(9)
u_{mf}	$0.5(\mu bf + \mu tf)$	(10)
u_{bf}	$\frac{nebf \cdot \mu}{D_p \rho_g}$	
nebf	$\frac{netf \cdot \mu}{D_p \rho_g}$	(10)
μtf	$[18.1^2 + 0.0192(\frac{D_p^3 \rho_g(\rho p-\rho_g)g}{\mu^2})]^{1/2} - 18.1$	
netf	$[24.0^2 + 0.0546(\frac{D_p^3 \rho_g(\rho p-\rho_g)g}{\mu^2})]^{1/2} - 24.0$	(10)
H_f	$\frac{(E_o^{1.46})(Vp_{max})^2(\rho_s)}{2g\ (\rho_s-\rho_g)}$	(12)
V_t (spout)	$\frac{(0.3)(0.2)(V_{max})DIS\ J}{(1-0.2)\qquad HH}$	
V_p (fountain)	$[\frac{V_{max}^2 - 2g(DISJ)(\rho p-\rho_g)}{E_o^{1.46}\rho_p}]^{0.5}$	
V_p (falling)	$[\frac{2g(\rho_p-\rho_g)}{E_o^{1.46}\rho_p} \cdot (H - DISJ)]^{0.5}$	

5) The oil shale particle is assumed to be a perfect spherical particle.

The computer program consists of three sections. Section 1 specifies all the data and information of the spouted bed reactor, the properties of sand (spouting media), oil shale and spouting gas. It also calculates the hydrodynamic properties for the spouted bed. Section 2 of the program calls the subroutine Temp2 to Temp5 to calculate and print out the solutions. Section 3 of the program stores all the subroutines. The calculations were done on three average oil shale sizes: 3mm, 1.5mm and 0.75mm; and three reactor temperatures: 450, 500 and 550°C. Other profiles can be obtained by simply changing the data information in line 44, 45 and 46 of the program.

APPENDIX B

B.1 Calculations for Isokinetic Gas Sampling

Isokinetic sampling means that the velocities of the gases in the main pipe is the same as the velocities of gases in the sampling tube. To ensure this, the volumetric flow rate of the gas in the main pipe is first estimated, and the volumetric flow rate of the sample is then calculated and adjusted to the temperature of the sampling gas rotameter. A sample calculation for Run #2 is shown as below:

Oil shale particle size = 0.5-1.0mm

Temperature of the reactor = 501°C

Temperature of the sampling tube = 400°C

Mass flow rate of spouting gas = 4.95g/s

Mass flow rate of oil shale (as received) = 0.369g/s

Mass flow rate of oil shale (MAF) = 0.095g/s

Water vapor and gas expected to evolve from oil shale = 0.019g/s

Total mass flow rate of gases = 4.969g/s

It can be seen that the spouting gas accounts for 99% of the gases, hence the mass flow rate and density of spouting gas are used for the purpose of this calculation.

Density of spouting gas at 501°C = 0.0004793g/cm^3

Volumetric flow rate of gases = 10367.20cm^3/s

Main pipe flow rate = 23.58cm^2

Velocity of the spouting gas = 439.66cm/s

Sampling tube cross-sectional area = $0.7cm^2$

Volumetric flow rate of sample gas, 500°C = $307.76cm^3/s$

Volumetric flow rate of sample gas, 21°C = $117.0cm^3/s$

Hence the sample gas rotameter setting is adjusted accordlingly.

B.2 Product Yield Calculation

The procedure used to calculate oil, gas and spent shale yields is outlined as below, and a simple computer program is written for this purpose.

$$\text{Oil Yield: } \frac{\text{oil}}{\text{Feed}} \times 100\%$$

$$\text{Spent Shale Yield: } \frac{\text{spent}}{\text{Feed}} \times 100\%$$

$$\text{Total Gas Yield: } \frac{TG - SG}{\text{Feed}} \times 100\%$$

TG = Total gas output, g/s

SG = Mass flow rate of spouting gas, g/s

APPENDIX C

Computer Programmes

C.1 Profile

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
      C ***************************************************************
      C                                                               *
      C    NAME OF THIS PROGRAM: PROFILE                              *
      C                                                               *
      C                                                               *
      C    THIS PROGRAM IS USED TO WORK OUT THE TEMPERATURE HISTORY OF *
      C    AN OIL SHALE PARTICLE IN THE 5 REGIONS OF A SPOUTED BED:   *
      C    1) SPOUT REGION                                            *
      C    2) FOUNTAIN REGION                                         *
      C    3) FALLING REGION                                          *
      C    4) ANNULLUS REGION                                         *
      C                                                               *
      C    THIS PROGRAM IS CONSISTED OF 3 SECTIONS:                   *
      C    SECTION 1) SPECIFIES ALL THE INFORMATION OF THE SPOUTED BED *
      C               BED REACTOR, PROPERTIES OF SAND (SPOUTING MEDIA)*
      C               AND PROPERTIES OF OIL SHALE.  IT ALSO WORKS OUT *
      C               THE HYDRODYNAMIC PROPERTIES (HM, UMS, UMF ETC)  *
      C               FOR THE SPOUTED BED                             *
      C                                                               *
      C    SECTION 2) CALLS THE SUBROUTINE TEMP2, TEMP3, TEMP4 AND    *
      C               TEMP5 TO CALCULATE AND PRINT OUT THE TEMPERATURE*
      C               HISTORY FOR THE OIL SHALE AT A GIVEN SIZE AND   *
      C               REACTOR TEMPERATURE                             *
      C                                                               *
      C    SECTION 3) STORES ALL THE SUBROUTINE TEMP2 TO TEMP5        *
      C                                                               *
      C ***************************************************************
      C
      C
            IMPLICIT REAL*8 (A-H,O-Z)
      C
            DIMENSION DP(3),TEMPG(3),TERM(3)
            DIMENSION BIOT2(20),BIOT3(20),BIOT4(20),BIOT5(20)
            DIMENSION DIS1(20), DIS2(20), DIS3(20), DIS4(20), DIS5(20)
            DIMENSION DTIME1(20),DTIME2(20),DTIME3(20),DTIME4(20)
            DIMENSION DTIME5(20)
            DIMENSION HP2(20),HP3(20),HP4(20),HP5(20)
            DIMENSION R1(20),R2(20),R3(20),R4(20),R5(20)
            DIMENSION T1(20,20),T2(20,20),T3(20,20),T4(20,20),T5(20,20)
            DIMENSION UP2(20),UP3(20),UP4(20),UP5(20)
      C
            REAL KP,KPP,NU
      C
      C     READ DATA
      C
            DATA DP/0.3D0,0.15D0,0.075D0/
            DATA TERM/567.96D0,784.35D0,355.2D0/
            DATA TEMPG/723.D0,823.D0,773.D0/
      C
      C     USE DO-LOOP TO ESTIMATE THE TEMPERATURE PROFILE
      C     FOR 3 DIFFERENT SIZES AT DIFFERENT TEMPERATURES
      C
      C       DO 9999 MM=1,3
                 TG=TEMPG(3)
      C        DO 999 M=1,3
                 DIA=DP(3)
                 UT=TERM(3)
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
      C
      C
      C ***************************************************************
      C                                                               *
      C     SECTION 1) SPECIFY THE BASIC INFORMATIN OF THE SPOUTED BED *
      C                REACTOR, SAND PARTICLES, OIL SHALE AND SPOUTING GAS *
      C                                                               *
      C ***************************************************************
      C
      C     INFORMATION OF THE SPOUTED BED REACTOR
      C
            DI=1.58DO
            DC=12.8DO
            DPIPE=1.58DO
            HPIPE=17.8DO
            APIPE=3.1416DO*(DPIPE**2.DO)/4.DO
            HH=33.DO
            ACOL=3.1416DO*(DC**2.DO)/4.DO
            ES=0.95DO
            EA=0.42DO
            EO=0.7DO
      C
      C     PROPERTIES OF THE SAND PARTICLES
      C
            DPS=0.1121DO
            RRS=DPS/2.DO
            DENS=2.68DO
      C
      C     PROPERTIES OF THE OIL SHALE
      C
            RR=DIA/2.DO
            DEN=2.DO
            KPP=1.25D-2/4.186DO
            CPP=1.13DO/4.186DO
      C
      C     PROPERTIES OF GAS
      C
            CP=(6.76DO+((0.606D-3)*TG)+((0.13D-6)*(TG**2.DO)))/28.DO
            DENG=1.DO*((28.0DO*0.85DO)+(44.0DO*0.15DO))/82.05DO/TG
            KP=0.0001257DO
            VIS=0.00033DO
      C
      C     FURTHER INFORMATION
      C     THE FOLLOWING DATA ARE TAKEN FROM STANELY WU'S THESIS
      C
            DIS5(1)=33.DO
            DIS5(2)=32.DO
            DIS5(3)=25.DO
            DIS5(4)=20.DO
            DIS5(5)=15.DO
            DIS5(6)=10.DO
            DIS5(7)=5.DO
      C
            UP5(2)=1.335DO
            UP5(3)=1.289DO
            UP5(4)=1.188DO
            UP5(5)=1.059DO
            UP5(6)=2.176DO
```

```
Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

      UP5(7)=0.838D0
C
C     TO CALCULATE THE HYDRODYNAMIC PROPERTIES OF THE SPOUTED BED
C     BASED ON SAND AS SPOUTING MEDIA
C
C     TO CALCULATE MAXIMUM SPOUTABLE BED HEIGHT, HM
C
      HM=0.105D0*((DC/DPS)**0.75D0)*((DC/DI)**0.4D0)*DC/(DENS**1.2D0)
C
C     TO CALCULATE MINIMUM SPOUTING VELOCITY, UMS
C
      UMS=(DPS/DC)*((DI/DC)**(1.D0/3.D0))*((2.D0*980.D0*HH*
     &     (DENS-DENG)/DENG)**(1.D0/2.D0))
      U=1.1D0*UMS
      Q=U*ACOL
C
C     TO CALCULATE THE DIAMETER OF SPOUT, DS
C
      EMF=0.5D0
      DENB=DENS*(1.D0-EMF)
      G=DENG*U
      DS=(0.118D0*((G*10.D0)**0.49D0)*((DC/100.D0)**0.68D0)/
     &    (DENB**0.41D0))*100.D0
      AS=3.1416D0*(DS**2.D0)/4.D0
C
C     TO CALCULATE MINIMUM FLUIDISATION VELOCITY, UMF
C
      CONST=(DPS**3.D0)*(DENG*(DENS-DENG)*980.D0)/(VIS**2.D0)
      NEBF=(((18.1D0**2.D0)+(0.0192D0*CONST))**0.5D0)-18.1D0
      UBF=NEBF*VIS/DPS/DENG
      NETF=(((24.D0**2.D0)+(0.0546D0*CONST))**0.5D0)-24.D0
      UTF=NETF*VIS/DPS/DENG
      UMF=0.5D0*(UBF+UTF)
C
      WRITE(6,991)DIA
 991  FORMAT(1H1,/,'DIA OF OIL SHALE PARTICLE =',F6.4,'CM')
      WRITE(6,992)UMS
 992  FORMAT(//,'MIN SPOUTING VELOCITY =',F8.4,'CM/SEC')
      WRITE(6,993)U
 993  FORMAT(//,'SPOUTING VELOCITY =',F8.4,'CM/SEC')
      WRITE(6,994)HM
 994  FORMAT(//,'MAX SPOUTABLE HEIGHT =',F7.4,'CM')
      WRITE(6,995)DS
 995  FORMAT(//,'DIAMETER OF SPOUT =',F6.4,'CM')
      WRITE(6,996)TG
 996  FORMAT(//,'REACTOR TEMPERATURE =',F7.3,'DEG K')
C
C
C ***************************************************************************
C                                                                           *
C    SECTION 2) CALL THE SUBROUTINES TO PERFORM THE CALCULATION AND         *
C               PRINT OUT THE RESULTS                                       *
C                                                                           *
C ***************************************************************************
C
C     INITIALISE ALL TEMPERATURES
C
        DO 111 I=1,10
```

```
Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

  167                T1(I,1)=771.900
167.011 C
  168       111    CONTINUE
  209       C
  210       C
  211       C ****************************************
  212       C                                        *
  213       C    CALL SUBROUTINE TEMP2 TO WORK OUT THE *
  214       C    TEMPERATURE PROFILE IN THE SPOUT      *
  215       C                                        *
  216       C ****************************************
  217       C
 217.2      C
 217.4             WRITE(6,606)CP
 217.6       606   FORMAT(//,F10.5)
 217.8      C
  218              CALL TEMP2(TG,DIA,CP,DENG,KP,VIS,RR,DEN,CPP,KPP,HH,ACOL,HM,Q,
  219           &  AS,ES,EA,T1,UMF,T2,DTIME2,DIS2,R2,UP2,TT2,HP2,BIOT2)
  220       C
  221       C     WRITE TITLE
  222       C
  223              WRITE(6,200)DIA
  224        200   FORMAT(1H1,'IN THE SPOUTING REGION FOR SIZE =',2X,F6.4,'CM')
  225       C
  226       C    WRITE OUT THE SOLUTIONS OF T2(I,J)
  227       C
  228              WRITE(6,201)
  229        201   FORMAT(//2X,'VEL CM/SEC',20X,'TEMP DEG K',28X,'HEIGHT CM',
  230           & 3X,'TIME',5X,'HP',4X,'BIOT NO')
  231       C
  232              DO 202 KK=1,10
  233              J=11-KK
  234              WRITE(6,203)UP2(J),(T2(I,J),I=1,10),DIS2(J),DTIME2(J),HP2(J),
  235           & BIOT2(J)
  236        203   FORMAT(//2X,F7.2,1X,10F6.1,2X,F6.3,2X,F7.5,2X,F7.4,2X,F5.2)
  237       C
  238        202   CONTINUE
  239       C
  240       C    WRITE OUT THE DELTA RADIUS FOR THE PARTICLE AT BOTTOM LINE
  241       C
  242              WRITE(6,204)(R2(I),I=1,10)
  243        204   FORMAT(//10X,10F6.3)
  244       C
  245       C    TO WRITE OUT THE SUB-TIME FOR PARTICLE TO REACH TOP LINE
  246       C    OF THE SPOUT
  247       C
  248              WRITE(6,205)TT2
  249        205   FORMAT(///,'SUB-TIME=',F8.4,'SEC')
  250       C
  251       C
  252       C ************************************************
  253       C                                               *
  254       C    CALL SUBROUTINE TEMP3 TO WORK OUT THE      *
  255       C    TEMPERATURE PROFILE IN THE FOUNTAIN REGION *
  256       C                                               *
  257       C ************************************************
  258       C
  259              CALL TEMP3(TG,DIA,DENG,KP,VIS,DENS,RR,DEN,CPP,KPP,U,UP2,T2,H,
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
      &  T3,DTIME3,DIS3,R3,UP3,TT3,HP3,BIOT3)
C
C     WRITE TITLE
C
        WRITE(6,300)DIA
 300    FORMAT(1H1,'IN THE FOUNTAIN REGION FOR SIZE=',2X,F6.4,'CM')
C
        WRITE(6,301)H
 301    FORMAT(//2X,'FOUNTAIN HEIGHT=',F6.3,'CM')
C
C     WRITE OUT THE SOLUTIONS OF T3(I,J)
C
        WRITE (6,302)
 302    FORMAT(//2X,'VEL CM/SEC',20X,'TEMP DEG K',28X,'HEIGHT CM',
     & 4X,'TIME',4X,'HP',4X,'BIOT NO')
C
        DO 303 KK=1,10
           J=11-KK
           WRITE(6,304)UP3(J),(T3(I,J),I=1,10),DIS3(J),DTIME3(J),
     &     HP3(J),BIOT3(J)
 304       FORMAT(//2X,F7.2,1X,10F6.1,2X,F6.3,2X,F6.4,2X,F7.5,2X,F5.2)
C
 303    CONTINUE
C
C     WRITE OUT THE DELTA RADIUS FOR THE PARTICLE AT BOTTOM LINE
C
        WRITE(6,305)(R3(I),I=1,10)
 305    FORMAT(//10X,10F6.3)
C
C     TO WRITE OUT SUB-TIME FOR PARTICLE TO REACH THE FOUNTAIN
C
        WRITE(6,306)TT3
 306    FORMAT(///,'SUB-TIME=',F6.4,'SEC')
C
C
C ********************************************************
C                                                        *
C      CALL SUBROUTINE TEMP4 TO WORK OUT THE             *
C      TEMPERATURE PROFILE IN THE FOUNTAIN FALLING REGION *
C                                                        *
C ********************************************************
C
C
        CALL TEMP4(TG,DENG,KP,VIS,DIA,DEN,CPP,KPP,DENS,H,EO,U,UP3,
     &  T3,T4,DTIME4,DIS4,R4,UP4,TT4,HP4,BIOT4)
C
C      WRITE TITLE
C
        WRITE(6,400)DIA
 400    FORMAT(1H1,'IN THE FALLING REGION FOR SIZE =',2X,F6.4,'CM')
C
        WRITE(6,401)
 401    FORMAT(//2X,'VEL CM/SEC',20X,'TEMP DEG K',28X,'HEIGHT CM',
     & 4X,'TIME',4X,'HP',4X,'BIOT NO')
C
C
        DO 402 KK=1,10
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
322                WRITE(6,403)UP4(KK),(T4(I,KK),I=1,10),DIS4(KK),DTIME4(KK),
323           &     HP4(KK),BIOT4(KK)
324            403      FORMAT(//2X,F7.2,1X,10F6.1,2X,F6.3,2X,F6.4,2X,F7.5,2X,
325           &     F5.2)
326          C
327            402   CONTINUE
328          C
329          C
330          C     WRITE OUT THE DELTA RADIUS FOR THE PARTICLE AT BOTTOM LINE
331          C
332                 WRITE(6,404)(R4(I),I=1,10)
333            404   FORMAT(//10X,10F6.3)
334          C
335          C     WRITE OUT SUB-TIME FOR PARTICLE TO DROP FROM FOUNTAIN
336          C
337                 WRITE(6,405)TT4
338            405   FORMAT(///,'SUB-TIME=',F6.4,'SEC')
339          C
340          C ******************************************************
341          C                                                     *
342          C    CALL SUBROUTINE TEMP5 TO WORK OUT THE TEMPERATURE *
343          C    PROFILE IN THE ANNULUS REGION                     *
344          C                                                     *
345          C ******************************************************
346          C
347                 CALL TEMP5(TG,DIA,DENG,KP,VIS,RR,DEN,CPP,KPP,HH,EA,ES,ACOL,AS,
348               &  UMF,HM,UP5,DIS5,T4,UP4,T5,DTIME5,R5,TT5,HP5,BIOT5)
349          C
350          C    WRITE TITLE
351          C
352                 WRITE(6,500)DIA
353            500   FORMAT(1H1,2X,'IN THE ANNULUS REGION FOR SIZE=',F6.4,'CM')
354          C
355                 WRITE(6,501)
356            501   FORMAT(//2X,'VEL CM/SEC',20X,'TEMP DEG K',28X,'HEIGHT CM',
357               & 4X,'TIME',4X,'HP',4X,'BIOT NO')
358          C
359                 DO 502 KK=1,7
360                    WRITE(6,503)UP5(KK),(T5(I,KK),I=1,10),DIS5(KK),DTIME5(KK),
361               &     HP5(KK),BIOT5(KK)
362            503      FORMAT(//2X,F7.2,1X,10F6.1,2X,F6.3,2X,F6.4,2X,F7.5,2X,
363               &     F5.2)
364          C
365            502   CONTINUE
366          C
367          C    WRITE OUT THE DELTA RADIUS FOR THE PARTICLE AT BOTTOM LINE
368          C
369                 WRITE(6,504)(R5(I),I=1,10)
370            504   FORMAT(//10X,10F6.3)
371          C
372          C    WRITE OUT TOTAL TIME FOR PARTICLE TO GO DOWN TO ANNULUS
373          C
374                 WRITE(6,505)TT5
375            505   FORMAT(///,'SUB-TIME=',F8.4,'SEC')
376          C
377          C    TO WORK OUT THE TOTAL TIME SPENT IN THE 5 REGIONS
378          C
379                 TIME=TT1+TT2+TT3+TT4+TT5
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
380             WRITE(6,600)TIME
381      600    FORMAT(///2X,'TOTAL TIME SPENT IN 5 REGIONS =',F8.4,'SEC')
382     C
383      999    CONTINUE
384     C
385      9999   CONTINUE
386             STOP
387             END
388     C
389     C ***************************************************************************
390     C                                                                           *
391     C     SECTION 3) STORE ALL THE SUBROUTINES                                  *
392     C                                                                           *
393     C ***************************************************************************
510     C
511     C
512     C **********************
513     C                       *
514     C     SUBROUTINE TEMP2  *
515     C                       *
516     C **********************
517     C
518     C
519               SUBROUTINE TEMP2(TG,DIA,CP,DENG,KP,VIS,RR,DEN,CPP,KPP,HH,ACOL,
520            &    HM,Q,AS,ES,EA,T1,UMF,T2,DTIME2,DIS2,R2,UP2,TT2,HP2,BIOT2)
521     C
522     C
523               IMPLICIT REAL*8 (A-H,O-Z)
524               DIMENSION A(100),B(100),C(100),D(100)
525               DIMENSION DTIME2(20),DIS2(20),R2(20),HP2(20),BIOT2(20)
526               DIMENSION T1(20,20),T2(20,20),UP2(20)
527               REAL KPP,NU,KP
528     C
529     C     SPECIFY CONDITIONS OF GRID
530     C
531               N=10
532               DR=RR/9.DO
533               DD=HH/9.DO
534               TT2=0.ODO
535               DTIME2(1)=0.ODO
536     C
537     C
538     C    INITIALISE ALL R(I)
539     C
540               DO 20 I=1,N
541      20          R2(I)=(I-1)*DR
542     C
543     C
544     C    INITIALISE ALL TEMPERATURES
545     C
546              DO 21 IK=1,10
547                 T2(IK,1)=T1(IK,1)
548      21      CONTINUE
549     C
550     C
551     C    WORK OUT THE VERTICAL DISTANCE
552     C
553               DO 22 I=1,11
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
  554      22       DIS2(I)=DD*(I-1)
  555     C
  556     C  TO WORK OUT SPOUTING VELOCITY AT THE TOP OF THE SPOUT, USH
  557     C
  558     C
  559           UA=UMF*(1.DO-((1.DO-(HH/HM))**3.DO))
  560           QA=UA*(ACOL-AS)
  561           QS=Q-QA
  562           USH=QS/AS/ES
  563     C
  564     C
  565     C   TO SET UP TRIDIAGONAL EQUATIONS TO SOLVE THE
  566     C   TEMPERATURE HISTORY FOR A SINGLE PARTICLE
  567     C
  568           DO 23 J=2,11
  569     C
  570     C
  571     C   TO WORK OUT THE UA AT EACH INTERVAL
  572     C
  573           IF (J .EQ. 11) GOTO 24
  574           UA=UMF*(1.DO-((1.DO-(DIS2(J)/HM))**3.DO))
  575           QA=UA*(ACOL-AS)
  576           QS=Q-QA
  577           US=QS/AS/ES
  578           UP2(J)=((0.3DO*0.2DO*USH)*(DIS2(J)/HH))/(1.DO-0.2DO)
  579           GOTO 25
  580      24   UA=UMF
  581           QA=UA*(ACOL-AS)
  582           US=QS/AS/ES
  583           UP2(J)=((0.3DO*0.2DO*USH)*(DIS2(J)/HH))/(1.DO-0.2DO)
  584      25   RV=DABS(US-UP2(J))
  585     C
  586     C   TO CALCULATE HP FOR THE OIL SHALE IN THE SPOUTING REGION
  587     C
  588           E=0.4DO
  589           RE=DIA*RV*DENG/VIS
  590           PR=CP*VIS/KP
  591           AA=2.DO/(1.DO-((1.DO-E)**(1.DO/3.DO)))
  592           BB=2.DO*E/3.DO
  593           NU=AA+BB*(PR**(1.DO/3.DO))*(RE**0.55DO)
  594           HP=NU*KP/2.DO/RR
  595           JJ=J-1
  596           HP2(JJ)=HP
  597           BIOT2(JJ)=HP*RR/KPP
  598     C
  599     C
  600           ALPHA=KPP/CPP/DEN
  601     C
  602     C   TO WORK OUT THE DT
  603     C
  604           DTIME2(J)=DD/UP2(J)
  605           TT2=TT2+DTIME2(J)
  606           DT=DTIME2(J)
  607           UP2(1)=0.ODO
  608     C
  609     C   SET COEFFICIENTS OF MATRICS
  610     C
  611     C   BOUNDARY CONDITION AT R=0
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
      C
            B(1)=-(6.DO*ALPHA/(DR**2.DO))-(1.DO/DT)
            C(1)=6.DO*ALPHA/(DR**2.DO)
      C
      C   BOUNDARY CONDITION AT R=N
      C
            A(N)=2.DO*ALPHA/(DR**2.DO)
            B(N)=(-1.DO/DT)-(2.DO*ALPHA*HP/R2(N)/KPP)-
           > (2.DO*ALPHA/(DR**2.DO))-(2.DO*ALPHA*HP/DR/KPP)
      C
      C   INITIALISE ALL VALUES OF A(I), B(I), AND C(I)
      C
            DO 26 IK=2,9
               A(IK)=(ALPHA/(DR**2.DO))-(ALPHA/R2(IK)/DR)
               B(IK)=(-2.DO*ALPHA/(DR**2.DO))-(1.DO/DT)
       26      C(IK)=(ALPHA/R2(IK)/DR)+(ALPHA/(DR**2.DO))
      C
               D(1)=-T2(1,J-1)/DT
                   DO 27 I=2,9
       27             D(I)=-T2(I,J-1)/DT
               D(N)=-(T2(N,J-1)/DT)-(2.DO*ALPHA*HP*TG/R2(N)/KPP)-
           >         (2.DO*ALPHA*HP*TG/DR/KPP)
      C
      C   CALL LIBRARY PROGRAMM TO SOLVE THE TRI-DIA EQNS
      C
            CALL TRISLV(N,A,B,C,D,O,&99)
      C
      C
      C   STORE THE SOLUTIONS T2(I,J)
      C
            DO 28 II=1,N
            T2(II,J)=D(II)
       28   CONTINUE
      C
       23   CONTINUE
      C
            GOTO 299
       99   WRITE(6,29)
       29   FORMAT(///2X,'ERROR MESSAGE')
       299  CONTINUE
      C
            RETURN
            END
      C
      C
      C *********************
      C                     *
      C    SUBROUTINE TEMP3 *
      C                     *
      C *********************
      C
      C
            SUBROUTINE TEMP3(TG,DIA,DENG,KP,VIS,DENS,RR,DEN,CPP,KPP,U,
           &  UP2,T2,H,T3,DTIME3,DIS3,R,UP3,TT3,HP3,BIOT3)
      C
            IMPLICIT REAL*8 (A-H,O-Z)
            DIMENSION A(100),B(100),C(100),D(100)
            DIMENSION BIOT3(20),DIS3(20),DTIME3(20),HP3(20),R(20)
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
      DIMENSION T2(20,20),T3(20,20),UP2(20),UP3(20)
      REAL KP,NU,KPP
C
C     TO CALCULATE THE HEIGHT OF FOUNTAIN REGION, H.
C
      UP3(1)=UP2(10)
      UP3(11)=0.0D0
      E0=0.7D0
      H=(E0**1.46D0)*(UP3(1)**2.D0)*DENS/(DENS-DENG)/2.D0/980.D0
C
C     TO WORK OUT THE TEMPERATURE OF DIFFERENT PARTICLE SIZE
C
C
C     SPECIFY CONDITIONS OF GRID
C
      N=10
      DR=RR/9.D0
      DD=H/9.D0
      TT3=0.0D0
      DTIME3(1)=0.0D0
C
C
C     INITIALISE ALL R(I)
C
      DO 30 I=1,N
   30    R(I)=(I-1)*DR
C
C
C     INTIALISE ALL TEMPERATURES
C
      DO 31 II=1,10
         T3(II,1)=T2(II,10)
   31 CONTINUE
C
C
C     WORK OUT THE VERTICL DISTANCE
C
      DO 32 I=1,11
   32    DIS3(I)=DD*(I-1)
C
C
C     TO SET UP TRIDIAGONAL EQUATIONS TO SOLVE THE TEMPERATURE
C     HISTORY FOR A SINGLE PARTICLE
C
      DO 33 J=2,11
C
C
      IF (J.EQ.11) GOTO 34
C
C     TO WORK OUT THE VELOCITY OF PARTICLE AT EACH INTERVAL IN
C     THE FOUNTAIN REGION
C
      UP3(J)=((UP3(1)**2.D0)-(2.D0*980.D0*DIS3(J)*(DENS-DENG)/DENS/
     >      (E0**1.46D0)))**0.5D0
C
C     TO WORK OUT THE DELTA TIME
C
      DTIME3(J)=DD/UP3(J-1)
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
728             TT3=TT3+DTIME3(J)
729             DT=DTIME3(J)
730       C
731        34   CONTINUE
732       C
733             RV=DABS(U-UP3(J))
734       C
735       C     TO CALCULATE HP FOR THE COAL PARTICLE IN FOUNTAIN REGION
736       C
737             RE=DIA*RV*DENG/VIS
738             NU=0.42D0+0.35D0*(RE**0.8D0)
739             HP=NU*KP/2.D0/RR
740             ALPHA=KPP/CPP/DEN
741             JJ=J-1
742             HP3(JJ)=HP
743             BIOT3(JJ)=HP*RR/KPP
744       C
745       C     SET COEFFICIENTS OF MATRICS
746       C
747       C     BOUNDARY CONDITION AT R=0
748       C
749               B(1)=-(6.D0*ALPHA/(DR**2.D0))-(1.D0/DT)
750               C(1)=6.D0*ALPHA/(DR**2.D0)
751       C
752       C
753       C     BOUNDARY CONDITION AT R=N
754       C
755               A(N)=2.D0*ALPHA/(DR**2.D0)
756               B(N)=(-1.D0/DT)-(2.D0*ALPHA*HP/R(N)/KPP)-
757            > (2.D0*ALPHA/(DR**2.D0))-(2.D0*ALPHA*HP/DR/KPP)
758       C
759       C     INITIALISE ALL VALUES OF A(I), B(I), C(I)
760       C
761               DO 35 IK=2,9
762                  A(IK)=(ALPHA/(DR**2.D0))-(ALPHA/R(IK)/DR)
763                  B(IK)=(-2.D0*ALPHA/(DR**2.D0))-(1.D0/DT)
764                  C(IK)=(ALPHA/R(IK)/DR)+(ALPHA/(DR**2.D0))
765        35    CONTINUE
766       C
767                D(1)=-T3(1,J-1)/DT
768       C
769               DO 36 I=2,9
770                  D(I)=-T3(I,J-1)/DT
771        36    CONTINUE
772       C
773       C
774               D(N)=-(T3(N,J-1)/DT)-(2.D0*ALPHA*HP*TG/R(N)/KPP)-
775            >       (2.D0*ALPHA*HP*TG/DR/KPP)
776       C
777       C
778       C     CALL LIBRARY PROGRAM TO SOLVE THE TRI-DIA EQUATIONS
779       C
780               CALL TRISLV(N,A,B,C,D,O,&99)
781       C
782       C
783       C     STORE THE SOLUTIONS T3(I,J)
784       C
785               DO 37 II=1,N
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
786                T3(II,J)=D(II)
787       37     CONTINUE
788      C
789       33     CONTINUE
790      C
791      C
792              GOTO 39
793       99     WRITE(6,38)
794       38     FORMAT(///2X,'ERROR MESSAGE')
795      C
796       39     RETURN
797              END
798      C
799      C
800      C
801      C **********************
802      C                       *
803      C     SUBROUTINE TEMP4  *
804      C                       *
805      C **********************
806      C
807      C
808              SUBROUTINE TEMP4(TG,DENG,KP,VIS,DIA,DEN,CPP,KPP,DENS,H,EO,U,
809             &  UP3,T3,T4,DTIME4,DIS4,R,UP4,TT4,HP4,BIOT4)
810      C
811              IMPLICIT REAL*8 (A-H,O-Z)
812              DIMENSION A(100),B(100),C(100),D(100)
813              DIMENSION BIOT4(20),DIS4(20),DTIME4(20),HP4(20),R(20)
814              DIMENSION T3(20,20),T4(20,20),UP3(20),UP4(20)
815              REAL NU,KP,KPP
816      C
817      C       SPECIFY CONDITIONS OF OIL SHALE
818      C
819               RR=DIA/2.DO
820               DEN=2.ODO
821               KPP=1.25D-2/4.186DO
822      C
823      C       SPECIFY CONDITION OF GRID
824      C
825               N=10
826               DR=RR/9.DO
827               DD=H/9.DO
828               TT4=O.ODO
829               DTIME4(1)=O.ODO
830               UP4(1)=O.ODO
831      C
832      C       INITIALISE ALL R(I)
833      C
834               DO 40 I=1,N
835       40       R(I)=(I-1)*DR
836      C
837      C
838      C       INITIALISE ALL TEMPERATURES
839      C
840               DO 41 II=1,10
841       41       T4(II,1)=T3(II,10)
842      C
843      C
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCId=TITA

```
      C     WORK OUT THE VERTICAL DISTANCE
      C
            DO 42 I=1,11
       42    DIS4(I)=DD*(I-1)
      C
      C
      C     TO SET UP TRIDIAGONAL EQUATIONS TO SOLVE THE TEMPERATURE
      C      HISTORY FOR A SINGLE PARTICLE
      C
            DO 43 J=2,11
      C
      C     TO WORK OUT THE VELOCITY OF PARTICLE AT EACH INTERVAL
      C      OF THE FALLING REGION
      C
            IF (J .EQ. 11) GOTO 44
      C
            UP4(J)=((2.DO*980.DO*(DENS-DENG)/DENS/(E0**1.46DO))*
     &         (H-DIS4(11-J)))**0.5DO
      C
       44   UP4(11)=UP3(1)
      C
      C
      C     TO WORK OUT THE DELTA TIME
      C
            DTIME4(J)=DD/UP4(J)
            TT4=TT4+DTIME4(J)
            DT=DTIME4(J)
      C
      C
      C     TO CALCULATE HP FOR THE OIL SHALE IN THE FALLING REGION
      C
            RV=DABS(U-UP4(J))
            RE=DIA*RV*DENG/VIS
            NU=0.42DO+0.35DO*(RE**0.8DO)
            HP=NU*KP/2.DO/RR
            ALPHA=KPP/CPP/DEN
            JJ=J-1
            HP4(JJ)=HP
            BIOT4(JJ)=HP*RR/KPP
      C
      C     SET COEFFICIENTS OF MATRICS
      C
      C     BOUNDARY CONDITION AT R=0
      C
            B(1)=-(6.DO*ALPHA/(DR**2.DO))-(1.DO/DT)
            C(1)=6.DO*ALPHA/(DR**2.DO)
      C
      C
      C     BOUNDARY CONDITION AT R=N
      C
            A(N)=2.DO*ALPHA/(DR**2.DO)
            B(N)=(-1.DO/DT)-(2.DO*ALPHA*HP/R(N)/KPP)-
     &   (2.DO*ALPHA/(DR**2.DO))-(2.DO*ALPHA*HP/DR/KPP)
      C
      C     INITIALISE ALL VALUES OF A(I),B(I),C(I)
      C
            DO 45 IK=2,9
               A(IK)=(ALPHA/(DR**2.DO))-(ALPHA/R(IK)/DR)
```

```
Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

898                B(IK)=(-2.DO*ALPHA/(DR**2.DO))-(1.DO/DT)
899                C(IK)=(ALPHA/R(IK)/DR)+(ALPHA/(DR**2.DO))
900       45     CONTINUE
901       C
902              D(1)=-T4(1,J-1)/DT
903              DO 46 I=2,9
904                 D(I)=-T4(I,J-1)/DT
905       46     CONTINUE
906       C
907       C
908              D(N)=-(T4(N,J-1)/DT)-(2.DO*ALPHA*HP*TG/R(N)/KPP)-
909            &  (2.DO*ALPHA*HP*TG/DR/KPP)
910       C
911       C      CALL LIBRARY PROGRAM TO SOLVE THE TRI-DIA EQUATIONS
912       C
913              CALL TRISLV(N,A,B,C,D,O,&99)
914       C
915       C      STORE THE SOLUTIONS T4(I,J)
916       C
917              DO 47 II=1,N
918                 T4(II,J)=D(II)
919       47     CONTINUE
920       C
921       43     CONTINUE
922       C
923       C
924              GOTO 49
925       99     WRITE(6,48)
926       48     FORMAT(///2X,'ERROR MESSAGE')
927       C
928       49     RETURN
929              END
930       C
931       C
932       C
933       C ********************
934       C                    *
935       C    SUBROUTINE TEMP5 *
936       C                    *
937       C ********************
938       C
939       C
940              SUBROUTINE TEMP5(TG,DIA,DENG,KP,VIS,RR,DEN,CPP,KPP,HH,EA,ES,
941            &  ACOL,AS,UMF,HM,UP5,DIS5,T4,UP4,T5,DTIME5,R,TT5,HP5,BIOT5)
942       C
943              IMPLICIT REAL*8 (A-H,O-Z)
944              DIMENSION A(100), B(100), C(100), D(100)
945              DIMENSION BIOT5(20),DIS5(20),DTIME5(20),HP5(20),R(20)
946              DIMENSION T4(20,20),T5(20,20),UP4(20),UP5(20)
947              REAL NU, KP, KPP
948       C
949       C
950       C      SPECIFY CONDITIONS OF GRID
951       C
952              N=10
953              DR=RR/9.DO
954              TT5=0.0DO
955              DTIME5(1)=0.0DO
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCid=TITA

```
      C
      C
      C     INITIALISE ALL R(I)
      C
            DO 50 I=1,N
               R(I)=(I-1)*DR
       50   CONTINUE
      C
      C
      C     INITIALISE ALL TEMPERATURE
      C
            DO 51 IK=1,10
               T5(IK,1)=T4(IK,10)
       51   CONTINUE
      C
      C     WORK OUT THE VERTICAL DISTANCE
      C
      C
      C    TO SET UP TRIDIAGONAL EQUATIONS TO SOLVE THE TEMPERATURE
      C    HISTORY FOR A SINGLE PARTICLE
      C
              DO 52 J=2,8
      C
      C    TO WORK OUT THE UA AT EACH INTERVAL
      C
              UP5(1)=UP4(10)
              UA=UMF*(1.D0-((1.D0-(DIS5(J-1)/HM)**3.D0)))
              QA=UA*(ACOL-AS)
              RV=DABS(UA-UP5(J-1))
      C
      C
      C    TO CALCULATE HP FOR THE OIL SHALE PARTICLE IN THE ANNULUS
      C
              RE=DIA*RV*DENG/VIS
              NU=0.42D0+0.35D0*(RE**0.8D0)
              HP=NU*KP/2.D0/RR
              JJ=J-1
              HP5(JJ)=HP
              BIOT5(JJ)=HP*RR/KPP
      C
              ALPHA=KPP/CPP/DEN
      C
      C    TO WORK OUT DT
      C
              IF (J .EQ. 8)GOTO 53
              DTIME5(J)=(DIS5(J-1)-DIS5(J))/UP5(J-1)
              TT5=TT5+DTIME5(J)
              DT=DTIME5(J)
       53   CONTINUE
      C
      C    TO SET COEFFICIENTS OF MATRICS
      C
      C    BOUNDARY CONDITION AT R=0
      C
              B(1)=-(6.D0*ALPHA/(DR**2.D0))-(1.D0/DT)
              C(1)=6.D0*ALPHA/(DR**2.D0)
      C
      C    BOUNDARY CONDTION AT R=N
```

Listing of PROFILE at 11:37:26 on MAY 28, 1987 for CCId=TITA

```
1014      C
1015              A(N)=2.DO*ALPHA/(DR**2.DO)
1016              B(N)=(-1.DO/DT)-(2.DO*ALPHA*HP/R(N)/KPP)-
1017           & (2.DO*ALPHA/(DR**2.DO))-(2.DO*ALPHA*HP/DR/KPP)
1018      C
1019      C     INITIALISE ALL VALUES OF A(I), B(I), AND C(I)
1020      C
1021              DO 54 IK=2,9
1022                 A(IK)=(ALPHA/(DR**2.DO))-(ALPHA/R(IK)/DR)
1023                 B(IK)=(-2.DO*ALPHA/(DR**2.DO))-(1.DO/DT)
1024       54        C(IK)=(ALPHA/R(IK)/DR)+(ALPHA/(DR**2.DO))
1025      C
1026                 D(1)=-T5(1,J-1)/DT
1027                     DO 55 I=2,9
1028       55               D(I)=-T5(I,J-1)/DT
1029                 D(N)=-(T5(N,J-1)/DT)-(2.DO*ALPHA*HP*TG/R(N)/KPP)-
1030           &           (2.DO*ALPHA*HP*TG/DR/KPP)
1031      C
1032      C
1033      C
1034      C     CALL LIBRARY PROGRAMM TO SOLVE THE TRI-DIA EQNS
1035      C
1036              CALL TRISLV(N,A,B,C,D,O,&99)
1037      C
1038              DO 56 II=1,N
1039              T5(II,J)=D(II)
1040       56     CONTINUE
1041      C
1042       52     CONTINUE
1043      C
1044              GOTO 58
1045       99     WRITE(6,57)
1046       57     FORMAT(///2X,'ERROR MESSAGE')
1047      C
1048       58     RETURN
1049              END
```

C.2 Entrance

Listing of ENTRANCE at 13:07:28 on JUN 11, 1987 for CCid=TITA

```
      C ******************************************************************
      C                                                                  *
      C     NAME: ENTRANCE                                               *
      C                                                                  *
      C     THIS PROGRAM IS USED TO ESTIMATE THE TEMPERATURE PROFILE     *
      C     FOR A PARTICLE IN THE ENTRANCE SECTION OF THE SPOUTED BED    *
      C                                                                  *
      C ******************************************************************

            IMPLICIT REAL*8 (A-H,O-Z)
            DIMENSION A(100),B(100),C(100)
            DIMENSION D(100), DTIME(100), DIS(100)
            DIMENSION R(100),T(100,100)
            DIMENSION DP(3),VELT(3),TEMPG(3)
            REAL KP,NU
      C
      C
      C     READ DATA
      C
            DATA DP/0.30D0,0.15D0,0.075D0/
            DATA VELT/567.9666D0, 784.358D0,355.02D0/
            DATA TEMPG/723.0D0,773.0D0,823.0D0/
      C
      C     TO WORK OUT THE TEMP PROFILE FOR TWO DIFFERENT GAS TEMPERATURE
      C
            DO 777 JJ=1,3

      C
      C
      C     SPECIFY CONDITIONS OF SPOUTING GAS
      C
            TG=TEMPG(JJ)
            KP=0.000150BD0
            DENG=1.D0*(28.D0*0.85D0 +44.D0*0.15D0)/82.05D0/TG
            VIS=0.00033D0
            CP=(6.76D0+((0.606D-3)*TG)+((0.13D-6)*(TG**2.D0)))/28.D0
      C
      C
      C     CONDITION OF SAND PARTICLE
      C
            DPS=0.11211D0
            RRS=DPS/2.D0
            DENS=2.68D0
      C
      C
      C     DATA ON THE REACTOR
      C
            DI=1.58D0
            DC=12.8D0
            HC=76.2D0
            ACOL=3.1416D0*(DC**2.D0)/4.D0
            HH=33.0D0
      C
      C
      C     DATA ON THE ENTRANCE REGION
      C
            DPIPE=1.58D0
            HPIPE=17.8D0
```

```
Listing of ENTRANCE at 13:07:28 on JUN 11, 1987 for CCid=TITA

     59              APIPE=3.1416D0*(DPIPE**2.D0)/4.D0
     60      C
     61      C     USE DO-LOOP TO ESTIMATE THE TEMPERATURE PROFILE
     62      C     FOR 3 DIFFERENT SIZES
     63      C
     64              DO 999 M=1,3
     65              DIA=DP(M)
     66              UT=VELT(M)
     67      C
     68      C
     69      C     WRITE TITLE
     70      C
     71              WRITE(6,101)DP(M)
     72        101   FORMAT(1H1,'IN THE ENTRANCE REGION FOR SIZE =',2X,F6.4,'CM')
     73              WRITE(6,111)TG
     74        111   FORMAT(//,1X,'THE TEMPERATURE OF THE GAS IS ',F6.1,' DEG K')
     75      C
     76      C
     77      C     SPECIFY CONDITIONS OF OIL SHALE PARTICLE
     78      C
     79              RR=DIA/2.D0
     80              DEN=2.0D0
     81              E=0.4D0
     82              KPP=1.25D-2/4.186D0
     83              CPP=1.13D0/4.186D0
     84      C
     85      C
     86      C     TO WORK OUT HM BASED ON SAND PROPERTIES
     87      C
     88              GEMA=1.
     89              HM=0.105D0*((DC/DPS)**0.75D0)*((DC/DI)**0.4D0)*DC/(DENS**1.2D0)
     90              WRITE(6,41)HM
     91        41    FORMAT(//'HM=',F8.4,'CM')
     92      C
     93      C     TO CALCULATE THE MINIMUM SPOUTING VELOCITY USING
     94      C       MARTHER GISHLER MODEL
     95      C
     96              UMS=(DPS/DC)*((DI/DC)**(1.D0/3.D0))*((2.D0*980.D0*HH*
     97             &       (DENS-DENG)/DENG) **(1.D0/2.D0))
     98              U=1.1D0*UMS
     99              Q=U*ACOL
    100              VEL=Q/APIPE
    101              V=VEL-UT
    102              RV=VEL-V
    103      C
    104      C
    105      C     TO CALCULATE HP FOR OIL SHALE PARTICLE
    106      C
    107              RE=DIA*RV*DENG/VIS
    108              PR=CP*VIS/KP
    109              AA=2.D0/(1.D0-((1.D0-E)**(1.D0/3.D0)))
    110              BB=2.D0*E/3.D0
    111      C
    112      C     IN THE ENTRANCE REGION
    113      C
    114              NU=2.D0+0.6D0*(RE**0.5D0)*(PR**(1.D0/3.D0))
    115              HP=NU*KP/2.D0/RR
    116              ALPHA=KPP/CPP/DEN
```

Listing of ENTRANCE at 13:07:28 on JUN 11, 1987 for CCid=TITA

```
      C
      C
      C     SPECIFY CONDITIONS OF GRID
      C
              N=10
              DR=RR/9.DO
              DT=HPIPE/9.DO/V
      C
      C
      C     SET ALL DELTA TIME
      C
                 DO 4 I=1,N
            4      DTIME(I)=DT*(I-1)
      C
      C
      C     INITIALISE ALL R(I)
      C
                 DO 5 I=1,N
            5       R(I)=(I-1)*DR
      C
      C
      C     INITIALISE ALL TEMPERATURES
      C
                 DO 10 I=1,N
           10       T(I,1)=298.DO
      C
      C
      C     WORK OUT THE VERTICAL DISTANCE
      C
              DO 6 I=1,N
            6     DIS(I)=V*DTIME(I)
      C
      C
      C     TO SET UP TRIDIAGONAL EQUATIONS TO SOLVE THE
      C     TEMPERATURE HISTORY FOR A SINGLE PARTICLE
      C
              DO 30 J=2,11
      C
      C
      C     SET COEFFICIENTS OF MATRICS
      C
      C     BOUNDARY CONDITION AT R=O
      C
                 B(1)=-(6.DO*ALPHA/(DR**2.DO))-(1.DO/DT)
                 C(1)=6.DO*ALPHA/(DR**2.DO)
      C
      C     BOUNDARY CONDITION AT R=N
      C
                 A(N)=2.DO*ALPHA/(DR**2.DO)
                 B(N)=(-1.DO/DT)-(2.DO*ALPHA*HP/R(N)/KP)-
            >   (2.DO*ALPHA/(DR**2.DO))-(2.DO*ALPHA*HP/DR/KP)
      C
      C
      C     INITIALISE ALL VALUES OF A(I), B(I) AND C(I)
      C
                 DO 20 IK=2,9
                    A(IK)=(ALPHA/(DR**2.DO))-(ALPHA/R(IK)/DR)
                    B(IK)=(-2.DO*ALPHA/(DR**2.DO))-(1.DO/DT)
```

Listing of ENTRANCE at 13:07:28 on JUN 11, 1987 for CCid=TITA

```
      20       C(IK)=(ALPHA/R(IK)/DR)+(ALPHA/(DR**2.DO))
C
                D(1)=-T(1,J-1)/DT
                    DO 40 I=2,9
      40              D(I)=-T(I,J-1)/DT
                D(N)=-(T(N,J-1)/DT)-(2.DO*ALPHA*HP*TG/R(N)/KP)-
     >               (2.DO*ALPHA*HP*TG/DR/KP)
C
C
C     CALL LIBRARY PROGRAM TO SOLVE THE TRI-DIA EQNS
C
        CALL TRISLV(N,A,B,C,D,O,&99)
C
C
C     STORE THE SOLUTIONS T(I,J)
C
          DO 50 II=1,N
          T(II,J)=D(II)
      50  CONTINUE
C
      30   CONTINUE
C       GO TO 500
C
      99  WRITE(6,103)
     103  FORMAT(//,'SOLUTIONS ARE')
     500  CONTINUE
C
C
C      WRITE OUT THE SOLUTIONS OF T(I,J)
C
          WRITE(6,301)
     301  FORMAT(//'SEC',20X,'TEMPERATURE DEG K',28X,' CM ')
C
          DO 200 KK=1,10
            J=11-KK
            WRITE(6,300)DTIME(J),(T(I,J),I=1,10),DIS(J)
     300    FORMAT(//1X,F5.4,2X,10F6.1,2X,F6.3)
C
     200  CONTINUE
C
C
C     WRITE OUT THE DELTA RADIUS FOR THE PARTICLE AT BOTTOM LINE
C
        WRITE(6,400)(R(I),I=1,10)
     400  FORMAT(//8X,10F6.3)
C
C
     999  CONTINUE
C
     777  CONTINUE
          STOP
          END
```

C.3 Calculate

Listing of CALCULATE at 14:22:12 on MAY 28, 1987 for CCid=TITA

```
      C ***************************************************************
      C                                                               *
      C    NAME OF THIS PROGRAM: CALCULATE                            *
      C                                                               *
      C    THIS PROGRAM IS USED TO CALCULATE THE DATA FOR ANALYSIS    *
      C    SECTION 1: TO CALCULATE OIL YIELD                          *
      C    SECTION 2: TO CALCULATE SPENT SHALE YIELD                  *
      C    SECTION 3: TO CALCULATE TOTAL GAS AND INDIVIDUAL GAS YIELDS *
      C                                                               *
      C ***************************************************************
      C
            REAL NF
      C
      C     READ DATA
      C
            SN=5.371
            CF=1801.5/80./60.
            FEED=
            WRITE(6,8)CF
        8   FORMAT(2X,'CF=',F7.4)
            CFMA=CF
            SG=0.158
            WRITE(6,333)CF
      333   FORMAT(2X,'CF',F7.4)
      C
      C ***************************************
      C                                       *
      C    SECTION 1: TO CALCULATE OIL YIELD  *
      C                                       *
      C ***************************************
      C
      C
            OYIELD=(OIL/FEED)*100.0
            WRITE(6,11)OYIELD
       11   FORMAT(/,'OIL YIELD=',F10.5)
      C
      C
      C ***********************************************
      C                                               *
      C    SECTION 2: TO CALCULATE SPENT SHALE YIELD  *
      C                                               *
      C ***********************************************
      C
            SYIELD=(SPENT/FEED)*100.0
            WRITE(6,22)SYIELD
       22   FORMAT(/,'SPENT SHALE YIELD=',F10.5)
      C
      C
      C ***************************************************************
      C                                                               *
      C    SECTION 3: TO CALCULATE TOTAL GAS AND INDIVIDUAL GAS YIELDS *
      C                                                               *
      C ***************************************************************
      C
      C     READ VOLUME PERCENTAGE OF INDIVIDUAL FROM GAS CHROMOTOGRAPH
      C
            VH2=0.03324
            VCO2=15.2390
```

Listing of CALCULATE at 14:22:12 on MAY 28, 1987 for CCid=TITA

```
      VO2=0.0000
      VN2=84.727
      VCH4=0.00
      VCO=0.0
C
C
      WRITE(6,1)
    1 FORMAT(1H1,21X,'H2',7X,'CO2',7X,'O2',8X,'N2',8X,'CH4',
     & 8X,'CO')
      WRITE(6,2)VH2,VCO2,VO2,VN2,VCH4,VCO
    2 FORMAT(//,2X,'VOL %',12X,6(F7.4,3X))
C
C     TO CORRECT FOR AIR LEAKED INTO THE SYSTEM
C
      AIR=VO2+(VO2*(0.79/0.21))
      COR=100./(100.-AIR)
C
      CVH=VH2*COR
      CVCO2=VCO2*COR
      CVN2=(VN2-(VO2*(0.79/0.21)))*COR
      CVCH4=VCH4*COR
      CVCO=VCO*COR
C
C     TO WRITE THE CORRECTED VOLUME PERCENTAGE OF INDIVIDUAL GAS
C
      WRITE(6,10)CVH,CVCO2,CVN2,CVCH4,CVCO
   10 FORMAT(/,2X,'CORRECTED VOL %',2X,2(F7.4,3X),10X,3(F7.4,3X))
C
C     TO CALCULATE WEIGHT PERCENTAGE FOR INDIVIDUAL GAS
C
      WH2=(2./82.07/293.)*CVH
      WCO2=(44./82.07/293.)*CVCO2
      WN2=(28./82.07/293.)*CVN2
      WCH4=(16./82.07/293.)*CVCH4
      WCO=(28./82.07/293.)*CVCO
      TW=WH2+WCO2+WN2+WCH4+WCO
C
C
      HF=100.*WH2/TW
      CO2F=100.*WCO2/TW
      NF=100.*WN2/TW
      CH4F=100.*WCH4/TW
      COF=100.*WCO/TW
C
C     TO WRITE THE WEIGHT PERCENTAGE OF INDIVIDUAL GAS
C
      WRITE(6,20)HF,CO2F,NF,CH4F,COF
   20 FORMAT(/,2X,'WEIGHT %',9X,2(F7.4,3X),10X,3(F7.4,3X))
      WRITE(6,30)TW
   30 FORMAT(/,2X,'TW=',F10.4)
C
C     WEIGHT FRACTION OF NITROGEN
C
      NF=(WN2+WCO2)/TW
      WRITE(6,7)NF
    7 FORMAT(2X,F10.5)
      TG=SN/NF
C
```

Listing of CALCULATE at 14:22:12 on MAY 28, 1987 for CCid=TITA

```
      C
      C     GAS PRODUCED DUE TO PYROLYSIS
      C
              PGAS=TG-SN
              WRITE (6,11)TG,PGAS
       11     FORMAT(2X,F10.5,5X,F10.5)
      C
      C     GAS YIELD
      C
              YIELD=100.*(TG-SN)/CFMA
      C
              WRITE(6,21)YIELD
       21     FORMAT(2X,'TOTAL YIELD OF GAS=',F7.4)
      C
      C     INDIVIDUAL GAS YIELD
      C
              YH=(TG/FEED)*(WH2/TW)*100.
              YCH4=(TG/FEED)*(WCH4/TW)*100.
              YCO=(TG/FEED)*(WCO/TW)*100.
      C
      C
      C     WRITE THE YIELD OF INDIVIDUAL GAS
      C
              WRITE(6,31)YH,YCH4,YCO
         31   FORMAT(/,2X,'YIELD %',11X,F7.4,32X,2(F7.4))
      C
      C
              RETURN
              END
```

C.4 Model

Listing of MODEL at 12:26:52 on MAY 28, 1987 for CCid=TITA

```
      C ******************************************************************
      C                                                                  *
      C     NAME OF THIS PROGRAM: MODEL                                  *
      C                                                                  *
      C     THIS PROGRAM USES UBC LIBRARY PROGRAM NL2SNO TO SOLVE FOR    *
      C     THE PARAMETERS K3 & E3, INORDER TO OBTAIN THE RATE CONSTANT  *
      C     FOR THE OIL TO GASES REACTION.                               *
      C     THE OTHER PARAMETERS K1, K2, E1, E2, FRACT1, FRACT2, AND     *
      C     KO ARE TAKEN FROM THE LITERATURES.                           *
      C                                                                  *
      C ******************************************************************
      C
      C
            IMPLICIT REAL*8 (A-H,K,O-Z)
            INTEGER I,L,N,KK
            COMMON/BLKA/FO(10),F1(10),F2(10),W(10),TEMP(10),SIZE(10),
           &            FEED(10),AEXPT(10),ACAL(10),MUM(10)
            DIMENSION P(6), IV(66),V(5000), R(10)
            EXTERNAL CALCR
      C
      C     READ IN DATA
      C
            DO 1100 MM=1,6
               READ(5,551)MUM(MM),FO(MM),F1(MM),F2(MM),W(MM),TEMP(MM),
           &   SIZE(MM),FEED(MM),AEXPT(MM)
      551   FORMAT(I4,1X,F6.4,1X,F6.4,1X,F5.3,1X,F6.1,1X,F5.1,1X,F4.2,
           &   1X,F6.1,1X,F6.2)
               WRITE(6,66)TEMP(MM),AEXPT(MM),FO(MM),F1(MM)
      66       FORMAT(1X,F10.4,2X,F10.4,2X,F10.4,2X,F10.4)
      1100  CONTINUE
      C
      C     TO DEFINE THE N, M, P, IV AND V
      C
            N=6
            M=2
            P(1)=1.7D14
            P(2)=2.D5
            CALL DFALT (IV,V)
            V(42)=1.0D-25
            IV(17)=1000
            IV(18)=1000
      C
      C     WRITE INITIAL GUESS VALUES
      C
            WRITE(6,666) (P(I), I=1,2)
       666  FORMAT('INITIAL GUESS=',1P2G16.8)
      C
      C    TO CALL FOR LIBRARY PROGRAM NL2SNO
      C
            CALL NL2SNO(N,M,P,CALCR,IV,V,IPARM,RPARM,FPARM)
      C
            WRITE(6,120) IV(1)
      120   FORMAT('RETURN CODE =', I10)
            WRITE(6,140) (P(I), I=1,2)
      140   FORMAT('SOLUTION:', 1P2G16.8)
      C
            EE=2.718281728DO
            RR=8.314DO
```

Listing of MODEL at 12:26:52 on MAY 28, 1987 for CCid=TITA

```
      K1=14.4D0
      K2=2.025D10
      E1=44560.D0
      E2=177580.D0
      T=4800.D0

C
C     TO CALCULATE THE PREDICTED OIL YIELD VALUE BASED ON
C     K3 AND E3 VALUES OBTAINED FROM THE NL2SNO PROGRAM
C
        DO 22 I=1,N
          TEMPA=TEMP(I)+273.D0
          T=4800.D0
          KC1=K1*EE**(-(E1/(RR*TEMPA)))
          KC2=K2*EE**(-(E2/(RR*TEMPA)))
          KC3=P(1)*EE**(-(P(2)/(RR*TEMPA)))
          WF=(13.D0*454.D0)+(W(I)/2.D0)
          FRACT2=0.62D0/0.9D0
          A=FO(I)*0.11D0/WF
          B=KC1+(F1(I)/WF)+(F2(I)/WF)
          C=0.9D0*KC1
          D=(F1(I)/WF)+(F2(I)/WF)+KC2
          C11=1.D0/B/D
          C12=1.D0/((D**2)-(B*D))
          C13=1.D0/((B**2)-(B*D))
          CB=C*A*(C11+(C12*(EE**(-D*T)))+(C13*(EE**(-B*T))))
          VOL=0.0322D0*1.3D0
          FN=0.000472D0*TEMPA/293.D0
          TT=VOL/FN
          PP=KC2*FRACT2*CB*WF/VOL
          Q=(FN/VOL)+KC3
          CA=(PP/Q)*(1.D0-(DEXP(-Q*TT)))
          OIL=(FN*PP/Q)*((T+((DEXP(-Q*T))/Q))-(1.D0/Q))
          ACAL(I)=OIL
   22   CONTINUE
C
C     WRITE THE FINAL RESULTS
C
        WRITE(6,1111)
 1111   FORMAT(10X,'TEMP',9X,'TIME',5X,'OIL CALCULATED',8X,'OIL EXPT')
C
        DO 40 KK=1,N
        WRITE(6,515)TEMP(KK),T,ACAL(KK),AEXPT(KK)
  515   FORMAT(5X,F10.4,4X,F10.4,4X,F10.4,8X,F10.4)
   40   CONTINUE
C
        STOP
        END


C ***********************
C                       *
C     SUBROUTINE: CALCR  *
C                       *
C ***********************
C
C
        SUBROUTINE CALCR(N,M,P,NF,R,IPARM,RPARM,FPARM)
```

Listing of MODEL at 12:26:52 on MAY 28, 1987 for CCid=TITA

```
      C
            IMPLICIT REAL*8 (A-H,K,O-Z)
            DIMENSION P(M), R(N)
            COMMON /BLKA/ FO(10),F1(10),F2(10),W(10),TEMP(10),SIZE(10),
           &              FEED(10),AEXPT(10),ACAL(10),MUM(10)
      C
      C
            EE=2.71828172800
            RR=8.31400
            K1=14.400
            K2=2.025D10
            E1=44560.00
            E2=177580.00
            T=4800.00

      C
      C     TO CALCULATE PREDICTED CK,CB AND CA VALUES BASED ON GUESSED
      C     K3 AND E3
      C
              DO 20 I=1,N
                 TEMPA=TEMP(I)+273.00
                 T=4800.00
                 KC1=K1*EE**(-(E1/(RR*TEMPA)))
                 KC2=K2*EE**(-(E2/(RR*TEMPA)))
                 KC3=P(1)*EE**(-(P(2)/(RR*TEMPA)))
                 WF=(13.00*454.00)+(W(I)/2.00)
                 FRACT2=0.6200/0.900
                 A=FO(I)*0.1100/WF
                 B=KC1+(F1(I)/WF)+(F2(I)/WF)
                 C=0.900*KC1
                 D=(F1(I)/WF)+(F2(I)/WF)+KC2
                 C11=1.00/B/D
                 C12=1.00/((D**2)-(B*D))
                 C13=1.00/((B**2)-(B*D))
                 CB=C*A*(C11+(C12*(EE**(-D*T)))+(C13*(EE**(-B*T))))
                 VOL=0.0322D0*1.300
                 FN=0.000472D0*TEMPA/293.00
                 TT=VOL/FN
                 PP=KC2*FRACT2*CB*WF/VOL
                 Q=(FN/VOL)+KC3
                 CA=(PP/Q)*(1.00-(DEXP(-Q*TT)))
                 OIL=(FN*PP/Q)*((T+((DEXP(-Q*T))/Q))-(1.00/Q))
                 ACAL(I)=OIL
      C
      C     TO CALCULATE THE DIFFERENCE BETWEEN EXPERIMENTAL AND PREDICTED
      C     OIL YIELD VALUE
      C
                 R(I)=ACAL(I)-AEXPT(I)
      C
       20       CONTINUE
                RETURN
      C
                END
```

C.5 Jac

Listing of JAC at 12:27:06 on MAY 28, 1987 for CCid=TITA

```
      C ***************************************************************
      C                                                               *
      C     NAME OF THIS PROGRAM: JAC                                 *
      C                                                               *
      C     THIS PROGRAM USES UBC LIBRARY PROGRAM JACOBIAN TO SOLVE   *
      C     FOR THE SET OF DIFFERENTIAL EQUATIONS TO CALCULATE KEROGEN,*
      C     BITUMEN, AND OIL AS A FUNCTION OF TIME AT A GIVEN SET OF  *
      C     OPERATING CONDITIONS.                                     *
      C                                                               *
      C     dW/dt  = YDOT(1)                                          *
      C     dCK/dt = YDOT(2)                                          *
      C     dCB/dt = YDOT(3)                                          *
      C     dCA/dt = YDOT(4)                                          *
      C                                                               *
      C                                                               *
      C ***************************************************************


            IMPLICIT REAL*8 (A-H,K,O-Z)
            EXTERNAL FUNC,PD
            COMMON/BLKA/FO(10),F1(10),F2(10),WW(10),TEMP(10),SIZE(10),
     &              FEED(10),AEXPT(10),ACAL(10),MUM(10),WF(10),WT
            COMMON/BLKB/KC1,KC2,KC3,FRACT1,FRACT2,FN,V,I
            COMMON/GEAR9/HUSED,NQUSED,NSTEP,NFE,NJE
            DIMENSION YO(112),A(10)
      C
      C     READ IN DATA, MM=NO OF DATA READ IN
      C
            MM=3
            DO 110 M=1,MM
               READ(5,55)MUM(M),FO(M),F1(M),F2(M),WW(M),TEMP(M),SIZE(M),
     &                   FEED(M),AEXPT(M)
         55    FORMAT(I4,1X,F6.4,1X,F6.4,1X,F5.3,1X,F6.1,1X,F5.1,1X,F4.2,
     &              1X,F6.1,1X,F6.2)
               WRITE(6,11)AEXPT(M),TEMP(M),F1(M),WW(M)
         11    FORMAT(2X,4(F10.4,2X))
        110  CONTINUE
      C
      C     DEFINE ALL PARAMETERS AND BASIC INFORMATION
      C
            DO 1001 I=1,MM
            EE=2.718281728DO
            K1=10.4DO
            K2=2.285D10
            K3=1.7D14
            E1=44560.DO
            E2=177580.DO
            E3=244319.45
            FRACT1=0.9
            FRACT2=0.62DO/FRACT1
            WF(I)=(13.DO*454.DO)+(WW(I)/2.DO)
            WT=WF(I)
            V=0.0322DO*1.3DO
            RR=8.314DO
      C
      C
            TEMPA=TEMP(I)+273.DO
            KC1=K1*DEXP(-(E1/(RR*TEMPA)))
```

Listing of JAC at 12:27:06 on MAY 28, 1987 for CCid=TITA

```
      KC2=K2*DEXP(-(E2/(RR*TEMPA)))
      KC3=K3*DEXP(-(E3/(RR*TEMPA)))
      FN=0.000472D0*TEMPA/293.D0

C
      WRITE(6,66)KC1,KC2,KC3
 66   FORMAT(//,'KC1=',F10.8,3X,'KC2=',F10.8,3X,'KC3=',F10.8)

C
C     SET VALUES FOR THE LIBRARY PROGRAM GEAR
C
      N=4
      H0=1.D-7
      EPS=1.D-4
      METH=2
      MITER=2
      MF=10*METH+MITER
      ML=3
      MU=3
      TOUT=100.D0
      INDEX=1
C
      T0=0.D0
      Y0(1)=13.D0
C
C     INITIALISE THE VALUES OF Y0 AT TIME=0
C
      DO 5 J=2,4
 5       Y0(J)=0.0D0
C
C     WRITE TITLE
C
      WRITE(6,41)
 41   FORMAT(5X,'TIME',8X,'W',12X,'CK',12X,'CB',12X,'CA')
C
C     CALL GEARB TO SOLVE PROBLEM
C

 10   CALL GEARB(N,T0,H0,Y0,TOUT,EPS,MF,INDEX,ML,MU,FUNC,PD,6)
C
      WRITE(6,20)TOUT,WT,Y0(2),Y0(3),Y0(4)
 20   FORMAT(2X,F8.2,4(3X,F10.5))

      IF(INDEX .EQ. 0)GOTO 40
        WRITE(6,30)INDEX
 30     FORMAT(//26X,'ERROR RETURN WITH INDEX =',I3)
      GOTO 50
 40     TOUT=TOUT+400.D0
        IF(TOUT .GE. 4900.D0)GOTO 50
      GOTO 10
 50   WRITE(6,60)NSTEP
 60   FORMAT(//21X,'PROBLEM COMPLETED IN',I5,'STEPS')
C
C     CALCULATE OIL AT THE FINAL TIME
C
      WRITE(6,69)Y0(3),Y0(1)
 69   FORMAT(2(F10.5,2X))
C
```

Listing of JAC at 12:27:06 on MAY 28, 1987 for CCid=TITA

```
      X=4800.D0
      P=FRACT2*KC2*YO(3)*WT/V
      Q=(FN/V)+KC3
      OIL=(FN*P/Q)*((X+((DEXP(-Q*X))/Q))-(1.D0/Q))
      ACAL(I)=OIL
      WRITE(6,44)OIL
 44   FORMAT('OIL =', F10.4)
C
 1001 CONTINUE
      DO 1 II=1,MM
      WRITE(6,1111)TEMP(II),ACAL(II)
 1111 FORMAT(//,F6.2,2X,F7.2)
 1    CONTINUE
      STOP
      END


C **********************
C                       *
C    SUBROUTINE FUNC    *
C                       *
C **********************

      SUBROUTINE FUNC(N,T,Y,YDOT)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(4),YDOT(4)
      COMMON/BLKA/FO(10),F1(10),F2(10),W(10),TEMP(10),SIZE(10),
     &            FEED(10),AEXPT(10),ACAL(10),MUM(10),WF(10),WT
      COMMON/BLKB/KC1,KC2,KC3,FRACT1,FRACT2,FN,V,I
C
C
      YDOT(1)=FO(I)-F1(I)-F2(I)
      YDOT(2)=(FO(I)*0.11D0/WT)-(((FO(I)/WT)+KC1)*Y(2))
      YDOT(3)=(FRACT1*KC1*Y(2))-(((FO(I)/WT)+KC2)*Y(3))
      YDOT(4)=(FRACT2*KC2*Y(3)*WT/V)-(((FN/V)+KC3)*Y(4))
      RETURN
      END


C ***************************
C                           *
C    DUMMY SUBROUTINE PD    *
C                           *
C ***************************

      SUBROUTINE PD(N,T,Y,P,NDIMPD,ML,MU)
      IMPLICIT REAL*8 (A-H,K,O-Z)
      DIMENSION Y(N),P(NDIMPD,N)
      RETURN
      END
```

C.6 Jac (Printout)

Increasing KC1

KC1= 5 x KC1 KC2=0.00337898 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00021	0.00038	2.77130
500.00	6051.00000	0.00022	0.00145	16.72927
900.00	6051.00000	0.00022	0.00173	20.44090
1300.00	6051.00000	0.00022	0.00179	21.37767
1700.00	6051.00000	0.00022	0.00181	21.61381
2100.00	6051.00000	0.00022	0.00182	21.67278
2500.00	6051.00000	0.00022	0.00182	21.68747
2900.00	6051.00000	0.00022	0.00182	21.69148
3300.00	6051.00000	0.00022	0.00182	21.69184
3700.00	6051.00000	0.00022	0.00182	21.69180
4100.00	6051.00000	0.00022	0.00182	21.69219
4500.00	6051.00000	0.00022	0.00182	21.69247

KC1=10 x KC1 KC2=0.00337898 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00011	0.00046	3.49169
500.00	6051.00000	0.00011	0.00148	17.03408
900.00	6051.00000	0.00011	0.00173	20.53415
1300.00	6051.00000	0.00011	0.00180	21.41725
1700.00	6051.00000	0.00011	0.00181	21.63994
2100.00	6051.00000	0.00011	0.00182	21.69574
2500.00	6051.00000	0.00011	0.00182	21.70991
2900.00	6051.00000	0.00011	0.00182	21.71281
3300.00	6051.00000	0.00011	0.00182	21.71394
3700.00	6051.00000	0.00011	0.00182	21.71461
4100.00	6051.00000	0.00011	0.00182	21.71447
4500.00	6051.00000	0.00011	0.00182	21.71394

KC1= 50 x KC1 KC2=0.00337898 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00002	0.00052	4.19059
500.00	6051.00000	0.00002	0.00149	17.25547
900.00	6051.00000	0.00002	0.00174	20.60514
1300.00	6051.00000	0.00002	0.00180	21.44784
1700.00	6051.00000	0.00002	0.00182	21.66002
2100.00	6051.00000	0.00002	0.00182	21.71425
2500.00	6051.00000	0.00002	0.00182	21.72718
2900.00	6051.00000	0.00002	0.00182	21.73055
3300.00	6051.00000	0.00002	0.00182	21.73167
3700.00	6051.00000	0.00002	0.00182	21.73151
4100.00	6051.00000	0.00002	0.00182	21.73124
4500.00	6051.00000	0.00002	0.00182	21.73124

KC1= 100 x KC1 KC2=0.00337898 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00001	0.00052	4.27888
500.00	6051.00000	0.00001	0.00149	17.28228
900.00	6051.00000	0.00001	0.00174	20.61495
1300.00	6051.00000	0.00001	0.00180	21.45220
1700.00	6051.00000	0.00001	0.00182	21.66309
2100.00	6051.00000	0.00001	0.00182	21.71656
2500.00	6051.00000	0.00001	0.00182	21.72962
2900.00	6051.00000	0.00001	0.00182	21.73265
3300.00	6051.00000	0.00001	0.00182	21.73393
3700.00	6051.00000	0.00001	0.00182	21.73416
4100.00	6051.00000	0.00001	0.00182	21.73372
4500.00	6051.00000	0.00001	0.00182	21.73339

Increasing KC2

KC1=0.01689492 KC2= 5 X KC2 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00010	3.40206
500.00	6051.00000	0.00105	0.00034	19.95759
900.00	6051.00000	0.00110	0.00036	21.69000
1300.00	6051.00000	0.00110	0.00037	21.82659
1700.00	6051.00000	0.00110	0.00037	21.83867
2100.00	6051.00000	0.00110	0.00037	21.83761
2500.00	6051.00000	0.00110	0.00037	21.83987
2900.00	6051.00000	0.00110	0.00037	21.83983
3300.00	6051.00000	0.00110	0.00037	21.84067
3700.00	6051.00000	0.00110	0.00037	21.84042
4100.00	6051.00000	0.00110	0.00037	21.83975
4500.00	6051.00000	0.00110	0.00037	21.83986

KC1=0.03378984 KC2= 10 X KC2 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00007	4.87035
500.00	6051.00000	0.00105	0.00017	20.42427
900.00	6051.00000	0.00110	0.00018	21.76849
1300.00	6051.00000	0.00110	0.00018	21.87208
1700.00	6051.00000	0.00110	0.00018	21.88049
2100.00	6051.00000	0.00110	0.00018	21.88077
2500.00	6051.00000	0.00110	0.00018	21.88094
2900.00	6051.00000	0.00110	0.00018	21.88112
3300.00	6051.00000	0.00110	0.00018	21.88088
3700.00	6051.00000	0.00110	0.00018	21.88068
4100.00	6051.00000	0.00110	0.00018	21.88069
4500.00	6051.00000	0.00110	0.00018	21.88081

KC1=0.16894918 KC2= 50 X KC2 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00002	6.78531
500.00	6051.00000	0.00105	0.00004	20.68129
900.00	6051.00000	0.00110	0.00004	21.81870
1300.00	6051.00000	0.00110	0.00004	21.90688
1700.00	6051.00000	0.00110	0.00004	21.91321
2100.00	6051.00000	0.00110	0.00004	21.91394
2500.00	6051.00000	0.00110	0.00004	21.91418
2900.00	6051.00000	0.00110	0.00004	21.91357
3300.00	6051.00000	0.00110	0.00004	21.91348
3700.00	6051.00000	0.00110	0.00004	21.91379
4100.00	6051.00000	0.00110	0.00004	21.91378
4500.00	6051.00000	0.00110	0.00004	21.91366

KC1=0.33789836 KC2= 100 X KC2 KC3=0.00037883

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00001	7.04378
500.00	6051.00000	0.00105	0.00002	20.70764
900.00	6051.00000	0.00110	0.00002	21.82087
1300.00	6051.00000	0.00110	0.00002	21.90879
1700.00	6051.00000	0.00110	0.00002	21.91601
2100.00	6051.00000	0.00110	0.00002	21.91758
2500.00	6051.00000	0.00110	0.00002	21.91746
2900.00	6051.00000	0.00110	0.00002	21.91720
3300.00	6051.00000	0.00110	0.00002	21.91753
3700.00	6051.00000	0.00110	0.00002	21.91772
4100.00	6051.00000	0.00110	0.00002	21.91764
4500.00	6051.00000	0.00110	0.00002	21.91760

Increasing KC3

KC1=0.00337898 KC2=0.00189415 KC3= 5 X KC3

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00014	0.92593
500.00	6051.00000	0.00105	0.00119	12.67593
900.00	6051.00000	0.00110	0.00163	18.23956
1300.00	6051.00000	0.00110	0.00176	19.84550
1700.00	6051.00000	0.00110	0.00179	20.28006
2100.00	6051.00000	0.00110	0.00180	20.38640
2500.00	6051.00000	0.00110	0.00180	20.41554
2900.00	6051.00000	0.00110	0.00180	20.42144
3300.00	6051.00000	0.00110	0.00180	20.42108
3700.00	6051.00000	0.00110	0.00180	20.42134
4100.00	6051.00000	0.00110	0.00180	20.42187
4500.00	6051.00000	0.00110	0.00180	20.42171

KC1=0.00337898 KC2=0.00378831 KC3= 10 X KC3

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00014	0.89680
500.00	6051.00000	0.00105	0.00119	11.96279
900.00	6051.00000	0.00110	0.00163	17.16337
1300.00	6051.00000	0.00110	0.00176	18.66119
1700.00	6051.00000	0.00110	0.00179	19.06403
2100.00	6051.00000	0.00110	0.00180	19.16432
2500.00	6051.00000	0.00110	0.00180	19.19162
2900.00	6051.00000	0.00110	0.00180	19.19713
3300.00	6051.00000	0.00110	0.00180	19.19735
3700.00	6051.00000	0.00110	0.00180	19.19782
4100.00	6051.00000	0.00110	0.00180	19.19849
4500.00	6051.00000	0.00110	0.00180	19.19836

KC1=0.00337898 KC2=0.01894153 KC3= 50 X KC3

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00014	0.71225
500.00	6051.00000	0.00105	0.00119	8.24347
900.00	6051.00000	0.00110	0.00163	11.65281
1300.00	6051.00000	0.00110	0.00176	12.63242
1700.00	6051.00000	0.00110	0.00179	12.88867
2100.00	6051.00000	0.00110	0.00180	12.95430
2500.00	6051.00000	0.00110	0.00180	12.97087
2900.00	6051.00000	0.00110	0.00180	12.97498
3300.00	6051.00000	0.00110	0.00180	12.97647
3700.00	6051.00000	0.00110	0.00180	12.97676
4100.00	6051.00000	0.00110	0.00180	12.97664
4500.00	6051.00000	0.00110	0.00180	12.97668

KC1=0.00337898 KC2=0.03788306 KC3= 100 X KC3

TIME	W	CK	CB	CA
100.00	6051.00000	0.00052	0.00014	0.56242
500.00	6051.00000	0.00105	0.00119	5.93075
900.00	6051.00000	0.00110	0.00163	8.31349
1300.00	6051.00000	0.00110	0.00176	8.99782
1700.00	6051.00000	0.00110	0.00179	9.17796
2100.00	6051.00000	0.00110	0.00180	9.22189
2500.00	6051.00000	0.00110	0.00180	9.23268
2900.00	6051.00000	0.00110	0.00180	9.23522
3300.00	6051.00000	0.00110	0.00180	9.23585
3700.00	6051.00000	0.00110	0.00180	9.23601
4100.00	6051.00000	0.00110	0.00180	9.23602
4500.00	6051.00000	0.00110	0.00180	9.23601