

## THE ALBERTA OIL SANDS - CANADA'S ENERGY CHALLENGE

by

R.D. (REG) HUMPHREYS

MEMBER ALBERTA OIL SANDS TECHNOLOGY AND RESEARCH AUTHORITY

AND INDEPENDENT CONSULTANT

### INTRODUCTION

With the growing energy shortages facing many countries today and particularly Canada and the U.S.A., it is imperative that we in Canada focus our attention on new potential reserves for alternate energy supplies. There are many possible sources available but the Alberta Oil Sands are probably the nearest to being ready for commercial development, thanks to a lot of hard work by a lot of very dedicated people like Dr. Karl A. Clark and companies with great determination and foresight like Great Canadian Oil Sands Limited and Syncrude Canada Limited.

### RESERVES AND RECOVERIES

The oil sands deposits have been known for centuries and have interested the white man from the days of the earliest fur traders and explorers. In total the four major deposits cover an area of over nineteen thousand (19,000) square miles and contain approximately one trillion barrels of in-place oil and are one of the worlds largest resources of hydrocarbons. The largest accumulation, the Athabasca deposit, outcrops along the Athabasca River and extends down-dip to the south and west to an overburden depth of about two thousand (2,000) feet. The other Alberta deposits, Peace River, Wabasca and Cold Lake are smaller in size and together contain about one half the amount of oil in the Athabasca deposit. Small sections of the Athabasca deposit only are suitable for open-pit recovery methods, but potential recoverable synthetic crude oil from these mineable sections amounts to 26.5

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billion barrels. This is small in comparison to the total potential recovery from the entire deposits but still some 3 - 4 times the amount of the present total Canadian conventional crude oil reserves. Possible in-situ recoveries from the tar sands total 250 billion barrels or more and could last Canada for hundreds of years at present rate of consumption.

#### THE CHALLENGE

With such an incentive as an assured supply of energy we can afford to spend extra time and effort in order to achieve the required production to relieve the impending shortage. The challenge is to develop the technology to produce enough oil at a reasonable market value and at the same time conserve the environment. This requires development of more sophisticated mining and extraction procedures, developing and proving up in-situ techniques and optimizing upgrading processes to give maximum yields of usable product from the bitumen recovered.

#### TAR SANDS PROPERTIES AND RESEVOIR CHARACTERISTICS

The Alberta deposits have been evaluated by the drilling of over 4000 wells, by extensive laboratory and field experimental work directed towards development of both mining and in-situ methods and by the work at The Great Canadian Oil Sands Limited mining project on a commercial scale. The oil sands are composed of a series of quartz sand deposits impregnated with varying amounts of a heavy, highly viscous bitumen. The sands are deposited on an irregular surface of limestone or shale and are generally overlain with overburden, varying in thickness from zero to two thousand feet. The bitumen has an API gravity of about 7 degrees and contains 5 or more weight percent sulphur and is relatively high in metals. The deposit is highly compacted and temperature within the ore body remains fairly constant at about 6° C. At this temperature the bitumen has a viscosity so high that it is immobile. Relatively little is known of the

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physical characteristics and behaviour of the ore body and much work must be done to determine more of the characteristics and properties in order to improve on mining techniques and develop viable in-situ processes.

#### OPEN PIT MINING

The only current commercial production from the oil sands is from the Great Canadian Oil Sands plant north of Fort McMurray in the Athabasca deposit, where yields have been running about 50,000 B.P.D. during the past several years. Syncrude Canada Limited is building a plant with planned production capacity of 100,000 B.P.D. by the early 1980's. Both operations require removal of tree growth, muskeg and remaining overburden before mining the tar sand for transportation to the extraction plant for bitumen recovery. The bitumen requires desulphurizing and upgrading. before it is suitable for pipeline shipment as refinery feed stock. The basic procedures in both plants are similar and vary in operating detail only.

Both operations face or will face several major problems which require solving before it can be said that the open pit mining method is completely successful.

The sludge problem with its high attendant cost of overburden removal and dyke building remains the greatest single obstacle to the success of the Great Canadian Oil Sands operation. Sludge accumulation and build-up requires the construction of high retaining basins which are constructed from selected suitable portions of the overburden layers. This requires the special handling, transportation, spreading and compaction of huge volumes of this material yearly which adds to the costs and does not give a final solution to the problem. The obvious answer of course, is to discover a simple inexpensive method for breaking this "emulsion" of clay, water, bitumen and residual caustic.

Upgrading and desulphurizing require high cost capital equipment which is relatively expensive to operate. Yields from the current up-

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grading operation are relatively low at 76%. Coke production is about twenty-eight percent and only a portion is burned as fuel and the rest stockpiled. Syncrude Canada Limited will install upgrading facilities that will improve the liquid product yield but coke production will be stockpiled because of its high sulphur content. Improved or new upgrading processes are required that will give higher liquid yields from the recovered bitumen and produce a balanced slate of products which utilizes 100% of the bitumen barrel. Stockpiling of coke can, at best, be only a temporary measure until such times as we learn how to take full advantage of production. Both projects make use of sizeable volumes of natural gas for the production of hydrogen which is used in the upgrading processes. Government authorities have indicated that the use of natural gas for such purposes in the future will be restricted and other sources of raw material (coke) must be utilized for hydrogen production.

#### IN-SITU

Many experimental projects have been conducted in the in-situ mode of operation in most areas of the oil sands deposits with varying results. One developer has a long standing project in operation in the Cold Lake deposit which is showing signs of success, although recoveries reported are as low as 7%. This may be satisfactory for initial pilot work but for long range operation this will not satisfy the conservation authorities. Other pilot projects have been carried out and claim better recoveries but these have not had the advantage of long term and sustained production. Up to this point there are no projects that can be classified as commercial or even semi-commercial but several claim an optimistic outlook for the future. To a large extent these pilot projects have been conducted in secret and there appears to be a measure of duplication from project to project. The projects all utilize some means to mobilize the oil by reducing the viscosity. Introduction of heat by injection of steam or hot gasses

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or by partial combustion of the bitumen in place are the major processes involved. Some utilize a solvent method for recovery but usually this has the shortcoming of major solvent losses in the process. Other pilots employ a combination of two or more methods and show some promise for the future.

#### THE ENVIRONMENT AND AOSERP

One of the major concerns in any process that may be utilized in developing this huge resource is the effect on the environment. Mining processes disturb large areas that must be rehabilitated and restored to acceptable condition. In-situ also disturbs some land area but considerably less than mining processes, nonetheless restoration must be considered. Both methods run the risk of water contamination and provisions must be made to assure that pollution is minimized. Upgrading operations from both methods can produce air pollution through sulphur and particulates emissions to the atmosphere and require an enormous amount of work so that new plants can remain within the strict Alberta standards.

One major problem facing environmental authorities has always been in setting realistic and meaningful standards. There has never been sufficient base data on which standards could be set. The Canadian Federal and Alberta Provincial Governments have combined in setting up a research program "directed to the practical solution of environmental problems resulting from oil sands development, and to the provision of scientific data for the use of government, industry and the public". The program will develop a comprehensive data base and background information for the formulation of an acceptable environmental program.

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DEVELOPING THE TECHNOLOGY

The Alberta Government has set up the "Alberta Oil Sands Technology and Research Authority" to develop the technology needed to establish a commercial in-situ method of oil sands recovery in Alberta. In addition it has been charged with the responsibility to investigate means to improve the surface mining technology particularly those having potential for reducing capital costs, for increasing the efficiency of separation and upgrading, or having improved environmental features. Methods for underground mining will also be investigated.

Since open pit mining and upgrading procedures have been developed and are in a relatively advanced stage, priority is being given to in-situ technology development. Applications have been received for funding in all areas of potential development and all are being considered. The in-situ applications have been reviewed and several have been selected for approval pending the successful negotiations with the applicant. The approved projects will be funded generally on a 50:50 basis with AOSTRA and industry being equal partners but with the Authority retaining the ownership of the technology developed.

Such a program should speed up the development of the in-situ technology and know-how, it should avoid wide spread duplication of effort and minimize overexpenditure of dollars and make available the technology at a reasonable cost for major tar sand development in in-situ areas.

Other technological developments in underground mining, upgrading, improvements in surface mining processes and environmental areas are being considered as time permits.

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THE FUTURE

The development of the tar sand industry is only beginning and we are only now realizing the number of problems and the magnitude of these problems to be overcome before we can say that we have a viable tar sands industry. The Federal and Provincial Governments are beginning to realize that this is a challenge worth facing and are beginning to show more active support. Industry has been attempting to develop the needed technology but it has been a slow process. With combined government/industry effort progress should be more quickly achieved and some of our problems solved.

## CHEMISTRY FOR TAR SANDS DEVELOPMENT

ROBERT SCHUTTE

SYNCRUDE RESEARCH, P.O. BOX 5790  
EDMONTON, ALBERTA T6C 4G3

I would like to suggest some possible research projects that would be of benefit to the oil sand industry as a whole. The Research Department of my company is fully occupied with efforts to ensure that the plant currently under construction (and scheduled to start production in March 1978) will operate satisfactorily. This takes us into studies of the geology of the formation, especially hydrogeology; extraction; tailings management; analytical research; and upgrading. Naturally we are acutely aware of the costs of oil sand development. And we are often reminded that knowledge specifically for application to the high cost areas of oil sands development has never been acquired.

Total investment in the Syncrude project for obtaining synthetic crude oil from the tar sands of northern Alberta will be \$2.048 billion for initial production of 105M bbl/d. Construction is more than 60% complete (Feb. 1977). Aside from hot water extraction procedures that we have developed independently, our technology has been adapted from practices followed in established industries. Considering the investment required this is not a good route to follow in the long run. Oil sands is capable of being such a big industry that research effort devoted to its particular problems is overdue. Syncrude alone will have one of the world's biggest mines removing 92 MM tons tar sand and 45 MM tons overburden per year. Our utilities plant is designed for 260 MW. Yet in spite of scale and the rising price of conventional crude, oil sand economics are still marginal. Research deliberately devoted to oil sands problems could lead to new equipment and process steps that would improve the economic outlook for the development of oil sand. Mining and extraction will be employed for working the top 200 feet or so of the deposit but deeper oil sand will have to be processed in-situ and this will require the acquisition of more knowledge to keep operations at acceptable costs.

A comparison of some statistics for the mining and in-situ plants looks like this. In both schemes the scale is large.

	MINING	IN-SITU
Area (acres)	8,000	>16,000
Production BPD	125,000	125,000 (at 50% recovery)
Steam used lb/hr	4,500,000	7,500,000 injected (1)
Major mining equipment	4 X 80 cu yard draglines 4 bucket wheel reclaimers >35,000 feet of conveyor belt	8000 wells (2 acre spacing) Oil gathering system Steam distri- bution system

In each of the two schemes upgrading of the isolated bitumen is needed to yield liquid hydrocarbon products.

Setting aside the question of what on this continent we should do to conserve energy, the fact remains that there is an urgent real demand for hydrocarbon fuels as conventional crude dwindles. It is also a fact that the oil sands of northern Alberta are a huge deposit of bituminous matter from which, by suitable treatment, fuel-grade hydrocarbons can be derived. Obviously mining tar sand and then manufacturing crude therefrom is more expensive than establishing land-based wells in accessible regions, and it is because costs of obtaining conventional crude have increased as less-accessible supplies have to be tapped that synthetic crude from oil sands has now become economically feasible.

If oil sands is to become the viable source of hydrocarbons that its extent and proximity to the Canadian market suggest that it can be, new solutions must be found to unacceptably expensive steps in the process. Otherwise, for new reasons, oil sand will remain what it has been for 200 years -- a known but unworkable bituminous deposit.

Areas of high cost cannot be dealt with solely by chemical invention. I am increasingly aware of our need in the Syncrude Research Department, for expertise in disciplines other than chemistry and chemical engineering. Because oil research is traditionally staffed by people with chemical training, we tend to concentrate on those problems that lend themselves to laboratory or pilot scale inquiry. In fact investment breaks down to:

Mining	34%
Extraction, Froth Treatment and Diluent Recovery	12%
Upgrading	30%
Offplots	24%
	<hr/>
	100%

It can be, and is, argued that mining is not our province but the responsibility of the mining industry. But the punitive cost of oil sand mining is in danger of blocking oil sands development. Ultimately such high cost must be attributed to failure to recognize the need for research.

As an example, my company will spend about \$80 million dollars on conveyors, and an as yet unknown amount on their maintenance. These conveyors will handle a material so harsh that it would be difficult to artificially formulate a worse composition for this mode of conveying, and working at temperatures ranging from -50°F to +100°F. For the benefit of tar sand development as a whole, several millions of dollars would be well spent on conveyor materials research and other uses of rubber or rubber substitute. The reason why this has not been done, I think, is that an oil sand industry is only now emerging, and approaches to the conveyor supplying industry have so far been made in a piece-meal fashion. Such a large army of construction workers is needed to build an oil sands plant that one

plant has to be completed before another can be started. Hence through lack of concerted investigation each plant is doomed to be equipped with conveyor that may be less than fully appropriate. The same reasoning applies to other features of oil sands technology.

### Steam

The piece-meal approach needs to be corrected even in chemical questions. Of the 600 billion barrels crude oil equivalent present in the Athabasca deposit, only 20 billion barrels can be recovered by a process involving a mining step. This is the preferred scheme where possible due to high recovery of around 93%. For the rest we must resort to in-situ methods (so far 50% recovery at best), which have as their common feature that they involve heating the deposit to render the bitumen fluid. Some proposed in-situ processes utilize steam which in turn calls for large quantities of water of sufficient purity to be used as boiler feed. Purifying water for boiler feed in electrical power generation is more demanding because not only will silica be deposited as scale, but some forms of silica will be volatile under the high pressures and high temperatures in modern boilers, only thereafter to be deposited downstream on such delicate equipment as turbine blades. Oil sands steam usage differs from that in conventional power generation because the steam is used and then allowed to escape: except in the utilities plant, no condensate is returned. Clearly for ourselves and for other developers inexpensive ways of producing copious supplies of purified water would be an important development.

Raw water of the Athabasca region contains soluble organic acids of high molecular weight and much dissolved silica in the form of silicic acids. Strongly basic ion exchange resins may be used to remove silica but if such resins are exposed to the dissolved organics, they foul irreversibly -- that is, they cannot be regenerated by simple caustic treatment. It is then necessary to add another resin system to guard the highly basic resin and to regenerate that. Besides introducing further capital expense, this brings operating complexity because the water eluted from the guard resin must be carefully monitored before it is advanced to the basic resin.

One answer to the resin-fouling problem lies in the use of ozone, for degradation of the large organic molecules. At Syncrude Research we have adjusted the molecular weight of the organics to the desired value by use of as little as 5 ppm ozone and success was demonstrated in a six-day experimental run where no noticeable resin fouling was observed (2).

Ozone is helpful, but if we go back a step we see that the problem is not so much in the water as in the resin. There is nothing inately harmful in contacting organic molecules with resins, but only contacting organic molecules with resins whose pore structure encourages too strong an affinity. In short, the resins available to use have been manufactured without Athabasca region water in mind and contain cavities that readily occlude the humic and fulvic acids with which we are plagued. Athabasca water needs tailor-made resins or some novel treatment.

## Reliability

The very scale on which Syncrude will operate constitutes a risk and a challenge. Unlike the conventional oil industry where the risk is in locating the oil, with us it is the reliability of the equipment. A new science of equipment reliability will have to be developed.

Syncrude has a train of 41 plants. If each of these were to operate at 99% reliability the total system could be depended upon to operate for only 66% of the time. At the high investment required it is uneconomical simply to have duplicate pieces of equipment. What we need is reliability engineering -- that is, some means for informing us of the health of equipment before such equipment fails. I understand that large computers will now diagnose failure of certain of their own components. Using a network of probes and monitors attached to equipment, this diagnostic practice needs to be extended to large mechanical systems.

Synthetic crude is more corrosive than its conventional counterpart. Stainless steel is not a good material from which process equipment should be fabricated because of its poor heat transfer properties. New alloys for synthetic crude would justify research effort.

I have already referred to a need in the tar sand industry for new conveyor belt material. It should be strong, resist abrasion, work at a demanding range of temperatures, resist attack by hydrocarbons, and release tar sand or at least not suffer when release agents are applied. Steam distribution systems are made expensive because expansion joints have to be let into the system. If in-situ recovery were to be employed over an area of 25 square miles this would be an enormous source of cost. There is an incentive to invent expansionless piping (possibly from ceramic or glass?).

## Upgrading

This is the operating by which the bitumen is converted to synthetic crude, suitable for treatment in a conventional oil refinery. Bitumen is first "cracked" and distilled above 900°F to yield light and heavy gas oils.

The assumption is that because 50% of bitumen is in the boiling range of conventional residuum, bitumen should be treated by residuum upgrading. With available technology this is correct. Nevertheless, about 25% of the energy available to the tar sand is lost in upgrading. We subject the bitumen to high temperature to crack the heavier molecules and to remove the carbon with a view to increasing the hydrogen/carbon ratio of the product. Unfortunately, side reactions are quite prominent and encourage production of

- olefins -- which have to be saturated at a later stage
- gases -- which consist of hydrogen and light hydrocarbons rich in hydrogen and constitute a serious loss of hydrogen from the reactive mixture, notwithstanding the fact that coking is intended to correct an alleged hydrogen deficiency.

Paraffins have a hydrogen/carbon ratio of approximately 2, benzene has 1.0. So in fact, bitumen, at a hydrogen/carbon ratio of around 1.5 is not deficient in hydrogen. It is coking that makes it so. It would appear that during coking, hydrogen migrates to give one by-product so starved of hydrogen that it must be rejected as a coke, and another, so rich in hydrogen that it is lost as refinery gas. Granted these are only side reactions, but serious in absolute terms. We will produce 800,000 tons per year of a coke of hydrogen/carbon ratio 0.3 and of low economic value, which started off as a constituent of useful hydrocarbons. Olefin production is so serious that in the subsequent hydrodesulfurization sixty percent of the hydrogen consumed is used merely to hydrogenate these olefins. We will use 35 MM cubic feet of natural gas per day to produce hydrogen. Both hydrogen migration and olefin production appear to be a function of temperature and hence a lower temperature cracking process is needed for oil sands upgrading.

Lewis acid catalysts, homogeneous with the mixture to be hydrocracked (3) (eg. fused zinc chloride) hold promise, but efficient catalyst recovery would be needed for economic reasons. Bed catalysts are at a disadvantage because of poisoning brought about by the metal content of the bitumen itself, and its ash content. The de-metallizing step, possibly using manganese nodules would probably solve this. Another possible application for catalytic action would be a reforming step. Although large volumes of hydrogen are needed to hydrogenate bitumen during hydrocracking, much of this could be regenerated by re-forming simultaneously with the creation of a valuable product, high in aromatics. Alternatively, it has been suggested that sulphur is evenly distributed along the length of the large molecules and that merely removing this sulphur from bitumen by hydrodesulfurization would bring about a ten-fold reduction in hydrocarbon molecular weight (4). If so, we are throwing away a great natural advantage that bitumen presents.

Although fluid coking followed by hydrodesulphurization is adequate for residuum in conventional crude, direct application to oil sands bitumen is really only a stop gap. As we move toward bitumen as a major hydrocarbon raw material, side reactions, which are a decided nuisance in the treatment of conventional residuum, will become a serious source of waste. The Catalytic Cracker (developed as recently as the early forties) was brought into use to cope with two new problems: expanded market for hydrocarbons of gasoline boiling range; and the increased use of heavier oil as refinery feedstock. Bitumen may be seen as the next step towards even heavier oil and the time seems ripe for the development of a brand new residuum conversion process.

Canada is fortunate in that as conventional crude supplies are depleted we have an intermediate source of hydrocarbons in the form of oil sands bitumen from which our liquid hydrocarbon needs can be satisfied. Other nations have to go directly to uncongenial hydrocarbon sources such as coal and oil shale. Oil sand poses technical and scientific problems but these are capable of being handled by Canadian research resources. I am sometimes asked what will be the future of the Syncrude Research Department once the first plant is operating and debottlenecked. My reply is that by that time we will have clear ideas about what the research problems of oil sands really are. The deposit contains about 600 million

barrels. Whether we convert it from a deposit to a resource will depend on whether we correctly choose new directions as a result of the initial experience we are gaining now.

#### References

- (1) Dillabough, J.A. and Prats, M. "Recovering Oil from Peace River Deposits". Oil and Gas Journal 72 (45) pp. 186-94 (11 Nov. 1974).
- (2) Filby, J.E. "Use of Ozone in the Preparation of Industrial Boiler Feed Water." Proceedings, I.O.I. Conference Chicago, June 2 to 4, 1976.
- (3) Desulfurization of Hydrocarbon Oils with Lewis Acids. Japanese Patent 74 24,203.
- (4) Strausz, O.P. "Some Aspects of the Chemistry of Alberta Oil Sand Bitumen". ACS San Francisco Meeting, August 20 - September 3, 1976, pp. 456-81.

CHEMICAL COMPOSITION OF GASES IN THE ALBERTA  
BITUMINOUS SAND

Kamal N. Jha and O.P. Strausz

Hydrocarbon Research Centre  
Department of Chemistry, University of Alberta  
Edmonton, Alberta, Canada, T6G 2G2

INTRODUCTION

The major bituminous sand formations in Canada are located within the heavy oil belt of northern Alberta. The two largest reservoirs, known as Athabasca and Cold Lake, are known to be interspersed with occasional small gas pockets indicating that secondary thermal or microbial alterations of the bitumen have taken place in the recent past or may still be occurring. The presence of the volatile materials, their composition and origin and their continuous formation and escape into the atmosphere pose challenging problems with regard to the past and current history of the formation and to the air quality of the region.

For the above reasons we have undertaken a detailed study of the composition of gases present in the bituminous sand, of gases produced in the low-temperature pyrolysis of the bituminous sand and of the separated asphaltene and maltene fractions.

The isotopic carbon ratios in two of the components of the gases and in the different fractions of the Athabasca and Cold Lake bituminous sands were measured in order to gain a better understanding of the alteration processes and the extent of maturity of these deposits.

EXPERIMENTAL

The experimental details for the collection and analysis of gases and the conversion of methane and carbon monoxide to carbon dioxide for isotopic measurements have been described before (1). The standard extraction procedures for bitumen, asphaltene and maltene from the Athabasca (2) and Cold Lake (3) oil sands were followed. The isotopic distribution of carbon in bitumen, asphaltene and maltene was determined as follows. Approximately 5 mg of the desired fraction weighed in a narrow quartz tube was pushed into the center of a wider quartz tube maintained at 980°C inside an electric furnace. Oxygen was flowed through the system at a rate of 7 cm<sup>3</sup>/min.

Oxidation of the material was complete within 20 minutes and the oxidized products, mainly carbon dioxide and sulfur dioxide, were condensed into a trap maintained at -161°C. Carbon dioxide was then removed from sulfur dioxide by vacuum distillation at -130°C and collected in a transfer tube. The isotopic ratios were measured with a 25 cm radius 90° sector magnetic mass analyzer equipped with a dual collection system. The digital output was handled with a TI 980 computer.

RESULTS AND DISCUSSION

The composition and yields of gases evolved upon heating the Cold Lake bituminous sand samples at 5°, 70°, 95°, 130°, 170° and 210°C for 5.5 hours each are presented in Table 1. At 5°C the volatile fraction contained CH<sub>4</sub>, CH<sub>3</sub>CHO, C<sub>3</sub>H<sub>8</sub>, *i*-C<sub>4</sub>H<sub>8</sub>, *i*-C<sub>4</sub>H<sub>10</sub>, C<sub>5</sub> and C<sub>6</sub> hydrocarbons. At elevated temperatures the following additional compounds were detected: C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>4</sub>H<sub>10</sub>, 1- and 2-C<sub>4</sub>H<sub>8</sub>, CO, COS and H<sub>2</sub>S. Gases collected at 5°C, which is the formation temperature, are considered to be constituents present in the formation while the others are expected to arise from pyrolysis of the bituminous sand. The yields of all products except acetaldehyde increase with rising temperature, implying that these are pyrolysis products as well.

The same products were obtained by heating Cold Lake maltene and asphaltene samples at 210° and 400°C and the results are given in Table 2. Most of the decomposition products were not detected at 210° because only 100 mg of samples were heated.

The yields of products at 400° are much larger than those at 210°C. The yields of some products are markedly affected by the reaction volume or more likely by the pressure in the system; for example, the yields of ethylene, propylene, propane and butane are enhanced at lower pressures. The total weight loss of asphaltene and maltene at 400°C was 29.9 and 34.5%, respectively, independent of pressure.

From comparison of the results, it is apparent that the amount of saturated hydrocarbons present in the Cold Lake deposit is greater than that in the Athabasca formation (1). On the other hand, the yields of carbon monoxide and carbon dioxide are much smaller in the Cold Lake samples than those in the Athabasca deposits. These results seem to imply that thermal or microbial degradation of the Cold Lake bitumen has occurred to a lesser extent than that in the Athabasca deposits.

Kinetic analysis of the data in Table 1 yielded Arrhenius parameters for the decomposition. They are given in Table 3 along with those obtained from the Athabasca study (1) for comparison. Since the Arrhenius parameters are favorable for a slow but significant rate of product formation at the ambient temperature of the reservoir, it follows that these materials were produced in the formation by the slow pyrolysis of the bituminous sand. The low values of the activation energies estimated for product formation in the Cold Lake samples are similar to those measured for the Athabasca bitumen. These low values may be attributed to the catalytic effect of the mineral matter present in the sample.

The carbon isotope ratios,  $C^{13}/C^{12}$ , of different fractions obtained from Athabasca and Cold Lake bituminous sands have been measured and are reported in Table 4. The  $\delta C^{13}$ \* values are corrected for the  $O^{17}$  contribution and are quoted relative to the Chicago PDB standard.

The  $\delta C^{13}$  values obtained for methane and carbon monoxide which were collected from bituminous sand, asphaltene and maltene at different temperatures, show a gradual increase with rising temperature. Those values for Athabasca bitumen and the separated asphaltene and maltene fractions are the same,  $\delta C^{13} = -29.6 \pm 0.10/_{\infty}$  at 980° whereas the corresponding values for Cold Lake maltene, asphaltene and bitumen are -31.6, -30.0 and -30.3 respectively. It is worth noting that the  $\delta C^{13}$  values obtained from the Cold Lake samples are slightly smaller than the corresponding ones from the Athabasca bitumen. This may imply that biological and/or chemical degradation of Cold Lake bitumen has occurred to a lesser extent than in the Athabasca bitumen.

The homogenization of the carbon isotope ratios in the bitumen, asphaltene and maltene may be due to mixing through migration and carbon isotope exchange reactions. Our values of  $\delta C^{13} = -29.6$  and  $-30.7$  for the Athabasca and Cold Lake bitumens respectively are very close to those obtained for different fractions of Saskatchewan and Alberta conventional oils (Mississippian and Devonian) which range between -30.6 and -26.6 (4). The sulfur isotope ratios,  $S^{34}/S^{32}$ , of several Saskatchewan crude oils and the Athabasca bitumen are also very similar (5).

The variation of the  $C^{13}/C^{12}$  ratios with temperature for methane, a pyrolysis product, can be explained in terms of the selective breaking of weaker C-C bonds at lower temperatures as a result of the kinetic isotope effect. It has been reported that methane produced by the bacterial degradation of oil has much lower  $\delta C^{13}$  values than those obtained in the present work (6). It is possible that the maturity, reservoir temperature and the strength of the C-C bonds cleaved are the primary factors influencing the isotopic distribution of gases in the bituminous sand.

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\* $\delta C^{13}$  ‰ (per mil) is defined as  $\left\{ \left( \frac{C^{13}}{C^{12}} \right)_{\text{sample}} / \left( \frac{C^{13}}{C^{12}} \right)_{\text{standard}} - 1 \right\} 10^3$ .

#### REFERENCES

1. Strausz, O.P., Jha, K.N. and Montgomery, D.S. Fuel, in press.
2. Selucky, M.L., Chu, Y., Ruo, T. and Strausz, O.P. "The Chemical Composition of Athabasca Bitumen", Fuel, in press.
3. Selucky, M.L., Chu, Y., Ruo, T. and Strausz, O.P. "The Chemical Composition of Cold Lake Bitumen", Fuel, in press.
4. Evans, C.R., Rogers, M.A. and Bailey, N.J.L. Chem. Geol., (1971) 8, 147.
5. Monster, Jan. AAPGB, (1972) 56, 941.
6. Dubrova, N. and Nesmelova, Z.N. Geokhimiya, (1968) 9, 1066.

TABLE 1

Composition of Gases Evolved from the Cold Lake Oil Sand  
as a Function of Temperature.<sup>a</sup>

	5°C	70°C	95°C	130°C	170°C	210°C
Methane	12.1	37.1	62.5	191.5	570.0	3,800
Ethylene	n.o. <sup>b</sup>	3.17	9.7	39.8	192.7	449.0
Ethane	n.o.	7.16	13.5	26.3	28.4	452.0
Acetaldehyde	9.0	54.5	146.6	84.0	18.8	7.22
Propylene	n.o.	4.13	12.0	68.1	n.d. <sup>c</sup>	494.0
Propane	3.49	10.2	16.7	153.7	n.d.	n.d.
<i>i</i> -Butane	3.49	5.52	6.68	8.42	13.9	n.d.
<i>i</i> -Butene	25.6	34.9	38.2	62.2	127.2	104.0
<i>n</i> -Butane	n.o.	63.8	71.3	79.8	130.5	246.3
Butenes	n.o.	90.0	147.4	152.2	152.4	521.4
Pentanes & Pentenes	1.34	5.34	16.04	36.6	62.1	231.0
C <sub>6</sub>	2,860	3,780	4,120	4,450	4,620	4,950
Carbon monoxide	n.o.	74.2	231.2	879.2	1,840	4,790
Carbonyl sulphide	n.o.	3.63	10.2	27.7	50.5	195.2
Hydrogen sulphide	n.o.	n.o.	n.o.	<85.0	<160	<1,930

<sup>a</sup> The sample was heated for 5.5 hours at each temperature.

Yields are expressed in units of 10<sup>-8</sup> mol/kg oil sand.

<sup>b</sup> Not observed.

<sup>c</sup> Not determined.

TABLE 2

Composition of Gases from Cold Lake Maltene  
and Asphaltene.<sup>a</sup>

	Maltene			Asphaltene		
	210° <sup>b</sup>	400° <sup>c</sup>	400° <sup>b</sup>	210° <sup>b</sup>	400° <sup>c</sup>	400° <sup>b</sup>
Methane	n.o. <sup>d</sup>	140,000	197,000	65.5	167,000	151,000
Ethylene	71.0	5,440	42,100	16.2	10,200	25,900
Ethane	n.o.	115,000	95,000	11.1	104,000	97,000
Acetaldehyde	n.o.	n.o.	n.o.	6.91	n.o.	n.o.
Propylene	n.o.	19,700	82,700	7.60	31,000	44,300
Propane	n.o.	77,800	91,900	9.10	67,200	73,500
<i>i</i> -Butane	n.o.	152.0	n.d. <sup>e</sup>	n.o.	259.0	n.o.
<i>i</i> -Butene	n.o.	17,700	13,900	n.o.	8,600	6,780
<i>n</i> -Butane	n.o.	18,600	52,400	14.3	20,800	33,800
Butenes	n.o.	55,500	61,900	8.13	47,700	49,700
Pentanes & Pentenes	16.0	69,100	75,900	314.0	59,700	58,400
C <sub>6</sub>	769.0	77,300	71,200	38.2	53,500	61,200
C <sub>7</sub>	n.o.	50,900	10,500	n.o.	36,400	6,600
Carbon monoxide	n.d.	n.d.	n.d.	340.0	n.d.	3,990
Carbon dioxide	135.4	529.0	615.0	369.0	2,900	1,850
Carbonyl sulphide	n.o.	60.0	44.0	n.o.	<0.1	24.0
Hydrogen sulphide	n.o.	<47,200	<33,400	<51.1	<86,900	<89,400
Oxygen	8.00	n.o.	438.0	6.94	n.o.	16.5
Nitrogen	17.90	n.o.	107.0	17.9	n.o.	94.6

<sup>a</sup> The samples were heated for 20 hours. Yields are expressed in units 10<sup>-8</sup> mol/g.<sup>b</sup> The volume of the cell was 155 cm<sup>3</sup> and contained ≈100 mg material.<sup>c</sup> The volume of the cell was 1.0 cm<sup>3</sup> and contained 15 mg of maltene or 5 mg of asphaltene.<sup>d</sup> Not observed.<sup>e</sup> Not determined.

TABLE 3

Arrhenius Parameters for Pyrolysis  
of Bituminous Sand

Product	A		E <sub>a</sub>		k <sub>5°C</sub>	
	[(5.5h) <sup>-1</sup> kg <sup>-1</sup> ]		[kJ/mol]		[(5.5h) <sup>-1</sup> kg <sup>-1</sup> ]	
	Cold Lake	Athabasca	Cold Lake	Athabasca	Cold Lake	Athabasca
CH <sub>4</sub>	1.7x10 <sup>9</sup>	3.6x10 <sup>9</sup>	53.8	56.9	1.7x10 <sup>-1</sup>	7.6x10 <sup>-2</sup>
C <sub>2</sub> H <sub>4</sub>	2.1x10 <sup>8</sup>	5.2x10 <sup>7</sup>	52.0	49.3	4.4x10 <sup>-2</sup>	2.8x10 <sup>-2</sup>
C <sub>3</sub> H <sub>6</sub>	5.3x10 <sup>7</sup>	7.9x10 <sup>8</sup>	46.8	57.7	9.4x10 <sup>-2</sup>	1.2x10 <sup>-2</sup>
<i>i</i> -C <sub>4</sub> H <sub>8</sub>	3.6x10 <sup>5</sup>	1.6x10 <sup>4</sup>	31.0	28.4	6.0x10 <sup>-1</sup>	7.3x10 <sup>-2</sup>
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	3.0x10 <sup>3</sup>	8.2x10 <sup>4</sup>	21.3	34.7	3.1x10 <sup>-1</sup>	2.5x10 <sup>-2</sup>
CO	7.9x10 <sup>7</sup>	1.1x10 <sup>8</sup>	39.3	36.8	3.6	13.2
COS	1.9x10 <sup>6</sup>	5.0x10 <sup>7</sup>	37.7	48.5	1.8x10 <sup>-1</sup>	4.0x10 <sup>-2</sup>

TABLE 4

Isotopic Ratios for C<sup>13</sup>/C<sup>12</sup> in the Fractions  
of Alberta Bituminous Sand

Temperature °C	Bituminous Sand Fraction	δC <sup>13</sup> (per mil)	
		Athabasca	Cold Lake
95	Bituminous Sand, CH <sub>4</sub> + CO <sub>2</sub>	-48.8 (1) <sup>a</sup>	
210	Bituminous Sand, CH <sub>4</sub> + CO <sub>2</sub>	-41.1±2.3(4)	
210	Bituminous Sand, CO + CO <sub>2</sub>	-32.0±2.4(4)	-37.3 (1)
210	Bitumen + Sand <sup>b</sup>		
	CH <sub>4</sub> + CO <sub>2</sub>	-47.8±0.9(3)	
	CO + CO <sub>2</sub>	-29.0 (1)	
400	Maltene, CH <sub>4</sub> + CO <sub>2</sub>	-41.9 (1)	-44.3 (1)
400	Asphaltene, CH <sub>4</sub> + CO <sub>2</sub>	-45.5±0.1(2)	-44.3±0.1(2)
980	Maltene, Total C + CO <sub>2</sub>	-29.7±0.1(3)	-31.6±0.1(3)
980	Asphaltene, Total C + CO <sub>2</sub>	-29.5±0.1(3)	-30.0±0.3(3)
980	Bitumen, Total C + CO <sub>2</sub>	-29.6±0.1(3)	-30.3±0.4(2)

<sup>a</sup> Numbers in brackets indicate number of analyses.

<sup>b</sup> Sand recovered after the extraction of oil from the Athabasca bituminous sand was mixed with bitumen in the proportion estimated in the bituminous sand.

## PHYSICAL PROPERTIES OF CONVENTIONAL AND BIODEGRADED OILS

I. Rubinstein and O.P. Strausz

Hydrocarbon Research Centre  
Department of Chemistry  
University of Alberta  
Edmonton, Alberta, Canada

### INTRODUCTION

During our studies on the origin and evolution of the Alberta oil sands we studied the bacterial attack on conventional crude oils, and came to the conclusion that the oil sand bitumen was the end product of the biodegradation of a liquid pooled oil (1). The biodegradation of a light, fluid conventional crude oil yielded a heavy, dense bitumen after bacterial attack, (2,3,4) which resembled the naturally occurring bitumen found in the Alberta oil sand formations (1).

The fact that biodegraded oils and oil sand bitumens have such different physical properties from conventional crude oils is of great importance to the petroleum industry. A fluid fossil fuel may be extracted from a reservoir by sinking a well and permitting the fluid to flow out of the ground under its own or assisted hydrostatic pressure, and it may be transported by pipeline or vessel to a remote plant for treatment. The oil sand bitumen, on the other hand, is a heavy tarry material, solid at ambient local temperature, which is held in an adhesive matrix around grains of sand in a solid geological formation underground. This requires difficult, and hence expensive, mining or *in-situ* recovery, and the bitumen released from the sand matrix must be treated and refined on-site since it is not easily transported to a remote refinery.

The three physical criteria of importance in this field of petroleum exploitation are Pour Point: -the temperature above which the oil is a liquid and will flow, Gravity: -the density of the material, and Viscosity: -its ability and resistance to flow.

We have investigated various oils, and bitumens and some of their major component fractions for these criteria, and noted their properties before and after biodegradation in an attempt to rationalize their physical behavior.

### MATERIALS AND METHODS

Samples investigated are shown in Table I. Prudhoe Bay is a conventional crude oil from Alaska, and its incubation for 168 hours with a culture of mixed bacteria yielded sample PB 168 (1). This latter material has been shown to resemble chemically the Alberta oil sand bitumens. Sample PB s.l. is the product of the incubation of Prudhoe Bay oil with a culture of the yeast *Saccharomyces lipolytica*. This organism removes completely the *n*-alkanes (5). Sample At is a typical oil sand bitumen from one of the four major deposits in Alberta. The Lloydminster crude oil is a heavy naphthenic crude oil found in a reservoir system in the Mannville formation in Eastern Alberta. It is thought to be related to the four oil sand formations bitumens (6,7) and is an example of an intermediate biodegradation product (1). The three component fractions, the saturate, aromatic and polar materials of the samples At and PB were isolated from the respective oils by column chromatography (1). Sample PB Sat. A.F. was a sample of PB Sat. from which the *n*-alkanes, *iso*- and *ante-iso* alkanes had been removed by molecular sieve inclusion (8) and urea adduction (9).

The Pour Point was determined by observing the temperature at which the liquid sample ceased to flow on cooling, and also the temperature at which this same sample, when frozen, commenced to flow on heating. The figures quoted are averages of these two values.

The gravity was determined by densitometry at 25°C. The values quoted are A.P.I. gravities calculated according to the formula 
$$\text{A.P.I. gravity} = \frac{141.5}{\text{specific gravity}}$$
 - 131.5. Hence water has a value of A.P.I. 10. More dense materials have lower values, less dense materials have values greater than 10.

Viscosities were measured at 38°C and 99°C with a Brookfield Viscosimeter on 5 ml samples, absolute values being corrected against known standards. Values quoted are in Saybolt Universal Seconds (s.u.s.) and are calculated using the formulae:

$$\frac{\text{Centipoise}}{\text{Specific Gravity}} = \text{Centistokes}$$

and S.U.S. = Centistokes x 4.635. Since oils and bitumens are not homogenous materials, the values quoted should not be regarded as absolute, but rather viewed for comparative purposes.

## RESULTS AND DISCUSSIONS

The chemical analyses of the materials investigated are illustrated in Figure 1. From this it may be seen that sample PB was a conventional crude oil containing a full complement of *n*-alkanes, acyclic isoprenoids, oligo- and polycyclic saturated alkanes, oligo- and polycyclic aromatics and polar materials. Biodegradations by the yeast (sample PB s.l.) removed solely the *n*-alkanes and minor amounts of small-ring aromatic materials. Biodegradation by the bacteria (sample PB 168) had removed all the *n*-alkanes and the acyclic isoprenoids, some mono and dicyclic saturates, and small ring aromatics, leaving the polar material unchanged (1).

Sample L1 was similar to sample PB s.l. in that the *n*-alkanes were absent, but the acyclic isoprenoids (the pristane and phytane family) were still present. However, as typical of the oils found in the Mannville formation of Alberta, there was a relatively large amount of polar material present. Similarly, sample At, the oil sand bitumen, resembled the fully biodegraded sample PB 168, excepting for, again, the larger amount of polar material present (1).

### a) Pour Point

The values obtained for the pour points of the samples are shown in Table II. The conventional crude oil, sample PB, had a pour point of -2°C. Removing the *n*-alkanes (sample PB s.l.) caused this figure to fall to -12°C; i.e. the oil was still liquid at an even lower temperature. Increasing the amount of polar material (as in sample L1) caused a marked increase in the pour point value to +3°C. Further biodegradation to completion (as in sample PB 168 and At) caused a further rise in the pour point, with the amount of polar material having little additional effect.

Looking at the values for the component fractions, it may be noted that the polar material had a very high pour point, and therefore the proportions present in a mixture had a marked effect on the overall pour point. The more polar material being present, the higher the pour point became.

Biodegradation caused a rise in the pour point values in the aromatic fraction, due to the removal of the lighter components (sample PB Aro, sample At Aro).

The most striking difference was observed in the saturate fractions. Sample PB Sat had a pour point of +1°C, due to the presence of the solid waxy *n*-alkane series. Removal of this (sample PB Sat A.F.) caused a marked fall in the pour point, hence the fall in values observed between samples PB and PB s.l. Further biodegradation (i.e. removal of the acyclic isoprenoids and mono- and di-cyclic saturates) caused a further decrease in the pour point values.

Thus biodegradation by the *Saccharomyces lipolytica* may be said to have "upgraded" the oil, in that its pour point had fallen due to the removal of the *n*-alkanes. Further biodegradation in the saturate and aromatic fractions caused a "downgrading" by increasing the pour point of the oil. The overriding factor involved in the pour point was the quantity of polar material present. The higher the percentage of polar material present, the higher the pour point became.

### b) Viscosity

The Viscosities obtained are tabulated in Table III.

Sample PB had a low viscosity, and thus flowed easily. Removing the *n*-alkanes (sample PB s.l.) increased this value from 208 to 1006. Adding polar material (sample L1) further increased this value to 3610. Complete biodegradation of sample PB increased the viscosity sharply to over five thousand (sample PB 168), and the addition of further polar material (sample At) more than doubled this figure. The values for the component fractions explain this in that biodegradation had only a minor effect on

the viscosity of the saturate and aromatic fractions. Since the polar material was a solid at 38°C, and was extremely viscous even at 99°C, its presence was the most important factor in the determination of the viscosity of an oil. Hence the Mannville oils (samples Ll and At) were all highly viscous at 38°C due to their high content of polar material, and were more viscous than their low-polar counterparts even at 99°C.

#### c) Gravity

Table IV lists the values obtained for the A.P.I. gravities of the oils. The conventional crude oil sample PB had a relatively high A.P.I. gravity, which fell to close to that of water on complete biodegradation with the bacteria (sample PB 168), and also on biodegradation with the *Saccharomyces lipolytica* (sample PB s.l.). The values for the samples At and Ll were likewise close to that of water. The values for the saturates (samples At Sat, PB Sat, PB Sat A.F.) revealed high values unaffected by biodegradation, and the values for the aromatic fractions fell only to a minor extent. It may thus be surmised that the concentration of polar material was the most important factor involved in the determination of the gravity of an oil (see Figure 1).

#### CONCLUSIONS

- i) Conventional crude oils are characterised in their physical properties by a high A.P.I. gravity, low pour point and low viscosity. Biodegraded oils and bitumens have low A.P.I. gravities, high pour points and high viscosities.
- ii) The most influential factor involved in the physical properties of oils is the amount of polar material present.
- iii) The selective removal of *n*-alkanes by the yeast *Saccharomyces lipolytica* caused an anomalous "upgrading" of the oil in that the pour point was decreased.

#### ACKNOWLEDGEMENTS

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#### LITERATURE CITED

- 1) Rubinstein, I., Strausz, O.P., Spyckerelle, C., Crawford, R.J. and Westlake, D.W.S. *Geochim. Cosmochim. Acta*. Submitted for publication.
- 2) Bailey, N.J.L., Jobson, A.M., and Rogers, M.A. *Chem. Geol.*, 11, 203 (1973).
- 3) Bailey, N.J.L., Krouse, H.R., Evans, C.R., and Rogers, M.A. *Amer. Assoc. Petroleum Geol.*, 57, 1276 (1973).
- 4) Evans, C.R., Rogers, M.A., and Bailey, N.J.L. *Chem. Geol.*, 8, 147 (1971).
- 5) Spyckerelle, C. and Rubinstein, I. Unpublished results.
- 6) Deroo, G., Tissot, B., McCrossan, R.G., and Der, F. *Can. Soc. Petroleum Geol. Memoirs*, 3, 148 (1974).
- 7) Montgomery, D.S., Clugston, D.M., George, A.E., Smiley, G.T., and Sawatzky, H. *Can. Soc. Petroleum Geol. Memoirs*, 3, 168 (1974).
- 8) O'Connor, J.G., Burrow, F.H., and Norris, M.S. *Anal. Chem.*, 34, 82 (1962).
- 9) Kimble, B.J., Maxwell, J.R., Philp, R.P., Eglinton, G., Albrecht, P., Ensminger, A., Arpino, P., and Oursson, G. *Geochim. Cosmochim. Acta*, 38, 1165 (1974).

Table I  
The Oils Examined

PB	Prudhoe Bay Crude. Location: Alaska (British Petroleum Ltd.)
PB 168	Prudhoe Bay Crude incubated 168 hours, mixed bacterial culture.
PB s.l.	Prudhoe Bay Crude incubated 21 days with <i>Saccharomyces lipolytica</i> culture.
L1	Lloydminster Crude. Location: 16-3-50-1 W4. Well depth 600 m. (Husky Oil Ltd.).
At	Athabasca Oil Sand Bitumen. Location: 24-92-10 W4. Quarry depth 22 m. (Great Canadian Oil Sands Ltd.).
PB Sat	Prudhoe Bay Saturate Fraction
PB Aro	Prudhoe Bay Aromatic Fraction
PB Pol	Prudhoe Bay Polar Fraction
PB Sat A.F.	Prudhoe Bay Saturate Fraction free of <u>n</u> -alkanes.
At Sat	Athabasca Saturate Fraction
At Aro	Athabasca Aromatic Fraction
At Pol	Athabasca Polar Fraction

Table II  
Pour Point Values (°C)

<u>Sample</u>	<u>Pour Point</u>	<u>Sample</u>	<u>Pour Point</u>	<u>Sample</u>	<u>Pour Point</u>
PB	-2	PB Sat	+1	At Sat	-55
PB s l	-12	PB Aro	-55	At Aro	-25
PB 168	+7	PB Pol	+50	At Pol	+45
L1	+3	PB Sat A.F.	-35		
At	+8				

Table III  
Viscosity Values 38°C; 99°C  
(Saybolt University Seconds)

<u>Sample</u>	<u>Viscosity</u>	<u>Sample</u>	<u>Viscosity</u>	<u>Sample</u>	<u>Viscosity</u>
PB	208 ; 131	PB Sat	<50 ; <50	At Sat	<50 ; <50
PB s l	1006 ; 215	PB Aro	<50 ; <50	At Aro	850 ; <50
PB 168	5280 ; 117	PB Pol	solid ; >20000	At Pol	solid ; >20000
L1	3610 ; 260	PB Sat A.F.	<50 ; <50		
At	11680 ; 513				

Table IV  
Gravity Values (°API)

<u>Sample</u>	<u>Gravity</u>	<u>Sample</u>	<u>Gravity</u>	<u>Sample</u>	<u>Gravity</u>
PB	27	PB Sat	36	At Sat	30
PB s 1	12	PB Aro	17	At Aro	4
PB 168	10	PB Pol	-10	At Pol	-10
L1	13	PB Sat A.F.	36		
At	10				

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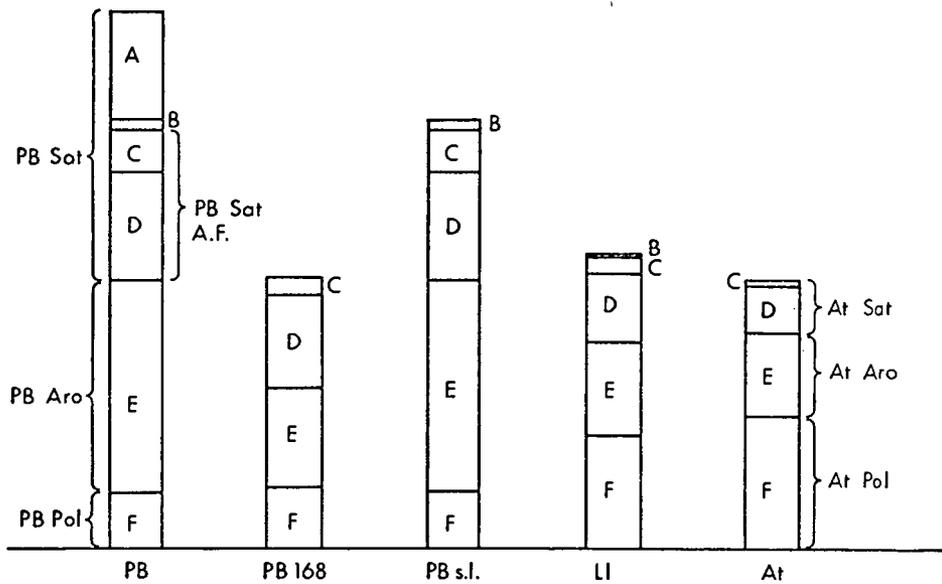


Figure I: Gravimetric analyses of the Oils and bitumens.

- A. Sieve adduct
- B. Urea adduct
- C. Thiourea adduct
- D. Thiourea non-adduct
- E. Aromatic Fraction
- F. Polar fraction

Saturate fraction

CHROMATOGRAPHIC SEPARATION AND CHARACTERIZATION OF HOPANES  
IN ATHABASCA BITUMEN

T.C.S. Ruo, M.L. Selucky, Y. Chu and O.P. Strausz

Hydrocarbon Research Centre  
Department of Chemistry, University of Alberta  
Edmonton, Alberta, Canada, T6G 2G2

INTRODUCTION

One of the more difficult tasks in the analysis of heavy crudes such as shale or oil sand bitumens is the detailed analysis of their saturated hydrocarbon fraction. Although this fraction is easily separated from the other constituents of the bitumen in two or even in one separation step, it represents a complex mixture of hydrocarbons which may, and in the case of heavy crudes often does, contain several classes of compounds ranging from simple straight chain alkanes, to various branched alkanes (and possibly the corresponding olefins which are eluted together with the saturates), to monocyclic, dicyclic and up to pentacyclic compounds. Separation of this complex mixture into the individual classes is a formidable task which, in the case of heavy crudes, is further complicated by the fact that the constituents of this fraction range from relatively low molecular weight compounds up to  $C_{40}$  and even higher hydrocarbons. Also, as the number of rings increases, the corresponding number of possible stereoisomers becomes very large. Thus, for example, GALLEGOS<sup>1</sup> showed that three hydrocarbons of molecular formula  $C_{30}H_{52}$  were present in the Green River shale oil: two had identical mass spectra, while the third differed only by the absence of a small M-43 peak in its mass spectrum. All three could be separated by GC. The slight differences in the mass spectra and the presence of common base ions (e.g. the majority of tetra- and pentacyclic terpanes have a major m/e 191 fragment in their mass spectrum) make discriminations based on GC/MS extremely difficult.

In heavy bitumens such as Athabasca or Cold Lake materials, and materials from the neighbouring areas, the major proportion of the hydrocarbons ranges between  $C_{16}$  and  $C_{30}$ . In this range GC/MS cannot easily furnish the entire structural data necessary for unambiguous identification of individual compounds, but other instrumental methods such as X-ray diffractometry or  $^{13}C$  n.m.r. can provide the required information. These methods however require preparative isolation of the compound of interest in quantities amounting to at least 5-15 mg. WSZOLEK et al. therefore studied preparative isolation of the steranes and hopanes from the Green River shale oil<sup>2</sup>.

Recent geochemical work has shown that many constituents of the saturated hydrocarbon fraction are hydrocarbons derived from naturally-occurring plant (e.g. terpenes and sterols) and possibly animal (viz. e.g. the recent identification of cholic acid by SEIFERT<sup>3</sup>) materials. Geochemists have pointed out repeatedly that such compounds, termed 'geochemical markers', might provide an insight into the genesis of the deposit and help to answer such questions as the relative maturity of the crude, and whether biodegradation has taken place. With regard to the latter, for example, it has been shown<sup>4</sup> that certain bacteria are capable of attacking and thus removing n-alkanes, branched alkanes and even monoaromatics with an alkane side-chain and since these compounds are absent in the Athabasca bitumen<sup>5</sup> it was concluded that complete biodegradation has taken place. However not too much importance should be vested in the presence or absence of other so-called geochemical markers since many terpanes and steranes are apparently always present in oils, irrespective of their origin and maturity.

In order to exploit the potential value of such classes of hydrocarbons for oil characterization studies, further refinements of existing analytical procedures were deemed necessary in order to allow routine (i.e. at least relatively fast and accurate) analyses and unambiguous identifications of the individual members of such classes of hydrocarbons. In view of the above-mentioned broad distribution of saturated hydrocarbons in the Alberta oil sand bitumens, we decided to first concentrate on the separation and determination of the hopanes and steranes using a combined GC/MS, HPLC and GPC approach.

## RESULTS AND DISCUSSION

A well established but tedious and lengthy<sup>6</sup> procedure for the isolation of penta-cyclic terpanes consists of the removal of possible olefinic contaminants on Ag<sup>+</sup>/silica, n-alkanes on 5A molecular sieve, of lower cyclic and branched open chain hydrocarbons by adduction with urea, and of higher cyclic compounds by adduction with thiourea. The hopanes remain in the thiourea non-adduct, while the steranes are distributed between the thiourea adduct and non-adduct. In previous work we have shown<sup>5</sup> that, from the total 'saturates' of Athabasca oil, 1.53% were retarded on Ag<sup>+</sup> loaded silica, 4.9% represented the thiourea adduct and 87.5% were isolated as the thiourea non-adduct after repeated adduction, for a total recovery of 94%. Thus the thiourea non-adduct represents the major portion of the saturate fraction. Due to the large spread in molecular weight of the saturates, it seemed obvious that some size separation should precede any other separation steps. A detailed study of the elution of saturates from a classical alumina column in which the eluate was collected in 10 separate fractions, each of which was checked by GC and HPLC (Figures 1 and 2) showed that the hopanes were preferentially eluted in fraction #7 and only small amounts were present in fraction #6. Since no n-alkanes are present in the Athabasca bitumen, fractions #5, 6 and 7 were treated with thiourea and the non-adduct was subjected to GC/MS scanning.

This scanning, based on the comparison of the intensities of the fragment ion m/e 191 and of the pair molecular ion plus an ion representing the side chain-containing fragment of the particular compound, suggested the presence of hopanes<sup>7</sup> but the results were hard to interpret due to incomplete separation and the presence of steranes and other material in the same range of retention times, c.f. Figure 3. In order to improve the separation, each of the fractions (#5, 6 and 7) were re-separated by GPC on 60, 100, 200 and 500 Å Styragel. Examples of the GPC chromatograms and the cut points of fractions #5, 6 and 7 are shown in Figures 4a, b and c. The gas chromatograms of these individual fractions are shown in Figures 5, 6 and 7 where it is seen that the hopanes are preferentially concentrated in one of the fractions (GPC fraction #8 from alumina fraction #7). Thus the lower molecular weight constituents were nearly completely removed, leaving a mixture of hopanes together with traces of other components as will be shown below, reasonably well separable on a conventional packed GC column (Dexsil-300). This finding was important for two reasons. First, it allowed us to obtain good mass chromatograms and mass spectra of the individual hopanes, the fragmentation patterns of which were in agreement with published data<sup>7</sup> on the 17 $\alpha$ (H), 21 $\beta$ (H)-, C<sub>27</sub>, C<sub>29</sub>-C<sub>35</sub> hopane series, and second, it suggested the possibility of a relatively easy preparative collection of enough material to run <sup>13</sup>C-n.m.r. and high resolution mass spectra of the individual compounds. For the preparative separation, a 1/4" by 8' column packed with 3% Dexsil-300 on Chromosorb W-AW was used with the thermal conductivity detector connected to the column outlet prior to the collection traps. The chromatogram is shown in Figure 8. Unfortunately the trapping train was only crudely set up and the collection efficiency was low. Comparison of the chromatograms of the isolated fractions with that of original hopane fraction, Figure 9, shows that the purity of the isolated C<sub>27</sub>, C<sub>29</sub> and C<sub>30</sub> hopanes was better than 90%. Moreover, these hopanes are the predominant representatives of the hopane series in Athabasca bitumen, in which the total content of hopanes is about 0.3-0.6%. High resolution mass spectra of the C<sub>29</sub> and C<sub>30</sub> compounds, Figure 10, have exact masses of 398.3911 (calc. 398.3912) and 412.40690 (calc. 412.40644) respectively, thus confirming the molecular formulae C<sub>29</sub>H<sub>50</sub> and C<sub>30</sub>H<sub>52</sub>. Comparison of the <sup>13</sup>C n.m.r. spectra with that of C<sub>30</sub> hopane<sup>8</sup>, Figure 11, shows that the hopanes in Athabasca bitumen are indeed the 17 $\alpha$ (H), 21 $\beta$ (H)-isomers.

Figure 12 illustrates the procedure adopted for GC-MS scanning of one of the GPC fractions containing C<sub>29</sub>, C<sub>30</sub> and C<sub>31</sub> hopanes. The respective molecular ions are m/e 191 and the fragments containing the side chain are, respectively, m/e 177, 191 and 205. We have also detected and preparatively isolated a C<sub>28</sub> compound which gave fragment ions and a molecular ion in accordance with the other homologues of the now unambiguously identified hopane series, but the retention time however does not conform to the retention times of this series. This suggests that the compound is not a C<sub>28</sub> hopane and the fact that it could not be crystallized suggests that the isolated product might in fact be a mixture.

A gas chromatogram of the hopane concentrate fraction on a SCOT column (N = 28,000), Figure 13, reveals the presence of a number of trace and minor constituents which, however, could hardly affect the purity of the isolated fractions for the purpose of  $^{13}\text{C}$  n.m.r. spectra or X-ray crystallography. Figure 13 clearly shows that the separation of the diastereoisomers at C-22 of  $\text{C}_{32}$  to  $\text{C}_{35}$  hopanes is complete, while the analogous separation of the  $\text{C}_{31}$  homologue would require efficiencies in the range of N = 80,000. It is also noteworthy that the ratios of the pairs of diastereoisomers change slightly along the series. From the limited data available however, the potential significance of these differences cannot be assessed. Figure 14 shows the same separation on a WCOT column (N = 80,000). The separation of C-22 diastereoisomers is nearly complete ( $t_R \sim 47$  min.). However, the  $\text{C}_{28}$  compound gives a single peak even at this high resolution. Apparently, the material isolated by preparative GC is appreciably contaminated by neighboring components.

Similarly, cross-scanning for steranes has been done by molecular ion and fragment ions m/e 217 and 231, and fragment ions m/e 149 and 151. The ion m/e 217 is a base fragment of steranes and m/e 231 is the base ion of sterane compounds bearing a skeletal methyl group. The ratio of m/e 149 and 151 ions allows discrimination between the  $5\alpha$  and  $5\beta$  stereoisomers of the sterane series. We have identified steranes ranging from  $\text{C}_{21}$  to  $\text{C}_{29}$  and work is still in progress. Figure 15 is an example of the GC/MS scanning of one of the GPC fractions in which the steranes are concentrated. Thus, in this fraction the following could be identified: a tetracyclic compound (terpane? m/e 191)  $\text{C}_{19}\text{H}_{32}$  (mass 260), a tricyclic compound (m/e 191)  $\text{C}_{20}\text{H}_{36}$  (mass 276), a tetracyclic hydrocarbon  $\text{C}_{20}\text{H}_{34}$  (mass 274), mixed peaks consisting of  $\text{C}_{21}$  methylsterane and  $\text{C}_{20}$  sterane,  $\text{C}_{22}$  methylsterane and sterane,  $\text{C}_{23}$  methylsterane and sterane, a  $\text{C}_{24}\text{H}_{42}$  tetracyclic terpane (m/e 191), a  $\text{C}_{27}\text{H}_{48}$  tetracyclic terpane (mass 372) and a  $\text{C}_{27}$  hopane. Also, minor amounts of  $\text{C}_{29}$ ,  $\text{C}_{30}$  and  $\text{C}_{31}$  hopanes were present.

It was important that a fairly good separation be achieved on a conventional GC column. The GC/MS equipment used for the measurements (MS-12 mass spectrometer interfaced to a Nova DS-50 data system) did not permit the use of WCOT columns without modifications to the sample introduction system in the MS. On the other hand the advantage of this system is the possibility of storing the large number of spectra (500 to 600 scans) and recalling any mass chromatogram or their combination off-line. The separation achieved on the classical liquid chromatography column and the resulting concentration of the hopanes in two of the fractions indicated that the length of time involved in the procedure could be substantially shortened if the efficiency of the column were increased. The hopanes should be easy to isolate under such circumstances since they are the highest molecular weight representatives of the compound spectrum of the saturate fraction. This expectation was confirmed by experiment. The total saturate fraction (about 1 g) was injected on a 2 cm i.d. x 4' column packed with 37-63  $\mu\text{m}$  particle size alumina and eluted with n-pentane using a Chromatronix pump at a flow rate of 18 ml/min. to give the chromatogram shown in Figure 16. Cutting into subfractions as shown in Figure 16 afforded two main fractions, the gas chromatograms of which are compared in Figure 17. These chromatograms show that upon proper cutting, the hopanes can be very well separated from the total saturates and be isolated in one preparative step in only 35 minutes. Thus, an increase in the number of theoretical plates to only about 400/m yielded a reasonably pure hopane fraction.

The use of high performance alumina columns (particle size 10 or 5  $\mu\text{m}$ ) would further improve the separation. However, the low loadability of such columns, the high back pressures generated when the column is used at optimum conditions and the high cost of such columns indicate that a compromise solution, e.g. the use of 18-32  $\mu\text{m}$  particle size in a preparative column, should give the best results. An additional problem related with the use of alumina columns which should not be overlooked is the strong influence of its water content on k-values. ENGELHARDT<sup>9</sup> described a simple assembly which is capable of adjusting the water content and thus k-values to a selected, constant value. We have, however, preferred to work with a non-linear isotherm as illustrated in the chromatogram in Figure 16 using fully activated (400°C) alumina and freshly dried eluent (n-pentane).

This procedure for the separation and identification of the hopane constituents in the saturated hydrocarbon fraction is relatively simple and fast, and moreover the

capillary GC results indicate that the component distribution can be accurately quantified. A large number of comparative analyses can be performed routinely, possible variations in the distribution and ratios of diastereoisomers can be accurately determined and therefore the importance of these variables with regard to the geochemical history of the bitumen can be evaluated on a more quantitative basis.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

1. E.J. Gallegos, *Anal. Chem.*, **43**, 1151 (1971).
2. P.C. Wszolek, E. Gelpi, and A.L. Burlingame, *Advances in Org. Geochemistry*, 1971, p. 229, Pergamon Press, Oxford (1972).
3. W.K. Seifert, E.J. Gallegos, and R.M. Teeter, *Angew. Chem., Int. Ed.*, **10**, 747 (1971).
4. D.W. Westlake, A. Jobson, R. Phillippe, and F.D. Cook, *Can. J. Microbiol.*, **20**, 915 (1974).
5. M.L. Selucky, Y. Chu, T. Ruo, and O.P. Strausz, *Fuel*, in print.
6. M.T.J. Murphy in "Organic Geochemistry", G. Eglinton and M.T.J. Murphy, Eds., Springer-Verlag, New York, N.Y., 1969, p. 74-85.
7. A. Ensminger, Ph.D. Thesis: Triterpenoides du schiste de Messel, L. Pasteur University, Strassbourg, 1974.
8. B. Balogh, D.M. Wilson, P. Christiansen, and A.L. Burlingame, *Nature*, **242**, 603 (1973).
9. P. Engelhardt, paper presented at 11th International Symposium on Advances in Chromatography, Houston, Texas, November, 1976.

#### APPENDIX

Experimental Details for Figures 1-17:

- Figure 1 - Gas chromatographic analysis of saturate fractions eluted from alumina. Left: 6' x 1/8" column, 3% Poly S-179 phase on Chromosorb W-AW (100/120 mesh);  $T_1$  220,  $T_2$  320°C;  $t_1$  5 min., rate 4°/min., F 32, Attn. 256x. Right: 6' x 1/8" column, 3% Dexsil 300 phase on Chromosorb W-AW (100/120 mesh);  $T_1$  220,  $T_2$  360°C;  $t_1$  1 min., rate 6°/min., F 21 ml/min., Attn. 256x. STD: mixture of n-alkanes  $C_{11}$ ,  $C_{13}$ ,  $C_{15}$ ,  $C_{19}$ ,  $C_{20}$ ,  $C_{22}$ ,  $C_{24}$ ,  $C_{28}$ ,  $C_{32}$  and  $C_{36}$  in n-hexane.
- Figure 2 - HPLC test for the presence of monoaromatics in the saturate fractions eluted from alumina. Column: 70 cm x 1/4" alumina Woelm + 3% H<sub>2</sub>O, particle size 18-32  $\mu$ m. Eluent: n-heptane, RI detector, P 220 psi, F = 6 ml/min.
- Figure 3 - Mass chromatograms (m/e 191, m/e 217) of the thiourea non-adduct of the saturate fraction #7 from alumina. Column: 6' x 1/8", 3% Dexsil 300 on Chromosorb W-AW (100/120). Conditions same as in Figure 1. GC/MS system: AEI MS-12 interfaced to an HP-5830A gas chromatograph via a heated transfer line and a Watson-Biemann type separator. Data system Nova DS-50.
- Figure 4 - a) GPC separation of fraction #5 from alumina.

b) GPC separation of fraction #6 from alumina.  
c) GPC separation of fraction #7 from alumina.  
Columns: 60 Å, 100 Å, 200 Å and 500 Å Styragel (Waters Assoc.) particle size 37-75 μm, 4' x 3/8" each, eluent methylene chloride, RI and UV (254 nm) detectors, F = 3 ml/min.

Figure 5 - Gas chromatograms of selected GPC fractions derived from fraction #5 from alumina.

Figure 6 - Gas chromatograms of selected GPC fractions derived from fraction #6 from alumina.

Figure 7 - Gas chromatograms of selected fractions derived from fraction #7 from alumina. All chromatograms in Figures 5-7 were run on a 3% Dexsil 300 column, conditions as in Figure 1.

Figure 8 - Preparative gas chromatogram of the hopane concentrate fraction. Column: 8' x 1/4", 3% Dexsil 300, TCD, isothermal 300°C, F = 60 ml/min. Cutting points are marked in the chromatogram.

Figure 9 - GC test of the purity of the isolated hopanes. Column same as in Figure 1, isothermal 300°C, F = 20 ml/min.  
2 = C<sub>27</sub> hopane, 4 = C<sub>29</sub> hopane, 5 = C<sub>30</sub> hopane.

Figure 10- a) High-resolution mass spectrum of C<sub>29</sub> hopane.  
b) High-resolution mass spectrum of C<sub>30</sub> hopane.  
Instrument: AEI MS-50, 70 eV, direct probe.

Figure 11- <sup>13</sup>C n.m.r. chemical shift line diagrams of C<sub>30</sub> hopane from Athabasca bitumen and published<sup>8</sup> spectra.

Figure 12- Mass chromatograms of GPC fraction #9 from alumina fraction #7.

Figure 13- Gas chromatogram of the hopane series on a SCOT column (N ~ 28,000) coated with OV-101 on Silanox-101, 0.2 μl sample, Attn. 128x; T<sub>1</sub> 200°C, T<sub>2</sub> 280°C; t<sub>1</sub> 10 min., rate 2°/min.

Figure 14- High-resolution GC of the hopane series on a WCOT column (N ~ 80,000), 0.2 μl sample, split ratio approx. 1:10, Attn. 16x, isothermal 280°C.

Figure 15- Mass chromatograms of GPC fraction #13 from alumina fraction #6. Column type and conditions as in Figure 1.

Figure 16- Preparative HPLC of the total saturate fraction from the Athabasca bitumen. Column: 4' x 2 cm i.d., alumina 37-63 μm (fully activated), eluent n-pentane; F = 18 ml/min., RI detector.

Figure 17- Gas chromatograms of fractions I and II from Figure 16 on a SCOT column (OV-101, Silanox-101); sample 0.2 μl.

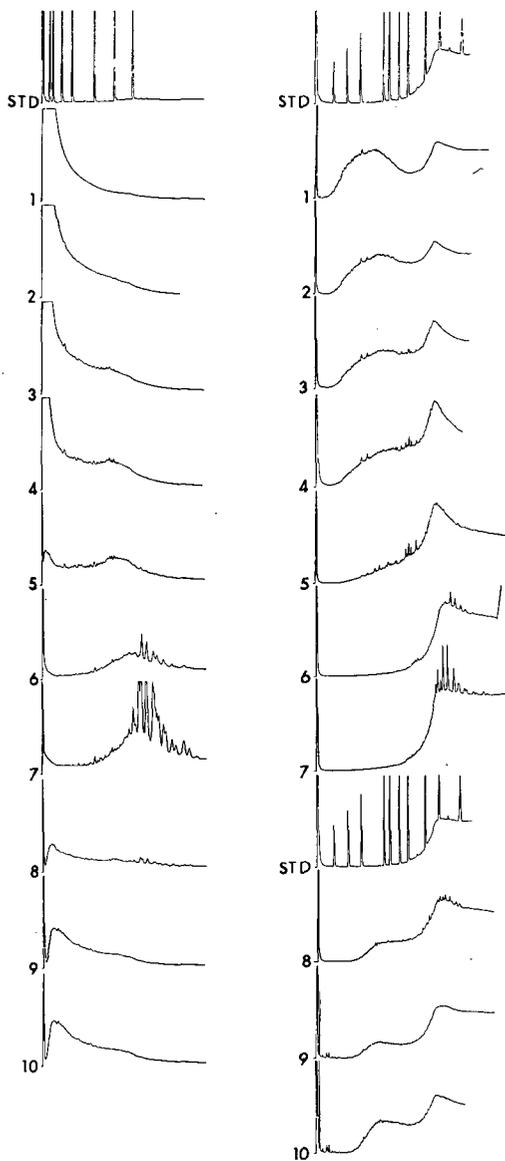


Fig. 1 - Gas chromatographic Analysis of saturate fractions eluted from alumina

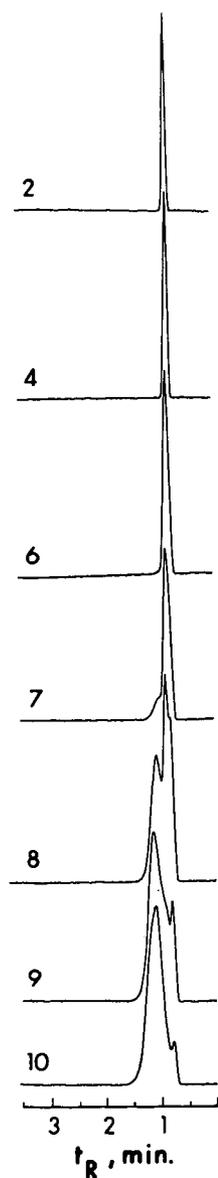


Fig. 2 - HPLC test for the presence of monoaromatics in the saturate fractions from alumina

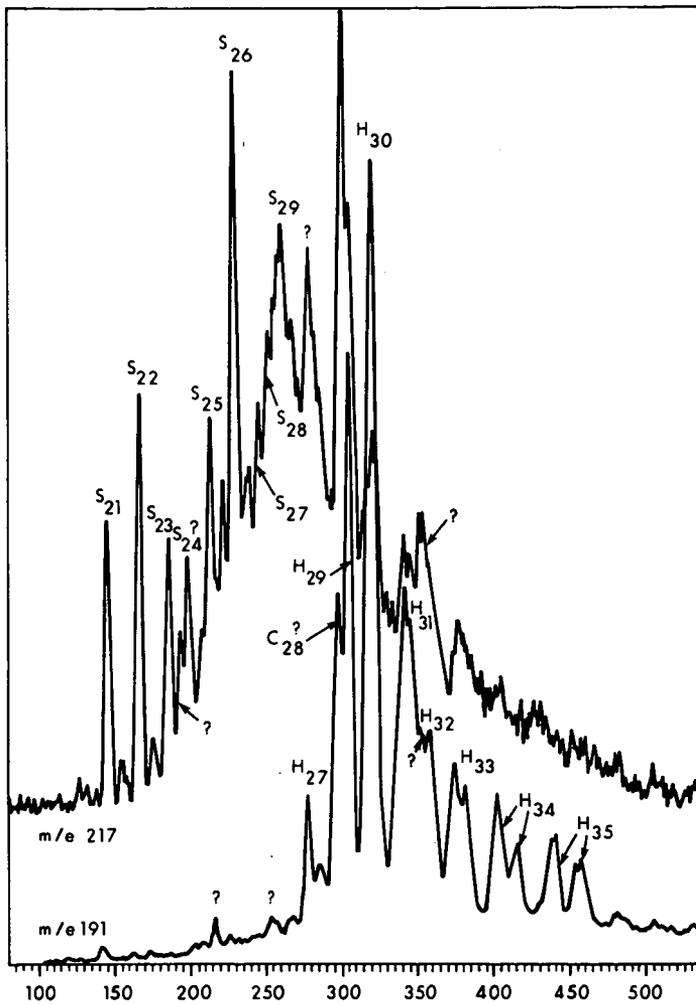


Fig. 3 - Mass chromatograms of the thiourea non-adduct of the saturate fraction #7 from alumina

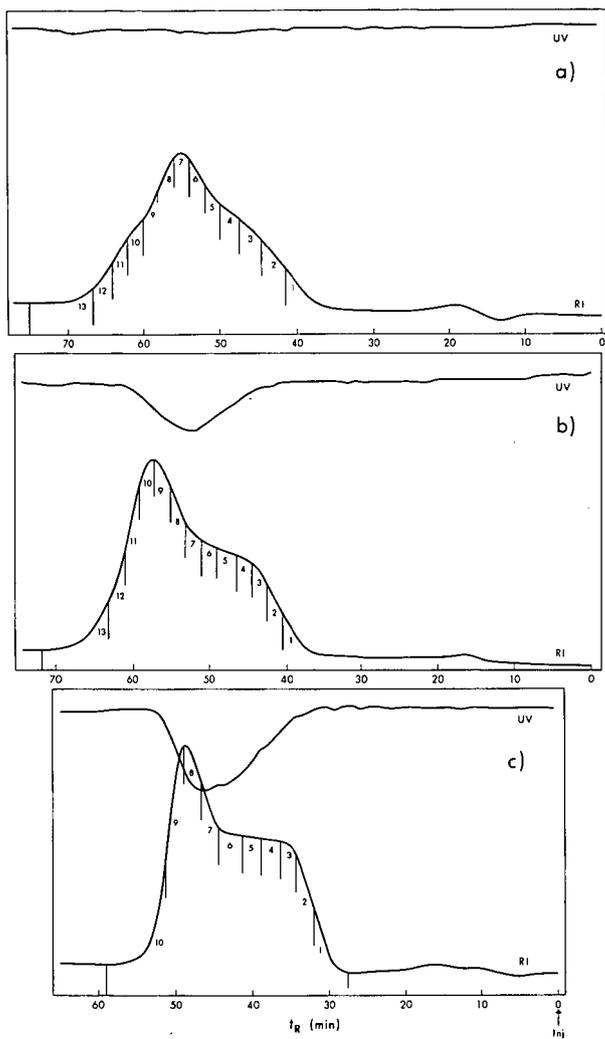


Fig. 4 - GPC separations of fractions #5 (a), #6 (b) and #7 (c) from alumina

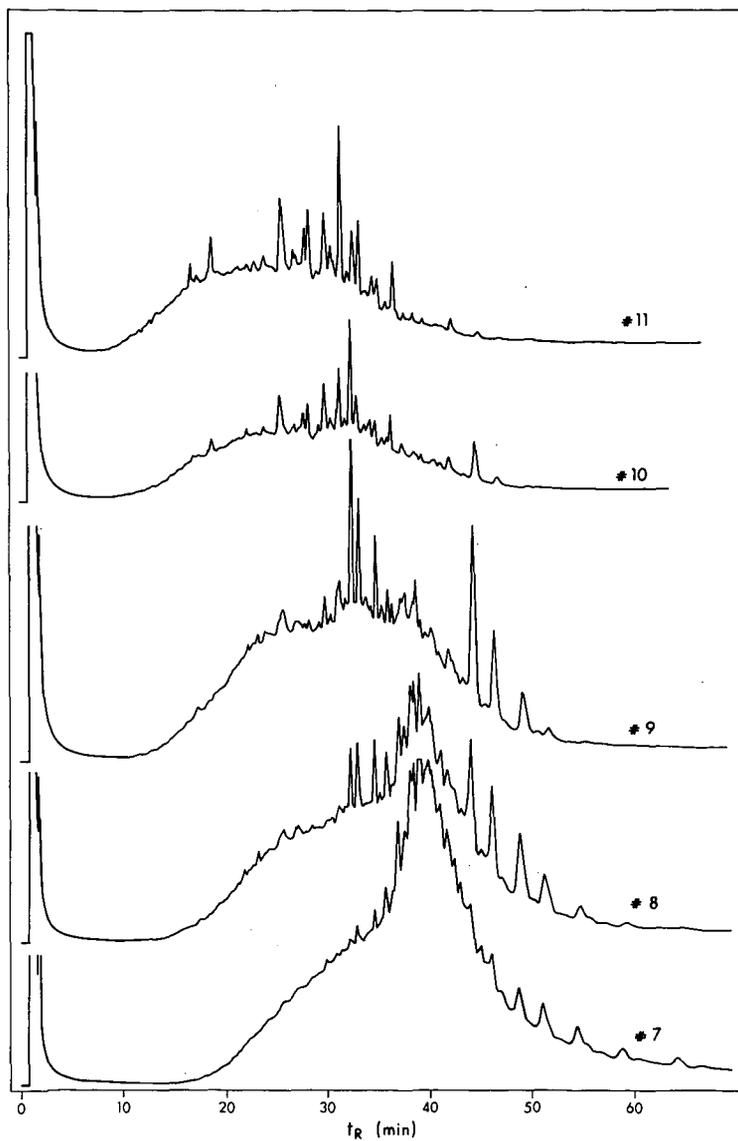


Fig. 5 - Gas chromatograms of selected GPC fractions derived from fraction #5 from alumina

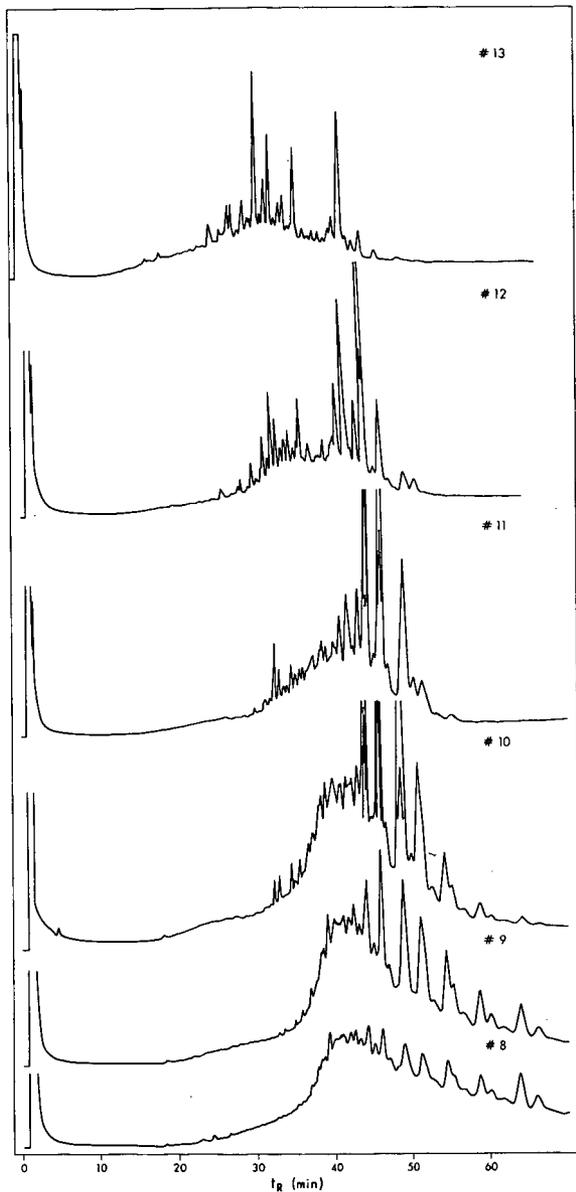


Fig. 6 - Gas chromatograms of selected GPC fractions derived from fraction #6 from alumina

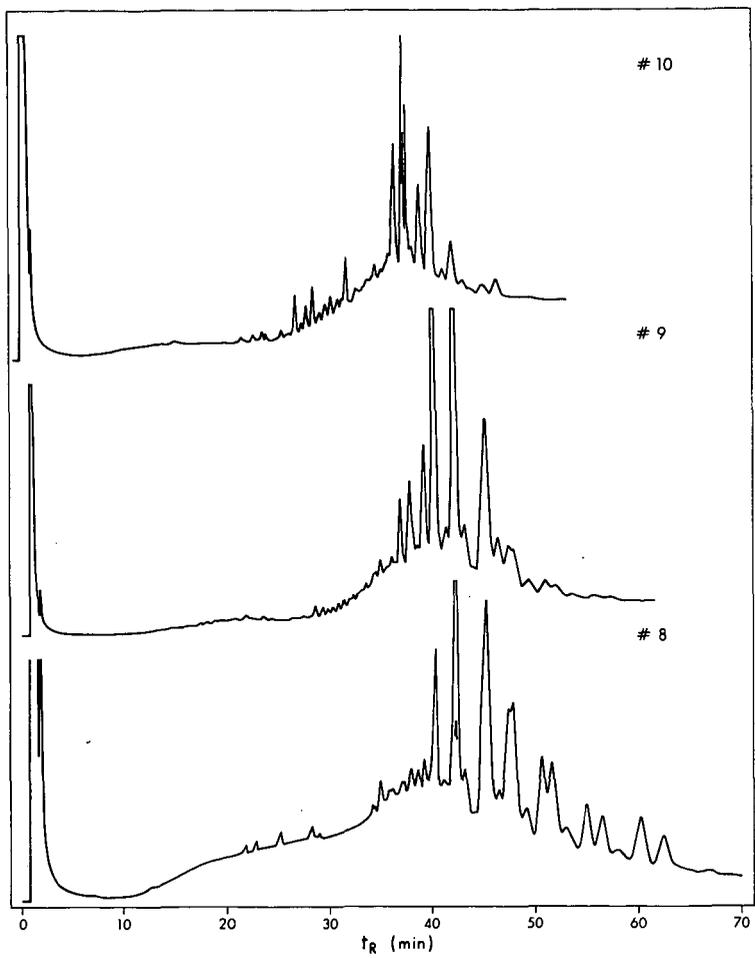


Fig. 7 - Gas chromatograms of selected GPC fractions derived from fraction #7 from alumina

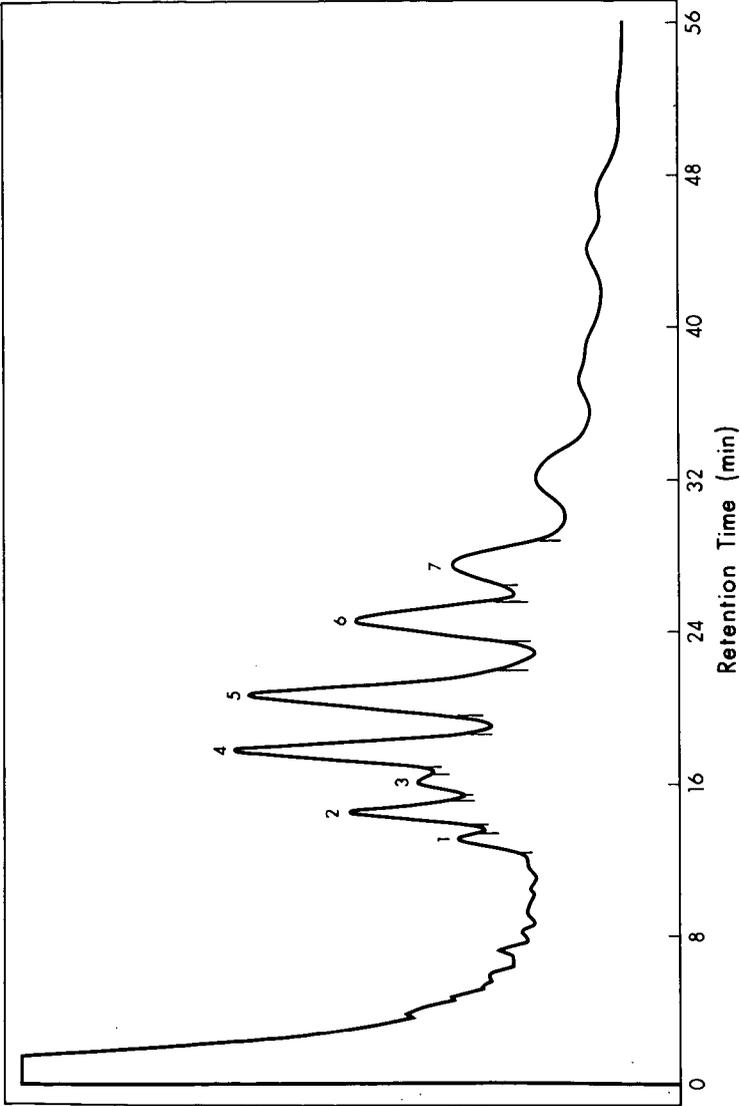


Fig. 8 - Preparative gas chromatogram of the hopane concentrate fraction

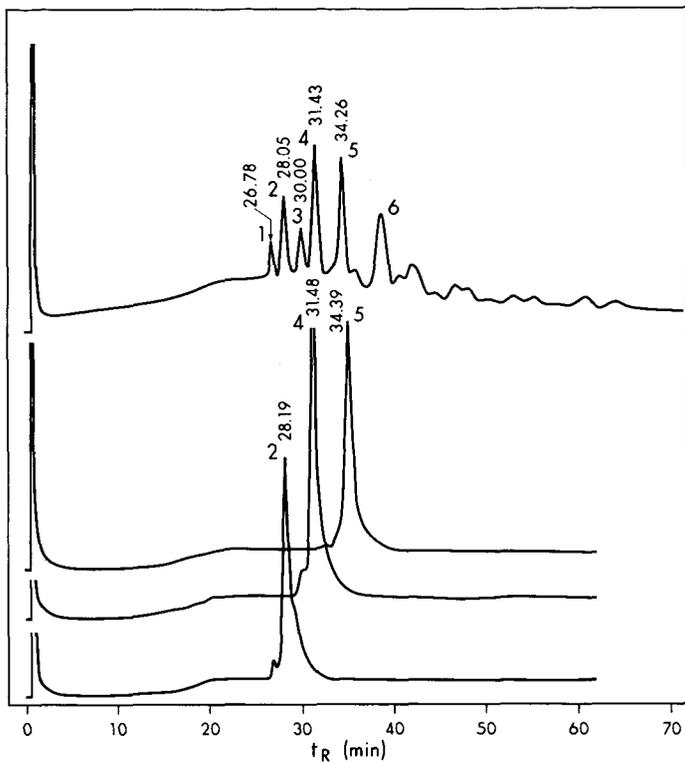


Fig. 9 - GC test of the purity of the isolated hopanes  
 2 =  $C_{27}$  , 4 =  $C_{29}$  and 5 =  $C_{30}$  hopane

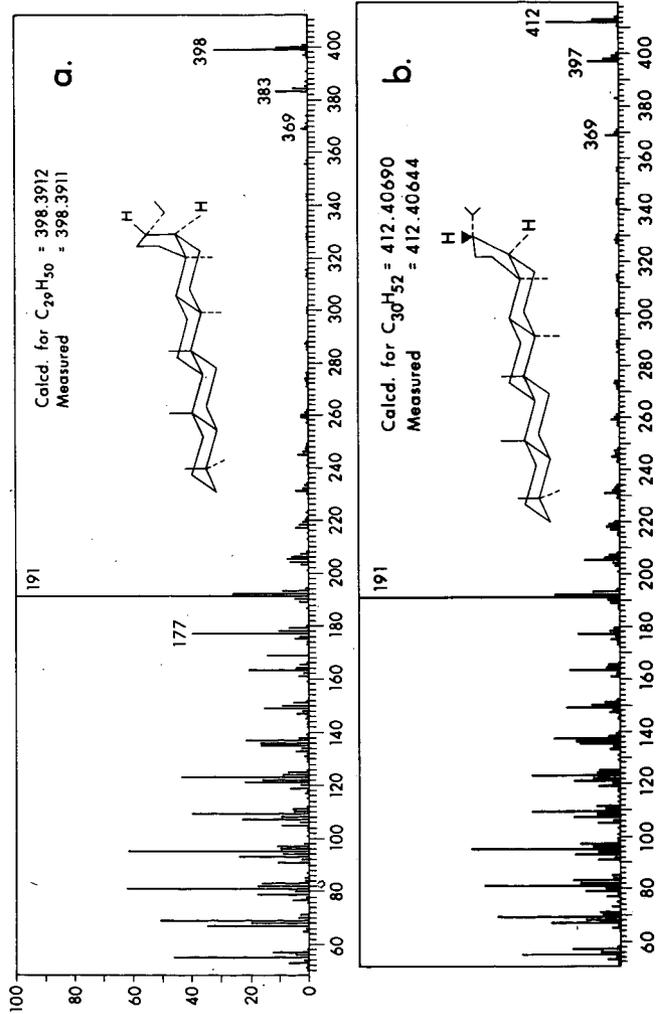


Fig. 10 - High-resolution mass spectra of  $C_{29}$  (a) and  $C_{30}$  (b) hopanes

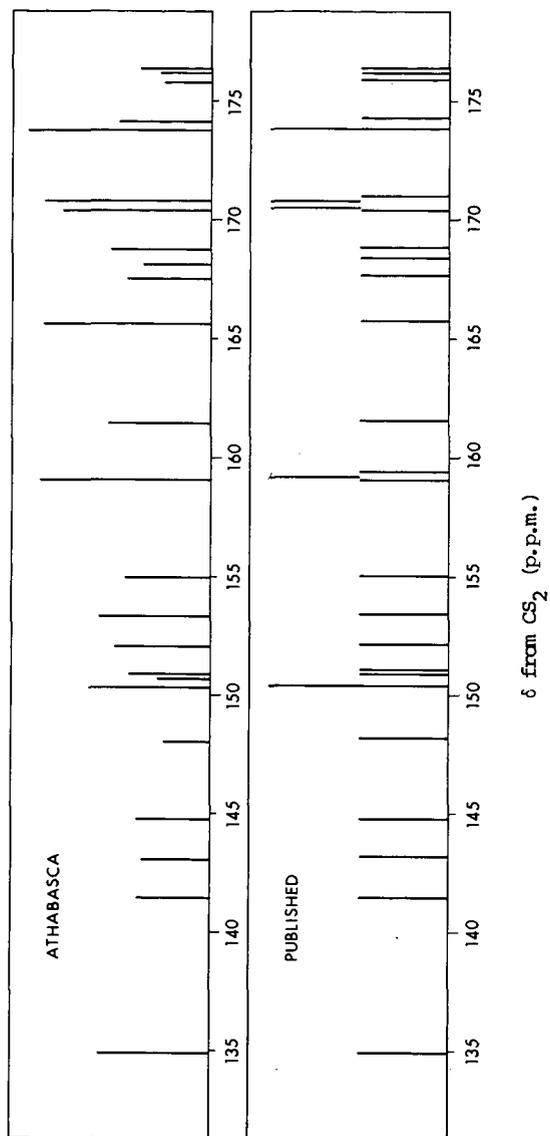


Fig. 11 -  $^{13}\text{C}$  n.m.r. chemical shift line diagrams of  $\text{C}_{30}$  hopane from Athabasca bitumen and published<sup>8</sup> spectra

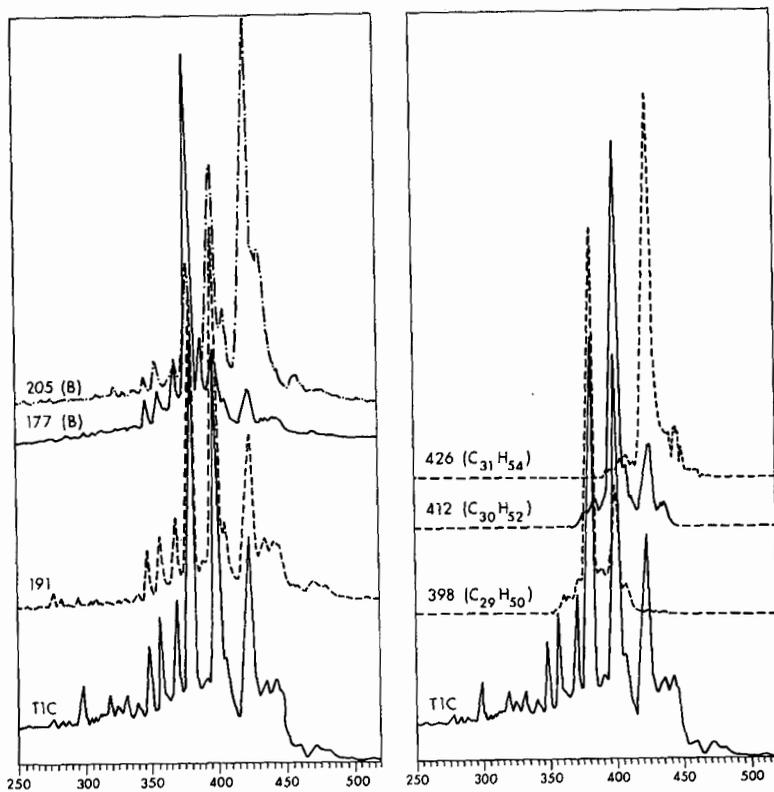


Fig. 12 - Mass chromatograms of GPC fraction #9 from alumina fraction #7

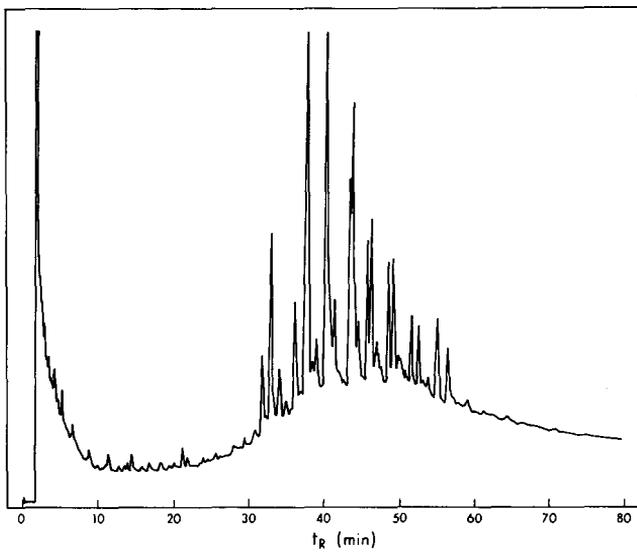


Fig. 13 - GC of the hopane series on a SCOT column

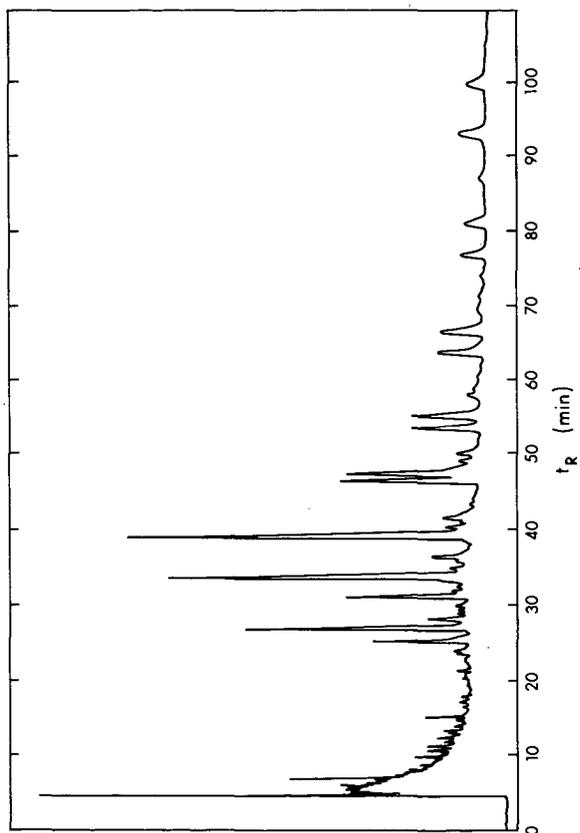


Fig. 14 - High-resolution GC of the hopane series on a WCOT column

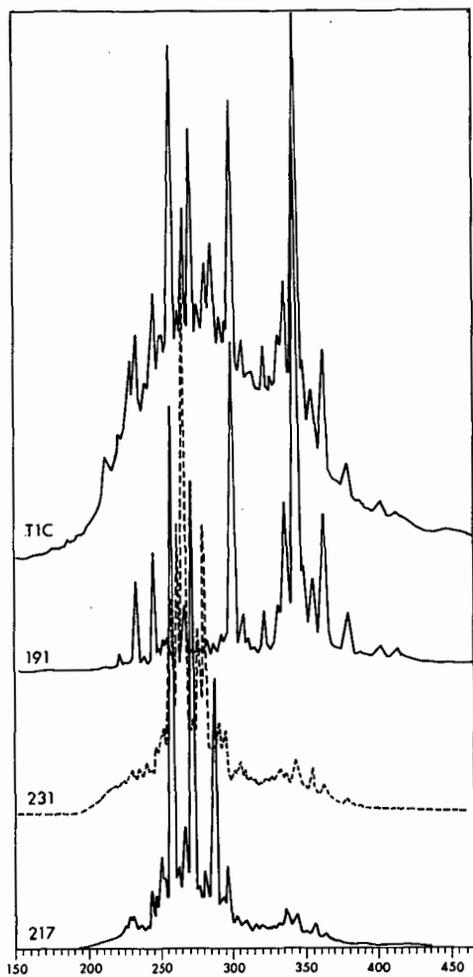


Fig. 15 - Mass chromatograms of GPC fraction #13 from alumina fraction # 6

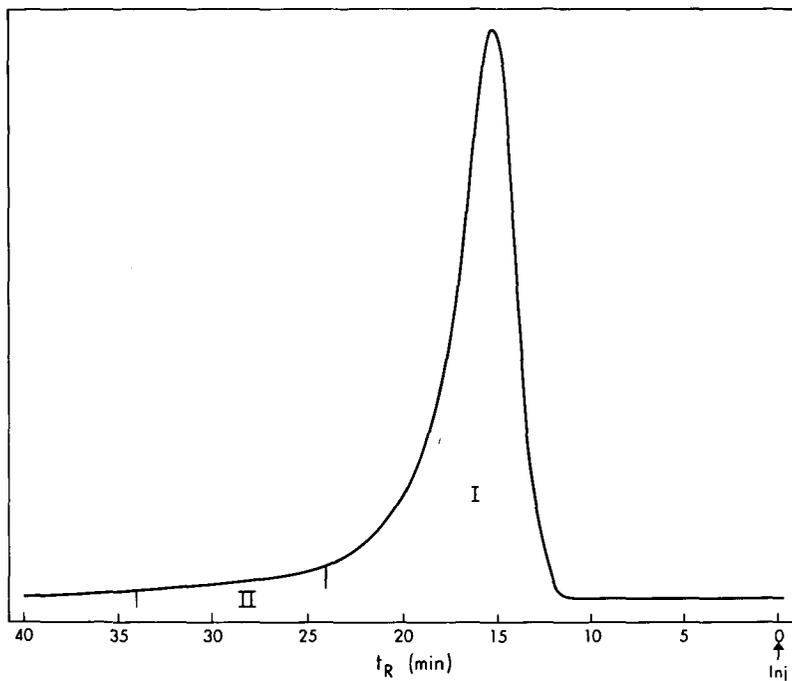


Fig. 16 - Preparative HPLC of the total saturate fraction from the Athabasca bitumen

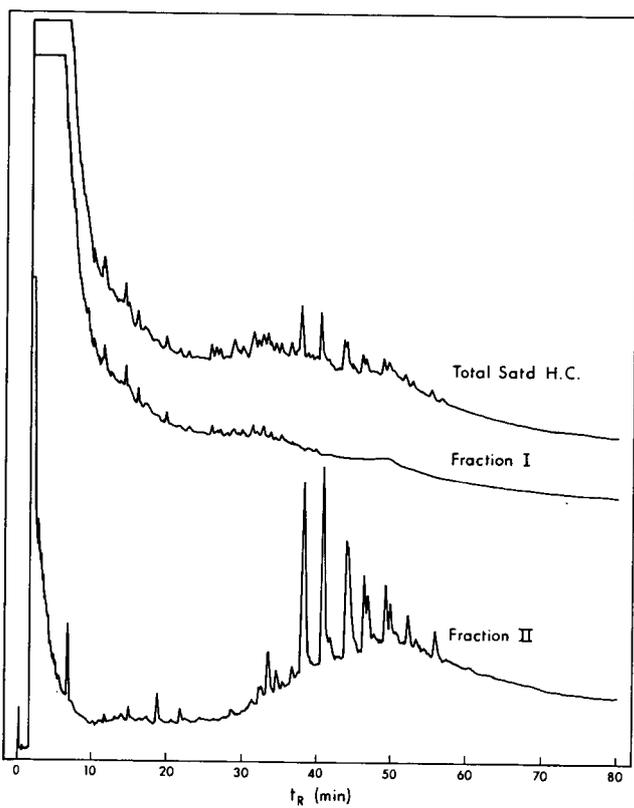


Fig. 17 - GC of fractions I and II from Fig.16 on a SCOT column

## POTENTIAL SHALE OIL PRODUCTION PROCESSES

by

H. C. Carpenter, H. B. Jensen, and A. W. Decora  
Laramie Energy Research Center  
U.S. Energy Research and Development Administration  
Laramie, Wyoming 82071

### ABSTRACT

The recovery of energy from oil shale has been investigated for well over a hundred years. Oil shale industries have existed in a number of countries including an infant industry in the eastern United States that was terminated after the discovery of petroleum in Pennsylvania. Research on oil shale processing has not kept pace with the increased demand for liquid hydrocarbons used as fuels and petrochemical feedstocks. With the present day demand for liquid hydrocarbons and the availability of petroleum, increasing interest in oil shale processing is evident. Potential shale oil production in the United States in the immediate future depends on aboveground retorts developed by the U. S. Bureau of Mines and by a limited number of private companies shortly after World War II. Recent developments in modified in situ retorting technology may also be an alternative method for shale oil production.

### INTRODUCTION

Increasing demand for hydrocarbons both for fuels and for chemical feedstocks and the current awareness of the finite nature of petroleum deposits results in renewed interest in alternate sources of fossil hydrocarbons. Oil shale is one of the alternate sources being considered because organic-bearing shales are located throughout the world. Production of oil from shale on a limited scale has occurred in several countries, but production has never reached a significant level related to the present day world requirements. In the United States, after an infant oil shale industry was terminated by the discovery of petroleum in Pennsylvania, the major activity was a research program started by the United State Bureau of Mines.

During World War II, this research activity was intensified and it is presently being continued by the United States Energy Research and Development Administration as well as by several agencies in the United States Department of the Interior. Several private companies in the United States, and Petrobras in Brazil, are presently conducting, or were in the recent past, conducting research on oil shale retorting processes. In this paper the potential of several of these processes for the production of shale oil will be reviewed.

### BACKGROUND

For well over 100 years, oil shale has been processed to produce hydrocarbon products. In 1859, a Scottish oil shale industry began using small vertical retorts to produce fuels, waxes, and chemicals. In Australia numerous operations were conducted, but the most significant was the Glen Davis plant operated in New South Wales. At one time about 100 vertical kiln retorts of the Pumpherson-Fell type were in operation processing 700 to 800 tons of 70-gallon-per-ton oil

shale per day (12).<sup>1</sup> During World War II, Australian operations produced over  $2 \times 10^8$  gallons of shale oil (6).

In Sweden a wartime operation with an initial capacity of 95,000 barrels of oil per year was established. This operation utilized aboveground retorts and an in situ operation (13). The in situ operation was based on a system of electrical heating that utilized the pressures generated by heating to force the products to recovery wells.

In China and the USSR oil shale processing has been in operation for many years. These operations produced oil and gas and, in Estonia (14-15), shale was used for firing a power plant. Data on recent operations in these countries are sparse.

A Brazilian oil shale research effort appears to be well advanced. Beginning in 1950, the Petrosix retorting process was expanded to a 2,200-ton-per-day demonstration facility by 1973.

#### RETORTING RESEARCH IN THE UNITED STATES

In 1944, the Synthetic Liquid Fuels Act authorized the Bureau of Mines to begin work on converting oil shale to liquid fuels. The oil shale work was divided essentially into two parts. The laboratory research and conducted at the Petroleum Experiment Station located in Laramie, Wyo., and a demonstration plant was constructed at the Anvil Points Facility near Rifle, Colo.

#### Development of the Gas-Combustion Retorting Process (7)

Recovery of shale oil from oil shale is based on a simple thermal decomposition of the solid organic substance in oil shale which is known as kerogen. When heated sufficiently the solid organic material decomposes to form oil, gas, and a spent shale consisting of carbonaceous and inorganic residue. These reactions have been used as a basis for a number of processes, but most of these processes have proved unsatisfactory from the standpoint of economics, or operability, or both. Oil shale retorts essentially are heat exchangers for transferring heat from a heating medium to the shale. They may be divided into four general classes based on the method of heat application.

Class	Method of Heat Application	Examples
I	Heat is transferred to the shale through a wall.	Pumpherson, Hayes, Berg
II	Heat is transferred to the shale from the combustion occurring in the retort by burning product gases and the residual carbon in the retorted shale.	N-T-U, Union Oil Co., Pintsch, Bureau of Mines gas-combustion
III	Heat is transferred to the shale by passing previously heated gases or liquids through the shale bed.	Swedish Industrial, Bureau of Mines gas-flow, Royster
IV	Heat is transferred to the shale by introduction of hot solids into the retorting bed.	Standard Oil Co. fluidized bed, Bureau of Mines hot-solids-contact, Aspeco, TOSCO

1 Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The most desirable process for retorting Colorado Oil shale should meet as many of the following requirements as possible:

1. It should be continuous.
2. It should have a high feed rate per unit cross-sectional area.
3. It should have high oil recovery efficiency.
4. It should require a low capital investment, and possess a high operating time factor with low operating costs.
5. It should be thermally self-sufficient; that is, all heat and energy requirements should be supplied without burning any of the product oil.
6. It should be amenable to enlargement into high-tonnage retorts rather than to a multiplicity of small units.
7. It should require little or no water because the Green River oil shale deposits are located in an arid region.
8. It should be capable of efficiently processing oil shale of a wide range of particle sizes to minimize crushing and screening.
9. It should be mechanically simple, easily operable.

At the Anvil Points Facility, the Bureau of Mines began an investigation that led to the development of the gas-combustion retorting process. This investigation included a study of the N-T-U process, the Royster process, and the gas-flow process before the gas-combustion process was developed. Of all of the processes studied, the gas-combustion process comes closest to fitting the above-listed desirable characteristics.

The gas-combustion retorting process is characterized by its use of continuous gravity flow of shale, direct gas-to-solids heat exchange, and heat supply by internal combustion. The essentials of the process are illustrated in figure 1. The retort is a vertical, refractory-lined shaft equipped with shale- and gas-handling devices. It is convenient to divide the retort into four functional zones, although there is no physical separation, and no definite dividing line between these zones.

Crushed and sized shale moves downward as a bed through the retort vessel, passing through the product cooling zone where the solid particles are heated almost to retorting temperature by the rising gases from the retorting zone. It then passes downward into the retorting zone where the organic matter is decomposed by heat to liberate oil vapor and gas. A carbonaceous residue from this reaction remains as part of the retorted shale particles. The retorted shale next proceeds to the combustion zone, where the sustaining heat for the process is produced by burning the organic residue on the shale plus a part of the product gas which is returned to the system. From this hot zone, the shale moves down through the heat recovery zone where its heat is transferred to the rising stream of recycle gas. The cooled, spent shale is discharged from the retort mechanically at a controlled rate, which governs the retort throughput.

Recycle gas is injected at the bottom of the vessel and rises through the spent shale in the heat recovery zone. In effect, this zone is a simple countercurrent, gas-to-solids heat exchanger. An air distribution device is located near the center of the retort where air, diluted with part of the circulating retort gas, is injected. This mixture is heated quickly by the hot spent shale; reaction of the oxygen with combustibles produces a hot flue

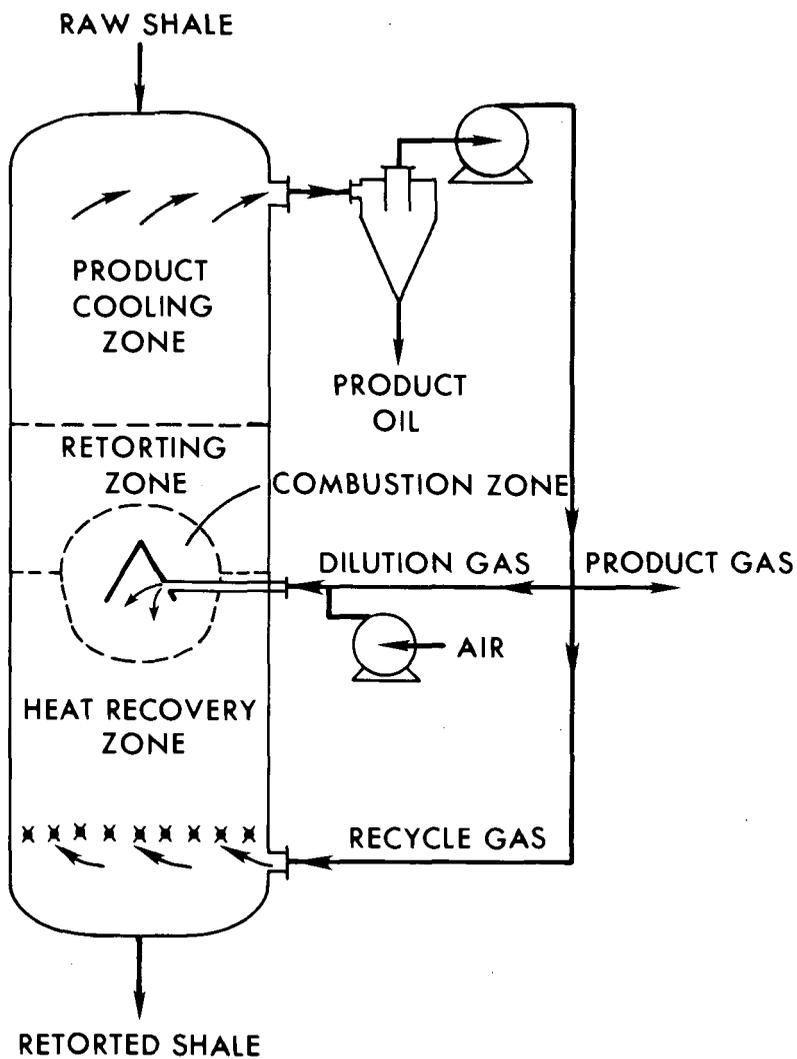


FIGURE 1. - GAS-COMBUSTION PROCESS.

gas. The hot flue and recycle gases rise in contact with the descending raw shale in the retorting zone, and the solids are heated enough to effect thermal decomposition of the kerogen in the shale. The liberated gases and oil vapors, commingled with the upward rising gas stream, are cooled by the entering raw shale. In the product cooling zone, the gas stream is cooled and the oil condenses as a fine mist or fog and is carried out of the top of the retort. Both the retorting and cooling zones are, in effect, counter-current gas-to-solids heat exchangers. However, their functioning is complicated by retorting reactions and by oil condensation.

The overhead stream from the retort passes first through oil-mist separators to recover the shale oil. The oil-lean gas then enters a blower from which it leaves at higher pressure and is divided into three streams. One part (dilution gas) is injected with air into the center of the retort. Another part (recycle gas) enters the bottom of the retort, and the remainder (net product gas) is vented from the system.

The typical material balance and pertinent temperatures are shown in table 1. These data reflect an actual test period during which 2,000 pounds

TABLE 1. - Typical gas-combustion retort material quantities and temperatures

	Weight, pounds	Volume, std cu ft	Temperature, °F
Material in:			
Shale	2,000	--	60
Recycle gas	1,134	14,850	129
Dilution gas	148	1,940	129
Air	294	3,840	91
Material out:			
Retorted shale	1,611	--	166
Product oil	196	--	129
Total retort gas	1,769	23,170	129

of raw shale, assaying 26.7 gallons per ton, were charged to the retort at 60°F. Under the retorting conditions of this test, 1,611 pounds of retorted shale were discharged at a temperature of 166°F, and 25.2 gallons of oil weighing 196 pounds were produced. The total volume of recycle gas, dilution gas, and air injected to the retort was 20,630 scf. The total gas discharge was 23,170 scf, representing a volume increase of 2,540 cu ft as the result of various reactions within the retort, such as the evolution of gas from cracking organic matter, and production of carbon dioxide from decomposing mineral carbonates. Net product gas vented amounted to 6,380 scf. The heating value of this gas varied from 80 to 100 Btu per scf and, with preheating, the gas could be used as fuel for gas turbines or waste-heat boilers. The weight of gas moved by the gas blower was about the same as the weight of raw shale charge.

Most of the studies were made at mass shale rates between 200 and 300 lb/(hr) sq ft. retort bed area. This is equivalent to a shale bed movement of about 3 to 4.5 feet per hour.

The reactions within the gas-combustion retort are complex, and a study of this phase of retorting was not completed when the project was terminated. Numerous combustion and related reactions are possible among the various gases, liquids, and solids present. These materials include air, carbon dioxide, carbon monoxide, hydrogen, water vapor, hydrocarbon gases, shale oil and bitumens, carbon, and various sulfur- and nitrogen-bearing materials, in addition to many minerals.

Because of the complexity of the combustion and thermal decomposition reactions, it was necessary to assume simplified conditions in calculating heat balances. Decomposition of part of the magnesium and calcium carbonates in the shale is an important endothermic reaction. Estimation of the extent of this reaction was relatively simple through comparison of the amount of carbon dioxide in the vent gas with that expected from combustion reactions. Other mineral reactions also may take place, such as oxidation of pyrites in the shale to produce sulfur dioxide or sulfates, and combination of silicates with calcium or magnesium oxides.

The gas-combustion process is notable for its high thermal efficiency. Because a large part of the sensible heat of the retorted shale is recovered, it is necessary to add only about 400,000 Btu per ton of shale. This low heat requirement is a distinct advantage, because it may be met by combustion of the easily burned portion of the carbonaceous residue near the surface of the retorted shale particles, and by combustion of a part of the gas. There is no indication that combustion rates limit the capacity of the gas-combustion process. The limits seem rather to be in such factors as increasing pressure drop through the bed, and the tendency for fine shale particles to become entrained in the gas stream as throughput is increased.

The endothermic carbonate decomposition reactions absorb about 160,000 Btu per ton of shale under normal gas-combustion retorting conditions. Thus the presence of mineral carbonates helps dissipate excess heat, when processing difficulties might otherwise result in temperatures high enough to cause severe fusion of shale. In general, carbonate decomposition tends to limit the maximum shale temperature to about 1,600°F, several hundred degrees below the fusion point of the inorganic matter that is present.

The mechanical simplicity of the gas-combustion retort is a particularly advantageous feature. The retort vessel is simple, and both gas and shale distribution devices are stationary. Raw and spent shale handling presents few problems because of the low temperatures and mechanical forces involved. The air distributor at the combustion zone is the most critical part of the system, and this requires special considerations in design, arrangement, material selection, and operation technique.

From the outset of the experimental work at Anvil Points, it was observed that the gas streams from retorts usually contained shale-oil mist. However, the potential benefit of the phenomenon was not realized until tests showed that the product oil could be removed as a mist carried in the gas stream. This discovery, a fundamentally new concept in oil shale retorting, suggested an approach to retorting and oil recovery that led to the development of the gas-combustion process.

Shale-oil mist forms in the retort just above the retorting zone, which in effect is a countercurrent heat exchanger. The downward moving oil shale is heated almost to retorting temperature, and the rising gases and vapors are

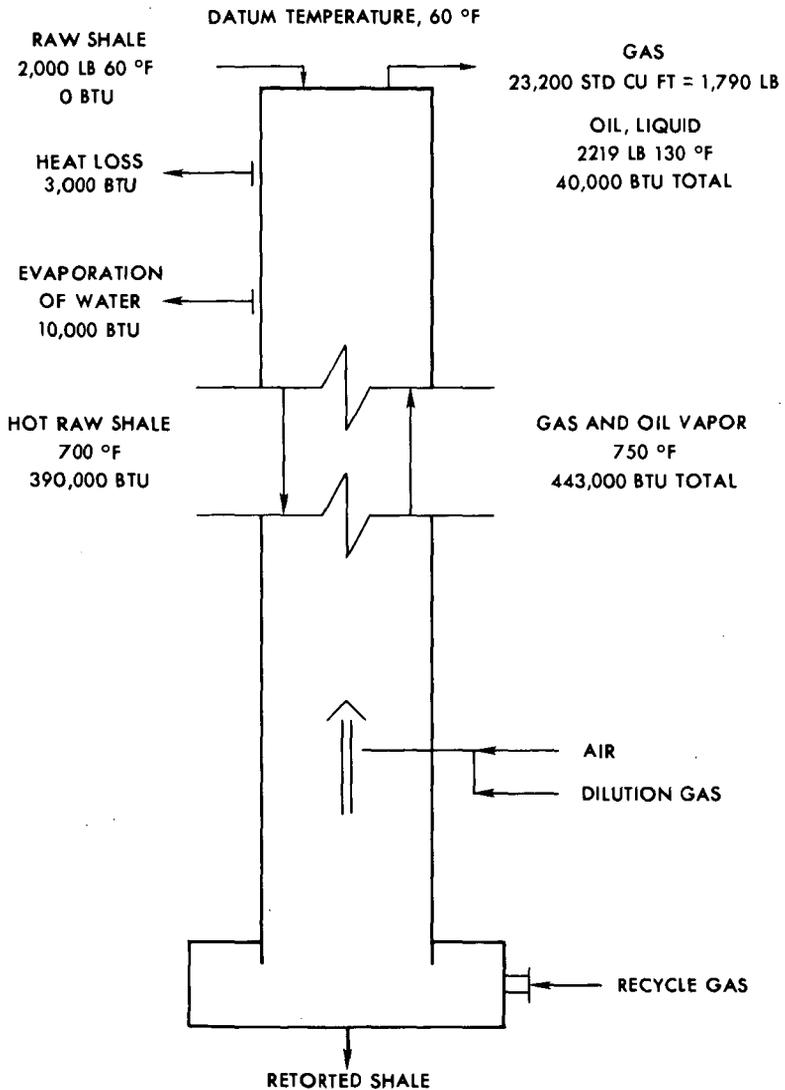


FIGURE 2. - MIST FORMATION SECTION OF THE GAS-COMBUSTION RETORT.

are cooled to the temperature of the retort outlet. Figure 2 is a diagram of this section. Conditions at the upper end are known because they can be measured directly, but there is no sharp separation of the zones of retorting and product cooling. For purposes of this discussion, a shale temperature of 700°F has been assumed as a dividing point. This is about the temperature at which the rate of kerogen decomposition becomes appreciable, so it may be considered the place at which the retorting zone begins.

Typical conditions existing around the mist-formation section are noted on figure 2. About 400,000 Btu's of heat are transferred from the gas stream to each ton of shale. Condensation of the oil vapor represents a substantial portion of this heat quantity, about 100,000 Btu. For the present purpose, it is assumed that no water vapor condenses in the upper part of the mist-formation section, even though this assumption probably is not always correct.

If the retort is operating satisfactorily, oil condenses in the upper section as a fine mist which is easily carried out with the gas.

The general requirements for efficient removal of mist from a retort can be determined from study of the upper section of the retort. The usual principle of mechanical entrainment does not operate because the gas velocity is too low to carry large oil drops, and any condensed oil deposited on shale particles will descend to the retorting zone with the moving bed. If the oil is to leave the retort as mist in the offgas stream, the droplets must be formed in the spaces between the shale particles, and must be small enough so that inertial separation does not occur as they are carried upward by the gases through several feet of shale bed.

Some condensation and deposition of oil on the pieces of shale is considered unavoidable. It is believed that even under the best conditions a thin film of oil is present on all particles of shale entering the retorting zone. A refluxing problem occurs when the amount of oil on the shale is great enough to drop or flow down through the bed of shale.

Oil on the pieces of shale is subjected to increasing temperature as the bed moves toward the retorting zone, and part of the oil redistills. However, the heavier fractions are thermally cracked before reaching their boiling point. Only about half of a gas-combustion crude oil distills at atmospheric pressure in the standard laboratory distillation test. Cracking of the heavier fraction forms lighter oil, gas, and coke. Most of the lighter oil is recoverable, but the gas and coke represent a loss in yield of primary product. Thus, refluxing, if uncontrolled, can result in substantial losses and altered products.

Runs may be classified either as refluxing or nonrefluxing, depending on the properties of the product and on operating characteristics. Equilibrium is stable under either type of operation, so that substantial changes are needed to shift from one type to the other. Within some operating ranges a refluxing type of equilibrium may exist or not depending upon conditions at the outset of a run. Data from runs 236 and 241, shown in table 2, illustrate this phenomenon. Run 241 was planned to duplicate 236, but the results were quite different even though the operating conditions apparently were matched. Comparison of the two runs shows that oil from run 241 was lighter, the viscosity and the carbon residue were lower, and the oil yield was greatly reduced. All of these differences indicate more cracking.

TABLE 2. - Comparison of refluxing and nonrefluxing tests

	Test number	
	236	241
Type of test	Nonrefluxing	Refluxing
Operating conditions:		
Shale grade, gpt	21.1	20.8
Shale size, in.	1/2 to 1	1/2 to 1
Raw shale rate, lb/hr	616	616
Air quantity, scf/ton shale	4,210	4,020
Recycle gas quantity, scf/ton shale	17,000	16,800
Results:		
Oil gravity, ° API	19.7	22.8
Oil viscosity at 130° F SSU	132	61
Oil Remsbottom carbon, wt-pct	5.2	.6
Oil yield, vol-pct Fischer assay	93	72
Retorted shale assay, gpt	.5	1.8
Product gas temperature, ° F	125	161

Secondary cracking in the retort produces a lighter, less viscous oil that has some quality advantages, but these are outweighed by the loss of yield. In addition, refluxing causes operational difficulties in that the coke that forms tends to bond the shale particles into large agglomerates, interfering with, and sometimes completely stopping, the flow of shale.

Refluxing also causes marked changes in the temperatures in the retort. Under refluxing conditions, there is an oil stream that moves downward through the shale bed. The volume of this oil may be appreciable. This downward flow of oil alters the heat distribution in the mist-formation section because of the thermal effects of revaporization and secondary cracking. The void space pattern in the shale bed also is affected by refluxing, even to the extent of causing as channeling, and the heat transfer coefficient between the hog gas and shale is reduced by the oil film. In comparison with nonrefluxing operation, refluxing conditions tend to increase the temperature near the top of the bed because of heat release through condensation, and to decrease the temperature lower down because of the heat load imposed by vaporization. Cracking reactions and other thermal effects, such as change in offgas temperature and carbonate decomposition, also affect the picture. It is apparent that formation of a stable mist is an essential part of the gas-combustion process, and that an understanding of the factors controlling mist formation is important for effective operation of the process.

A summary of the results of operations by the Bureau of Mines at Anvil Points using two different sized retorts are shown in table 3. Examination of this table shows that the oil yield in volume-percent of Fischer assay was about 7 to 11 percent lower for the 150-ton-per-day plant than for the 6-ton-per-day plant. Since the runs shown are representative of smooth,

TABLE 3. - General data summary, evaluation runs on the 150 ton/day plant

Test number	150 ton/day plant				6 ton/day plant			
	25(1-5)	26(1-2)	26(3-5)	27(1-3)	28(1-4)	28(5-6)	222(A-J)	304(A-D)
Length of test, hours	120	48	72	72	96	48	240	72
Rates and quantities:								
Shale size, in.	3/8-3	1-2	1-2	1-2	1-2	1-2	1/2-1 1/2	1/2-1 1/2
Bed height, ft and in.	9,11	9,11	9,11	9,11	7,2	7,2	7,0	7,0
Raw shale rate, lb/(hr)ft <sup>2</sup>	299	222	299	350	299	300	233	229
Air rate, scf/ton shale	3,940	4,230	3,910	3,840	4,010	4,290	3,760	3,840
Dilution gas rate, scf/ton shale	2,860	3,800	2,950	3,140	3,100	4,040	--	1,940
Recycle gas rate, scf/ton shale	13,340	12,400	12,650	12,660	12,500	10,260	16,620	14,850
Temperatures, ° F:								
Product outlet	162	142	141	143	141	126	123	129
Retorted shale out	376	348	356	345	378	447	185	166
Raw shale in	40	34	32	30	28	25	--	85
Recycle gas	241	247	250	246	224	213	122	129
Dilution gas	83	90	92	92	79	86	--	129
Air	128	129	131	144	110	98	84	91
Yields:								
Oil, vol-pct Fischer assay	82.8	92.3	86.2	86.7	85.1	86.1	94.1	95.0
Gas, scf/ton shale	6,040	6,440	6,000	6,020	6,100	6,090	5,810	6,380
Retorted shale, wt-pct of raw shale	81.8	82.9	82.3	82.1	83.3	83.0	77.9	76.5
Liquid water, lb/ton shale	.2	5.0	.9	1.1	4.9	11.2	25.7	18.8
Miscellaneous:								
Retort pressure drop, in. H <sub>2</sub> O/ft bed	.90	.37	.73	1.02	.58	.45	.34	.40
Carbonate decomposition, wt-pct	24.9	24.1	26.9	25.6	23.3	23.6	26.1	37.6

extended operating periods in both plants, the data shown are indicative of the maximum yields that could be expected at the stage of process development from the equipment and procedures used in this study. Yields from the 150-ton-per-day plant were improved by using a narrow-sized-range shale. However, the performance still did not equal that achieved with the smaller unit. The reason for this decrease in yield in the larger unit appears to be primarily the result of secondary cracking. Some evidence of secondary cracking was shown by differences in oil properties. The gravity of the oil produced in the large plant was 21° API or greater while that produced in the small plant was 20° API in kess. The viscosities and Ramsbottom carbon contents of the oils also indicated more extensive cracking in the 150-ton-per-day plant. Comparison of the product gas streams from each of these two retorts also indicated that the larger retort may have been troubled by extensive secondary cracking. The 150-ton-per-day retort produced a gas containing more light hydrocarbons than the 6-ton-per-day retort.

Secondary cracking not only forms light gases, but also forms coke which contributed to the greater quantity of carbon which was found on the spent shale from the 150-ton-per-day retort.

Another problem related to the operation of a moving bed retort is the flow of solids through the retort vessel. Because of segregation of various particle sizes, wall effects, the resistance to solid flow of air/gas distributors, and other operational problems, there is a tendency for localized heating to result in clinker formation. These clinkers further impede the flow of solids and ultimately result in bridging which completely stops the flow through the retort vessel. The bridged material must be removed mechanically before the retorting process can be continued.

By the mid-1950's, work by the Bureau of Mines on the gas-combustion process was terminated; however, in 1964, the Anvil Points Facility was reactivated and operated under contract to the Government by six major oil companies (10-11). This work further defined the effects of operating variables and continued to indicate that the gas-combustion process is technically feasible. The Anvil Points Facility was again leased in the early 1970's to Development Engineering, Inc. for development and demonstration of the Paraho Oil shale retorting process.

#### The Paraho Process

The Paraho process is very similar to, and can be considered, a further development of the gas-combustion process. Major improvements of the Paraho process over the gas-combustion process are related to better process control, including solid and fluid flow. This more precise control tends to minimize operational problems such as bridging and loss of liquid product by refluxing on the cold shale. The Paraho process can also be successfully operated in an externally heated mode where the energy for the process is provided by burning part of the recycle gas stream in an external heater.

In the externally heated mode, the quality of the recycle gas can be improved. Liquid oil recoveries remain essentially unchanged.

### The Union Oil Company Process

To overcome the problems of bridging and secondary cracking of product oil, Union Oil Co. devised a retorting process based on a retort which utilizes a rock pump. This rock pump is a piston-type feeder which forces solid oil shale particles upward into an inverted, cone-shaped vessel which is open to the atmosphere at the top. Spent shale solids overflow the retort vessel's top rim after having been retorted in the lower regions of the vessel.

Air enters the moving bed at the top of the vessel and flows downward countercurrent to the flow of solids. Because of the influence of gravity refluxing is less likely to occur and secondary cracking is much less of a problem. The rock pump tends to break up any bridging in the material and forces spent shale from the vessel. Over the years the Union Oil process has been modified. In 1974, Union Oil Co. announced an improvement to the process that was called the SGR process.

The SGR process, which stands for steam-gas-recycle, uses essentially the same retort design as the internally heated process except that the top of the retort was covered to prevent air from being admitted. The spent shale was transferred to a separate vessel where oxygen and steam reacted with the residual carbon left on the spent shale. The hot synthesis gas that was produced in this upper vessel was injected into the shale in the retort to provide all necessary heat for retorting the incoming shale.

In the Union "B" process, heated recycle gas is used to provide the necessary heat for retorting oil shale.

### The TOSCO 11 Retorting Process

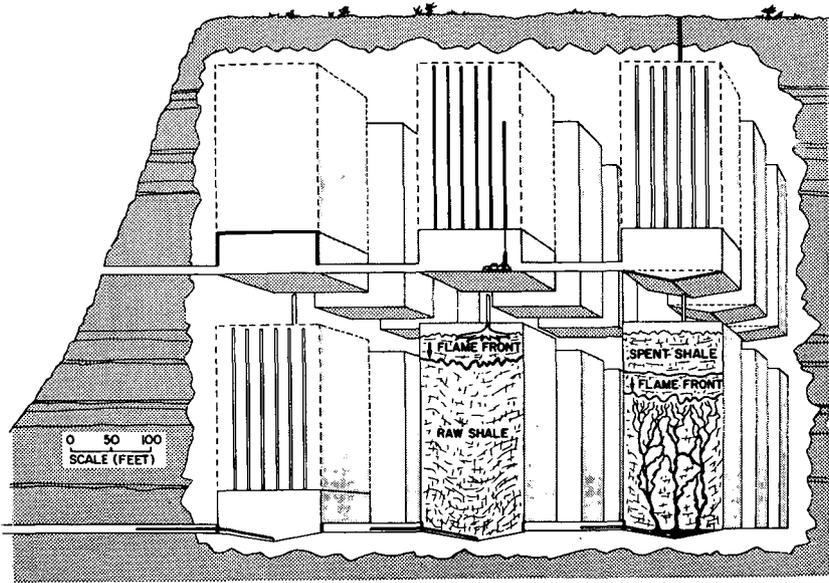
The TOSCO 11 retorting process is also an externally heated process. In this process the retorting vessel was a rotating drum in which raw oil shale is heated by being contacted with ceramic balls that are used as a heat transfer medium. The balls are heated in an external vessel by burning residual carbon on spent shale particles. Because combustion air is not admitted into the retorting vessel, the gases produced are not diluted with nitrogen and, therefore, have a higher heating value. The oil product tends to have a slightly higher API gravity and a lower pour point than shale oil from the gas-combustion process. The recovery of hydrocarbon values from the raw shale is high.

### The Petrosix Retorting Process

The Petrosix retorting process, which was developed in Brazil, is also an externally heated process similar to the gas-combustion process and also to the externally heated Paraho process.

### In Situ Retorting Processes

Retorting oil shale underground by in situ methods has been considered because this method appears to have several potential advantages over above-ground processing. Many shale deposits are deeply buried and may be too lean, or the strata may be too thin to be produced economically by ordinary mining techniques. These deposits can only be produced by some in situ



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|--|--|---|
| <p style="text-align: center;"><b>1</b></p> <p style="text-align: center;">20% OF<br/>ANTICIPATED<br/>MODULE VOLUME<br/>IS REMOVED<br/>FROM BASE</p>                         | <p style="text-align: center;"><b>2</b></p> <p style="text-align: center;">MODULE<br/>IS DRILLED<br/>IN<br/>PREPARATION<br/>FOR FRACTURING</p>                             | <p style="text-align: center;"><b>3</b></p> <p style="text-align: center;">A SHALLOW SLOPING<br/>PIT IS MINED OUT<br/>AND A SHAFT IS<br/>DRILLED INTO BLOCK<br/>FROM ABOVE</p>          |
| <p style="text-align: center;"><b>4</b></p> <p style="text-align: center;">PIPING SYSTEM<br/>FOR OIL RECOVERY<br/>IS PLACED IN PIT<br/>AND SHAFT OPENINGS<br/>ARE SEALED</p> | <p style="text-align: center;"><b>5</b></p> <p style="text-align: center;">MODULE IS DETONATED<br/>AND BROKEN SHALE<br/>IS IGNITED<br/>FROM ABOVE<br/>WITH NATURAL GAS</p> | <p style="text-align: center;"><b>6</b></p> <p style="text-align: center;">COMPRESSED AIR FORCES<br/>FLAME FRONT DOWN<br/>AND SHALE OIL<br/>IS RELEASED BELOW<br/>THIS BURNING ZONE</p> |

FIGURE 3. - SIMPLIFIED SEQUENCE FOR MODIFIED IN SITU OIL SHALE RETORTING.

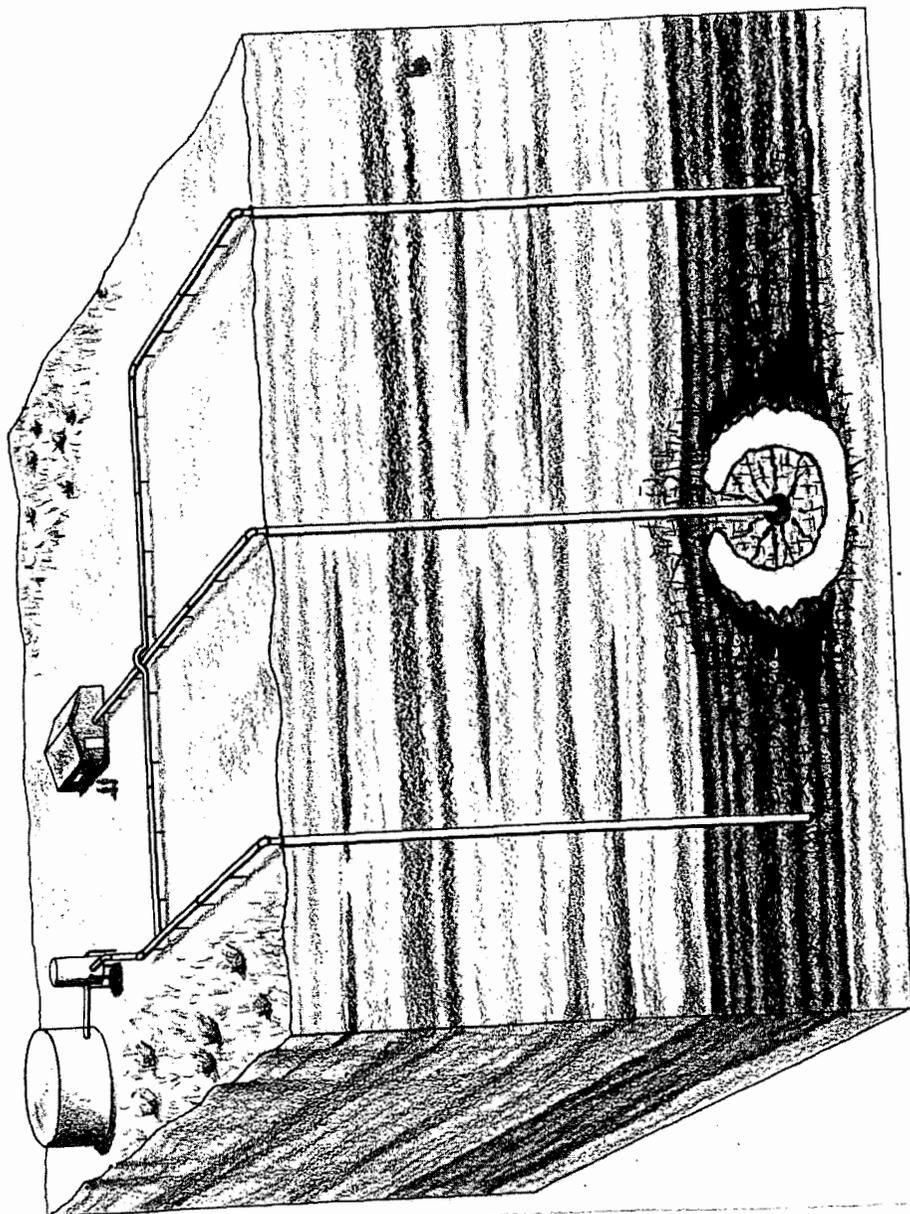


FIGURE 4. - TRUE IN SITU RETORTING PROCESS.

method. There may be advantages of in situ methods in richer, thicker deposits of oil shale also. Because the aboveground installation is less expensive and less complicated, the in situ process is less capital intensive. Because the spent material remains underground there is less problem associated with the disposition of waste products. To be successful, an in situ retort requires sufficient permeability to permit the flow of retorting fluids into and out of the retort, so that heat may be distributed evenly throughout the shale bed. This permeability must be maintained throughout the life of the retort and it must be limited so that the flow of fluids can be contained within the desired volume.

Recently, the term "modified in situ retorting" have come to be applied to an in situ retort in which a part of the material has been removed to allow for expansion during fracturing of the oil shale bed. The term would also be applied to underground retorts prepared by solution mining of soluble salts, either by natural or artificial means.

The remaining in situ processes where very little or no material is removed prior to fracturing have come to be termed "true in situ processes." For the true in situ process, fracturing and maintaining permeability is a much more difficult problem. Some limited work was performed by Sinclair Oil Co. on a true in situ process in Green River oil shale (4). These tests were conducted at Haystack Mountain near Grand Valley, Colo., and have been described, but no technical results were presented.

Extensive experimental work on this process has been conducted by the Laramie Energy Research Center under the Bureau of Mines and the Energy Research and Development Administration. These tests, conducted in Green River oil shale near Rock Springs, Wyo., have been reported extensively in the literature (1-3,8-9,16). These experiments have not produced large quantities of oil but have demonstrated that underground combustion can be initiated and sustained and liquid products can be produced from this type of processing. The outstanding example of modified in situ processing is the work conducted by Occidental Oil Co. (5). In this method, underground mining is used to remove sufficient material to allow for proper expansion of oil shale rubble during the formation of the retort. Figure 3 presents an artist's concept of how a modified in situ retorting sequence could be developed underground. Figure 4 is a concept of how a true in situ oil shale retort might operate. After fracturing, the oil shale is ignited in a central well and combustion is sustained by injecting air. The heated combustion products flow outward toward recovery wells retorting the oil shale and forcing the shale oil to flow in the same direction.

## DISCUSSION

The technical feasibility of producing liquid hydrocarbon products from aboveground retorts has been established. Many of these processes, the gas-combustion process, the Paraho process, the Union Oil process, and the TOSCO 11 process have operated successfully at rates as high as approximately 1,000 tons per day. The Petrosix process has been operated at rates above 2,000 tons per day.

To make significant contributions to today's energy demand, these processes must be scaled up by approximately 10 to 20 times. This scale-up would result in a commercial-sized module and a successful operation of a module would produce realistic data that could be used to develop an economic analysis of an oil shale retorting process. Scaling a process up by a factor of 10 to 20 is not unusual, but a retort handling 20,000 tons per day of broken oil shale has never been constructed and operated. The problems connected with the flow of this amount of solids countercurrent to a flow of retorting fluids will require extensive engineering development. This development will require time and if oil shale is to make a significant contribution to our energy requirements in the near term, the development work should be started as soon as possible.

The picture, as far as in situ retorting is concerned, is roughly similar to aboveground retorting. Modified in situ methods show great promise and are applicable to many shale deposits, especially formations that are thick and readily accessible for the required mining operation. True in situ methods require a great deal more research before they can be considered for commercial application.

Shale oils produced by all of these retorting methods have many similar characteristics. The most extensive work has been done on gas-combustion crude oils and these oils are made up of about 40 percent hydrocarbons and the remaining 60 percent are organic compounds containing oxygen, nitrogen, and sulfur. The oils are deficient in gasoline boiling range material and only about half of it can be recovered overhead during distillation. The crude shale oil could be used directly as burner fuel and this may well be one of the uses during the early stages of development. Because the most urgent needs are for finished fuels required for transportation, gasoline, jet fuels, diesel fuel, and others, research on upgrading and refining to these products is essential.

## CONCLUSIONS

In conclusion, oil shale has been known and processed for more than one hundred years. It is widely distributed throughout the world and could well be an abundant substitute for the diminishing supply of petroleum. There are engineering development problems that must be solved before this resource can compete in the marketplace. Technical feasibility has been shown by several aboveground retorting processes and by modified in situ retorting. All of these processes must be demonstrated on a larger scale to prove operability and to provide reliable economic data. As the retorting processes are developed, refining methods must also be developed to convert this valuable resource to the desired hydrocarbon products.

#### REFERENCES

1. Burwell, E. L., H. C. Carpenter, and H. W. Sohns. Experimental In Situ Retorting of Oil Shale at Rock Springs, Wyo. BuMines TPR 16, June 1969, 8 pp.
2. Campbell, G. G., W. G. Scott, and J. S. Miller. Evaluation of Oil Shale Fracturing Tests Near Rock Springs, Wyo. BuMines RI 7397, 1970, 21 pp.
3. Carpenter, H. C., E. L. Burwell, and H. W. Sohns. Engineering Aspects of Processing Oil Shale by In Situ Retorting. Presented at 71st National Mtg, AIChE, Dallas, Tex., Feb. 20-23, 1972.
4. Grant, B. F. Retorting Oil Shale Underground--Problems and Possibilities. Colo. School of Mines Quarterly, v. 59, 1964, pp. 39-46.
5. McCarthy, H. E., and C. Y. Cha. Oxy Modified In Situ Process Development and Update. Colo. School of Mines Quarterly, v. 71, 1976, pp. 85-100.
6. Mapstone, G. H. Wartime Shale Oil Production at Marangaroo, N.S.W. Proc. of the Second Oil Shale and Cannel Coal Conf., Institute of Petroleum, Glasgow, Scotland, 1950.
7. Matzick, Arthur, R. O. Dannenberg, J. R. Ruark, J. E. Phillips, J. D. Lankford, and Boyd Guthrie. Development of the Bureau of Mines Gas-Combustion Oil-Shale Retorting Process. BuMines Bull. 635, 1966, 199 pp.
8. Melton, N. M., and T. S. Cross. Fracturing Oil Shale with Electricity. Colo. School of Mines Quarterly, v. 62, 1967, pp. 45-62.
9. Miller, J. S., and W. D. Howell. Explosive Fracturing Tested in Oil Shale. Colo. School of Mines Quarterly, v. 62, 1967, pp. 63-74.

10. Ruark, J. R., H. W. Sohns, and H. C. Carpenter. Gas-Combustion Retorting of Oil Shale Under Anvil Points Lease Agreement: Stage I. BuMines RI 7303, 1969, 109 pp.
11. Ruark, J. R., H. W. Sohns, and H. C. Carpenter. Gas-Combustion Retorting of Oil Shale Under Anvil Points Lease Agreement: Stage II. BuMines RI 7540, 1971, 74 pp.
12. Staff of National Oil Proprietary Ltd., Glen Davis. The Development of the Oil Shale Industry at Glen Davis, New South Wales, Australia. Presented at the Second Oil Shale and Cannel Coal Conf., Glasgow, Scotland, 1950.
13. Svenska Skifferolje Aktiebolaget (The Swedish Shale Oil Company). Company brochure, printed by Ludvig Larsson Boktryckeri Eftr., Orebro, 1958.
14. Umbria, E. J. Estonian Oil Shale. Ind. Eng. Chem., v. 54, January 1962, pp. 42-48.
15. Volkov, T. M., I. J. Vainaste, V. M. Yefimov. Oil Shale Processing in the Soviet Union. USSR Oil Shale Presentation given in the offices of the Resources Sciences Corp., Tulsa, Okla., December 1975.
16. Wise, R. L., B. C. Sudduth, J. M. Winter, L. P. Jackson, and A. Long. Preliminary Evaluation of Rock Springs Site 9 In Situ Oil Shale Retorting Experiment. Presented at 51st Ann. Fall Mtg, SPE-AIME, New Orleans, La., Oct. 3-6, 1976.

COMPOSITIONAL VARIATION OF RETORTED SHALE OILS WITH STRATIGRAPHY:  
WYOMING CORE, NORTHERN GREEN RIVER BASIN

L. P. Jackson, J. R. Morandi, and R. E. Poulson

Energy Research and Development Administration  
Laramie Energy Research Center  
P.O. Box 3395, University Station  
Laramie, WY 82071

INTRODUCTION

Current plans for the commercial development of oil shale resources are designed to obtain the maximum amount of oil from the least amount of shale. Within the United States, the industry would use the thick, rich seams which are reasonably close to the surface in the Green River Formation in the Rocky Mountain region. This formation is made up of four principal basins, the Piceance Creek Basin in Colorado, the Uinta Basin in Utah, and the Green River and Washakie Basins in Wyoming. The construction of mining operations, both surface and subsurface, to support aboveground retorting processes will be designed in such a manner that the thickest seams of rich shale will be used. Modified in situ retorts will be designed to develop the tallest rubble chimneys technically feasible. True in situ retorting sites will be located in those shale seams which are inaccessible to the other technologies and will produce the maximum amount of high quality product oil.

Of all the possible variables which can affect the quality of shale oil, the retorting method is by far the most significant (1, 2).<sup>1</sup> It is also known that shale type can affect oil quality. A detailed study of Colorado shale oils and Paraiba Valley (Brazil) shale oils showed significant differences between the two in such characteristics as residuum content, nitrogen content, distribution of nitrogen by boiling range in the oil and hydrocarbon types (3). Consideration of the quality of the shale from a given location has generally been confined to the variations in yield (gallons of oil per ton of shale) and its mining and retorting properties.

To date, the stratigraphic variation of oil shale as it relates to oil quality has received little attention. Robinson and Cook (4, 5, 6) have published a three part study on the variations of the organic source material within three basins in the Green River Formation. Differences in the organic source material between basins were noted and variations with depth within basins were also observed. To date, three systematic, depth-related studies on shale oils have been completed. Two are concerned primarily with the decreasing specific gravity of some (but not all) oils with increasing depth (5, 7) the other study deals with the nitrogen compound types in Green River oil shale and its kerogen degradation products (8).

Smith (7) compared the oil from a 30 foot section of the Mahogany Zone and a composite oil from two discontinuous lower zone sections (total length 310 ft). The analysis was done on Fischer Assay oils composited from drill cuttings. The two composite oils were produced from shales 1,030 feet apart. Variations were noted in specific gravity, elemental composition for nitrogen and sulfur, viscosity and boiling range distribution. In the other study (8), it was found that the nitrogen types in low temperature thermal degradation products of shale (>200°C) were mostly very weak bases and neutral nitrogen types.

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<sup>1</sup> Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The current study was undertaken to provide information on potential variations in oil quality and composition with increasing depth of burial of the source rock. Such variations would be encountered by any production facility which obtains its raw materials from the vertical development of an oil shale deposit by mining or in situ retorting.

Knowledge of these potential variations is useful for two reasons. First, it will help assure that the technology chosen for any particular site will be sufficient to handle these product variables and allow optimum resource recovery as production proceeds down through the shale bed. Secondly, sound planning is essential to guarantee that oil shale development occurs in a manner which precludes any significant environmental degradation. The evaluation of the potential impact of oil shale products and effluents on the biosphere is just beginning to produce preliminary results (9). As an aid in answering environmental questions by the time full scale development begins, this study will provide the initial data on oil characteristics as produced through a vertical shale bed. This will allow potential problems to be recognized as soon as they are delineated by the environmental impact research effort and will permit the most rapid development of the control technology which must supplement the production technology for orderly development of the resource.

#### EXPERIMENTAL

A core was obtained in the Northern Green River Basin in T 21 N, R 107 W, Sweetwater Co., WY. The lithographic description was obtained on the core at approximately one foot intervals and the Fischer Assay was carried out on the sections containing kerogen by the Oil Shale Characteristics Division, Modified Fischer Assay Laboratory of the Laramie Energy Research Center. The Fischer Assay oils were collected in 11 composite oils comprising the oil produced from shale seams of similar appearance. The 11 composite oils were obtained from the three principal members of the Green River Oil Shale Formation appearing in this basin. The first two composite oils, L1 and L2, are from the Laney member, the next eight composite oils, WP1 to WP8 are from the Wilken's Peak member, the last oil is T1 and is from the Tipton member which is the lowest strata.

The 11 oils produced by the modified Fischer Assay analysis of the oil bearing strata of the core were characterized by major and trace element analysis, pour point, viscosity, and specific gravity. Boiling range distribution of the total oils and hydrocarbon type analysis as a function of percent composition and boiling range distribution was determined as described elsewhere (10). The nonaqueous titration of the bases was done in acetic anhydride-benzene (1 to 1) with perchloric acid (11, 12) and the acids were titrated with tetrabutylammonium hydroxide in 1 to 1 benzene-acetonitrile (13). These data provide information relevant to site selection, production, and refining technology, environmental planning, and control technology.

#### RESULTS AND DISCUSSION

A description of the various sections of core and the resulting oils is given in Table 1. The pour point data demonstrates a pattern found in the analyses of these oils, namely the oils L1 and L2 lie at one extreme and WP1 lies at the other extreme while WP2 through WP8 lie in between in irregular order, T1 is usually found at either extreme. This pattern is also found in the elemental analysis for nitrogen and sulfur (Table 2), saturate hydrocarbon analysis (Table 3), polar, material analysis (Table 3), and acid-base analysis (Table 4 and Table 5). The list of physical properties on the oils is completed by Table 6 which gives the percent composition of the oils by 200°F boiling range increments.

TABLE 1. - Description of Wyoming core and Fischer Assay oils

Section	Depth <sup>1</sup>	Length <sup>2</sup>	Gal/ton	Viscosity <sup>3</sup>	Sp. gr.	Pour pt.
L1	771.5	38.1	5.3	228	0.964	90
L2	870.5	59.6	10.3	112	0.917	85
WP1	1064.7	44.3	13.5	84	0.918	50
WP2	1109.0	48.6	15.1	106	0.921	60
WP3	1157.6	41.2	11.0	86	0.923	60
WP4	1250.0 <sup>4</sup>	26.2	8.0	172	0.923	75
WP5	1276.4	45.6	15.9	118	0.928	70
WP6	1322.0	193.0	6.1	102	0.927	65
WP7	1515.0	101.0	8.9	94	0.933	65
WP8	1616.0	94.0	7.3	124	0.919	70
T1	1710.0	7.0	4.5	82	0.907	85

<sup>1</sup> Top of section, depth in feet.

<sup>2</sup> Excluding barren sections, length in feet.

<sup>3</sup> S.U.S at 100°F.

<sup>4</sup> 51.2 ft of core missing between WP3 and WP4.

TABLE 2. - Analysis of major elements in Fischer Assay oils from Wyoming core

Section	C	H	H/C	N	S	O <sup>1</sup>
L1	84.06	10.77	1.54	1.66	1.62	1.89
L2	82.85	11.26	1.63	1.59	1.86	2.44
WP1	84.42	11.23	1.60	2.26	0.76	1.33
WP2	83.84	11.39	1.63	2.11	1.14	1.52
WP3	83.79	11.13	1.59	2.03	1.40	1.65
WP4	84.26	11.14	1.59	2.12	0.97	1.51
WP5	84.06	11.11	1.59	2.32	0.99	1.52
WP6	84.02	11.00	1.59	2.03	0.68	2.27
WP7	84.45	11.07	1.59	2.21	0.53	1.74
WP8	84.66	11.06	1.58	1.86	0.57	1.85

<sup>1</sup> By difference.

### Variations in Oil Properties

As shown in Table 1, the lengths of the various sections range from 7.0 to 193.0 feet, with the lengths being determined by intervals of lithologic homogeneity. The first two sections, total length 97.7 feet, are located in the Laney member of the Green River Formation. The Laney member is an oil shale marlstone section which begins at the base of the Bridger Formation and continues to the top of the sodium-salt mineral oil shale section known as the Wilken's Peak member. The Wilken's Peak member is composed of Lacustrine sediments containing oil shale marlstone and trona (sodium carbonate and sodium bicarbonate), shortite, and other exotic carbonate mineral combinations. Eight sections with a total length of 500.1 feet were obtained from this section. An interval of 51.2 feet was missing from the core near the top of the Wilken's Peak member and is not included in these results. The Tipton member is very thin in this region and yielded only one 7.0 ft section of core. This sample should not be considered representative of the oil shales which make up the Tipton. The results of the analysis on the oil from this section is not discussed and included for comparison only.

TABLE 3. - Analysis of Fischer Assay oils for percentage saturate hydrocarbon, polar, and nonpolar material

Section	Polar	Nonpolar <sup>1</sup>	Saturates <sup>2</sup>
L2	43	57	11.1
WP1	55	45	8.90
WP2	53	47	9.67
WP3	50	50	10.2
WP4	54	46	9.80
WP5	54	46	9.73
WP6	54	46	9.85
WP7	52	48	9.76
WP8	51	49	9.98
T1	40	60	13.3

<sup>1</sup> Removed from Florisil column with cyclohexane.

<sup>2</sup> By absorption.

TABLE 4. - Acid type analysis of Fischer Assay oils from Wyoming core<sup>1</sup>

Section	Acid type, Meq/g oil		
	Weak acids	Very weak acids	Total acids
L1	0.045	0.302	0.347
L2	0.034	0.228	0.262
WP1	0.021	0.206	0.227
WP2	0.021	0.196	0.217
WP3	0.020	0.207	0.227
WP4	0.025	0.228	0.253
WP5	0.015	0.222	0.237
WP6	0.014	0.232	0.246
WP7	0.014	0.226	0.240
WP8	0.028	0.258	0.286

<sup>1</sup> Determined by nonaqueous titration with tetrabutyl ammonium hydroxide in benzene-acetonitrile.

The oil shales from this region of Wyoming are generally classed as very lean to lean indicating that their oil yield on retorting is low. This is supported by the assay data in Table 1 where the values range from 5.3 gallons per ton in L1 to 15.9 gallons per ton in WP5. The viscosity at 100°F, specific gravity and pour point of L1 are all unusually high when compared to the other oils but aside from this one example no relationship appears to exist among these properties and their depth of burial or yield in gallons per ton.

The elemental analysis of the oils are given in Table 2 and several comments can be made comparing these data and the material presented in Tables 3 through 6. (a) The oils with a H/C ratio of 1.60 or more, L2, WP1, and WP2 show a significant increase in the amount of material with a boiling point of less than 400°F (Table 6). (b) The amount of total nitrogen in the oil is directly proportional to the total bases and total basic nitrogen in the oils (Table 5). (c) The oils from the Laney member contain less than 2% nitrogen and the weak/very weak base ratio is about one whereas the Wilken's Peak oils contain greater than 2% nitrogen and the

TABLE 5. - Base type analysis of Fischer Assay oils from Wyoming core<sup>1</sup>

Section	Base types, Meq/g oil			Basic nitrogen type, wt%			Nonbasic <sup>4</sup> N, wt%
	Weak <sup>2</sup>	Very weak <sup>3</sup>	Total	Weak <sup>2</sup>	Very weak <sup>3</sup>	Total	
L1	0.486	0.373	0.859	0.681	0.522	1.203	0.46
L2	0.435	0.501	0.936	0.610	0.710	1.320	0.27
WP1	0.832	0.399	1.231	1.169	0.559	1.728	0.52
WP2	0.752	0.436	1.188	1.054	0.610	1.664	0.45
WP3	0.732	0.420	1.152	1.025	0.588	1.613	0.42
WP4	0.698	0.416	1.114	0.977	0.583	1.560	0.56
WP5	0.764	0.470	1.234	1.069	0.658	1.727	0.59
WP6	0.736	0.388	1.124	1.030	0.543	1.573	0.50
WP7	0.771	0.438	1.209	1.108	0.613	1.721	0.49
WP8	0.650	0.416	1.066	0.910	0.582	1.492	0.37

<sup>1</sup> Determined by nonaqueous titration with perchloric acid in acetic anhydride-benzene (1:1).

<sup>2</sup> pK<sub>a</sub> = +8 to +2, pyridines, quinolines, anilines, alkylated pyrroles.

<sup>3</sup> pK<sub>a</sub> = +2 to -2, pyrroles, indoles, amides.

<sup>4</sup> Determined by difference using total N analysis from table 2, nitriles, carbazoles.

TABLE 6. - Composition by boiling range for the oils obtained by Fischer Assay of Wyoming core<sup>1</sup>

Section	Boiling range fractions, percent of total				Residue
	ibp to 400	400 to 600	600 to 800	800 to 1,000	
L1	1	20.8	31.4	31.1	16.5
L2	12.0	23.9	27.5	24.0	13.1
WP1	15.5	24.3	26.1	21.9	12.2
WP2	13.0	23.6	26.1	21.4	15.9
WP3	7.8	22.4	28.0	26.7	15.1
WP4	3.6	23.4	29.5	28.1	15.4
WP5	7.0	22.7	28.4	27.6	14.3
WP6	6.7	24.0	28.9	28.3	12.1
WP7	7.6	24.1	29.0	28.9	10.4
WP8	6.2	23.5	30.9	30.8	8.6
T1	8.9	24.9	28.9	22.1	15.3

<sup>1</sup> Determined by simulated distillation.

weak/very weak base ratio is about two (Table 5). (d) The amount and types of acids present in the oils do not follow the sequence of percent oxygen in the oils (Table 4). (e) With the exception of WP1, the amount of nonpolar material in the oils generally decreases with the nitrogen content of the oil but sulfur has little or no effect (Table 3).

The variation in the oils when analyzed by simulated distillation for boiling range distribution is given in Table 6. The L1 section is deficient in material boiling below 400°F. Sections L2, WP1, and WP2 show 12.0 to 15.0 percent of material boiling below 400°F with 21.4 to 24.0 percent in the 800 to 1,000°F range. The remaining oils are generally heavier, showing less than 8% below 400°F and more than 28% in this 800-1,000°F range. Section WP8 shows less than 9% material boiling above 1,000°F while the other oils vary between 16.5% and 10.4%.

### Processing Considerations

The bulk properties which relate to handling the oils specific gravity, pour point, and viscosity are given in Table 1 and show very little variation from one section to another. These values are well within the range expected for shale oils so that handling these products in a production facility will present no new problems.

When the initial shale-oil product is refined, either on or off the site, provisions will have to be made to handle a high-nitrogen feed with modest sulfur levels. These facts are already well known and it seems from the data in Table 2 that the variations in nitrogen and sulfur levels are not sufficient to cause any problems in the refining step not already predicted. In Table 2 the hydrogen-to-carbon ratios are very nearly the same for all oils so it is apparent that hydrogen demand for a hydrotreating plant will depend primarily on the final levels of nitrogen and sulfur in the hydrotreated product. The role of nitrogen and sulfur in the refining of shale oils has been discussed by Poulson (14). Some of the sulfur levels in these oils are slightly higher than those mentioned in that paper but it is generally acknowledged that the sulfur will present no problems because it will be removed before denitrification is complete.

The data in Tables 4 and 5 were obtained by means of nonaqueous titrimetry on the total crude oils. This method was chosen for its applicability to whole oils and to shale oil distillates (15, 16). The data is detailed and therefore gives a good picture of the oil with respect to nitrogen content. The total oils follow the trends established for the various distillation cuts, that is, total bases exceed the total acids, very weak acids predominate over weak acids, and weak bases predominate over very weak bases. Since denitrification is the most troublesome factor in refining, the relative amounts of weak and very weak bases in the oils are worth noting because it is known that weak bases (pyridines and quinolines) are more easily reduced than very weak bases (pyrroles and indoles) at low temperature and pressure, while the situation is reversed at high temperatures and pressures (17). The ratio of weakly basic nitrogen to very weakly basic nitrogen varies from 2.09 to 0.86 in the oils, this changing quality of the feedstock may require a hydrotreater design which is flexible to assure efficient operation of that phase of production. If a fixed hydrotreater design is chosen because of operating and/or economic considerations, judicious consideration will have to be given as to which shale seams will be exploited.

Another result of this study is presented in Table 6. If a given set of retorting parameters are chosen as the most ideal for a particular facility, the boiling range distribution of the product can be markedly affected by the choice of shale seams which are processed. The amount of material in the IBP to 600°F range (naphtha to light distillate) can be increased from about 30 percent of total oil to about 38 percent by selecting the shales in the seams represented by L2, WP1, and WP2. Residuum (1,000°F+) can be lowered from about 16 percent to less than 9. This type of product mix flexibility can occur without changing retorting conditions and could be capitalized on, making an industry much more responsive to changing fuel demands. This varying product mix with stable retort conditions may also have significant economic implications.

### Environmental Considerations

As stated earlier, the potential impact of shale products on the biosphere is just beginning to be delineated and evaluated. With this qualification, a few general comments can be made at this time concerning the environmental implications of the varying product quality of these oils.

The physical properties of these oils do not differ markedly from any other known shale oil, so no unusual problems should arise from the retorting or processing of oils from this region as compared to any other. As for unique chemical properties which may be significant, none are apparent. The oils have been analyzed for all stable elements and they are very similar to oils with which we are familiar (18). The analyses were obtained by spark source mass spectrometry. Table 7 gives

TABLE 7. - Elemental analysis of three oils produced by Fischer Assay on Wyoming core<sup>1</sup>

Element	Section		
	L2	WP3	WP7
Molybdenum	-	0.46	-
Arsenic	5.8	2.7	5.4
Zinc	-	0.40	-
Nickel	0.43	3.1	3.3
Cobalt	-	0.56	0.62
Iron	17	26	29
Calcium	1.1	8.8	3.5
Potassium	0.61	6.5	2.8
Chlorine	-	-	0.28
Sulfur	0.54	5.0	1.2
Phosphorus	-	0.77	1.7
Silicon	8.5	40	15
Aluminum	4.4	11	1.1
Magnesium	0.79	7.9	4.6
Sodium	1.4	4.9	2.8

<sup>1</sup> All values in ppm; elements for which values are not listed are less than 0.25 ppm.

the results of analysis on these oils. The character of the organic materials is under active investigation as to compound types and specific examples of each type. This work will allow the evaluation of the biological effects of these oils to be made as soon as the suspect agents in shale oil are identified. The suspect nature of the various components of petroleum is well known (19) and the analysis for these materials in shale oils is proceeding.

In an investigation of the mutagenic effects of a shale oil and a petroleum crude, the basic material in the shale oil (8% of the total oil) was significantly more active on a weight basis than the corresponding basic material in the petroleum (>1.0% of the total oil) (20). Since this is the first report of this type it is very important that additional data be gathered on other samples before the results are generalized to all petroleum or shale oils. As the biological significance of the various basic materials in shale oils is reported further, a more comprehensive statement of the possible environmental impact of the variations of oil with depth of burial will be possible. The results of the study on compound types and specific compounds found in these shale oil fraction will be forthcoming in the near future.

#### SUMMARY

A series of oils produced by Fischer Assay of a core representing 11 major strata of Northern Green River Basin--Green River Formation oil shale have been

analyzed for physical and chemical properties. Three major points concerning the retorting and processing of various strata of shale can be made. First, the physical properties of all oils are similar and as such, the oils will require much the same handling. Second, the types of basic nitrogen vary significantly in their concentration which may require a flexible hydrotreating facility to operate at maximum efficiency. Under the static retorting conditions of the Fischer Assay, product mix varies significantly with the shale strata being used as source material.

Shale from these different strata can be handled and processed in the same way, requiring no unique environmental control technology. Total elemental analysis reveals no significant variations between strata and no potentially harmful elements in unusual concentration.

#### LITERATURE CITED

1. Stevens, R. F., Dinneen, G. U., and Ball, J. S., U.S. BuMines Rept. of Inv. 4477 (1949).
2. Jensen, H. B., Poulson, R. E., and Cook, G. L., Preprints, Div. Fuel Chem., ACS, 15, No. 1, 113 (1971).
3. Dinneen, G. U., Allbright, C. S., and Ball, J. S., Chem. Eng. Data, 2, No. 1, 91 (1957).
4. Robinson, W. E. and Cook, G. L., U.S. BuMines, Rept. of Inv. 7492 (1971).
5. Ibid, U.S. BuMines, Rept. of Inv. 7820 (1973).
6. Ibid, U.S. BuMines, Rept. of Inv. 8017 (1975).
7. Smith, J. W., Bull. Am. Assa. Petr. Geol., 47, 804 (1963).
8. Cummins, J. J., Poulson, R. E., and Robinson, W. E., Preprints, Div. Fuel Chem., ACS, 20, No. 2, 154 (1975).
9. Symposium on Management of Residuals from Synthetic Fuels Production, May 25-27, 1976, Denver Research Institute, Denver, Colorado, to be published.
10. Jackson, L. P., Allbright, C. S., and Poulson, R. E., Preprints, Div. Petr. Chem., ACS, New Orleans Meeting, March 20-25, 1977, to be published.
11. Wimer, D. C., Anal. Chem., 30, 77 (1958).
12. Buell, B. E., Anal. Chem., 39, 756 (1967).
13. Buell, B. E., Anal. Chem., 39, 762 (1967).
14. Poulson, R. E., Preprints, Div. Fuel Chem., ACS, 20, No. 2, 183 (1975).
15. Poulson, R. E., Jensen, H. B., Duvall, J. J., Harris, F. L., and Morandi, J. R., Analysis Instrumentation, 10, Instrument Society of America, Pittsburgh, PA (1972).
16. Morandi, J. R. and Poulson, R. E., Preprints, Div. Fuel Chem., ACS, 20, No. 2, 162 (1975).
17. Frost, C. M. and Jensen, H. B., Preprints, Div. Petr. Chem., ACS, 18, No. 1, 119 (1973).
18. Proceedings of the EPA/NBS Workshop on Standard Reference Materials for Oil-Shale Environmental Concerns, Gaithersburg, MD, Nov. 1975, D. A. Becker, ed., In Press.
19. Searle, C. E., Chemical Carcinogens, ACS, Monograph, No. 173, ACS, Washington, DC (1976).
20. Guerin, M. R. and Epler, J. L., presented in part at the First Conference on Determining Fugitive Emissions Measurements Needs, Hartford, CT, May 17-19 (1976).

## A LABORATORY APPARATUS FOR CONTROLLED TIME/TEMPERATURE RETORTING OF OIL SHALE

Norman Stout, George Koskinas, and Stephen Santor

Lawrence Livermore Laboratory, University of California, Livermore, California/94550

### INTRODUCTION

The Lawrence Livermore Laboratory (LLL) is currently developing technology for modified in-situ retorting of oil shale.(1) Under this concept, a column of oil shale would be broken up using mining techniques, and then the rubblized oil shale would be retorted either through combustion or hot-inert-gas methods.

As part of the research effort we have designed and built an oil shale assay apparatus that can be used to simulate and evaluate the effects of various heating schedules that might be encountered in-situ.(2)

Our apparatus is a modification of the standard Fischer assay vessel and apparatus.(3,4) Changes were made primarily to simulate phenomena common in in-situ retorting (e.g., the descent of gas and possibly liquid products through reacting shale under variable thermal conditions). The collection system allows for complete gas and liquid product recovery (and hence, for good mass balance). The apparatus can be operated in either autogenous (self-generated) gas or gas-sweep conditions.(2)

In the following discussion, we describe the apparatus and compare our experimental results with those from a typical Fischer assay apparatus.(3) We refer to our assay method as the Koskinas, Stout, Santor (KSS) assay.

### APPARATUS

The KSS apparatus is shown in Fig. 1. It has three major parts: a retort chamber, a furnace and controller unit, and a gas manifold and oil collection system. The design and construction of each component is described in detail below.

#### RETORT CHAMBER

Our retort differs from the usual Fischer assay retort in three respects. First, the product is collected from a delivery tube at the bottom of the retort chamber. Second, our retort is a stainless steel chamber, sealed by welding and hence capable of operating leak-free at high temperatures (1000°C) for long periods of time (> 1 month). Third, the simple physical design of the chamber is compatible with a cylindrical furnace readily available commercially.

The retort chamber (Fig. 2) is made in two parts: the body (with downspout) and the lid. The main body is a cylindrical stainless steel pipe 3.8 cm (1.25 in.) in diameter with a stainless steel frit of 165- $\mu$ m mesh, 0.45 cm (3/16 in.) thick, heliarc welded in the bottom. The frit provides a porous path for gases and liquids flowing from the retort, while retaining solid particles in the chamber. The downspout is 0.64-cm-diameter (1/4-in.) type 304 stainless steel pipe, 25.4 cm (10 in.) in length. It has a 0.64-cm (1/4-in.) Cajon Ultratorr O-ring fitting on the exit end. The lid is a flat disk with a thermocouple well at the center. The thermocouple well dimensions are such that when the retort is assembled, the tip is roughly in the middle of the retort chamber. A stainless-steel-sheathed, chromel-alumel (type K) thermocouple is inserted into the well.

The lid is heliarc-welded onto the body after the sample has been put into the retort. To maintain the sample in its natural state and to eliminate any degradation during welding, there is a small void space between the sample and the cap.

A large copper block is clamped to the vessel to minimize heating of the sample near the weld.

### FURNACE

The furnace used (see Fig. 1) is 25.4 cm (10 in.) high and 15.24 cm (6 in.) in diameter. It has an aluminum oxide tube with a 4.1275-cm (1 5/8-in.) inside diameter, wound with kanthol wire 0.127 cm (0.05 in.) in diameter. The furnace has a maximum temperature range of 1200°C. Two chromel-alumel thermocouples (type K) are used for control and temperature measurement. Bubbled alumina beads are used as filler and insulating material around the heating element. The outside wall is made of aluminum, and the top and bottom ends are of transite. A programmable controller, Data Trak Model 5310, made by Research Inc., Minneapolis, Minnesota, is used to control the heating schedule.

### MANIFOLD AND OIL COLLECTION SYSTEM

The gas manifold is designed to use electropneumatic valves and strain-gauge pressure transducers so that the data collection and system operation can be easily automated. To avoid errors in mass balance, the volume of the manifold was kept below 10 cm<sup>3</sup>. The oil collection is connected to a bellows and to the gas manifold by 0.3175-cm-diameter (1/8-in.) stainless steel tubing. The bellows allows the gases generated in the autogenous atmosphere heatings to flow out of the retort chamber with only moderate pressure changes (67 to 100 kPa, 0.67 to 1 atm). When the gas reaches roughly one atmosphere in the bellows, it is transferred to a 2-l stainless steel collecting bottle.

The oil collector is a graduated, 12-cm<sup>3</sup> centrifuge cone, placed inside a glass thimble. A small amount of glass wool is inserted in the top of the thimble to condense any oil mist produced during the assay.

### SAMPLE PREPARATION

Sample uniformity directly affects our ability to judge the accuracy of the KSS technique and apparatus and to make comparisons with commercial assay results. We will therefore describe the sample preparation in some detail.

We obtained oil shale from the Anvil Points Mine near Rifle, Colorado. A number of pieces weighing from 4 to 12 kg each were crushed and sieved; material passing a 20-mesh screen (841 μm) was retained and the coarser material was discarded. The density of the 21.0 kg of retained material was 2.28 g/cm<sup>3</sup>, corresponding to a predicted yield of 88.0 t/t (20.0 gallons/ton). (5) The initial batch was separated into aliquots by a spin riffing technique. (6) The spin riffler is shown in Fig. 3, and the separation scheme is shown in Fig. 4. The first split gave six aliquots weighing about 3.5 kg each. These 3.5-kg aliquots were split into 585-g batches as needed. A third split gave samples of about 95 g each, which were used in the retorting experiments. Four of these 95-g aliquots were sent to Commercial Testing and Engineering Company for Fischer assay.

Two of the 95-g aliquots were split further into 8-g and 0.6-g aliquots for mineral carbonate, total carbon and hydrogen analyses. The results of 12 determinations of total carbon gave 15.97 wt% carbon;  $\sigma$  of a measurement,  $\pm 0.076$ ; and 95% confidence limits of the mean,  $\pm 0.048$ . We did 49 determinations of acid-evolved CO<sub>2</sub>. The results showed 22.19 wt% CO<sub>2</sub>,  $\sigma$  of a measurement,  $\pm 0.18$ , and 95% confidence limits of the mean,  $\pm 0.05$ . The organic carbon calculated from these analyses is 9.914  $\pm$  0.05 wt%. Organic hydrogen content was uncertain because of the uncertainty in water content.

The unused 3.5-kg and 585-g aliquots were kept in sealed containers so as to exclude air during storage.

## PROCEDURE

A 95-g aliquot of oil-shale powder was weighed exactly and placed in the retort chamber. The retort lid was welded to the chamber and the retort reweighed. The retort and sample were then dried at 100°C in a vacuum for 1 h, cooled to room temperature, and reweighed. (Typical weight loss due to drying was 0.23% of sample weight.) All of the components of the product-collection systems were then weighed, and the retort was placed in the furnace and connected to the collection system and manifold setup. The furnace openings were lightly plugged with insulating material (Fiberfrax). The system was then evacuated, checked for leaks, and backfilled with argon to a pressure of 67 kPa (0.67 atm). The sample was then heated in the Fischer assay mode (12°C/min to 500°C, with a final holding period of 30 min at 500°C). (3,4) After the system had cooled, the weights of all products (gas, oil, and water) were determined. The oil collector was centrifuged to separate the oil and water phase. Most of the oil was removed with a pipette, and the oil remaining with the water phase was extracted with benzene followed by hexane. The hexane was allowed to evaporate, and the weight of the water was determined. The water phase was then discarded.

The spent shale was spin-riffled into aliquots, one of which was analysed for C, H, N, and S. Oil density was determined using a 3-cm<sup>3</sup> pycnometer. An oil aliquot was taken for analyses, and the remainder was stored at 0°C under argon. The product gas was weighed and then analysed by mass spectrometry. The gas mass was corrected for the initial amount of argon and the amount of gas remaining in the retort-bellows system. We found this correction to be trivial.

An overall material balance was calculated by comparing the weight loss during heating to the total mass of the products collected. Typically, the results ranged from 99.0 to 101.0%. If the spent shale is counted as a product, the material balance results will range from 99.9 to 100.1%. A typical run sheet is shown in the appendix.

## RESULTS AND DISCUSSION

### EXPERIMENTS IN THE FISCHER ASSAY MODE

The results of our assays in the Fischer assay mode are summarized in Tables 1 and 2. The mass yields, in kg/t, were measured directly. The volume yields, in gal/ton, were calculated from the mass yields via:

$$\text{Yield}_{(\text{vol})} \text{ gal/ton} = \text{Yield}_{(\text{mass})} \frac{\text{kg}}{\text{t}} \times \frac{0.239653 \text{ gal}\cdot\text{t}\cdot\text{g}}{\rho \text{ g/cm}^3 \text{ ton}\cdot\text{kg}\cdot\text{cm}^3} \quad (1)$$

The volume yield depends on the oil density, which in turn depends on the temperature. We normally measure oil densities at 21°C (70°F). Since the oil industry reports densities at 15.6°C (60°F), we measured several oils at both 21°C and 15.6°C and found the densities to be 1% higher at 15.6°C. The 15.6°C densities listed in Table 1 are calculated values.

The results from the four commercial Fischer assays are listed in Table 3. To compare the commercial assay values with our work, we calculated mass yields from the reported volume yields and densities. We assumed that both values were measured at the same temperature.

Our work gave a mean yield of 84.07 kg/t and the commercial results gave 83.25 kg/t. Using the "t" test (7) of significance between two sample means and the standard deviation of the measurement shown in Table 1, we can determine

that there is a 60% probability that the two assay values are the same.

The uncertainty in our KSS assay procedure for a single determination is about 1.2%. The uncertainties in the total carbon and acid-evolved CO<sub>2</sub> are 0.5% and 0.8%. We believe that the analytical procedures are more precise than these numbers imply, and that the major contribution to statistical scatter comes from the spinning technique used in sampling.

J. Ward Smith (3) reported  $\sigma$  of  $\pm 0.3\%$ , and 95% confidence limits of the mean of  $\pm 0.3\%$  in his paper on Fischer assay procedures. Goodfellow and Atwood (4) reported 95% confidence limits of 0.8 to 1.6% on a series of assays. Furthermore, they state, "Our experience has been that most problems with precision and accuracy can be traced to inadequate sample preparations procedures." We certainly agree. The results discussed above are summarized in Fig. 5.

The oils from our assays were analysed for C, H, N, and S. Although we did not attempt to carry out a complete elemental balance as did Smith, (3) it is interesting to compare our products with his work and with the work of Goodfellow and Atwood. (4) Our oil had a composition of CH<sub>1.63</sub>N<sub>0.02</sub>S<sub>0.003</sub>. Smith's oils were CH<sub>1.55</sub>N<sub>0.02</sub>S<sub>0.003</sub>. Our data on the distribution of organic carbon among the products (oil, char, and gas) were also slightly different from those of Smith (3) and of Goodfellow and Atwood. (4)

The organic carbon originally present in the shale (9.914 wt%) was distributed 73.2% in oil, 19.7% in char, and 7.1% in gas (by difference). Smith's distribution was 66% in oil, 23.5% in char, and 10.5% in gas. Goodfellow and Atwood reported 64.6% in oil, 24.6% in char, and 11% in gas (by difference).

In 1974, Cook (8) reported correlations between elemental analysis of raw shales and Fischer assay yields for 152 samples of Green River oil shale, and our oil yield, in wt%, calculated from the organic carbon content of the raw shale, falls within the uncertainty limits of Cook's correlation.

#### USE OF KSS RETORT APPARATUS FOR NONROUTINE RESEARCH

Beyond routine Fischer assays, the apparatus described above is versatile enough to handle a variety of unique experiments. We have recently reported a series of experiments (2) on the effects of long-term heat soaking on oil yield from powdered shale samples. Heating times ranged from 8 to 800 h and temperatures up to 400°C. In some cases, a controlled sweep of inert gas was used. In all experiments, the KSS apparatus was used, and it gave excellent material balances (see Ref. 2 for results).

Using a nonisothermal technique, (9) we have also made a kinetic study of oil production. Comparing the results of this study with those from a number of other isothermal experiments, we found excellent agreement. In these kinetic studies, we were able to use the KSS apparatus without any modifications, and the kinetic experiment simulated the real in-situ condition (nonisothermal heating).

More recently, we have completed studies on the effects of different heating rates and gas sweep atmospheres on oil yield from powdered oil shale in 1-in. cores. (2) Again, the KSS apparatus was used without modification. The results of this last investigation give insight into the mechanism of oil degradation during long-term in-situ retorting experiments.

#### CONCLUSIONS

We have designed, built, and tested a simplified laboratory retort system (KSS apparatus) that simulates conditions involved in in situ oil shale processing.

The apparatus is of simple design, and it can be used with commercially available cylindrical furnaces. The welded closure is rugged and leak-tight. When operated in the Fischer assay mode, our apparatus gives results indistinguishable from those of a Fischer assay. The KSS apparatus is versatile. It can provide excellent mass balance in a wide variety of retorting experiments. Various sweep gases can be used. The heating schedule is completely programmable, and the apparatus can run unattended for long periods (> 1 month).

#### ACKNOWLEDGMENTS

We wish to thank our analytical department, and especially Lewis Gregory, for their support of this work. We also thank Robert Opila, who did many of the assay experiments, and too Jack Campbell for his encouragement.

#### REFERENCES

1. A. E. Lewis and A. J. Pothman, Rubble In-Situ Extractions (RISE): A Proposed Program for Recovery of Oil From Oil Shale, Lawrence Livermore Laboratory, Rept. UCRL-51768 (1975)
2. N. D. Stout, G. J. Koskinas, T. H. Paley, S. D. Santor, R. J. Opila, and A. J. Rothman, Pyrolysis of Oil Shale: The Effects of Thermal History on Oil Yield, Lawrence Livermore Laboratory, Rept. UCRL-77831 (1976)
3. J. W. Smith, Analytical Method for Study of Thermal Degradation of Oil Shale, U.S. Bureau of Mines Report of Investigations, No. 5932 (1962)
4. L. Goodfellow and T. Atwood, Col. Sch. Mines Quart. 69 (2), 205 (1974)
5. J. W. Smith, Chem. Eng. Data Ser. 3, 306 (1958)
6. C. A. Slettevold and A. H. Biermann, Characterizations of ASTM Round-Robin Tungsten-Powder Samples, Lawrence Livermore Laboratory, Rept. UCRL-51812 (1975)
7. E. L. Bauer, A Statistical Manual for Chemists, Academic Press, New York, (1971)
8. E. W. Cook, Fuel 53, 16 (1974)
9. J. H. Campbell, G. Koskinas, and N. Stout, The Kinetics of Decomposition of Colorado Oil Shale: 1. Oil Generation, Lawrence Livermore Laboratory, Rept. UCRL-52089 (1976)

TABLE 1

KSS Assay Results

SAMPLE NO. <sup>a</sup>	MATERIAL BALANCE (%)	YIELD (kg/t)	YIELD <sup>b</sup> (gal/t)	DENSITY (g/cm <sup>3</sup> )	
				at 21 <sup>o</sup> C	at 15.6 <sup>o</sup> C <sup>d</sup>
(4-5)-4	-	84.98	22.2 <sup>d</sup>	-	-
(1-1)-4	-	85.33	22.3 <sup>d</sup>	-	-
(1-6)-1	98.6	83.67	22.3	0.890 <sup>e</sup>	0.899
(4-5)-5	101.4	83.44	22.0	0.900 <sup>e</sup>	0.909
(1-5)-1	98.9	83.25	21.9	0.903	0.912
(1-6)-6	101.0	85.44	22.4	0.908	0.917
(4-6)-2	99.9	82.56	21.5	0.912	0.921
(1-6)-2	99.8	84.09	21.9	0.912	0.921
(4-6)-4	99.6	83.27	21.7	0.908	0.917
(1-3)-6	100.7	84.68	22.2	0.905	0.914
Mean Value		84.07	22.0	0.908	0.917
σ of a Measurement		0.99	0.3		
95% Confidence Limits of the Mean		0.71	0.2		

<sup>a</sup>Sample numbers refer to the sample-splitting scheme shown in Fig. 4.

<sup>b</sup>Yield in gal/ton calculated at 15.6<sup>o</sup>C from mass yield and density.

<sup>c</sup>Density at 15.6<sup>o</sup>C = density at 21<sup>o</sup>C (measured) x 1.01.

<sup>d</sup>Yield in gal/ton calculated using mean density, 0.917 g/cm<sup>3</sup>.

<sup>e</sup>Density estimated by visual measurement of oil volume; not used in calculation of mean density.

TABLE 2

Analytical Summary

Sample	Elemental Analysis, wt%						% of Original Organic Carbon Present
	Total Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	
Raw Shale	15.97	9.914	1.43	0.34	0.14	-	100
Spent Shale	8.84	2.19	0.19	0.17	0.15	-	19.7
Oil	86.38	86.38	11.22	2.06	0.67	-	73.2
Gas <sup>a</sup>	57.9	57.9	12.3	-	-	29.8	7.1 (by difference)

<sup>a</sup>24.2 vol % CO<sub>2</sub>; 26.1 vol % H<sub>2</sub>; 18.4 vol % CH<sub>4</sub>;  $\sum_n C_n = 25.9$  vol % (average composition for  $\sum C_n = C_{3.2} H_{7.5}$ )

TABLE 3

Results of Fischer Assay  
Performed by Commercial Testing and Engineering Co.

Sample No. <sup>a</sup>	YIELD <sup>b</sup> (kg/t)	YIELD (gal/t)	DENSITY <sup>c</sup> (g/cm <sup>3</sup> )
(1-1)-3	84.02	22.2	0.907
(1-1)-5	83.05	21.8	0.913
(4-5)-2	82.78	21.8	0.910
(4-5)-6	83.16	21.9	0.910
Mean Value	83.25	21.9	0.910
$\sigma$ of a Measurement	0.54	0.2	
95% Confidence Limits of the Mean	0.85	0.3	

<sup>a</sup>Sample numbers refer to the sample-splitting scheme shown in Fig. 4

<sup>b</sup>Yield in kg/t calculated from volume yield and density

<sup>c</sup>Density measurement at an unknown temperature - see text

APPENDIX: Typical Material Balance Sheet for Oil Yield Experiments  
(Fischer Assay Heating Schedule)

Item	Weight (g)
1. Retort and lid	296.5312
2. Tare and sample	227.3068
3. Tare	125.5600
4. Sample (2 - 3)	101.7468
5. Assembled full retort (1 + 4)	398.2780
6. Assembled and welded retort before drying	398.2472
7. Weight change due to welding (5 - 6)	0.0308
8. Assembled and welded retort after drying	397.9693
9. Weight loss due to drying (6 - 8)	0.2779
10. Weight of retort after heating	386.8700
11. Weight loss on heating (8 - 10)	11.0993
12. Collection tube, oil, and water	27.2546
13. Collection tube and water	19.5628
14. Collection tube (clean)	18.8655
15. Weight of water (13 - 14)	0.6973
16. Weight of oil (12 - 13)	7.6918
17. Thimble, glass wool, and oil	74.4964
18. Thimble and glass wool (clean)	73.6902
19. Oil in thimble (17 - 18)	0.8062
20. Downspout, stopper, and oil	25.3609
21. Downspout and stopper (clean)	25.3030
22. Oil in downspout (20 - 21)	0.0579
23. Total oil collected (16 + 19 + 22)	8.5559
24. Gas bulb (full)	919.4503
25. Gas bulb (evacuated)	917.6485
26. Gas collected (24 - 25)	1.8018
27. Gas correction	0.0312
28. Total product collected (26 + 27 + 23 + 15)	11.0862
29. Pycnometer and oil	28.9494
30. Pycnometer (clean)	26.2119
31. Oil density, g/cm <sup>3</sup> [(29 - 30)/3.0 cm <sup>3</sup> ]	0.9125
32. Material balance, % (28 x 100/11)	99.88
33. Oil yield, kg/t (23 x 1000/4)	84.0901
34. Oil yield, gal/ton (33 x 0.239653/31)	22.085

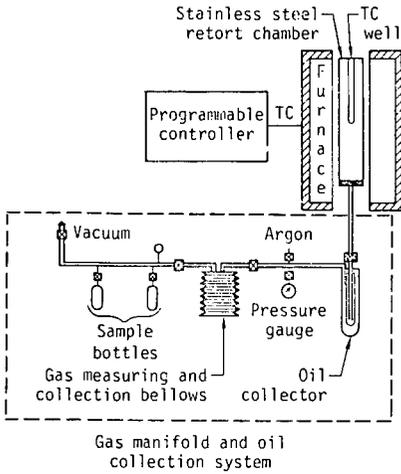


Fig. 1. Schematic of the KSS oil shale assay apparatus.

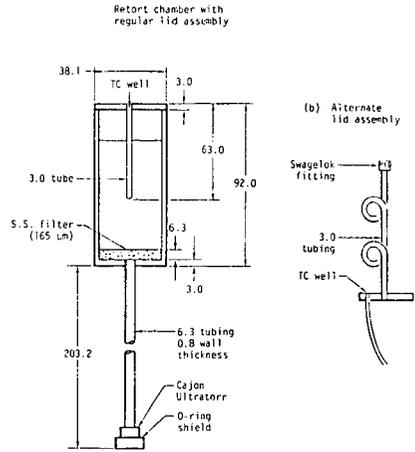


Fig. 2. Retort chamber assembly (dimensions in mm).

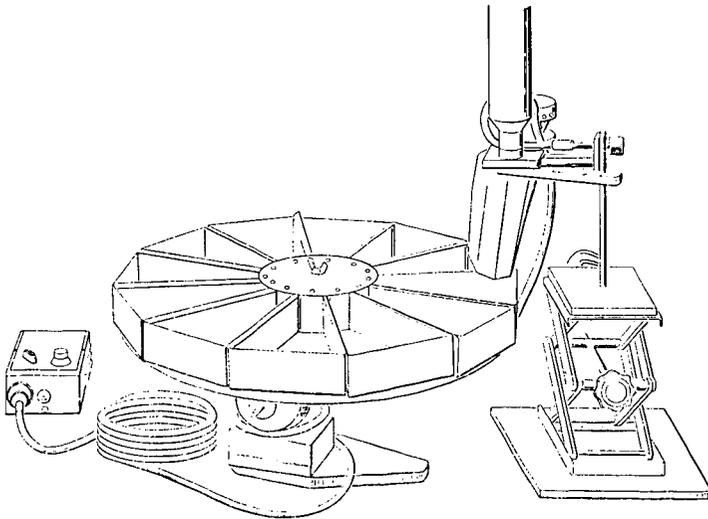


Fig. 3. Spin-riffing apparatus.

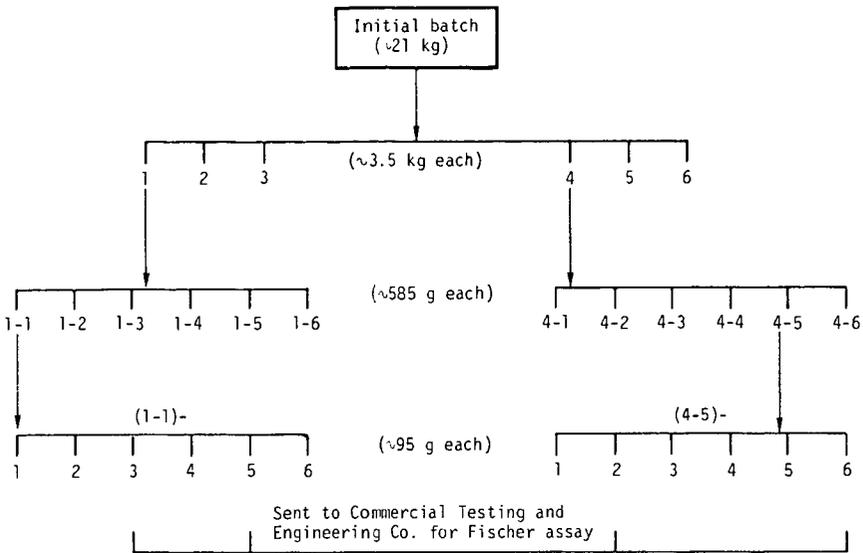


Fig. 4. Sample-separation flow chart.

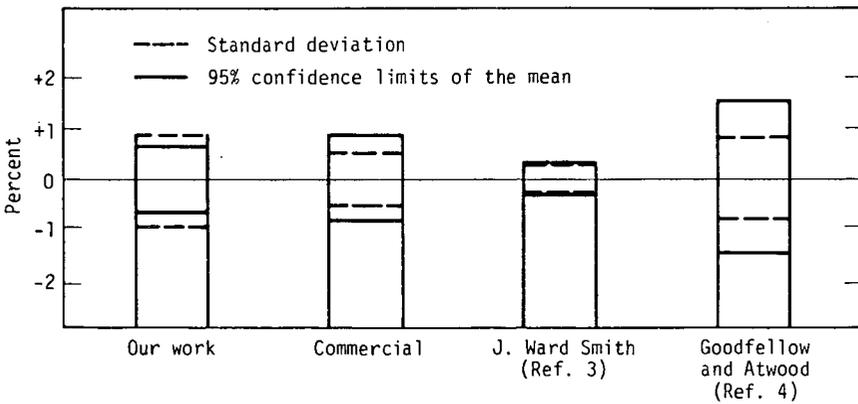


Fig. 5. Comparison of the accuracy of assay results from various sources.

**OIL-SHALE'S PROPERTIES, PECULIARITIES, AND POSSIBILITIES.** John Ward Smith,  
U.S. ERDA, Laramie Energy Research Center, P. O. Box 3395, University Station,  
Laramie, Wyoming 82071

The world's oil shales represent a tremendous store of fossil fuel energy, estimated to be many times larger than that offered by coal. Oil shale has an immediate advantage in that its primary product is oil which can feed directly into our established consumption patterns. Although oil shale is difficult to define unambiguously, oil shale is best described as a sedimentary rock containing solid, combustible organic matter in an inorganic mineral matrix. The organic matter, frequently called kerogen, is largely insoluble in petroleum solvents, but decomposes when heated to yield oil, gas, water, and residual carbon. World resources are summarized and the history and status of world-wide development efforts outlined. Oil shale is a strange rock whose properties are modified and even controlled by its organic matter content. Density varies with organic volume - general oil-shale relationships are discussed. The hydrogen available to make hydrocarbons in the organic matter controls how much oil can be produced from any oil shale. A general relationship between C-H ratio and conversion of organic matter to oil is described. The organic matter of the oil shales in United States' Green River Formation is extremely rich in hydrogen. This deposit in Colorado, Utah, and Wyoming is the World's largest oil-shale resource. Its physical, chemical and thermal character and properties are summarized. Common misconceptions about the shale are debunked - it does not increase in size when heated to produce oil, it does not have liquid oil in it, and the organic matter differs very little throughout the formation. Dawsonite and nahcolite, minerals capable of yielding co-products with the oil from oil shale are described and the variation in the nature of the formation leading to application of different development methods at different sites is described.

## SULFUR IN HEAVY OILS, OIL SANDS AND OIL SHALES

Wilson L. Orr

MOBIL RESEARCH AND DEVELOPMENT CORPORATION  
FIELD RESEARCH LABORATORY  
DALLAS, TEXAS, 75221

### INTRODUCTION

Sulfur, after carbon and hydrogen, is often the most abundant element in fossil organic materials, whereas in biological tissues and their degradation products oxygen and nitrogen usually are more abundant than sulfur. In rare cases, the sulfur content on a weight basis even exceeds the hydrogen content. Nevertheless, sulfur in petroleum appears to be non-essential, *i.e.*, it is not a necessary component for the formation of petroleum and related bitumens because some of these materials contain only trace amounts.

The chemistry of sulfur in fossil fuels and related materials is of interest for two major reasons: 1) For its behavior during processing and in applications: It can cause problems in processing and has deleterious effects on the environment in many applications, and 2) For its geochemical significance, *i.e.*, for understanding processes which determine its abundance, distribution, and chemical combination (forms) during both the formation and alteration of fossil organic materials in geologic environments.

Emphasis in this paper is on the second area -- the geochemistry of sulfur in crude oils, oil sands and related materials. The first section of this paper briefly summarizes some of the factual knowledge concerning the abundance and forms of sulfur in these materials, especially in crude oils. Following this is a more speculative section discussing opinions and our understanding of the geochemical processes believed to control and modify the abundance and forms of sulfur. In spite of much research and a great body of factual knowledge, many important questions are still debated and diverse views will be found in the literature.

### THE NATURE AND ABUNDANCE OF SULFUR IN FOSSIL FUELS

Crude oils and bitumens vary in sulfur content from less than 0.05 to more than 14%, although relatively few produced crude oils contain more than 4% sulfur. Most oils contain from 0.1 to 3% sulfur. Similar variations in sulfur content are found in lignites, coals and the organic matter (kerogen) in oil shales and other sedimentary rocks.

Comprehensive reviews concerning sulfur and sulfur compounds in petroleum have been given by Dean and Whitehead (1), Rall *et al.* (33) and Zobell (43). Drushel also reviewed sulfur compound types in petroleum with emphasis on analytical methods (12). Challenger's monograph on the organic chemistry of sulfur (6) includes much of the early work on sulfur in fossil fuels as well as aspects of biochemistry and biogeochemistry of sulfur. The biogeochemistry of sulfur has been more recently summarized by Orr (28). Monographs are available also on microbiological processes in the formation of sulfur deposits (19) and on the biochemistry of inorganic sulfur compounds with emphasis on microbiology (35).

Hydrogen sulfide<sup>\*</sup> and elemental sulfur dissolved in crude oils usually are a very minor portion of the total sulfur if they are present at all (24,

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\* Oils containing detectable amounts of hydrogen sulfide or mercaptans (thiols) are referred to as "sour crudes". High sulfur oils without these components should not be called sour (24). However, hydrogen sulfide in a sour crude oil is easily oxidized by air to elemental sulfur during surface handling and processing. Later, during thermal treatment, H<sub>2</sub>S may form again from thermal reactions of the elemental sulfur with other components and/or from thermal decomposition of unstable sulfur compounds.

It is reasonable that the sulfurization of organic matter can occur at any stage in the geological history of a given material if proper conditions prevail. However, many advocates for a late introduction apparently do not appreciate the magnitude of sulfur incorporation into initial sedimentary organic matter in certain environments. For example, humic acids extracted from young marine sediments contain from 0.8 to 6 %S, and these acidic polymeric materials make up from 20 to 60% of the organic matter in many sediments (26). Humic acids may be considered major precursors of kerogen which in turn can be the major precursor of petroleum (41).

Gransch and Posthuma (16) conclude that most of the sulfur in crude oils originates from organically combined sulfur in the kerogen of source rocks, and therefore the major sulfur compounds and hydrocarbons are formed together. They give a number of examples illustrating that high-sulfur kerogens produce high-sulfur oils and vice versa. They also concluded from laboratory experiments that more sulfur compounds are formed during the early stages of oil generation from a given kerogen than during the later stages of its decomposition. Thus the sulfur content of an oil is a function of both the initial sulfur content of its source kerogen and its state of maturation or evolution. I believe these conclusions are essentially correct and are accepted by a large number of geochemists. Nevertheless, there are subsequent changes and alterations in oils after they are formed, possibly during their migration, and after their accumulation in reservoirs. Many questions remain about the nature and importance of these effects. Evidence of late sulfurization and competing desulfurization of oils during thermal maturation in some high temperature reservoirs has been demonstrated (27, 29), but since this does not relate directly to heavy oils it will not be discussed.

Studies of sulfur isotope ratios ( $^{34}\text{S}/^{32}\text{S}$ )\* have contributed to our understanding of the origin of sulfur in petroleum and support the view for its early incorporation into oil precursor materials. These studies indicate that a large portion of the sulfur has been derived from reduced sulfur ( $\text{H}_2\text{S}$  and/or  $\text{S}^0$ ) showing a typical isotopic fractionation attributed to microbial reduction of sulfate under conditions where the supply of sulfate is not largely reduced (i.e., in an open system) (27, 36, 37, 38).

It has been established that the  $\delta^{34}\text{S}$  values of sea water have fluctuated considerably with geologic periods (17, 37, 38) and that  $\delta^{34}\text{S}$  values of sulfur in crude oils show parallel fluctuations with geologic age but are commonly  $15 \pm 5$  ‰ lighter isotopically than sea water sulfate of the same age. These observations are most reasonably explained by isotopic fractionation during microbial reduction of sea water sulfate at the time of sediment deposition. The  $\text{H}_2\text{S}$  and/or  $\text{S}^0$  thus formed became incorporated into sedimentary organic matter with retention of its isotopic ratio. Later with the formation of petroleum by thermal processes resulting from deeper burial, the sulfur compounds formed with the hydrocarbons retain the isotopic ratio reflecting the original isotopic fractionation.

The amount of sulfur initially incorporated into sedimentary organic matter may be expected to be determined by 1) the abundance of sulfate in the water, 2) the Eh of the environment near the sediment-water interface which is one of the controls on the intensity of microbial sulfate reduction, 3) the

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\* Sulfur isotope ratios are reported as deviations ( $\delta$  - values) in parts per mil (‰) from a standard according to the relationship:

$$\delta^{34}\text{S}(\text{‰}) = \left[ \frac{^{34}\text{S}/^{32}\text{S}_{(\text{sample})}}{^{34}\text{S}/^{32}\text{S}_{(\text{standard})}} - 1 \right] 1000$$

The standard is troilite from the Canyon Diablo meteorite which has an absolute  $^{34}\text{S}/^{32}\text{S}$  ratio accepted as 0.0450045. The  $\delta^{34}\text{S}$  values can be either positive or negative with respect to the standard.

nature and abundance of organic matter which not only affects the extent of sulfate reduction but also influences the degree to which reduced sulfur species will become organically combined through reactions with reactive functional groups, and 4) the abundance of iron or other elements (cations) which compete with organic matter for the reduced sulfur. Thus, with the variations which can occur in these factors, and accepting the concept that sulfur in the sedimentary organic matter is the major source of sulfur in any oil derived therefrom, it is easy to understand that crude oils as initially formed can have wide variations in sulfur content. These variations, therefore, reflect conditions of the initial sedimentary environments.

There is another school of thought which would attribute a large part of the sulfur in crude oils to late sulfurization resulting from microbial sulfate reduction occurring in relatively shallow petroleum reservoirs (2, 8, 14). Microbial sulfate reduction certainly has been demonstrated in petroleum reservoirs (1, 2, 3, 8, 14) and as a result oil field waters are often very deficient in sulfate. However, the extent to which the resulting hydrogen sulfide reacts with the oil is difficult to evaluate. It is probably variable and often negligible. Petroleum no longer contains the abundance of reactive function groups which existed in younger organic materials in the early source environments. Its sulfurization is expected to be very slow and possibly negligible in low temperature reservoirs where microbial activity occurs. For example, Gransch and Posthuma (16) illustrate that there is not a dramatic difference in sulfur content between "flank oils" and "cap-rock oils" associated with Gulf Coast salt domes especially if any dissolved elemental sulfur is discounted in the cap-rock oils. Sulfate reduction is known to have been very active in many of the cap-rocks as evidenced by deposits of elemental sulfur and secondary calcite (14).

Although it is difficult to extrapolate laboratory experiments to geologic conditions, the experiments reported by Bestougeff and Combaz are of interest (5). They demonstrated great differences in the ease of sulfurization of different organic materials and the relative inertness of oils and oil fractions. Low boiling fractions are very inert but high boiling fractions and residues (fractions enriched in asphaltic heteroatomic and aromatic compounds) are more reactive to sulfurization by hydrogen sulfide, elemental sulfur and polysulfides. These observations support the view that sulfurization of oils in low temperature reservoirs is not easy and that any sulfur which may be introduced should be largely in the heavy ends of the oil.

#### **B. Effects of Biodegradation and Water-Washing on Sulfur in Fossil Fuels**

These crude oil alteration processes have been adequately discussed in the literature (1, 2, 8, 13, 32, 42) and only selected aspects can be reviewed here. These processes are discussed together because they commonly occur together in oil reservoirs. An active aquifer facilitates both processes.

Water-washing refers to the extractive removal of crude oil components which, of course, depends on their solubility in the aqueous phase. Biodegradation refers to the oxidation of crude oil components by bacteria and therefore has biochemically controlled selectivity which may be different for various microbial communities.

Microbial activity has an upper temperature limit whereas water-washing does not. Nevertheless, active aquifers associated with petroleum reservoirs are commonly shallow and temperatures are therefore sufficiently low for microbial activity. The aquifer may supply oxygen for aerobic bacteria and/or sulfate for anaerobic sulfate reducing bacteria.

Microbial utilization of hydrocarbons by aerobic microorganisms has been known for many years by microbiologists (3, 8, 40), but the utilization of hydrocarbons by anaerobic microorganisms is debated and is difficult to demonstrate in the laboratory (8). Nevertheless, field studies and natural observations provide strong evidence of microbial reduction of sulfate (an anaerobic process) in many situations where petroleum hydrocarbons are the most likely organic substrate available (8, 14, 19, 32). Furthermore, there is ample evidence that in many such cases secondary calcite has been formed which has carbon isotope ratios indicating that its carbon must have been derived from the oxidation of

hydrocarbons (14). It must be concluded that microbial oxidation of crude oils in the subsurface does occur and may involve both aerobic and anaerobic microorganisms.

Interest in biodegradation of crude oils in reservoirs received a new stimulus by the rather definitive study of the Bell Creek Field reported by Winters and Williams in 1969 (42). In this case the biodegradation was attributed largely to aerobic microorganisms because of relationships between changes in oil composition and locations of wells in the field. Shallower oils closer to the aquifer outcrop were more degraded than deeper oils further from the outcrop. Variations of oxygen with distance from the outcrop were considered to be a controlling factor.

Most recently, Philippi (32) has taken a strong position suggesting that all "primary" crude oils are paraffinic, and that all "naphthenic" crude oils are the result of microbial attack on the primary oils. He also believes that anaerobes are effective in these transformations. Bailey *et al.* (1) also assume that bacteria can metabolize most types of hydrocarbons including aromatics and naphthenes although n-alkanes are most readily attacked. Thus, it has become common for geochemists to accept certain criteria as evidence of microbial degradation. Major gross criteria are a relative decrease in n-alkanes, an increase in density (decrease in API gravity), and an increase in cycloalkanes, aromatics and heteroatomic compounds (N, S, and O compounds). Isoprenoids, *e.g.*, pristane and phytane, initially show an apparent increase relative to n-alkanes because of their slower utilization but subsequently they decrease relative to cycloalkanes and other compounds. Philippi and others have discussed additional criteria based on the relative amounts of various compound types and/or isomer ratios. Unfortunately, no absolutely stable marker is known which would allow assessment of absolute changes rather than relative changes.

Our interest in this paper centers mainly on the increase in sulfur content of oils during biodegradation. We subscribe to the thesis that the increase in sulfur content occasioned by biodegradation is largely due to losses of non-sulfur compounds rather than to an introduction of additional sulfur. Some consequences of this thesis and evidence for its support are given below. However, it should be clear that definitive data are still lacking and the problem needs further study.

In reported suites of oils believed to represent undegraded and biodegraded oils from a common source, the sulfur content often increases by a factor of 2 or 3 (1, 2, 13, 16)<sup>2</sup>; the factor may be greater in very heavy asphalts and tar sands but definitive data are not available to my knowledge. If this increase is merely a concentration of sulfur compounds from the relative loss of non-sulfur compounds, it requires that 50 to 70% of the initial oil must be destroyed. In most cases this is greater than that possible from selective removal of n-alkanes alone and therefore appreciable losses of iso- and cyclo-alkanes and aromatics are required. If some of the sulfur compounds are also utilized, then, of course, losses must be even greater. In the absence of an absolute marker or complete material balance information, we cannot draw a final conclusion. Nevertheless, such large losses may be possible.

The limited data on sulfur isotope ratios for Midway-Sunset oils shown in Fig. 8 are consistent with the above suggestion that the sulfur increase during biodegradation does not necessarily involve the introduction of new sulfur formed by microbial reduction of sulfate. These three oils, which vary in sulfur content from 0.51 to 1.08% and in API gravity from 26.1 to 15.1°, have essentially identical sulfur isotope ratios. This suggests that either little or no new sulfur was introduced or the rather unlikely coincidence that the sulfur introduced

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\* It is of some interest that the increase in %N and in optical activity appears to be of the same order of magnitude.

had the same sulfur isotope ratio as that in the original oil. Further isotopic studies of this type including measurements on associated hydrogen sulfide and sulfates should help delineate situations where sulfurization does or does not occur during biodegradation of crude oils.

Another bit of evidence supporting the above position may be found in the homogeneity of sulfur isotopes in crude oils. Monster (23) demonstrated that sulfur isotope ratios were almost identical in the asphaltenes and various chromatographic fractions from a few crude oils. If the conclusions of Bestougeff and Combaz (5) are valid, one would expect the newly introduced sulfur to be mostly in the more polar and higher molecular weight fractions. Therefore, a homogeneous distribution of sulfur isotope ratios would not be expected unless the reacting hydrogen sulfide and/or elemental sulfur had the same isotope ratios as that of the sulfur initially in the oils. The oils examined by Monster are regarded as biodegraded oils. They included two of the Mission Canyon (MC-5) oils studied by Bailey *et al.* (2) and the Athabasca oil sand. Only a few oils have been examined for homogeneity of sulfur isotopes. Another case is the Fourbear oil from the Big Horn Basin. In this case very little difference in sulfur isotope ratios was found in distillations cuts and the distillation residue (see Fig. 11 in reference 27). This is one of the heaviest and probably most biodegraded oils in the Big Horn Basin.

A third argument for our thesis may be the fact that biodegraded heavy oils and tar sands do not necessarily have a high sulfur content. This was emphasized by Clairret *et al.* (7) in reporting on the heavy oils of the Emerald Field and some nearby but deeper light oils. The light oils with only about 0.12% S were concluded to be the type of oil which during biodegradation in the Emerald Field produced heavy oils with about 0.8% S. These authors make the following statement (Translated from French text): We are led to suppose that the sulfur enrichment in the course of biological degradation is largely only an effect of concentration of the products not consumed by microorganisms, and does not imply any appreciable introduction of sulfur from outside.

#### C. Sulfurization and Desulfurization Processes in High Temperature Reservoirs

Changes in abundance and forms of sulfur which occur during thermal maturation of crude oils are important for understanding the geochemistry of sulfur in oils, bitumens, pyrobitumens and natural gases. However, because these processes have little to do with heavy oils or the other subject materials except by way of contrast, we simply mention their existence and reference discussions dealing with them (27, 29, 30).

In high temperature reservoirs desulfurization always accompanies thermal maturation of oils. The sulfur is lost partly as hydrogen sulfide and partly as precipitated reservoir bitumens or pyrobitumens. Under certain conditions hydrogen sulfide may accumulate and sulfurization may compete with desulfurization. This can lead to a dynamic steady-state sulfur system. These interesting high temperature processes are important in understanding deep oils, condensates and natural gases. They can lead to gases unusually rich in hydrogen sulfide and condensates unusually rich in thiols.

#### SUMMARY AND CONCLUSION

We have briefly reviewed the geochemistry of sulfur as it relates to crude oils and other fossil fuels.

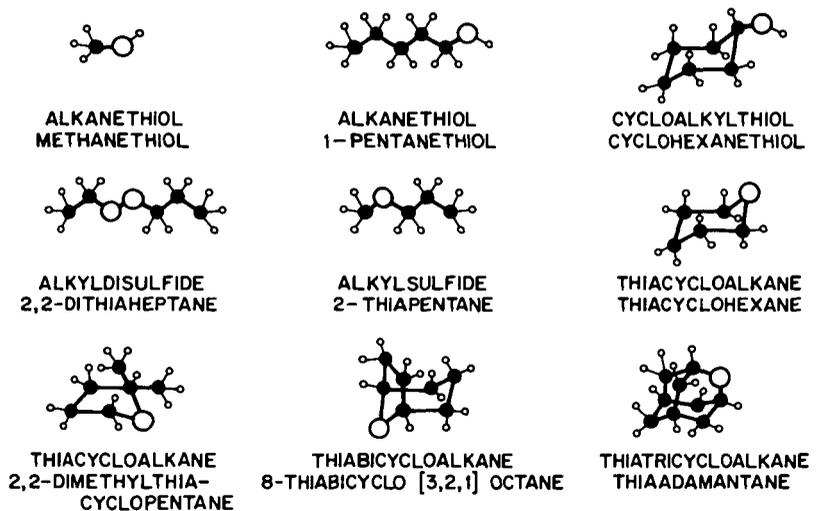
Heavy oils and asphaltic oil sands are believed to have been formed largely by biodegradation of lighter oils. The sulfur content of a heavy oil and/or oil sand is believed to be determined largely by the sulfur content of the undegraded precursor oil and the extent of biodegradation which involves a preferential removal of non-sulfur components. New sulfur probably is not added to the residual oil during biodegradations but its concentration is increased mainly because of the removal of other components.

## REFERENCES

- (1). Bailey, N. J. L., M. A. Jobson and M. A. Rogers. Bacterial degradation of crude oil: Comparison of field and experimental data. *Chem. Geol.* v. 11, 1973, pp. 203-221.
- (2). Bailey, N. J. L., H. R. Krouse, C. R. Evans and M. A. Rogers. Alteration of crude oil by waters and bacteria: Evidence from geochemical and isotopic studies. *Am. Assoc. Petrol. Geologists Bull.*, v. 57, 1973, pp. 1276-1290.
- (3). Beerstecher, E. Petroleum Microbiology, Elsevier Press, Inc., 1954, 375 pp.
- (4). Bestougeff, M. Constitution des composés soufrés cycliques du pétrole. *Proc. 5th. World Petrol. Congr., Sect. V, Paper 12*, 1959.
- (5). Bestougeff, M. and A. Combaz. Action d' $H_2S$  et de S sur quelques substances organiques actuelles et fossiles. In Advances in Organic Geochemistry 1973, (B. Tissot and F. Bienner, Eds.). Editions Technip., Paris, 1974, pp. 747-759.
- (6). Challenger, F. Aspects of the Organic Chemistry of Sulfur. Butterworth Scientific, London, 1959, 253 pp.
- (7). Claret, J., J. B. Tchikaya, B. Tissot, G. Deroo, and A. van Dorsselaer. Un exemple d'huile biodegradée à basse teneur en soufre: Le gisement d'Émeraude (Congo). Preprint of paper given at 7th International Meeting on Organic Geochemistry, Madrid, Sept. 1975. (Proceedings in press).
- (8). Davis, J. B. Petroleum Microbiology, Elsevier Pub. Co., 1967, p. 604.
- (9). Dean, R. A. and E. V. Whitehead. Status of work in separation and identification of sulfur compounds in petroleum and shale oil. 7th World Petrol. Cong.: Panel Discussion 23, Paper 7, 1967.
- (10). Deroo, G., B. Tissot, R. G. McGrossan and F. Der. Geochemistry of the heavy oils of Alberta. In Oil Sands Fuel of the Future, Mem. 3, Canadian Soc. Petrol. Geologists, 1973, pp. 148-167.
- (11). Drushel, H. V. Sulfur compound type distribution in petroleum using an in-line reactor or pyrolysis combined with gas chromatography and a microcoulometric sulfur detector. *Anal. Chem.* v. 41, 1969, pp. 569-576.
- (12). Drushel, H. V. Sulfur compounds in petroleum - known and unknown. Preprints ACS Div. Petroleum Chem. Div. v. 15, No. 2, C-12 (1970).
- (13). Evans, C. R., M. A. Rogers and N. J. L. Bailey. Evolution and alteration of petroleum in western Canada. *Chem. Geol.*, v. 8, 1971, pp. 147-170.
- (14). Feely, H. W. and J. L. Kulp. Origin of Gulf Coast salt dome sulfur deposits. *Am. Assoc. Petrol. Geologists Bull.*, v. 41, 1957, pp. 1802-1853.
- (15). Gal'pern, G. D. Organic sulfides in petroleum. *Intn. J. Sulfur Chem.* B, 1971, 1971, p. 115-
- (16). Gransch, J. A., and J. Posthuma. On the origin of sulfur in crudes. In Adv. in Organic Geochemistry 1973. (B. Tissot & F. Bienner, Eds.), Editions Technip. Paris, 1974, pp. 727-739.

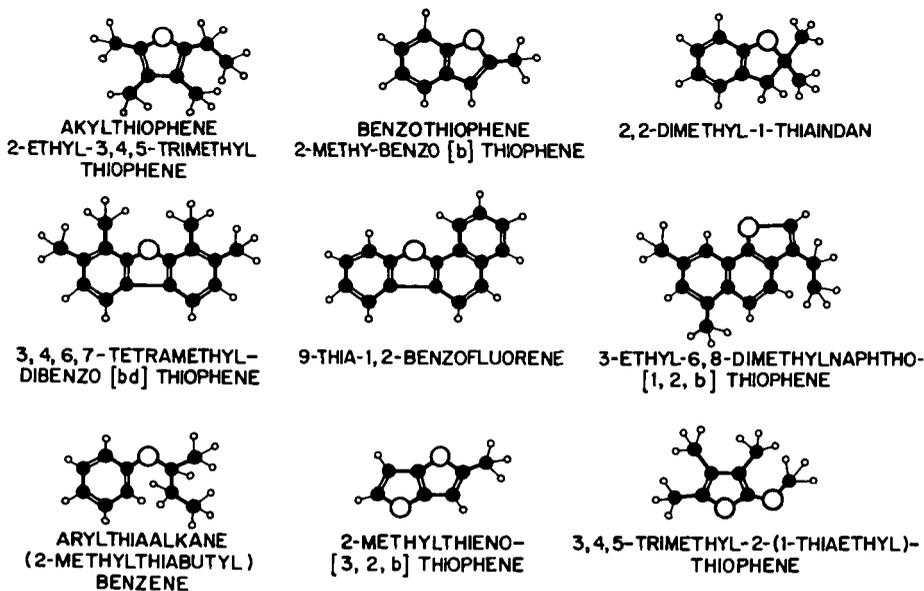
- (17). Holser, W. T. and I. R. Kaplan. Isotope geochemistry of sedimentary sulfates. *Chem. Geol.*, v. 1, 1966, pp. 93-135.
- (18). Ho, T. Y., M. A. Rogers, H. V. Drushel and C. B. Koons. Evolution of sulfur compounds in crude oils. *Am. Assoc. Petrol. Geologists Bull.* v. 58, No. 11, 1974, pp. 2338-2348.
- (19). Ivanov, M. V. Microbiological Processes in the Formation of Sulfur Deposits. Jerusalem, Israel Program for Scientific Translations 1968 (Available from U.S. Dept. of Commerce).
- (20). Koots, J. A. and J. G. Speight. Relation of petroleum resins to asphaltenes. *Fuel*, v. 54, 1975, pp. 179-184.
- (21). Lumpkin, H. E. Analysis of a trinuclear aromatic petroleum fraction by high resolution mass spectrometry. *Anal. Chem.*, v. 36, 1964, p. 2399-2401.
- (22). Martin, R. L. and J. A. Grant. Determination of thiophenic compounds in petroleum samples. *Anal. Chem.*, v. 37, 1965, p. 644-649.
- (23). Monster, J. Homogeneity of sulfur and carbon isotope ratios  $S^{34}/S^{32}$  and  $C^{13}/C^{12}$  in petroleum. *Am. Assoc. Petrol. Geologists Bull.*, v. 56, 1972, pp. 941-949.
- (24). Nelson, W. L. Sulfur distribution of oils throughout the world. *Oil & Gas J.*, v. 65, Feb. 13, 1967, pp. 122-123.
- (25). Nelson, W. L. Sulfur distribution in extreme or freak crude oils. *Oil and Gas J.*, v. 65, no. 49, 1967, pp. 92-93.
- (26). Nissenbaum, A. and I. R. Kaplan. Chemical and isotopic evidence for the in situ origin of marine humic substances. *Limnol. Oceanogr.*, v. 17, 1972, p. 574-
- (27). Orr, W. L. Changes in sulfur content and isotopic ratios of sulfur during petroleum maturation - Study of Big Horn Basin Paleozoic oils. *Am. Assoc. Petrol. Geologists Bull.*, v. 58, 1974, pp. 2295-2318.
- (28). Orr, W. L. Biogeochemistry of sulfur. In Handbook of Geochemistry (K. H. Wedpohl, Ed.). Vol. 11-1, Sec. 16-L. Springer-Verlag, Berlin, 1974.
- (29). Orr, W. L. Geologic and geochemical controls on the distribution of hydrogen sulfide in natural gas. *Proc. 7th International Meeting on Organic Geochemistry*, Madrid, Sept. 1975 (In press).
- (30). Orr, W. L. Sulfur in petroleum and related fossil organic materials. *Preprints ACS Div. of Petroleum Chem.* v. 21, No. 3, 1975, pp. 417-421.
- (31). Pack, R. W. The Sunset-Midway Oil Field. California. Part I. Geology and Oil Reserves. USGS Prof. Paper 116, 1920, 173 pp.
- (32). Philippi, G. T. On the depth, time and mechanism of origin of the heavy to medium-gravity naphthenic crude oils. *Geochim. et Cosmochim. Acta.*, v. 41, 1977, pp. 33-52.
- (33). Rall, H. T., C. J. Thompson, H. J. Coleman and R. L. Hopkins. Sulfur compounds in crude oil. *US Bureau of Mines Bull.* 659, 1972, 187 pp.

- (34). Rogers, G. S. The Sunset-Midway oil field California: Part II. Geochemical relations of the oil, gas and water. USGS Prof. Paper 117, 1919, 103 pp.
- (35). Roy, A. B. and P. A. Trudinger. The Biochemistry of Inorganic Compounds of Sulfur. Cambridge Univ. Press, 1970, 400 pp.
- (36). Thode, H. G., J. Monster and H. B. Dunford. Sulfur isotope abundances in petroleum and associated materials. Am. Assoc. Petrol. Geologists Bull., v. 42, 1958, pp. 2619-2641.
- (37). Thode, H. G. and J. Monster. Sulfur-isotope geochemistry of petroleum, evaporites and ancient seas. In Fluids in Subsurface Environments (A. Young and J. E. Galley, Eds.). Am. Assoc. Petrol. Geol. Memoir 4, 1965, pp. 367-377.
- (38). Thode, H. G. and J. Monster. Sulfur isotope abundances and genetic relations of oil accumulations in Middle East basins. Am. Assoc. Petrol. Geologists Bull., v. 54, 1970, pp. 627-637.
- (39). Vredenburg, L. D. and E. S. Cheney. Sulfur and carbon isotopic investigation of petroleum Wind River Basin, Wyoming. Am. Assoc. Petrol. Geologists Bull., v. 55, 1971, pp. 1954-1975.
- (40). Walker, J. D., R. R. Colwell and L. Petrakis. Biodegradation rates of components of petroleum. Can. J. Microbiology, v. 22, 1967, pp. 1209-1213.
- (41). Welte, D. Recent advances in organic geochemistry of humic substances and kerogen. In Advances in Organic Geochemistry 1973, Editions Technip, Paris, 1974, pp. 3-13.
- (42). Winters, J. C. and J. A. Williams. Microbial alteration of petroleum in the reservoir. Preprints ACS Petrol. Chem. Div., v. 14, no. 4, 1969, pp E22-E31.
- (43). Zobell, C. E. Organic geochemistry of sulfur. In Organic Geochemistry (I. A. Breger, Ed.). Macmillan Co., New York. 1963., pp. 543-578.



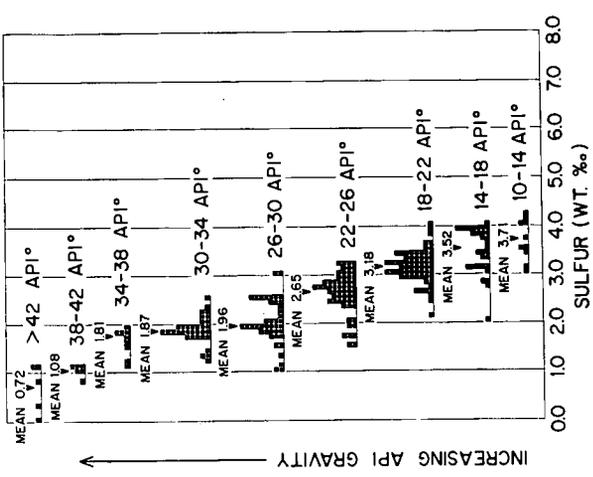
### EXAMPLES OF ALIPHATIC SULFUR COMPOUNDS IN PETROLEUM

Figure 1.



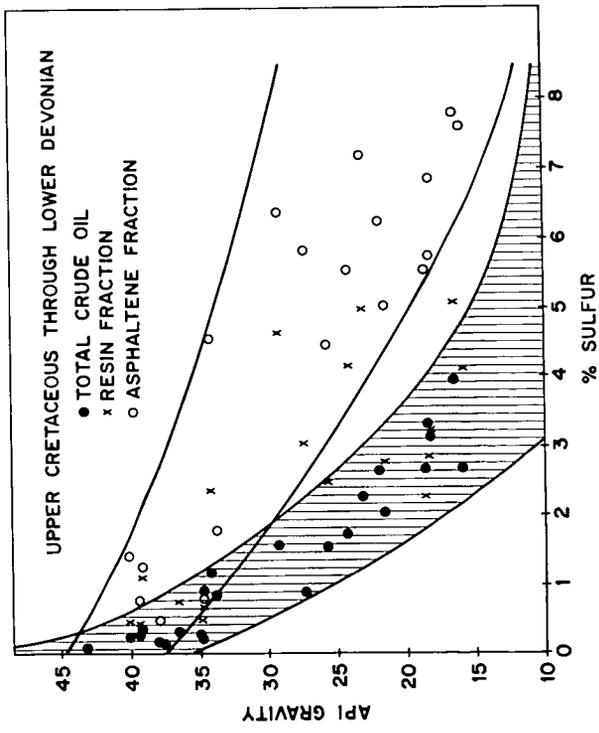
### EXAMPLES OF AROMATIC SULFUR COMPOUNDS IN PETROLEUM

Figure 2.



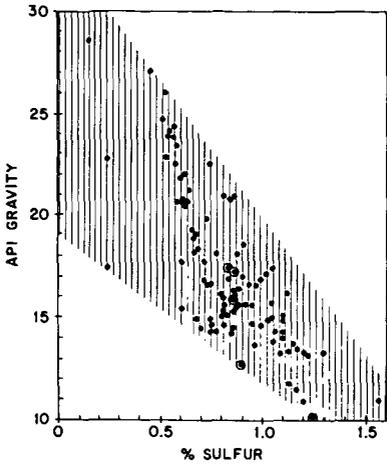
**BIG HORN BASIN PALEOZOIC OILS**

Figure 4.



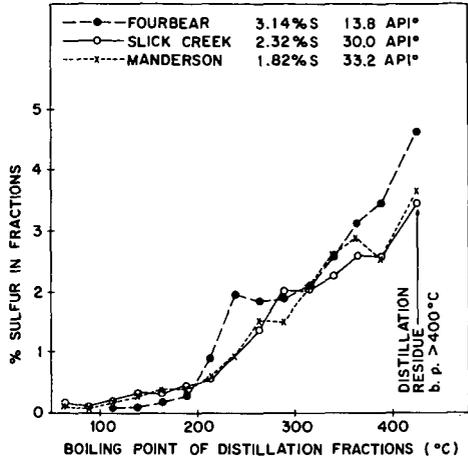
**ALBERTA CRUDE OILS**  
(MOOTS & SPEIGHT, 1975)

Figure 3.



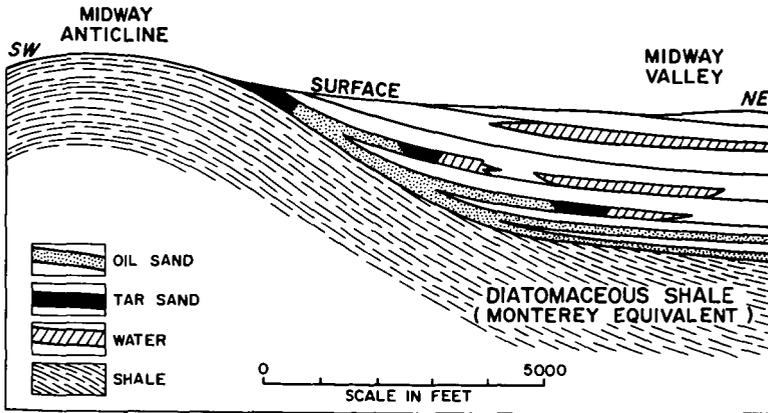
**MIDWAY-SUNSET OILS (CALIF.)**  
 REDRAWN FROM ROGERS (1919)

Figure 5.



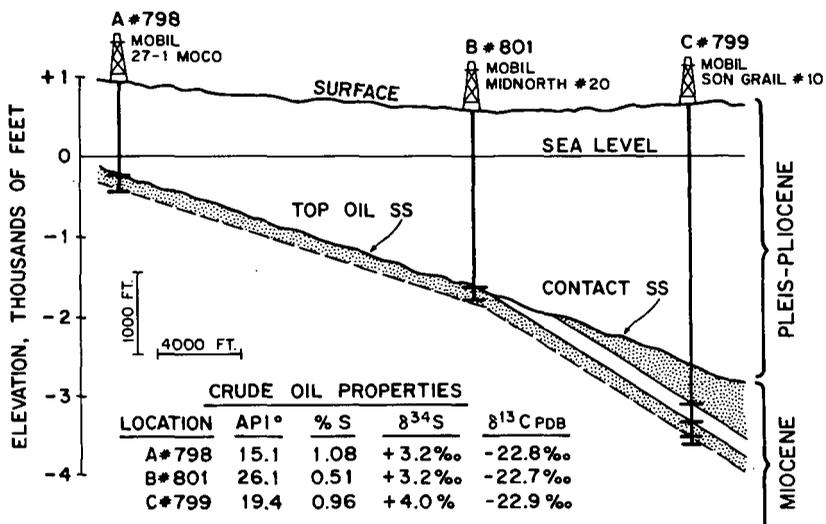
**BIG HORN BASIN OILS (WYO.)**

Figure 7.



**DIAGRAM SHOWING RELATIONS OF OIL, TAR & WATER ZONES  
 IN VICINITY OF FELLOWS (MIDWAY-SUNSET FIELD)**  
 FROM ROGERS (1919) FIG. 13, p. 115

Figure 6.



CROSS SECTION OF MIDWAY-SUNSET FIELD

Figure 8.

# OPTICAL ACTIVITY OF SHALE OIL FOR PARAMETER STUDY IN RETORTING

Dale L. Lawlor

Laramie Energy Research Center  
Energy Research and Development Administration  
P. O. Box 3395, University Station  
Laramie, Wyo. 82070

## INTRODUCTION

Optical activity has been observed in petroleum and in isoprenoid compounds, steranes, and triterpanes extracted from oil shale (1-3). Optical activity is a property that can reflect the molecular integrity of a former biological system and has been used to evaluate the geochemical history of petroleum from different geological ages (1). Optical isomer data have been used as a biological clock in geochronological research (4) and have been used to determine the possible origin of certain carbonaceous chondrite meteorites (5). The key to studying these organic systems is the slow decay of the optically active molecules, as a result of low-level heat (geological time), into optically neutral mixtures. Retorting of oil shale kerogen accelerates this decay process. This paper describes the use of optical activity data as a means of studying this conversion of kerogen into shale oil. Studies at the Laramie Energy Research Center have demonstrated that shale oil produced from bench-scale and field in-situ experiments is optically active. New insights into the retorting process may now be possible by following the changes in optical activity.

## EXPERIMENTAL

### Preparation of Shale Oils

The three sets of shale oils studied were from two laboratory retorting experiments and one field retorting experiment. The laboratory experiments were conducted in the controlled-state retort (CSR), described in detail by Duvall (6). In brief, the retort is an electrically heated, 3-in. by 13-ft stainless steel pipe. The electric heaters are spaced each 6 inches and are monitored by thermocouples inserted in a 1-inch pipe through the center of the 3-inch pipe. Nitrogen, admitted at the top of the retort, is used as a sweep gas.

The first set of oils was prepared by filling the retort with 1/8- to 1/2-inch, 36.5-gal/ton shale from the Anvil Points, Colo., mine and by retorting under the conditions shown in Table I. The shale was heated from the top downward; the produced oil flowed by gravity with assistance from the nitrogen sweep gas and was collected at the bottom of the retort. The collected oil was transferred to a distillation flask and was distilled to remove water and naphtha. The naphtha was separated from the water and was returned to the oil. Properties of the dried oil are shown in Table II. Naphtha and light distillate fractions after tar acid and tar base removal were fractionated, using silica gel chromatography, into saturates, olefins, and aromatics.

TABLE I. - CSR retorting conditions

Heating rate, °F/min	Maximum temp., °F	Zone velocity, in./hr	Sweep gas, ft <sup>3</sup> /hr	Sweep gas, SCF/ft <sup>2</sup>
2	1,000	3	1.5	24
20	1,000	12	14	224

TABLE II. Properties of CSR crude oils

Retort heating rate, °F/min	Oil yield, % of Fischer assay	Specific gravity 60/60°F	Pour point, °F	Viscosity, 100°F SUS	Viscosity, 130°F SUS	Molecular wt.*
2	96.4	.925	45	148	69	282
20	87.6	.921	35	263	131	219

\*Vapor-phase osmometry in benzene

The second set of oils was prepared by filling only the bottom 6-inch zone of the retort with 1/8- to 1/2-inch shale and the next 6-inch zone with ceramic beads. Oils were prepared using heating rates of 0.1, 1, 2, 4, and 10°F per minute and a N<sub>2</sub> flow rate of 14 ft<sup>3</sup> per hour. A maximum spent-shale temperature of 1200°F was reached. The collected oils were dried by centrifugation.

The third set of oils was collected from the in-situ retorting Site 9 near Rock Springs, Wyo.(7). A 40-ft zone of fractured oil shale was retorted in advance of a combustion front that propagated radially from a central air injection well toward surrounding production wells. One production well, No. 7, located 50 feet from the injection well, was sampled four times during a 2-month period. The collected oils were dried by centrifugation.

#### Preparation of Saturate Fraction

The procedure is basically that used by Redfield (8). A 0.5-g sample of dried oil was dissolved in 1 ml of cyclohexane and placed on a 2- by 75-cm column of 150 g of 28- to 200-mesh silica gel (Matheson Grade 10) prewet with n-hexane (Burdick and Jackson Laboratories, Inc.). The column was eluted with 240 ml of n-hexane at a flow rate of 7 to 8 ml per minute. The n-hexane-eluted saturate fraction was concentrated to 20 ml by evaporation under N<sub>2</sub>, and the concentrated solution was used for optical activity measurements.

#### Optical Activity Measurements

Optical activity was measured on the saturate fraction using a 10-cm, strain-free quartz cell in a Jasco J-20 spectropolarimeter in the optical rotary dispersion mode. Data were recorded in the 250- to 600-nm wavelength range. A solvent blank after each run was used to determine the baseline. The observed rotation from 300 to 600 nm wavelengths was converted to degrees of specific rotation,  $[\alpha]^{25}$ , by the following formula:

$$[\alpha]^{25} = \frac{\alpha}{l \cdot c}$$

where  $\alpha$  = observed rotation,  $l$  = sample path length in decimeters, and  $c$  = concentration of sample in g per ml; i.e., the weight of oil charged to the silica gel column divided by the volume of the saturate solution in the cell.

### RESULTS AND DISCUSSION

Shale oils are deeply colored, and thus are not easily amenable to optical activity measurement. Fortunately, the optically active molecules, steranes, di-, tri-, and tetraterpanes (3), are found essentially in the transparent saturate

fraction so that measurements can be made on this fraction. These molecules partly degrade to racemic or optically inactive mixtures during the retorting process.

Optical activity measurements on the first set of oils show that optically active molecules do survive the retorting process, and this occurs to varying degrees. The data plotted in Figure 1 show less activity in the 20°F-per-minute oil at all wavelengths. This activity difference indicates more degradation or cracking in the 20°F-per-minute oil than in the 2°F-per-minute oil.

Other evidence of increased cracking with increased heating rate is shown in Table II where the oil yield, the pour point, and the molecular weight decrease. More definitive cracking evidence is seen in the olefin increase (Table III) from 48 to 54 percent for the naphtha and from 49 to 65 percent for the light distillate.

TABLE III. - Hydrocarbon-type analysis of neutral oils

Retort heating rate, °F/min	Vol. percent					
	Naphtha			Light distillate		
	Saturates	Olefins	Aromatics	Saturates	Olefins	Aromatics
2	38	48	14	30	49	21
20	32	54	14	24	65	11

The second set of oils was chosen for a more detailed study of the effect of heating rate on optical activity. Five heating rates were chosen, and duplicate samples of the resulting oils were separated and measured. The results, Table IV, show good reproducibility since rotational differences between duplicate samples are generally less than 0.1° of rotation. A plot of the data, Figure 2, shows a consistent trend toward decreasing activity with increasing heating rates. The top curve, representing the oil prepared at a 0.1°F per minute heating rate, ranges from above 3.2°[α]<sup>25</sup> to about 0.6°[α]<sup>25</sup>. The 10°F-per-minute heated oil ranges from 1.9 to 0.4°[α]<sup>25</sup>. Shale oils prepared from the controlled state retort show changes in optical activity as an inverse function of heating rate. The oils produced at higher rates show the least activity, implying more thermal energy exposure to the product oil, which causes more oil degradation.

Optical activity measurements were made on four oils collected from the Rock Springs, Site 9, in-situ retorting experiment (Fig. 3). Using data plotted from the 450-nm wavelength, differences are apparent in the oil composition from the four dates over a time span of over two months. These differences seem to reflect changes in operation that altered the rate of combustion. During the period April 5 to 22, propane was burned in the injection well to establish combustion and retorting. The produced oil, because of exposure to hot combustion gases, showed a low optical activity of about 0.3 degrees. Conversion from propane to air-only injection on April 23 probably resulted in a cooler retorting system which produced the higher optically active oil collected on May 5. Propane injection was resumed on May 8, and later air injection in a different well produced hotter combustion conditions, resulting in the lower optically active oils sampled on May 25 and June 8. These conclusions are tentative and do warrant further data evaluation and experimentation. The in-situ oils in general show one-third to one-half the optical activity of the controlled-state produced oils and, therefore, apparently have experienced more degradation or cracking.

TABLE IV Optical activity,  $[\alpha]_{25}^D$ , of five shale oils prepared at different heating rates

Heating rate, °F/min	Degrees specific rotation, $[\alpha]_{25}^D$						
	300	350	400	450	500	550	600
0.1	3.26 ± 0.15	2.28 ± 0.12	1.61 ± 0.08	1.21 ± 0.05	0.96 ± 0.03	0.77 ± 0.03	0.62 ± 0.01
1*	2.59	1.76	1.29	1.02	0.83	0.67	0.68
2	2.56 ± 0.01	1.76 ± 0.01	1.28 ± 0.01	0.96 ± 0.03	0.78 ± 0.01	0.62 ± 0.03	0.55 ± 0.04
4	2.10 ± 0.08	1.38 ± 0.03	1.00 ± 0.02	0.76 ± 0.01	0.58 ± 0.04	0.46 ± 0.03	0.38 ± 0.02
10	1.90 ± 0.08	1.28 ± 0.06	0.90 ± 0.04	0.68 ± 0.01	0.52 ± 0.04	0.41 ± 0.00	0.37 ± 0.04

\*Single determination only

#### SUMMARY

The possibility of using optical activity data to study cracking during oil-shale retorting was confirmed by examining shale oils prepared at different heating rates using the bench-scale controlled-state retort. The results show a relationship between shale oil optical activity and heating rate. The oils prepared from in-situ field experiments have optical activity values that are inversely proportional to the suspected underground retorting temperatures and indicate more severe and variable retorting conditions than the controlled state retort system. Further use of optical activity data may be useful in understanding the retorting process in the laboratory and in controlling the process in the field.

#### ACKNOWLEDGMENTS

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#### LITERATURE CITED

1. W. D. Rosenfeld, *J. Am. Oil Chem. Soc.*, 44, 703 (1967).
2. I. R. Hills, E. V. Whitehead, and D. E. Anders, *Chem. Commun.*, 752 (1966).
3. B. Hitchon, "Origin and Refining of Petroleum," *Adv. in Chem. Series 103*, Washington, 1971, p. 30f.
4. P. E. Hare and P. H. Abelson, *Carnegie Inst. of Wash., Yearbook 66*, 526 (1967).
5. K. A. Kvenvolden, J. Lawless, K. Pering, E. Peterson, J. Flores, C. Ponnampuruma, I. R. Kaplan, and C. Moore, *Nature*, 228, 92 (1970).
6. J. J. Duvall and H. B. Jensen, *Quart. Colo. School of Mines*, 70, (3), 187 (1975).
7. R. L. Wise, B. C. Sudduth, J. M. Winter, L. P. Jackson, and A. Long, *Soc. Petrol. Eng. of AIME*, Paper No. SPE 6067, New Orleans, Oct. 3-6, 1976.
8. W. D. Redfield, personal communication.

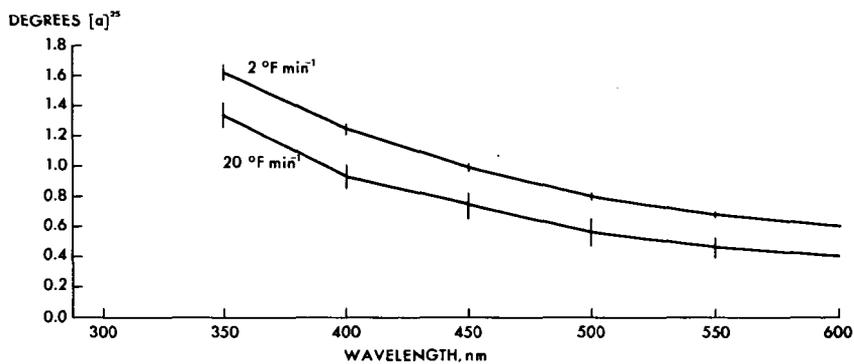


FIGURE 1. - OPTICAL ACTIVITIES, 2 CSR CRUDES.

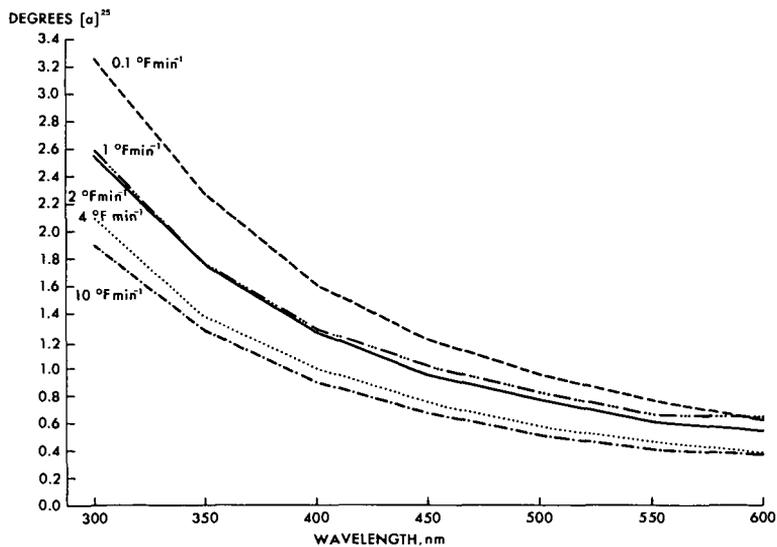


FIGURE 2. - OPTICAL ACTIVITIES, 5 CSR CRUDES.



THE EFFECTS OF SOME ALKALI METAL PROMOTORS ON COKE DEPOSITION AND THE CATALYTIC ACTIVITY OF A  $\text{CoO-MoO}_3\text{-Al}_2\text{O}_3$  CATALYST. James F. Kelly and Marten Ternan, Energy Research Laboratories, Dept. of Energy, Mines and Resources, c/o 555 Booth Street, Ottawa, Canada, K1A 0G1.

In the catalytic hydrocracking of Athabasca bitumen, coke formation on the catalyst surface leads to rapid catalyst deactivation. In an attempt to reduce catalyst deactivation by coke deposition, a series of  $\text{Al}_2\text{O}_3$  supported catalysts (2.2%  $\text{MoO}_3$ -1.15%  $\text{CoO}$ ) promoted with lithium, sodium or potassium carbonate was prepared and evaluated. Metal salts and carbonates were added to alumina by spraying aqueous solutions of the appropriate species onto alumina monohydrate in a mix-muller. Catalyst evaluation experiments were performed in a bottom-feed continuous-flow tubular reactor operated at  $450^\circ\text{C}$ ,  $1.39 \times 10^4$  kPa and a liquid volumetric space velocity of  $0.29 \text{ ks}^{-1}$  based on the total empty reactor volume. All catalyst samples were presulphided with bitumen at  $430^\circ\text{C}$  before evaluation. An experimental approach to the determination of the amount of coke deposited on the catalyst during reaction in the presence of bitumen is described. The effects of the investigated carbonate promoters on measured catalyst coke levels are discussed, as well as the resulting changes in the catalytic hydrodesulphurization and hydrodenitrogenation activities due to these promoters.

## Effect of Shale Alterations in Oil Recovery. Ionic Treatments.

W. Kubacki

Instituto de Investigaciones Petroleras  
Facultad de Ingenieria  
Universidad del Zulia  
Maracaibo, Venezuela.

### INTRODUCTION

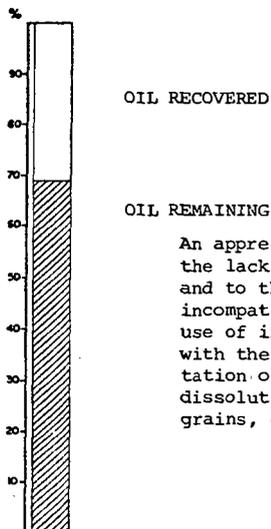
The permeability and porosity of the sedimentary rock in an oil field are responsible for the storage, detection and migration of oil and gas. Previously, it was believed that these properties were not changed even if one or more of the rock components, such as silica clays, reacted with the fluids used during oil recovery. However, we know now that this is not completely valid since the permeability can be affected by the treatment undergone by the porous medium. These problems which originate from alteration phenomena should be investigated mineralogically and chemically in order to understand the physical equilibrium between the oil field shale, the formation water, and the oil. If the chemical reactions which can occur between the liquid used in the treatment and the oil field formation are not known or considered, and if the mineralogical data on the deposit are lacking, a serious waste of time and money can result.

An oil reservoir is generally found in sedimentary rocks such as conglomerates of sand, sandstone, clays, limestone, and dolomites. We will discuss the properties of oil reservoirs of the silicate type, and, among them, the clay types and those consisting of sand mixed with swellable clays known as "sensitive formations" which are found in the surrounding area of an oil field.

#### I. Oil recovery and chemical-mineralogical parameters, the control of which will allow an increase in oil recovery.

The alteration of silicate rocks by the water of invasion can be avoided or minimized by taking preventive measures aimed at controlling the cause.

#### Extent of world oil recovery and estimated losses:<sup>1</sup>



An appreciable portion of the oil is not recovered due to the lack of chemical-mineralogical knowledge of the formation and to the damage caused by the use of operational practices incompatible with the impermeable strati of clay such as: use of inadequate fluids that undergo adverse reactions with the formation causing the dispersion of clays, precipitation of salts resulting from chemical reactions, the dissolution or hydration of the cementing materials of the grains, etc.

Table I

## Chemical-Mineralogical Parameters Affecting Oil Recovery

Type of Operation	Chemical-Mineralogical phenomena which can occur
Drilling	Alteration of the underground formation due to migration of mud towards the formation. Reduction of the permeability of the well surroundings.
Electrical Recordings	Electrochemical phenomena effects (membrane potential) and electrokinetics (mud migration) on the inflection of the "Sp" curve renders the detection of hydrocarbons difficult.
Secondary Recovery	During the injection of water, if it is incompatible with the clay or with the water of hydration of the clay, a reduction in alkalinity, and dispersion of the formation can occur; later, the production fluid will cause transport, deposition and blockage of the porous media. If micellar fluids are used, adsorption will bring about failure of the operation. On the other hand, the removed and dispersed clays lead to the production of sand which, in turn, will cause the obstruction of pipes and valves.
Stimulation of the Wells	If the fluids used in the operations of acidification and fracturing are not compatible with the chemical composition of the formation, they can cause unexpected chemical reactions, the products of which reduce the permeability by blocking the porous medium and lead to the failure of the operation.

II. Effect of hydration of the clay lattice.

The water molecule is a dipole with a positive and negative center of charge (see Figure 1). The distance between the center of gravity of the oxygen atom and that of the hydrogen atom in water is  $0.96\text{\AA}$  and the HOH angle is  $104.5^\circ$ . In the crystalline lattice of silicates the molecule of water behaves as if it had two negative charges in the corners of a tetrahedron which bond with metallic ions; on the other side they bond to oxygen atoms<sup>2</sup> (see Figures 1b and 2).

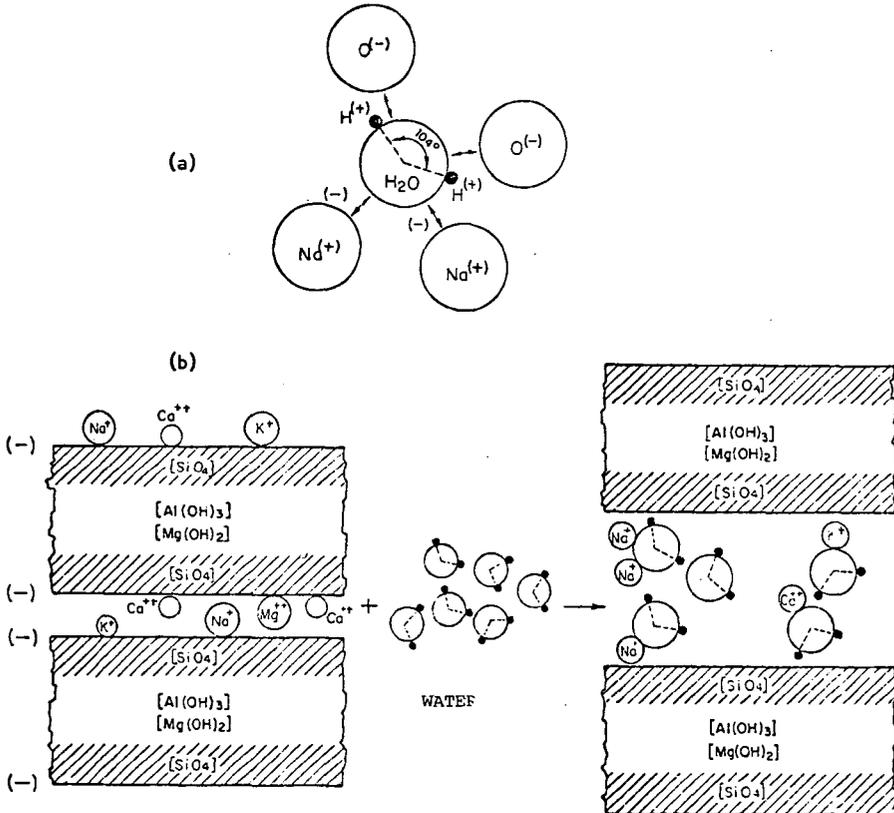


Figure 1. Electrostatic Bond Strength between the clay and the water table.

a) Water dipole. Distribution of electrical charges.

b) Phenomenon of positive ion binding between the layers. Swelling of the clay.

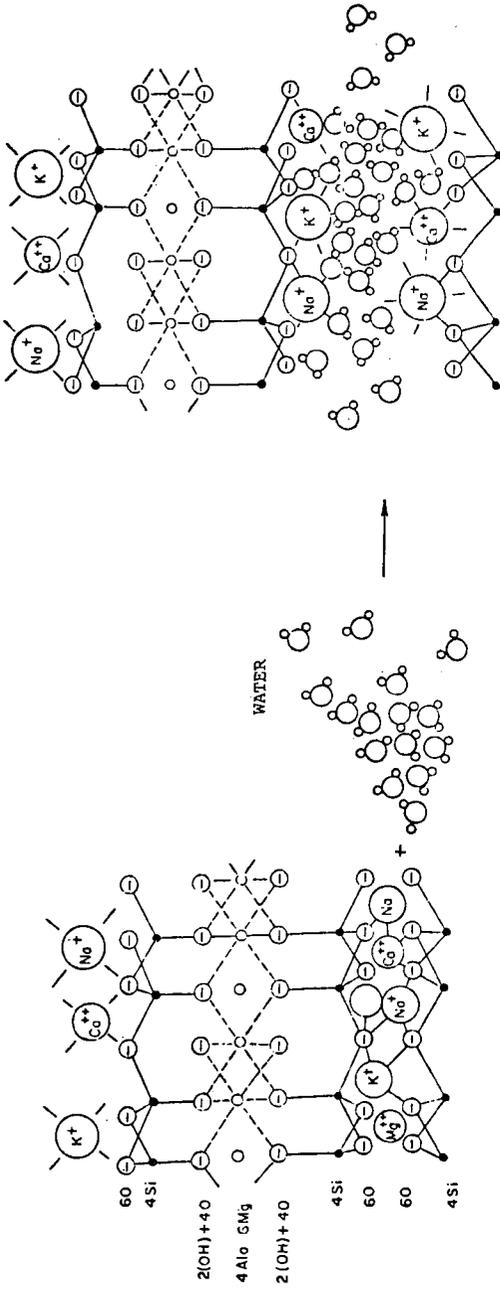


Figure 2. Phenomenon of swelling of clays due to water penetration at the level of the crystallographic unit cell.

### III. Clay differentiation.

Most of the silicates of the so-called "layer" type are characterized by structural similarities. The crystals belong to the same symmetry group and show the same type of geometric distribution of the structural elements such as, for example, the unit cell, which has the same symmetry and the same relation of axes<sup>2</sup>. From the crystallographic point of view, the silicates of the layer type have the same number of ions and the same relation for the radii of cations and anions.

The difference in the sensitivity towards alteration or hydration is caused by the pressure due to ions of isomorphic interchange placed in the exterior of the crystal lattice. These ions act as a cement, binding the structural units by electrostatic forces, and are directly responsible for the structural compactness and hardness of the rock.

Clays of sedimentary origin, previously situated in marine waters, are formed of various types mixed in different proportions. The most sensitive components of the clays are montmorillonite, illite and their mixtures. They constitute up to 80% of the total weight of the clay rock and often cause serious problems during the operation of the oil field. Due to the presence of monovalent ions, these minerals easily absorb water, the base of the conventional operating fluids, and as a result they hydrate and disperse. The first step in the colloidal dispersion of clays consists of a reduction in the bond strength between hydrated structural layers, and in the second step they are separated and the rock is dispersed. This dispersion is not the same for every type of clay.

Generally, the expandable clays are present in relatively small amounts and the problems of structural expansion, the so-called "swelling", are not so alarming as people tend to believe.

Colloidal dispersion and the migration of particles, however, can be much more damaging because serious problems can be caused by very small quantities of clay. These particles of clay dispersed in the flux channels are eventually deposited in a porous constriction, producing a collapse.

Lately, research has focussed on mixed operational fluids consisting of polymer and brine, which react only slightly with the rock. This fluid should be selected for the particular conditions of the oil field such as:

- 1) chemical composition of the formation;
- 2) chemical content of the formation water;
- 3) pH of the water of formation;
- 4) temperature and pressure of the oil field;
- 5) the unpredictable reactions "in situ";
- 6) the erosive action of the fluids;
- 7) the residence time in the "sensitive" region.

Recently it has been found<sup>3</sup> that pressure and high temperature accelerate the effects of the colloidal dispersion of clays (see Figure 3). Unfortunately it is rare for geochemical laboratories to consider these parameters and to simulate the conditions of the oil field.

Table 2 shows the differentiation of clays by the presence of the isomorphic interchange ion, and Table 3 shows the physical characteristics of clay formations when there is an invasion of fresh water. Until recently this differentiation and classification which are encountered in practice have not been considered<sup>4,5</sup>.

Table II

## Differentiation of Clays

Type of Clay	Ions of the Isomorphic Exchange Structural Components	Effect Produced By Water of Invasion	Remarks
Montmorillonite	$(H_3O, Na, K, Ca) -$ $(Al, Mg, Fe, Ni, Zn, Cr)_{2-3}$ $/(Si, Al)_4O_{10}/(OH)_2 \cdot nH_2O$	Easy hydration and elimination of alkaline ions with swelling and colloidal dispersion.	The predominance of Na ions which are easily interchanged by the ambient water.
Illite	$(H_3O, K) Al$ $/(Si, Al)_4O_{10}/(OH)_2$	Easy penetration of water between layers but it hydrates with more difficulty. It has less tendency to disperse.	The only clay type of material which contains a lot of radioactive K* which can be detected by gamma ray profile. Potassium is predominant.
Chlorite	$Mg_2Al(Mg, Al)_3$ $/(Si, Al)_4O_{10}/(OH)_6$	Difficult penetration of water between layers because of the presence of polyvalent Mg and Al ions.	
Kaolinite	$Al_4 (Si_4O_{10}) (OH)_8$	It contains structural water which weakens the cohesion of the layers so that it is easily dispersed.	It is the most pure clay. It does not contain ions of interchange, and does not swell.
Mica	$K(Mg, Fe)_3$ $(AlSi_3O_{10}) (OH, F)_2$	The invasion of water produces swelling more easily than dispersion due to the elimination of interchangeable ions (OH and F).	The interchange of the anion $F^-$ by $OH^-$ or the reverse takes place which destabilizes the structure and the electrostatic charges.
Isomorphic Mixture	Kaolinite/Illite Illite/Montmorillonite Kaolinite/Chlorite Montmorillonite/Chlorite/Kaolinite	Isomorphic mixtures of clays are present in nature. The physico-chemical properties of the mixture depend on the relative amounts of each clay.	

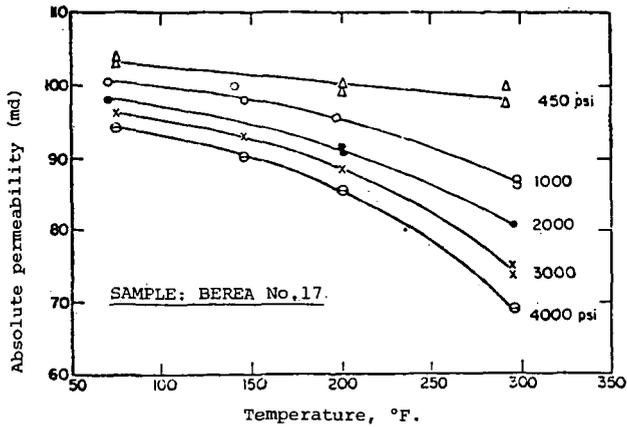


Figure 3. Effect of pressure and temperature on the permeability of the oil field (affected by clays).

Table III

Class	Characteristics	Clay Contents
1	Soft rock. It is easily dispersed in a colloid state.	High concentration of montmorillonite. Low concentration illite.
2	Soft rock. It is relatively easily dispersed in a colloidal state.	Medium concentration montmorillonite. High concentration of illite.
3	Medium-soft rock. It is moderately dispersed. Strong swelling.	High concentrations of illite and chlorite.
4	Medium-hard rock. Little colloidal dispersion. Medium swelling.	Medium concentration of illite and chlorite.
5	Hard rock. No colloidal dispersion, little swelling.	High concentration of illite. Medium concentration of chlorite.



The Na<sup>+</sup> ions, present because of the isomorphous changes at the crystalline aluminum-silicate lattice level, are easily dissolved in fresh water. If there is an isomorphous substitution of the type 2Na<sup>+</sup> + Ca<sup>2+</sup>, the Ca<sup>2+</sup> ions act as a new binding agent between the clay layers, and its reactions with water will be altered. Let us compare the dissolution of different oxides in 100 ml of fresh water at 20°C (see Table 4).

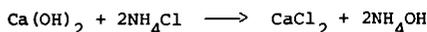
Table IV  
Solubility of oxides in 100 ml water at 20°C

Type of Oxide	SiO <sub>2</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	CaO	MgO	Al <sub>2</sub> O <sub>3</sub>
Solubility in mg.	insol.	65,700	76,700	151	0.89	insol.

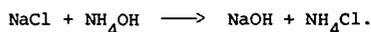
The low solubility of CaO (151 mg CaO compared to 65,700 mg Na<sub>2</sub>O<sup>2,6</sup>) causes an increase in the electrostatic coherence between the clay layers and ensures that the elements of electrostatic coherence are maintained in the crystal lattice.

The technology of the proposed interchange will consist of injection of calcium hydroxide Ca(OH)<sub>2</sub> and, since reactions giving products of lower enthalpy are favoured, CaCl<sub>2</sub> can be precipitated while at the same time the sodium that exists between the clay layers is dissolved<sup>2</sup>. The reactions which take place during this injection are the following:

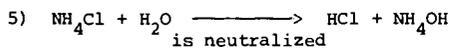
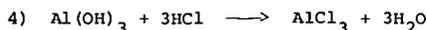
- 1) Injection in the oil field of the solution



- 2) Spontaneous dissolution of sodium salts in ammonium hydroxide and substitution for Ca<sup>2+</sup>



If colloids of the silicate acid type are present, the reactions can be a function of pH and enthalpy as follows:



If reactions 1) and 2) take place in aqueous solution, NaCl is substituted by the precipitated CaCl<sub>2</sub> and NaCl diffuses into the ammonium hydroxide. The reaction sequence is determined by the reaction enthalpy (see Table 5)<sup>6</sup>. Thus of the two salts CaCl<sub>2</sub> and NaCl, the preference for forming hydroxides with NH<sub>4</sub>OH depends on the value of ΔH°<sub>298</sub>, which is greater for NaOH.

Table V  
Enthalpies of Ionic Reactions

Type of Salt	$\Delta H^{\circ}_{298}$ kcal/mol
Ca <sup>2+</sup> Cl <sub>2</sub> <sup>-</sup>	190.60
Na <sup>+</sup> Cl <sup>-</sup>	98.82
Ca <sup>2+</sup> (OH) <sup>-</sup>	235.60
Na <sup>+</sup> (OH) <sub>2</sub> <sup>-</sup>	101.96
H <sub>2</sub> <sup>+</sup> SiO <sub>3</sub> <sup>2-</sup>	267.80
H <sub>2</sub> <sup>+</sup> SiO <sub>4</sub> <sup>4-</sup>	340.60

### Conclusion

In the commercial development of an oil field a chemical-mineralogical study should precede the engineering study. One of the problems encountered in oil field operations such as drilling, completion, and reconditioning is the damage to the oil producing formation due to the reduction of the permeability of the surroundings. This damage can impede the detection of some hydrocarbons in an exploratory well, or diminish the productivity of a functioning well. Furthermore, the extent of damage will often affect the viability of secondary recovery operations.

The permeability and porosity of the oil field rocks are responsible for the storage and migration of oil and gas. The explanation of field problems should be searched for by chemical and mineralogical studies because it is easier to take preventive measures than to reestablish a damaged permeability by chemical treatment.

### REFERENCES

1. R.E. Snyder, Formation Damage Control: Opportunity for Profits, World Oil, March (1976), P. 33.
2. W. Kubacki, Mineralogia de Yacimientos. Facultad de Ingenieria, LUZ (1975), Maracaibo, V-la.
3. F.J. Casse and H.J. Ramey, The Effect of Temperature and Confining Pressure on Single Phase Flow in Consolidated Rocks. SPE, P.N. 5877 (1976), P. 1-15.
4. J.H. Berkman and A. Abrams, An Oil-Coating Process to Stabilize Clays in Fresh Waterflooding Operation. JPT., September (1975).
5. F.O. Jones, Influence of Chemical Composition of Water on Clay-Blocking of Permeability. JPT., April (1964).
6. H.G. Reed, Stabilization of Formation Clays with Hydroxy Aluminium Solutions, JPT., July (1972).
7. A.R. Jennings, The Effect of Surfactant Bearing Fluids on Permeability Behavior in Oil-Producing Formation. SPE, P.N. 5635 (1975).
8. Anonimo, Fundamentals of the Interpretation of Profiles, Schlumberger Limited, New York, N.Y. (1969).
9. R.F. Krueger, L.C. Vogel, and P.W. Fischer, Effect of Pressure Drawdown on Clay-Up of Clay or Silt-Blocked Sandstone. JPT., March (1967). P. 397.

## THE ROLE OF ASPHALTENES IN SHALE OIL

T.F. Yen, C.S. Wen, J.T. Kwan and E. Chow

University of Southern California  
University Park, Los Angeles, California 90007

Asphaltene is ubiquitously present in bitumens regardless of whether or not the sample is naturally occurring or thermally altered. It might be noted that most naturally occurring bitumens have undergone a thermal maturation process during diagenesis.<sup>1</sup> Therefore, thermal process is important in the generation of asphaltene and resin molecules from any fossil fuel sources. Oil shale from lacustrine formation, such as that of the Green River Formation contains 2% to 4% of bitumens. There is asphaltene in bitumen from Green River Oil Shale but the content is only 9% to 12%. This causes the overall content of asphaltene in raw oil shale to be as low as two to five parts per thousand.

During retorting the kerogen undergoes thermal decomposition to oil, gas and insoluble coke. The intermediate is a fairly large amount of pyrobitumen which does contain asphaltene. Since asphaltene is prone to form coke, the reduction of pyrobitumen may account for the increase of coke formation. In this manner the asphaltene is formed in conventional oil shale.

Although the content of asphaltene or resin in shale oil may be low, they are responsible for the dark color as well as the viscosity. Asphaltene in shale oil may be unique since it is high in nitrogen content and, consequently, there will be a high ash content. Furthermore, nitrogen polycyclics may be carcinogenic since they are unique in shale oil asphaltene. The polarity of the nitrogen polycyclics may also exhibit the specific properties of emulsification of water and complexing of metals. It is within this context that the present study is undertaken.

### EXPERIMENTAL

A total of three shale oil samples was used for this study. The oil shales used for the study are all from the Green River Formation. The first one was obtained from Paraho Project, Paraho Syncrude (PS). The chemical composition of the oil is as follows: %C, 85.8; %H, 11.3; %S, 0.5; %N, 1.4; %O, 0.99; %ash and carbon residue, 2. The API gravity at 70°F is 27.8; SSU viscosity at 210°F is 48.0. The flash point is 290°F. Water content is 2.8%. Semi-quantitative spectrographic analysis indicates that silicon, sodium, iron, calcium, nickel, vanadium and aluminum are major constituents. The second sample was a residue left from the processing of the PS through a delayed coker, henceforth referred to as residue oil (RO). The third sample was the oil obtained from Don's Welding, a small one-ton vertical retort in San Bernardino. This sample is referred to as DW. The difference between the DW and the PS is that the former also contains arsenic, copper and zinc.

Isolation of asphaltene was in accordance with the traditional procedure of precipitation with 20-fold volume of n-pentane, and followed by centrifugation and Soxhlet-extraction of the solid with n-pentane. The crude asphaltene was dissolved in benzene, hot-filtered and the benzene filtrate was lyophilized to remove the benzene.

## CHARACTERIZATION

Various methods are employed for the characterization of shale oil asphaltene. Table I lists the results of isolated asphaltenes and their ultimate analyses. The percentages of carbon, hydrogen, nitrogen, and sulfur, as well as the ash content in the asphaltenes, were determined through elemental analysis in which high contents of nitrogen are found in samples. An empirical formula for each asphaltene sample was determined from vapor pressure osmometry (VPO) measurement. Since the complex molecule of asphaltene tends to associate strongly even in the dilute solution, the usual analytical procedures fail to differentiate between the molecular weight and particle weight. A technique of gel permeation chromatography (GPC) with  $\mu$  Styragel column in a dilute solution under high pressure has been carried out to obtain asphaltene molecular weight of a single unit sheet. Figure 1 shows molecular weight distributions of three samples in which DW shale oil asphaltenes contain a larger percentage of high molecular weight fraction. Semiquantitative analyses of metals present in asphaltenes are listed in Table II. Apparently metal is an integral part of asphaltenes.

A typical infrared spectrum of potassium bromide pellet from PS asphaltene is given in Figure 2. A number of similarly well defined bands are shown in all samples. The broad absorption band centered at  $3220\text{ cm}^{-1}$  is assigned as hydrogen-bonded O-H or N-H which interpretation has been reported in coals<sup>2,3</sup> and coal asphaltenes.<sup>4</sup> Two low-intensity bands at  $3010$  and  $3050\text{ cm}^{-1}$  represent aromatic C-H stretching. Wiberly<sup>5</sup> has shown that the aromatic C-H band shifts to values as high as  $3052\text{ cm}^{-1}$  as ring number decreases. The strong absorption bands falling between  $2840$  and  $2950\text{ cm}^{-1}$  are due to naphthenic and/or aliphatic C-H vibration. The two vibrations of the methyl group are located at  $2950$  and  $2885\text{ cm}^{-1}$ , and the methylene band, which is the strongest, at  $2915\text{ cm}^{-1}$ . Another methylene frequency occurs at  $2840\text{ cm}^{-1}$ . An intense absorption band located at  $1600\text{ cm}^{-1}$  has been assigned partly caused by a conjugated C=C band and partly by carbonyl, C=O group. Two very intense bands at  $1455$  and  $1375\text{ cm}^{-1}$  are due to bending frequency of symmetric C-CH<sub>3</sub> and/or methylene, and symmetry C-CH<sub>3</sub>, respectively. The group of bands located at  $1255$ ,  $1090$  and  $1030\text{ cm}^{-1}$  may be assigned to aromatic oxygenated compounds, such as aromatic ethers.<sup>2</sup> Differences of absorption intensities of these bands among three asphaltene samples are apparent from Fig. 3. Three fairly definite bands in the spectrum of PS asphaltene in comparison to ill-defined weak bands in the spectra of DW and RO asphaltenes are consistent with the highest value of O/C ratio in PS asphaltene (Table I). The long wavelength bands at  $860$ ,  $800$  and  $750\text{ cm}^{-1}$  are considered aromatic out-of-plane frequencies and are important with regard to the nature of the structure of aromatic clusters. The four-adjacent C-H bending band at  $720\text{ cm}^{-1}$  and the five-adjacent band at  $695\text{ cm}^{-1}$  are very weak in spectra (Fig. 3). The long-chain alkyl band at  $735\text{ cm}^{-1}$  is only present in the spectrum of RO asphaltene. This long-chain methylene structure in RO asphaltene is further confirmed by the X-ray diffraction.

A number of parameters can be obtained by resolving the  $\gamma$ - and (002)-bands in the X-ray scattering pattern (see Table III). The (002)-spacing which appears in graphite and carbon blacks is accepted as representing the spacing between the layers of condensed aromatic system.<sup>5-7</sup> The  $\gamma$ -band centered around  $(\sin\theta)/\lambda = 0.10\text{-}0.11\text{ \AA}^{-1}$  has been assigned to be associated with spacing in the saturated portion.<sup>5,8</sup> Accordingly, a comparative estimate of the aromaticity,  $f_a$ , can be made from the areas of the resolved peaks corresponding to the  $\gamma$ - and the (002)-

bands.<sup>5</sup> The distance between aromatic sheets,  $d_m$ , is obtained from the maximum of the (002)-band and the distance between the saturated portion of the molecule,  $d_s$ , is obtained by using the value from the  $\gamma$ -band. X-ray diffraction also permits a determination of the average height of the stack of aromatic sheets,  $l_c$ , and the average diameter of the aromatic sheets,  $l_a$  based on the Scherrer crystallite size formula<sup>9</sup> or on the Diamond's curve.<sup>10</sup> The X-ray diffraction pattern of the RO asphaltene is strikingly different from the others; it shows the sharp doublet of (100)- and (200)-bands at 4.15 and 3.70 Å as shown in Fig. 4. Yen<sup>11</sup> in his study of native asphaltic molecule, has reported these two peaks as wax-like long-chain alkyl compounds. In comparison with the doublet bands, the results of X-ray diffraction of the three samples are very similar. It is to be noted that PS asphaltene has a smaller value of  $l_a$ , the layer diameter, among them.

The hydrogen-distribution data obtained by NMR has been applied to the analysis of carbon structure, with particular emphasis on estimating several important structural parameters as listed in Table IV. A typical NMR spectrum of PS asphaltene is provided in Fig. 5 in which subgroups are assigned for aromatic and saturated hydrogen resonances.<sup>12</sup> From the area under the component peaks, it is possible to estimate values for the degree of substitution of the aromatic sheets. The aromaticities obtained from NMR data depend largely on two parameters: one being the ratio of hydrogen to carbon for the  $\alpha$ -paraffinic groupings, and the other refers to the ratio for all nonaromatic groupings other than  $\alpha$ -position. In this investigation, these two ratios were given the value 2 for all asphaltenes. Data from NMR also permit the determining of the shape of the condensed aromatic sheets by estimating the value of the ratio of aromatic hydrogen to carbon of the hypothetical unsubstituted aromatic sheet. The results for asphaltenes are tabulated in Table IV. The other structural parameters including total numbers of aromatic ring carbon, substituted aromatic ring carbon, and aromatic ring per molecule, as well as the average number of carbon atoms per saturated substituent are shown in the same table. The  $H_I/CA$  value for RO asphaltene is lower than those of the PS and DW asphaltenes. The number of rings in the condensed aromatic ring system per molecule varies from one, as in the case of DW asphaltene, to 3-4 in the case of the RO asphaltene.

#### DISCUSSION

In fossil fuel conversion, it is generally recognized that asphaltene is the transition stage from fossil fuel source to oil products. Therefore, the asphaltene generation and elimination is one of the main and important control factors of the conversion process. Present knowledge of the skeletal structural of the shale oil asphaltene is presented in this paper.

In contrast with the carbon skeletons of kerogen which has very low  $f_a$  value,<sup>13</sup> the aromaticity of asphaltene ranges from 0.4 to 0.5. The high temperature retorting of oil shale tends to yield more aromatic hydrocarbons than those which are present in the original raw oil shale, the latter has undergone maturation. The thermally induced aromatization for the difference in properties of asphaltene series is well recognized.<sup>14</sup> For example, asphaltene fraction can be converted into carbene fraction and resin fraction can also be converted into asphaltene fraction.<sup>15</sup> All these conversions can be accomplished by thermal processes.

The proton NMR spectra of the shale oil asphaltene are similar to those of the petroleum asphaltene and of the coal-derived asphaltenes as well. The degree of substitution,  $\sigma$  or  $C_{SU}/H_I$  of the shale oil asphaltene is larger than 0.5. It falls closer to petroleum asphaltene than coal asphaltene, since the majority of the latter is less than 0.5. In contrast, the cluster compaction parameter,  $H_I/C_A$  or HCC, of shale oil asphaltene is higher and closer to coal asphaltene than to petroleum asphaltene. The value of  $H_I/C_A$  for petroleum asphaltene ranges from 0.3 to 0.5 and those for coal asphaltenes 0.6 to 0.8. It is recognized that coal asphaltene contains more or less smaller kata-condensed cluster.<sup>18</sup> The petroleum asphaltene has large, peri-condensed systems.<sup>12,17</sup> The value of 1.0 or 0.95 is not possible; one of the reasons of such high values is possibly the higher contents of nitrogen atoms in the system which may effect the computation; other reasons being the assumption of X, Y coefficients of 2. Another parameter, the substituents chain length,  $N_{SC}$  or  $C_6/C_{SU}$  for the shale asphaltene is medium-sized, i.e. between 2 to 3 carbons. For comparison, the coal asphaltene is about 1 to 2 carbon atoms (methyl or ethyl); and the petroleum asphaltene is 4 to 6 carbon atoms. In general, for NMR data alone, one can state that the shale oil asphaltene contains heavily substituted linked or kata-condensed system.<sup>16</sup> The system is small and the substituents average between 2 to 3 carbons.

What is more striking is the fact that in one of the shale oil asphaltenes studied (RO), there is actually either the long-chain paraffin or substituent present as indicated by the sharp bands at 3.70 and 4.15 Å by X-ray diffraction. This is further supported by the observation of polymethylene peak in the infrared spectra of RO asphaltene. In previous work, such crystalline sharp peaks have been found in a few petroleum asphaltenes,<sup>11</sup> especially when asphaltene has undergone thermal processing by visbroken process. At present the delayed coker processing of shale oil may also form considerable amount of paraffins which are coprecipitated down with other asphaltene molecules.

The layer diameter for the shale oil asphaltene is 7-12 Å by Diamond's curve fitting of the X-ray diffraction data. This value is compatible to NMR data in which the aromatic number varies from 1 to 3. The inconsistent data between number of aromatic carbons per molecule and ring number per molecule probably are due to the high content of nitrogen atoms in the system.

The high nitrogen content of shale oil asphaltene could affect the mineral content or ash content in asphaltenes. This property also will contribute to the surface and colloidal nature of shale oil to form emulsions with water. Finally, the hydrogen bonding is found both in shale oil asphaltene and in coal asphaltene. Purified petroleum asphaltene does not possess hydrogen bonding. Hydrogen bonding in shale oil asphaltene also originates from its high content of nitrogen.

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. J. Connan, "Thermal Evolution of Natural Asphalts", in Bitumens, Asphalts and Tar Sands, (G. V. Chilingar and T. F. Yen, ed.), Elsevier, Chapter 3, 1977.
2. R. A. Friedel and J. A. Queiser, Anal. Chem., 28, 22, 1956.
3. R. A. Friedel and H. L. Retcofsky, "Spectrometry of Chars-Structure Studies", in "Spectrometry of Fuels", (R. A. Friedel, ed.), Plenum Press, New York, Chapter 5, 1970.
4. S. R. Taylor, L. G. Galya, B. J. Brown and N. C. Li, Spectro. Lett., 2(11), 733, 1976.
5. T. F. Yen, J. G. Erdman and S. S. Pollack, Anal. Chem., 33, 1587, 1961.
6. S. S. Pollack and L. E. Alexander, J. Chem. & Eng. Data, 5, 88, 1960.
7. S. Ergun and V. H. Tiensuu, Fuel, 38, 64, 1959.
8. T. F. Yen and J. G. Erdman, "Asphaltene (Petroleum) and Related Substances: X-ray Diffraction" in Encyclopedia of X-rays and Gamma-rays, Reinhold, 1963, p. 65.
9. H. P. Klug and L. E. Alexander, "X-ray Diffraction Procedure", Wiley, New York, 1956.
10. R. Diamond, Acta. Cryst., 10, 359, 1957.
11. T. F. Yen, Nature Physical Science, 233(37), 36, 1971.
12. T. F. Yen and J. G. Erdman, ACS, Div. Petroleum Chem., Preprints, 7(3), B-99, 1962.
13. J. T. Kwan and T. F. Yen, ACS, Div. Fuel Chem., Preprint, 21 (7), 67, 1976.
14. T. F. Yen, "Chemistry of Asphaltene in Coal Liquids", in Preprints Workshop on Coal Chemistry, Stanford Research Institute, 1976, p. 144.
15. T. F. Yen and S. R. Sprang, Geochim. Cosmochim. Acta, in press, 1977.
16. T. F. Yen and J. P. Dickie, J. Inst. Petroleum, 54, 50, 1968.
17. T. F. Yen, J. G. Erdman and A. J. Saraceno, Anal. Chem., 34, 694, 1962.
18. T. F. Yen, I. Schwager, J. T. Kwan and P. A. Famanian, Characterization of Coal Derived Asphaltene, Pittsburgh Analytical Conference, 1977.

TABLE I Elementary Analyses of Shale Oil Asphaltenes

Asphaltene	PS	RO	DW
Yield (wt)%	1.19	2.01	1.69
Elemental Analysis <sup>b</sup>			
Carbon	75.58	81.25	79.73
Hydrogen	7.51	8.26	8.17
Nitrogen	3.41	4.31	3.49
Sulfur	0.72	0.81	1.15
Oxygen <sup>c</sup>	6.73	3.04	4.64
Ash	5.99	2.35	2.82
Atomic Ratio			
H/C	1.19	1.22	1.23
N/C	0.039	0.046	0.037
S/C	0.004	0.004	0.005
O/C	0.067	0.028	0.044
Molecular Weight <sup>d</sup>			
	709	630	605
Empirical Formula			
	C <sub>50.1</sub> H <sub>59.4</sub> N <sub>2.0</sub> O <sub>3.4</sub> S <sub>0.2</sub>		
	C <sub>43.7</sub> H <sub>52.7</sub> N <sub>2.0</sub> O <sub>1.2</sub> S <sub>0.2</sub>		
	C <sub>41.3</sub> H <sub>50.5</sub> N <sub>1.6</sub> O <sub>1.3</sub> S <sub>0.2</sub>		

TABLE II Semi-quantitative Analysis of Metals from Shale Oil Asphaltenes (ppm)

Asphaltene	DW	PS	RO
Si	12,000	25,000	10,000
Fe	130	1,500	120
Mg	15	230	21
Ca	4	620	8
Na	ND 50	TR 50	ND 50
Al	8	91	91
As	47	59	74
Ni	62	52	68
V	8	5	4
Cu	34	9	36
Zn	100	ND 10	140
Co	4.1	15	6.8
Loss on Ignition (%)			
	97.2	94.1	97.7

<sup>a</sup>Average of at least 2 runs. <sup>b</sup>Expressed in weight percentage. <sup>c</sup>By difference. <sup>d</sup>By VFC in benzene.

TABLE III Aromaticity and Crystallite Parameters for Shale Oil by X-Ray Diffraction

Asphaltene	DW	PS	RO
f <sub>a</sub>	0.39	0.43	0.42
d <sub>m</sub> <sup>a</sup>	3.57	3.57	3.57
d <sub>y</sub> <sup>a</sup>	4.17	4.41	4.41
L <sub>c</sub> <sup>a</sup>	15	15	16
M	5	5	5
L <sub>a</sub> <sup>a,b</sup>	19	13	20
L <sub>a</sub> <sup>a,c</sup>	12	7	12

<sup>a</sup>All expressed in Å.

<sup>b</sup>From Scherrer's Eqn.

<sup>c</sup>From Diamond's Curve.

TABLE IV Values for Structural Parameters of Shale Oil Asphaltenes from NMR Data

Asphaltene	DW	PS	RO
f <sub>a</sub> <sup>a</sup>	0.49	0.50	0.47
σ <sup>b</sup>	0.58	0.62	0.56
HCC <sup>c</sup>	1.00 <sup>h</sup>	0.95 <sup>h</sup>	0.86
CAR <sup>d</sup>	20.4	20.4	20.7
CSR <sup>e</sup>	11.8	11.9	8.6
NAR <sup>f</sup>	1.03	1.52	3.64
NSC <sup>g</sup>	2.10	2.23	3.13

<sup>a</sup>Aromaticity; <sup>b</sup>Degree of Substitution as C<sub>50</sub>/H<sub>1</sub>

<sup>c</sup>Aromatic hydrogen to carbon ratio of the hypothetical unsubstituted aromatic portion, H<sub>1</sub>/C<sub>A</sub>

<sup>d</sup>Total number of aromatic ring carbon per molecule;

<sup>e</sup>Total number of substituted aromatic ring carbon per molecule;

<sup>f</sup>Total number of aromatic ring carbon per molecule;

<sup>g</sup>Average number of carbon atoms per saturated substituent, C<sub>5</sub>/C<sub>50</sub>

<sup>h</sup>Based on coefficients X, Y of 2. If more than 2, this value will be considerably less.

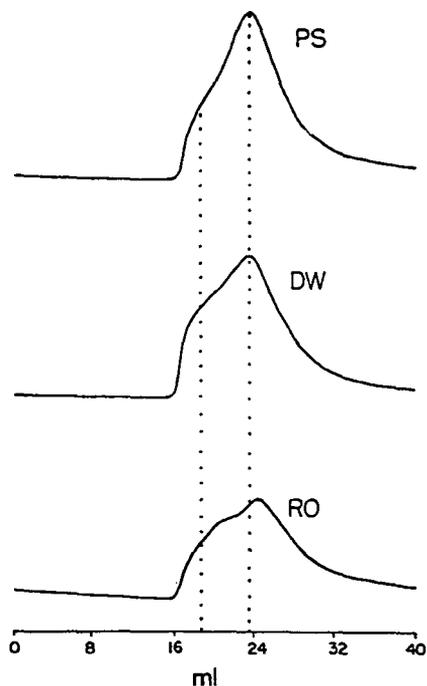


Fig. 1. Molecular Weight Distribution Patterns of three Shale Oil Asphaltenes Determined from HPLC. (the lower numbers of elution volume represents higher molecular weight).

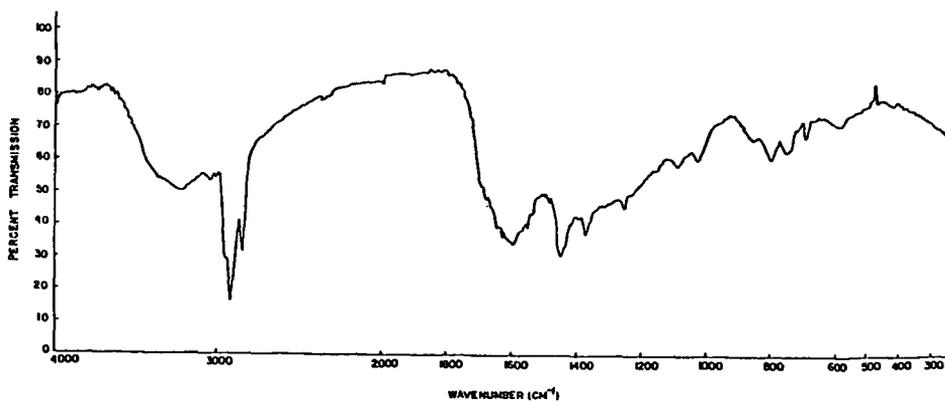


Fig.2. Infrared Spectrum of a Paraho Syncrude Asphaltene, (KBr Solid Phase).

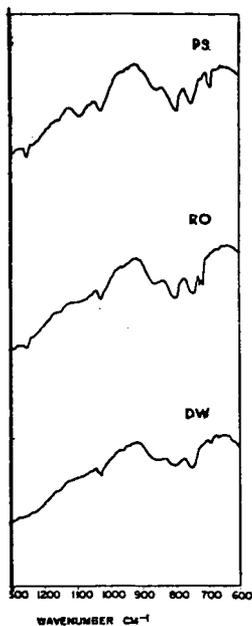


Fig. 3. Aromatic C-H Bending Vibrations of Three Shale Oil Asphaltenes.

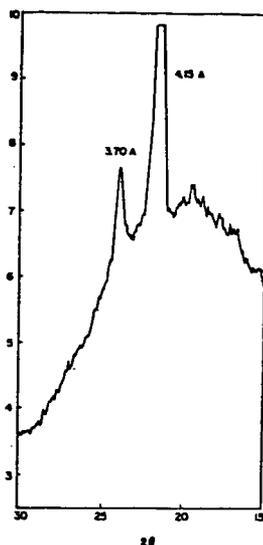


Fig. 4. X-ray Diffraction Scan of the Medium Angle Region of a Residue Oil Asphaltene from a Delayed Coker. (Sharp Bands indicate Crystalline Peaks).

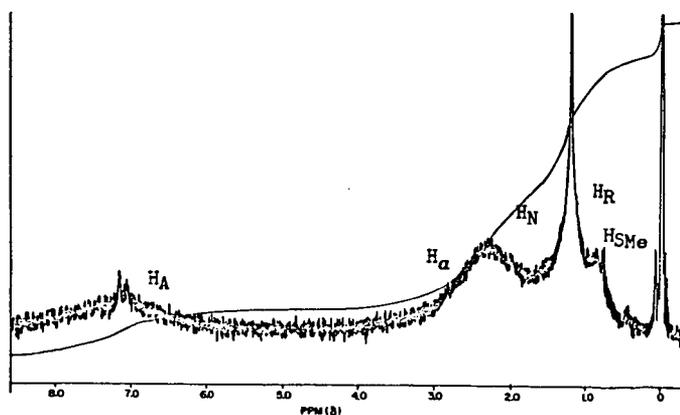


Fig. 5. Proton NMR Spectrum of a Paraho Synerude Asphaltene.

PROPERTIES OF ASPHALTENES  
FROM VARIOUS ALBERTA CRUDE OILS

T. Ignasiak, A.V. Kemp-Jones and O.P. Strausz

Hydrocarbon Research Center  
Department of Chemistry  
University of Alberta  
Edmonton, Alberta  
Canada

INTRODUCTION

Asphaltene is defined as the high molecular weight pentane-insoluble fraction of petroleum. In general, of all the petroleum fractions, asphaltene contains the greatest percentage of sulfur, oxygen and nitrogen. The structure and composition of asphaltene may vary considerably with the origin and mode of formation of the source reservoir.

Very few comparisons of asphaltene properties are available in the literature (1-4). Recently, a detailed investigation of the properties of Athabasca asphaltene was carried out (5). Chemical and spectroscopic evidence led to the proposal of an average structure in which relatively small hydrocarbon units are linked together by sulfur bridges. Since, in addition to the Athabasca deposit, there are other important oil sands and heavy oils in Alberta which also have high asphaltene contents, it was therefore of interest to study these asphaltenes and to compare their properties with those of Athabasca asphaltene.

The asphaltene sources investigated were the Cold Lake and Peace River oil sands, and Lloydminster crude oil. These asphaltenes have been further compared with the asphaltenes from Pembina light crude oil and a tar produced by steam cracking of gas oil.

EXPERIMENTAL

The samples used were: (1) Cold Lake crude oil obtained by cold bailing from well Leming G-7 prior to steam stimulation; (2) a Peace River core obtained from Well OBS-5, location 4-21-85-18 W5 (Cadotte), depth 1868-1872 ft.; (3) Lloydminster base crude oil, sample 5431; (4) Pembina vacuum reduced pitch received January 9, 1976 from Imperial Oil Enterprises Ltd., Strathcona; (5) a tar produced by steam cracking gas oil, sample PS-76-020.

The asphaltenes were prepared as described previously (5) for Athabasca asphaltene. When the sample was found to contain large amounts of clay, a 5% solution of the asphaltene in benzene was centrifuged at 4000 rpm for several hours, and decanted, and the asphaltene was then reprecipitated with pentane.

The experimental conditions for the reductive acylation and silylation are given in detail in a previous paper (5).

The molecular weights were determined by vapor pressure osmometric method at a nominal asphaltene concentration of 20 mg/ml in benzene. Infrared spectra were determined at 0.004 M concentration in carbon tetrachloride solution in a 5 mm cell.

The  $^{13}\text{C}$  NMR spectra, recorded as described previously (5), can be integrated numerically using a subroutine provided by Bruker Scientific.

RESULTS AND DISCUSSION

Elemental analyses and average molecular weights for the asphaltene samples used in this study are shown in Table I. The analyses of the Cold Lake, Peace River and Lloydminster asphaltenes show little to distinguish them from Athabasca asphaltene, the main difference being a trend toward higher molecular weights and a higher sulfur content in the Peace River sample. The asphaltene from the light Pembina oil is different however. It represents only a minute percentage of the oil, as expected from

the viscosity, and is very low in sulfur content. The average molecular weight is lower than that of Athabasca asphaltene, and definitely lower than the average molecular weight of the high sulfur asphaltenes. It is clear that any conclusion about the structure of Athabasca asphaltene should not be extended to the trace amount of asphaltene in light oils.

The Pembina asphaltene has properties, e.g. m.w. and heteroatom content, intermediate between those of the heavy oil asphaltenes and steam cracking tar asphaltene. This very viscous refinery tar contains a large amount of asphaltene, which is even lower in heteroatoms than the asphaltenes from the light oils, and has a low molecular weight and low H/C ratio.

The routine (2% solution in a 0.5 mm cell) IR spectra of the asphaltenes studied appeared to be quite similar. Some differences, however, in the hydrogen stretching region at 3600-3000  $\text{cm}^{-1}$  become apparent from 0.004 M solutions of asphaltenes measured in a 5 mm cell (Figure 1). The IR spectrum of Cold Lake asphaltene was not suitable for interpretation because of extremely high background interference. Asphaltene precipitated from Peace River bitumen shows a broad hydrogen bonding absorption with a maximum centered about 3250  $\text{cm}^{-1}$ ; its shape and intensity approximates that of Athabasca asphaltene (6). The free phenolic and/or alcoholic absorptions at 3600  $\text{cm}^{-1}$  and the free NH absorption at 3480  $\text{cm}^{-1}$  are observable in the spectrum of Lloydminster asphaltene, and the hydrogen bonded absorption is clearly reduced as compared to Athabasca and Peace River asphaltenes. In Pembina asphaltene the relative intensity of the free OH absorption is very weak and no hydrogen bonding is visible.

Thus, the almost complete association of the OH and likely NH functional groups seems to be a characteristic feature of asphaltene originating from Alberta oil sands. The difference in the role which hydrogen bonding plays in the molecular aggregation of Athabasca, Cold Lake, Peace River asphaltenes and those from Lloydminster and Pembina crudes is clearly demonstrated by the silylation reaction. On silylation, hydroxyl groups are generally easily converted to trimethylsilyl derivatives. This is accompanied by the disappearance of IR absorption in the hydrogen stretching region and the appearance of the absorption of trimethylsilyl ethers. The IR spectra of silylated Athabasca, Peace River and Lloydminster asphaltenes all show a remarkable reduction in the hydrogen bonding absorption and the free OH absorption disappears in the latter. As seen from data given in Table II, the molecular weights of silylated Athabasca, Cold Lake and Peace River asphaltenes have been drastically reduced, roughly by half, pointing to the intermolecular character of the hydrogen bonding. The decrease in the molecular weight of Lloydminster asphaltene is less significant and none occurs for Pembina asphaltene, as expected from their IR spectra.

There is not much variation in the oxygen contents (average of 2%) of the asphaltenes studied (Tables I and II), and the number of silyl groups attached to asphaltenes, calculated from either integration of the PMR spectrum or changes in the H/C ratios and ash contents, indicates that from 60 to 64% of the oxygen in Athabasca, Cold Lake and Peace River asphaltenes, 71% in Lloydminster and 23% in Pembina asphaltenes is accessible for silylation. Some of this "silylated" oxygen may originate from oxygen functional groups other than hydroxyl (7). The disappearance on silylation of the small but distinct carbonyl absorption at 1725  $\text{cm}^{-1}$ , which is present in all except Athabasca asphaltenes may suggest the existence of readily enolized ketones, for example.

That most of the nitrogen in asphaltenes is present in the form of NH groups is concluded from the IR absorption at 3480  $\text{cm}^{-1}$  previously (8) assigned to free NH groups. The changes in this region before and after silylation indicate that the NH groups play an important role in hydrogen bonding in Athabasca, Cold Lake and Peace River asphaltenes, and almost none in Lloydminster and Pembina asphaltene; in general they are not easily silylated.

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the heavy oil asphaltenes are qualitatively similar to those of the Athabasca asphaltene (5). The quantitative proportions of aromatic hydrogen and carbon are shown in Table III. The NMR spectra of the refinery tar show that it contains 47% aromatic hydrogen and 87% aromatic carbon which emphasizes its difference from Athabasca asphaltene. These values make it of interest for the application of the structural analysis method we reported previously (5). The H/C ratio of 0.71 means that there are 65 double bond equivalents (DBE)/100 C. Using the value of 0.72 for DBE/aromatic carbon which was assumed for Athabasca asphaltene (5),

and the 87% aromatic carbon from  $^{13}\text{C}$  NMR, gives  $87 \times 0.72 = 62.6$  DBE/100 C due to aromatic carbon atoms. This is sufficiently close to the 65 total DBE/100 C that the DBE due to alicyclic carbon atoms can be assumed to be zero. To some extent this is expected from the method of preparation of the steam cracking asphaltene, and lends support to the value of 0.72 for DBE/aromatic carbon which we assumed for Athabasca asphaltene. A structure consistent with the H/C ratio and the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra is as shown in Figure 2. It has H/C ratio 0.72 (0.71 observed), 88% aromatic carbon (87% observed) and 50% aromatic hydrogen (47% observed). To obtain a proportion of aromatic hydrogen as low as 47% with 87% aromatic carbon requires that virtually all the aliphatic groups are methyl groups, to maximize the substitution on the aromatic rings.

To further compare the various heavy oil asphaltenes, they were reduced and octylated following the procedure (5) used for Athabasca asphaltene. Reaction of the Athabasca asphaltene with potassium in tetrahydrofuran in the presence of naphthalene gave an impressive decrease in the m.w. of the asphaltene which, on the basis of some other auxiliary studies involving determination of oxygen distribution and model reduction of sulfur compounds, could be attributed to the cleavage of non-ring sulfur. From the results shown in Table IV some differences become apparent. In all cases the m.w. of the product, corrected for octyl groups added and by-products, is higher than that found for Athabasca asphaltene, although there is still a substantial decrease in m.w. on reduction. The m.w., number of octyl groups added, desulfurization, and weight increase all follow the same pattern, with the order of reactivity being Cold Lake > Peace River > Lloydminster. Since the sulfur content of these asphaltenes is similar to that of Athabasca asphaltene (Table I), it follows that a greater proportion of the sulfur atoms are in rings. The percentage of sulfur in bridges was estimated from the ratio of the number of bonds cleaved on reduction to the number of sulfur atoms present in a molecule.

The number of bonds cleaved (N) was derived from the experimental molecular weights using an equation:  $N = \text{MW starting}/\text{MW reduced} - 1$ , in which the molecular weight of the silylated asphaltenes was taken as MW starting.

#### CONCLUSIONS

In the present study it has become clearly established that asphaltenes from Alberta heavy oil deposits have much in common, including concentration in the bitumen, elemental composition, high molecular weight, high sulfur content and an oxygen distribution such that most of the oxygen is in hydroxyl groups. Asphaltenes from the typical oil sands exhibit very strong hydrogen bonding properties, partly intermolecular in character, whereas in the Lloydminster asphaltene, the hydroxyl association is much less pronounced.

The results from reductive octylation indicate that all these sulfur-rich asphaltenes possess a sulfur-polymer framework. The amount of sulfur in bridges, however, varies, decreasing in the order Athabasca > Cold Lake > Peace River > Lloydminster, which may reflect some diagenetic differences among the asphaltene sources.

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#### REFERENCES

- (1) Bestougeff, M.A., Bull. Soc. Chim. Fr., 4773 (1967).
- (2) Koots, J.A., and Speight, J.G., Fuel, 54, 179 (1975).
- (3) Erdman, J.G., and Ramsey, V.G., Geochim. Cosmochim. Acta, 25, 175 (1961).
- (4) Chernova, T.G., Shishenina, E.P., and Maryasin, I.L., Khim. Tekhn. Topliv. i Masel, 11, 59 (1973).
- (5) Ignasiak, T., Kemp-Jones, A.V., and Strausz, O.P., J. Org. Chem., 42, 312 (1977).

- (6) Ignasiak, T., Strausz, O.P., and Montgomery, D.S., submitted to Fuel.  
 (7) Peterson, J.C., Barbour, R.V., Dorrence, S.M., Barbour, F.A., and Helm, R.V.,  
 Anal. Chem., 43, 1491 (1971).  
 (8) Peterson, J.C., Fuel, 46, 295 (1967).

TABLE 1

Elemental Analyses and Molecular  
 Weights of Various Asphaltenes

Asphaltene Source	% of Source	% Wt., d.a.f.					Ash	H/C	MW
		C	H	N	S	O			
Athabasca	16	80.3	8.0	1.2	8.2	2.5	1.5	1.20	5920
Cold Lake	15	80.2	7.8	1.1	8.3	2.5	4.2	1.17	8140
Peace River	17	79.4	8.0	0.8	9.1	2.6	4.0	1.22	9510
Lloydminster	9	81.2	8.0	1.0	8.4	1.5	1.2	1.18	9300
Pembina Pitch	3	86.8	9.2	0.9	1.0	2.0	0.1	1.27	3100
Steam Cracking Tar	20	91.8	5.4	0.0	0.6	0.4	1.2	0.71	1380

TABLE 2

The Effect of Silylation on Various Asphaltenes

Asphaltene Source	MW After Silylation	Number of atoms or groups/100 C atoms		% of Oxygen Silylated
		Oxygen	Trimethyl- silyl	
Athabasca	3680	2.3	1.5	64
Cold Lake	4600	2.4	1.5 <sup>1</sup>	63
Peace River	4430	2.5	1.6	64
Lloydminster	7150	1.4	1.0	71
Pembina	3070	1.7	0.4 <sup>2</sup>	23

- <sup>1</sup> NMR spectrum is broadened and unresolved, the number of silyl groups was determined from changes in the H/C ratio and ash content.  
<sup>2</sup> The NMR of silylated Pembina asphaltene does not show any absorption near  $\delta_0$ , though there was some change in H/C ratio and ash content.

TABLE III

Content of Aromatic Hydrogen and Aromatic Carbon in Various Asphaltenes

Asphaltene	% ArH	% ArC
Athabasca	8	42
Cold Lake	- <sup>a</sup>	30
Peace River	9	35
Lloydminster Crude	5	42
Steam Cracking Tar	47	87

<sup>a</sup> Spectrum broadened and unresolved, probably due to an unusually high content of paramagnetic molecules. This effect was also visible in the <sup>13</sup>C spectrum.

TABLE IV

Reductive Octylation of Alberta Asphaltenes<sup>1</sup>

Asphaltene	MW Octyl Free	No. of Octyl Groups Added/100C	Weight Increase %	% of Sulfur Removed	No. of Bonds Cleaved	% of Sulfur in Bridges
Athabasca	580	9.4	120	37	5.3	65
Cold Lake	1280	7.9	65	52	2.6	22
Peace River	1590	7.1	53	45	1.8	14
Lloydminster	2010	6.3	48	32	2.6	13

<sup>1</sup> Data are the means of two experiments.

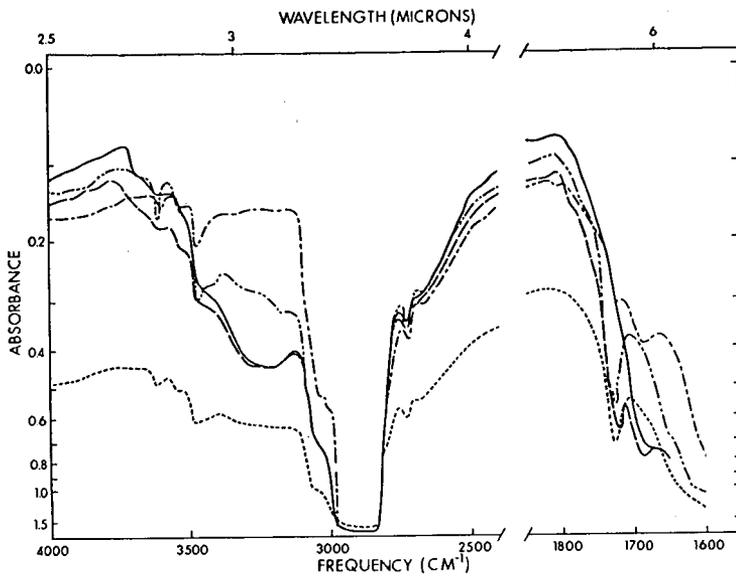


FIGURE 1

Infrared spectra of some Alberta asphaltenes - the hydrogen and carbonyl stretching regions.

Athabasca	—————
Cold Lake	- - - - -
Peace River	- · - · -
Lloydminster	- - - - -
Pembina	- - - - -

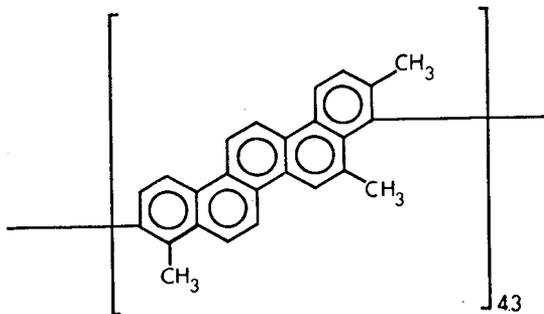


FIGURE 2

INVESTIGATION OF POSSIBLE ROUTES  
TO ASPHALTENE IN NATURE

A.V. Kemp-Jones and O.P. Strausz  
Hydrocarbon Research Center  
Department of Chemistry, University of Alberta  
Edmonton, Alberta, Canada, T6G 2G2

INTRODUCTION

The literature contains relatively little evidence to indicate how asphaltene is formed in nature. In particular the frequent proposals of an asphaltene structure consisting of polynuclear aromatic sheets (1,2,3) have not been accompanied by suggestions as to what chemical reactions might produce such structures. Knowing how asphaltene is formed in nature might provide some indication of how to reverse the process.

We have proposed the average structure I for Athabasca asphaltene on the basis of a detailed chemical and spectroscopic study (4). A possible route to such a structure is the aromatization and condensation of smaller molecules of biological origin with sulfur and/or hydrogen sulfide. Hydrogen sulfide is produced in nature by sulfate-reducing bacteria, which often use petroleum as the energy source (5). Heating terpenes with sulfur or selenium at high temperatures to convert them to more readily identifiable aromatic hydrocarbons is a well-established method in structure elucidation. Heating cholesterol with selenium produces the Diels hydrocarbon, methylcyclopentanophenanthrene, which was found in petroleum by Mair. Mair has noted the general similarity between the structure of certain petroleum hydrocarbons and those produced by heating terpenes with sulfur (6). In one experiment Douglas and Mair reported heating cholesterol with sulfur and obtaining "petroleum-type hydrocarbons" (7). They also reported obtaining dark viscous materials with high sulfur content. We have carried out similar experiments to determine whether asphaltene is formed under these conditions.

EXPERIMENTAL

Reaction of Cholesterol with Sulfur

Powdered cholesterol (40 g), sulfur (20 g) and, in most experiments, clay (20 g) were shaken until thoroughly mixed and then heated under nitrogen at 170° for 7 days. The mixture was cooled, diluted with benzene (about 3:1) until mobile and centrifuged to remove the clay. The benzene solution was shaken overnight with mercury and centrifuged to remove mercury sulfide, if any, and mercury. Excess mercury was always present. The benzene solution was concentrated to a benzene:product ratio of 1:1 and diluted with 60 volumes of n-pentane. The material which precipitated was collected by filtration, washed with n-pentane, and then Soxhlet extracted for three days with ether. The residual solid was dried at 50°C and <1mm Hg for two days. Typical analysis: C, 74.0; H, 7.7; S, 17.0; O, 1.3.

Reaction of Dimethylnaphthalene with Sulfur

Technical grade dimethylnaphthalene from Terochem Laboratories, Edmonton, was used. It was completely soluble in pentane and had the correct carbon and hydrogen analysis but contained 0.3% nitrogen. The dimethylnaphthalene (200 g, 1.28 moles) and powdered sulfur (17.2 g, 0.54 mole) were heated at 140° for 3 days while exposed to the air. The product was diluted with benzene and the insoluble material ("coke") was filtered off (10.25 g). The total volume was reduced to 400 ml and the mixture was diluted with 6 l. of pentane. The precipitate was

collected and boiled with 10% aqueous sodium sulfite containing a few drops of ethanol for 4 hours to remove sulfur. The residue was extracted with benzene, dried, filtered and the benzene evaporated to leave the product (3.95 g, 2% yield). Analysis: C, 80.5; H, 5.0; N, 1.4; S, 10.7; O, 2.4.

#### Reaction of Maltenes with Sulfur

The maltenes from Athabasca bitumen (33.9 g) and sulfur (1.7 g) were stirred mechanically in a 200 ml flask with reflux condenser under nitrogen for 1 hour, then heated to 170° for 20 hours. The mixture was diluted with benzene, in which it was completely soluble, and shaken overnight with mercury. The solution was decanted and diluted with pentane to precipitate the product, which was Soxhlet extracted with pentane and dried. Yield 0.84 g. Analysis, after correcting for 1.9% ash, C, 79.7; H, 7.9; N, 1.0; S, 9.4; O, 2.1. MW 7813.

#### Reduction of Synthetic Asphaltene with Lithium Aluminum Hydride

1 g of synthetic asphaltene, containing 5 mg-atoms of sulfur, was added to a solution of 7 mmoles of lithium aluminum hydride in 27 mls of tetrahydrofuran. The mixture was stirred under nitrogen at room temperature for 5 hours and then refluxed for 16 hours. After cooling, 9% HCl was added, cautiously at first, until the inorganic material separated as a white paste. The solution was decanted, rinsing the paste with dichloromethane. The solvent was evaporated, the residue was dissolved in dichloromethane and washed with 9% HCl. The dichloromethane was evaporated and the residue redissolved in 25 mls of tetrahydrofuran. A solution of KOH (350 mg, 3 pellets) in 5 ml of 98% ethanol was added. After stirring 10 minutes, 1.25 mls of octyl iodide was added and the mixture was stirred overnight. Most of the solvent was evaporated and the residue was partitioned between dichloromethane and 9% HCl. The dichloromethane was evaporated and the residue was pumped at 50°C and 0.1 mm Hg under a dry-ice/acetone cold finger to remove most of the octyl iodide. GC analysis with hexadecane as internal standard showed that the product contained 3.12% of octyl iodide. Recovered 1.04 g. Analysis, corrected for 2.8% ash, C, 77.1; H, 9.3; O, 1.5; S, 12.1. MW, found 974, after correcting for octyl iodide present 1129, after correcting for octyl groups added 952.

### RESULTS AND DISCUSSION

Our first attempt to prepare a synthetic asphaltene involved heating dimethylnaphthalene with sulfur. The major part of the pentane-insoluble product was also insoluble in benzene ("coke"), but a small yield of benzene-soluble material was also obtained. This asphaltene was quite different from natural asphaltene, having a molecular weight of only 486, an H/C ratio of 0.78, and a sulfur content of 11%. The H nmr spectrum was also completely different from that of Athabasca asphaltene.

However a material strikingly similar to natural asphaltene can be obtained by heating cholesterol with sulfur. The yield of synthetic asphaltene obtained under various conditions, together with the number average molecular weight, H/C ratio and sulfur content are shown in the Table. The yield of asphaltene is substantially increased when clay is present. Preliminary experiments suggest that kaolin is more effective than montmorillonite, contrary to expectation. The number average molecular weight of the synthetic asphaltene is about 2000, whereas that of Athabasca asphaltene is 3000 after allowing for hydrogen bonding. The H/C ratio has been reduced from 1.7 in the starting material, cholesterol, to an average of 1.25 which compares with 1.19 for Athabasca asphaltene and an average of 1.16 for 33 analyzed samples in the literature (8). The major difference between the synthetic and natural asphaltene is that the synthetic asphaltene contains an average of 17% sulfur while the highest value recorded for a natural asphaltene is 9.6% (8b). Attempts to obtain an asphaltene with lower sulfur content from cholesterol were not successful. When the amount of sulfur

TABLE  
 Reactions of Cholesterol (40 g) with Sulfur  
 Under Various Conditions

Reaction Conditions				Yield(g)	MW	% S	H/C
Sulfur(g)	Clay(g)	Temp.(°C)	Time (days)				
20	20	170	7	9.5	1905	17.0	1.24
20	20	170	7	8.4	2093	17.0	1.24
			Average	9.0	1999	17.0	1.24
15	20	170	7	1.3	2060	16.9	1.27
15	20	170	7	2.0	1809	15.9	1.26
15	20	170	7	1.1	1904	16.4	1.25
			Average	1.5	1924	16.4	1.26
20	0	170	7	3.6	1631	19.0	1.27
20	20	150	30	3.7	1893	24.2	1.37

was reduced to 10 g (with 40 g of cholesterol), no asphaltene was produced. If the amount of sulfur was reduced to 15 g, the yield of asphaltene dropped substantially, but the sulfur content decreased only slightly from an average of 17.0% to 16.4%, barely outside the experimental variance. The high sulfur content, roughly twice that of natural asphaltene, suggested that disulfide groups might be present. To test this possibility the synthetic asphaltene was treated with lithium aluminum hydride which would reductively cleave any disulfide groups to thiols (9) and cause a decrease in the molecular weight, if the disulfide group is not in a ring. The product was alkylated with octyl iodide to protect any thiol groups generated. This procedure caused a decrease in the molecular weight from 1905 to 952, after allowing for the weight of the octyl groups added (3.1 per molecule), showing that only one disulfide group per molecule is present. Addition of three octyl groups implies that no more than three thiol groups were generated, which corresponds fairly well to the two thiol groups expected from cleavage of one disulfide bond, and shows that there are few if any disulfide groups in rings. Reduction of the synthetic asphaltene with potassium and naphthalene in tetrahydrofuran, which cleaves carbon-sulfur bonds (4), decreased the molecular weight to 416, very close to the cholesterol molecular weight of 387. This shows that the polymer is held together by sulfide bridges, rather than by carbon-carbon bonds. 4.6 sulfur atoms per molecule must be involved in such bridges, with one a disulfide bridge, to cause the observed decrease in molecular weight, so that the remaining 5.5 sulfur atoms per molecule may be in rings.

The IR, NMR and UV spectrum of the synthetic asphaltene are quite similar to those of Athabasca asphaltene, as shown in the Figures. The <sup>1</sup>H NMR spectrum of the synthetic asphaltene shows that 6% of the hydrogen atoms are aromatic, quite close to the 8% found for Athabasca asphaltene. The <sup>13</sup>C NMR spectrum of the synthetic asphaltene shows that 32% of the carbon atoms are aromatic compared to 42% for Athabasca asphaltene. These figures are consistent with the slightly higher H/C ratio for the synthetic asphaltene. A difference between the synthetic and Athabasca asphaltene is apparent when the <sup>1</sup>H NMR spectrum is arbitrarily divided into "benzylic", "saturated CH<sub>2</sub>", and "saturated CH<sub>3</sub>" regions at δ4.50-1.75 for "benzylic", δ1.75-1.05 for "saturated CH<sub>2</sub>" and δ1.05-0.0 for "saturated methyl". (The spectrum does show minima at about δ1.05 and 4.50 but not at δ1.75). The three regions are in the ratio 0.72:1:0.54 for Athabasca asphaltene and 0.82:1.0:0.90 for the synthetic asphaltene, i.e. there appears to be more "saturated methyl" absorption in the synthetic asphaltene. The synthetic asphalt-

tene also shows an intense EPR signal similar to the main peak in the spectrum of Athabasca asphaltene.

In view of the high sulfur content of the asphaltene produced by heating cholesterol with sulfur, we have investigated the properties of the asphaltene produced by heating the Athabasca maltene with sulfur under the conditions reported by Bestougeff for Hassi-Messaoud maltene (10). The asphaltene produced in this way had an average molecular weight of 7813, 9.4% sulfur and an H/C ratio of 1.18. These values are very close to those of Athabasca asphaltene. Apparently there are some molecules present in the maltene which can be polymerized by sulfur without incorporating sulfur into the units of the polymer. These molecules are probably in the resins, where the molecules with reactive functional groups are concentrated. Since little is known about the structure of the molecules in the resins, we do not know what kind of molecules are responsible. However the experiment provides further support for the suggestion that polymerization of smaller molecules with sulfur is a possible route to asphaltene in nature.

#### CONCLUSIONS

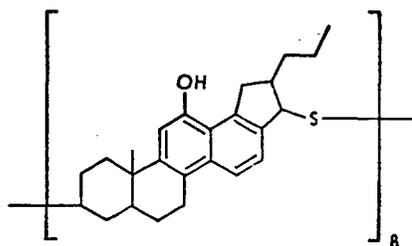
Reaction of cholesterol with sulfur produces material very similar to natural asphaltene. The synthetic asphaltene consists of small units held together by sulfur bridges, as was previously found for Athabasca asphaltene. Reactions of this type are a reasonable route to asphaltene in nature, and are the only route supported by experimental evidence.

#### ACKNOWLEDGEMENTS

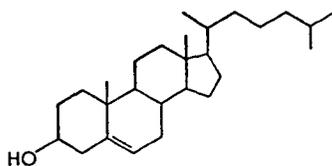
We are grateful to the National Research Council for financial support, and to the Alberta Oil Sands Technology Research Authority for a fellowship to one of us (A.V. K-J.). Mr. Cleve Murray provided technical assistance.

#### REFERENCES

- (1) Yen, T.F., *Energy Sources*, 1, 447 (1974).
- (2) (a) Erdman, J.G., *Adv. Org. Geochem.*, 215 (1964).  
(b) idem, "Hydrocarbon Analysis", ASTM Spec. Tech. Publ. 389, 259 (1965).
- (3) Speight, J.G., *Fuel*, 50, 102 (1971).
- (4) Ignasiak, T., Kemp-Jones, A.V., and Strausz, O.P., *J. Org. Chem.*, 42, 312 (1977).
- (5) (a) Kuznetsov, S.I., Ivanov, M.V., and Lyalikova, N.N., "Introduction to Geological Microbiology", McGraw-Hill, New York, 1963.  
(b) Davis, J.B., "Petroleum Microbiology", Elsevier, Amsterdam, 1967.
- (6) Mair, B.J., *Geochim. Cosmochim. Acta*, 28, 1303 (1964).
- (7) Douglas, A.G., and Mair, B.J., *Science*, 499 (1965).
- (8) (a) Erdman, J.G., and Ramsey, V.G., *Geochim. Cosmochim. Acta*, 25, 175 (1961).  
(b) Padovani, C., Berti, V., and Pinetti, A., *Proc. 5th World Pet. Congr.*, Sec. V, 273 (1959).  
(c) Koots, J.A., and Speight, J.G., *Fuel*, 54, 179 (1975).
- (9) Arnold, R.C., Lien, A.P., and Alm, R.M., *J. Am. Chem. Soc.*, 72, 731 (1950).
- (10) (a) Bestougeff, M., *Bull. Soc. Chim. Fr.*, 4773 (1967).  
(b) idem, *Proc. 7th World Pet. Congr.*, 9, 129 (1969).



I



Cholesterol

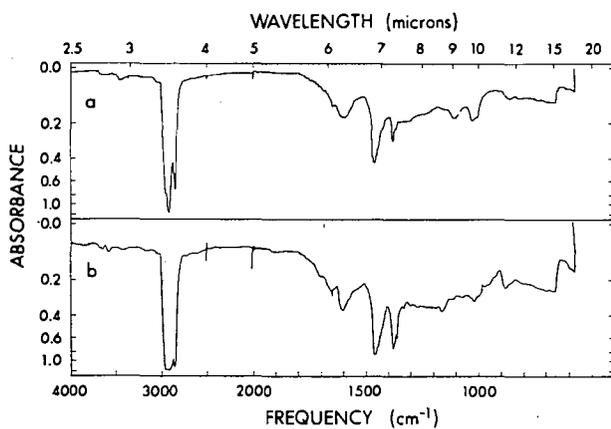


Figure 1. (a) IR spectrum of Athabasca asphaltene (2.7% in  $\text{CHCl}_3$ ).  
 (b) IR spectrum of synthetic asphaltene prepared from cholesterol and sulfur (2.7% in  $\text{CHCl}_3$ ).

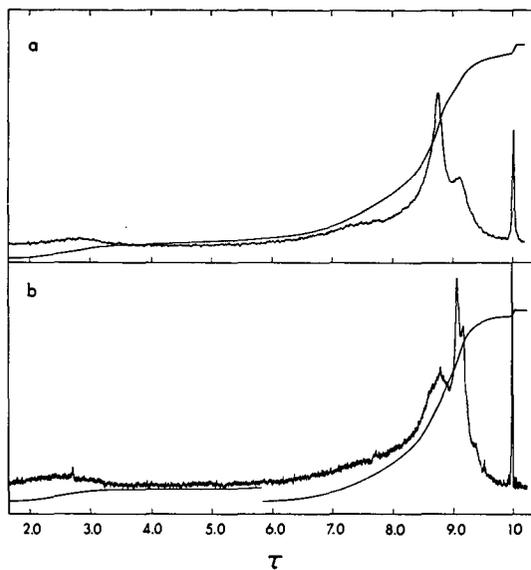


Figure 2. (a) <sup>1</sup>H NMR spectrum of Athabasca asphaltene.  
 (b) <sup>1</sup>H NMR spectrum of synthetic asphaltene prepared from cholesterol and sulfur.

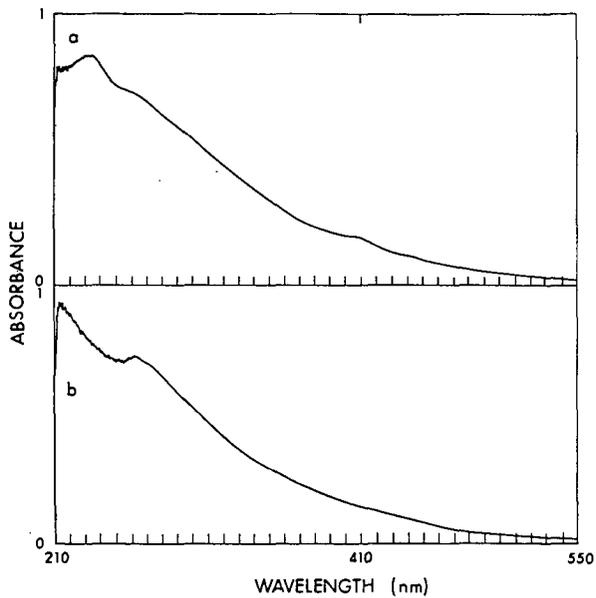
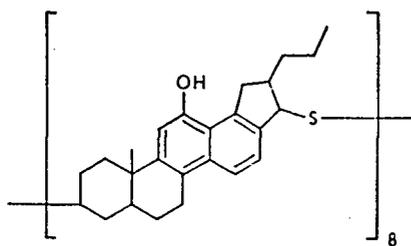
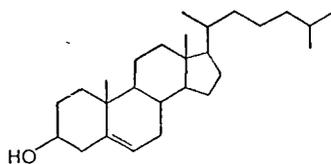


Figure 3. (a) UV spectrum of Athabasca asphaltene (16 mg/l in tetrahydrofuran).  
 (b) UV spectrum of synthetic asphaltene prepared from cholesterol and sulfur (15 mg/l in tetrahydrofuran).



I



Cholesterol

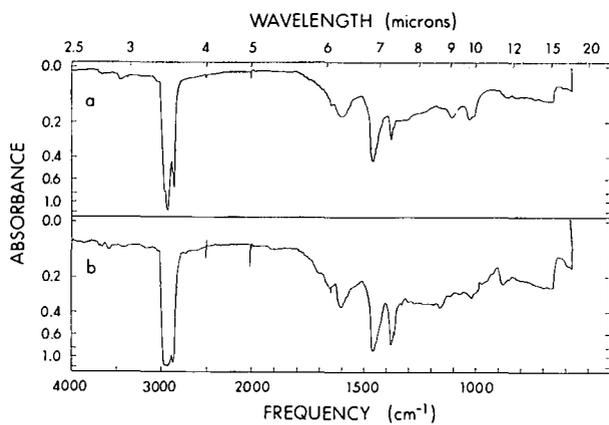


Figure 1. (a) IR spectrum of Athabasca asphaltene (2.7% in  $\text{CHCl}_3$ ).  
 (b) IR spectrum of synthetic asphaltene prepared from cholesterol and sulfur (2.7% in  $\text{CHCl}_3$ ).

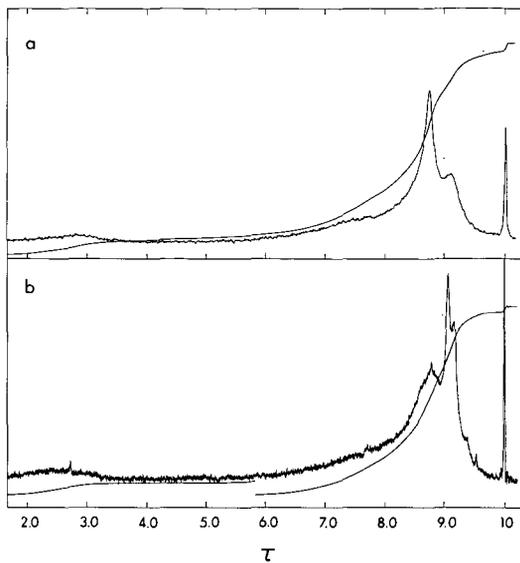


Figure 2. (a)  $^1\text{H}$  NMR spectrum of Athabasca asphaltene.  
 (b)  $^1\text{H}$  NMR spectrum of synthetic asphaltene prepared from cholesterol and sulfur.

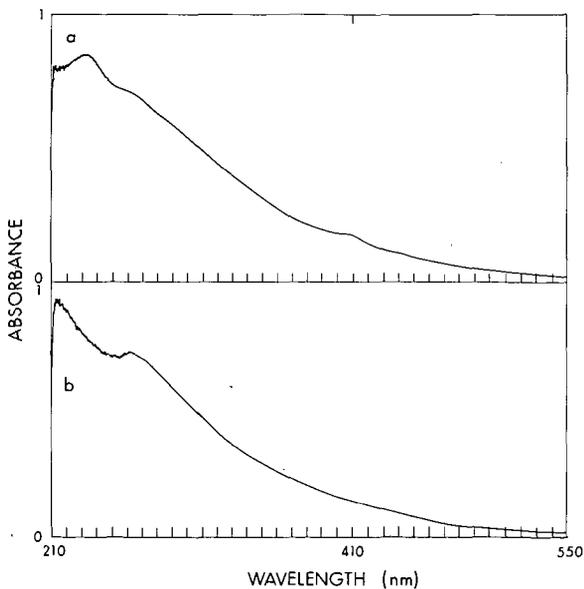


Figure 3. (a) UV spectrum of Athabasca asphaltene (16 mg/l in tetrahydrofuran).  
 (b) UV spectrum of synthetic asphaltene prepared from cholesterol and sulfur (15 mg/l in tetrahydrofuran).

## CHEMICAL CHANGES DURING THERMAL HYDROCRACKING OF ATHABASCA BITUMEN

A.E. George, G.T. Smiley and H. Sawatzky

Canadian Fossil Fuel Research Laboratory,  
Research on Bituminous Substances Section,  
Energy Research Laboratories, CANMET,  
Department of Energy, Mines and Resources,  
Ottawa, Canada.

### INTRODUCTION

Non-catalytic thermal hydrocracking is a method of upgrading Athabasca bitumen. It reduces or eliminates waste coke production and, if combined with gasification of the residue, is less polluting than the currently used coking processes. In a previous report (1) we described some of the chemical conversions that take place during the hydrocracking of the bitumen. The work described here is a continuation of the previous studies on the hydrocracked products.

### EXPERIMENTAL

A schematic diagram of the procedure and the breakdown to compound-types is shown in Figure 1.

#### Samples:

1. Athabasca bitumen obtained from the Great Canadian Oil Sands' hot water separation process.
2. Five samples of hydrocracked bitumen, selected to represent increasing severities of treatment as expressed in pitch conversion to distillable fractions.

#### Thermal Hydrocracking

The hydrocracking pilot plant and its operation have been described in a previous report (2) by our colleagues in the Process Engineering Section of the Canadian Fossil Fuel Research Laboratory of the Energy Research Laboratories. Athabasca bitumen and hydrogen are fed at the bottom. The resulting products, both liquid and vapour, flow from the top of the reactor to a hot separator. The condensed material in this receiver is withdrawn continuously as a heavy oil product (HOP) through a pressure reducing valve into an atmospheric receiver. The uncondensed vapours flow from the hot separator to a cold receiver where the light oil product (LOP) is withdrawn continuously. The gas stream from the cold receiver, consisting mainly of hydrogen and containing impurities such as uncondensed hydrocarbon gas, hydrogen sulphide and ammonia, is oil-scrubbed. The scrubbed hydrogen is joined by fresh make-up hydrogen and is then recycled to the reactor at a constant controlled rate. Five liquid samples of both the light and heavy oil products representing increasing degrees of hydrocracking were selected for investigation. Three of these samples are representative of steady state conditions at a liquid hourly space velocity of 2 and temperatures of 435, 445 and 455°C. Similarly, the other two samples were obtained at a liquid hourly space velocity of 1 and temperatures of 445 and 460°C. All the samples resulted from processing at 2000 psi operating pressure and a hydrogen recycle rate of 1.5 cu ft/hr. at the same operating pressure and a temperature of 25°C. The hydrogen purity was 85%. The distribution of product between light and heavy oil depends on the hot-receiver temperature, the gas/liquid ratio entering the receiver, and the degree of cracking to which the product is subjected (3).

## Distillation

Light oil product (LOP) was separated by distillation (ASTM D216-54) to light ends boiling below 200°C and a fraction boiling above 200°C. The heavy oil product (HOP) did not contain any light ends boiling below 200°C. The distillation residue of the HOP boiling above 524°C under atmospheric pressure is defined as pitch.

## Deasphalting

The asphaltene portion of the heavy oil (HOP) was precipitated by the addition of twenty volumes of pentane to one volume of oil. The asphaltenes were separated by filtration, extracted with pentane in a Soxhlet Extractor and dried first on a water bath and then under reduced pressure at 50°C. The main pentane solubles and washings were combined and n-pentane was completely evaporated from these maltenes.

## Compound-Type Separation

The light ends distilling below 200°C were analysed for saturate, aromatic and olefinic contents on silica gel using the fluorescent indicator adsorption method (ASTM D1319-70), and the following fractions were collected:

- (i) saturated hydrocarbons
- (ii) mixture of saturated and olefinic hydrocarbons
- (iii) olefinic hydrocarbons
- (iv) mixture of olefinic and aromatic hydrocarbons
- (v) aromatic hydrocarbons
- (vi) mixture of aromatic hydrocarbons and polar compounds

The light oil product (LOP) boiling above 200°C and the deasphalted heavy oil product (maltenes of HOP) were separated into compound-type concentrates of saturates, monoaromatics, diaromatics, polyaromatics and basic compounds in a dual-packed (silica gel and alumina gel) liquid-solid chromatographic column developed by the API project 60 (4), and modified in this laboratory (5), Figure 1.

The number of moles of the various types of structures were determined using average molecular weights that were obtained by vapour-pressure osmometry for the light and heavy oil fractions. The average molecular weights of the light oil fraction below 200°C were determined from gas chromatographic simulated distillation data, assuming that the material distilling when half of the sample had distilled represented the average molecular weight. The aromatics in the light ends distilling below 200°C were assumed to be mononuclear aromatics.

The number of sulphur-bearing structures in each fraction was determined assuming that there was one sulphur atom per molecule; the number of sulphur-free structures was then obtained by difference. Sulphur contents of compound-types were determined by the microbomb method (6).

## Characterization of the Hydrocracked Products

### 1. Capillary Gas Chromatography

The various fractions collected from the FIA separations were subjected to capillary gas chromatography on a 100 ft OV-101 column, and the column effluent was characterized by mass spectrometry (CEC-21-104).

## 2. Gas-liquid Chromatography (Packed Columns)

The main fractions of the hydrocarbon types collected from the liquid-solid chromatographic separation (LOP above 200°C and deasphalted HOP) were chromatographed on an OV-1 packed column using both flame ionization and coulometric sulphur detectors.

## 3. Separation on Anion-Cation Exchange Resins

The heavy oil product of a severely hydrocracked bitumen was subjected to chromatography on both anion and cation exchange resins in order to concentrate the nitrogenous and polar compounds according to a procedure similar to that developed by the API project 60 (7), but modified to reduce the time of analysis (8). The results were compared with results obtained on applying this separation scheme to the bitumen feedstock.

## 4. Infra-red Spectrometry

Some comparisons were made of the IR spectra on a Beckman IR-12. Methylene chloride solutions of the samples were scanned for the carbazole and carboxylic acid bands.

## 5. High Resolution Mass Spectrometry

The diaromatics of the hydrocracking product (445°C, LHSV 1) were studied by high resolution mass spectrometer (Model MS-9) for identification of individual components.

# RESULTS AND DISCUSSION

## Gross Composition

In thermal hydrocracking of Athabasca bitumen the lighter materials are formed at the expense of the heavier ones as shown in Table 1. The pitch fraction is defined as that fraction boiling above 523.9°C as determined in a Podbielniak flash equilibrium still (2). The extent of conversion is determined by the percentage of pitch converted to products distilling below 523.9°C.

## Compound-Type Changes

In Table 2 the changes that occur in the chemical type distribution on a weight basis are shown. The saturated hydrocarbons (including the olefins) increased at the expense of the other classes of compounds, particularly the polynuclear aromatic and polar compounds and most of this increase (46%) took place at the least severe treatment (435°C) studied. The basic compounds decreased to less than half the amount in the feed during the mildest treatment but, since this class constitutes such a small proportion of the total bitumen, it does not make a substantial contribution to other compound types on degradation. The asphaltenes were not appreciably affected by the treatments at 435°C. The mononuclear aromatic compounds increased somewhat, while the dinuclear aromatic compounds decreased slightly.

Under the more severe conditions, the production of saturated hydrocarbons appears to accelerate as a function of the percentage of pitch conversion as shown in Figure 1. The asphaltenes diminish markedly when subjected to the more severe thermal treatments. The polynuclear aromatic and polar compounds continue to decrease on a weight basis with increasing severity of treatment, while the dinuclear aromatics undergo a small decrease and the mononuclear aromatic compounds increase slightly.

On a molar basis the situation is different, as shown in Table 3. The number of moles per 100 gm of products of all aromatic hydrocarbons increases as a function of severity of hydrocracking. Some of this increase is due to cleavage of lower molecular weight aromatic hydrocarbons from the higher molecular weight complex materials. The other possibility is that they could have been formed during aromatization reactions in which some structures, such as asphaltenes or large polynuclear aromatic clusters, become hydrogenated by hydrogen transfer.

The number of moles of both dinuclear and polynuclear aromatic hydrocarbons increase substantially during the less severe treatments, and during the most severe treatment the increase is not as substantial as in the lower conversion rates. The moles of mononuclear aromatic hydrocarbons increase steadily with the increase in severity of conditions.

When the changes in the number of moles of the various types are plotted against the percentage pitch conversion, the plots as shown in Figure 2 are obtained. The interesting feature of this figure is that the largest increases in the number of moles of mononuclear aromatic hydrocarbons, and also in the weight of saturated hydrocarbons, occur during the most rapid decline of the asphaltenes.

Asphaltenes are considered to consist mainly of large substituted aromatic structures (8) and to contain more heteroatoms than other bitumen fractions. Therefore it would be expected that their cleavage during cracking would increase the number of polynuclear aromatic and polar structures. While there is a steady molar increase in these compounds, there is no apparent direct relationship between their increase and the rate of asphaltene degradation.

The substantial increase in the number of moles of mononuclear aromatic compounds tends to indicate some relationship to asphaltene destruction. Since it is not believed that the asphaltenes contain many phenyl groups, a hydrogenation step of the large aromatic structures in the asphaltenes before undergoing cracking must be considered.

Mononuclear aromatic hydrocarbons are possibly formed during hydrogen transfer reactions in which asphaltenes undergo some hydrogenation, while cycloalkanes are aromatized. Cyclohexanes are not good hydrogen donors but decalins are (9). If a dicyclic alkane is a good donor, then more highly cyclic alkanes should be even better donors. If olefinic bonds are involved in the ring systems their tendency for aromatization is increased (10). It is known that the Athabasca saturated hydrocarbons are highly cyclic (11) and that the hydrocracked saturates contain substantial olefins. Thus mono-aromatization of the saturated hydrocarbons (including olefins) appears plausible.

The asphaltene aromatic clusters might also have undergone some hydrogenation during milder treatments in which cycloalkyl mononuclear (tetralins) or other cycloalkyl aromatic compounds lost hydrogen that led to the increase in di- and polynuclear aromatic moles. This would then suggest that the number of moles of mononuclear aromatic hydrocarbons produced is greater than indicated in Table 3.

The FIA results of the light ends below 200°C were as shown below:

		<u>Saturates</u>	<u>Olefins</u>	<u>Aromatics &amp; Polar</u>
LHSV - 1,	400°C	60.6	26.8	12.7
	435	59.2	29.3	11.5
	445	69.7	19.2	11.1
	455	69.6	18.9	11.5
LHSV - 2,	445	73.0	15.9	11.1
	460	75.3	13.8	10.8

It can be seen that the olefin content of the light ends decreases with severity of cracking which may be caused by the aromatization reactions discussed earlier.

These light ends were virtually non-existent in the bitumen feedstock and thus were totally the products of hydrocracking. In Figure 3, the chromatogram of light ends obtained under mild conditions (400°C, LHSV-1, pitch conversion 27.69) is shown. Most of the main peaks (30% of the LOP) are due to normal alkanes. This proportion of normal alkanes appeared to increase slightly with an increase in hydrocracking severity.

Figure 4 shows the gas chromatogram of the aromatic compounds and the numbered peaks represent the following compounds.

1. n-propyl benzene
2. 1-methyl-4-ethyl benzene
3. 1,3,5-trimethyl benzene
4. 1,2,4-trimethyl benzene
5. } mixture of a methyl- isopropyl benzene and
6. } a trimethyl thiophene
7. a dimethyl-ethyl benzene
8. a dimethyl-ethyl benzene and dimethyl-ethyl thiophene
9. mixture of tetra-methyl benzene and tetramethyl thiophene
10. dimethyl indane and tetramethyl benzene

The chromatogram of the polar materials is shown in Figure 5. These materials are composed mostly of thiophenes but they also contain benzene and xylene isomers. The numbered peaks were identified as follows:

1. thiophene and benzene
2. ethyl thiophene
3. tetrahydrothiophene
4. p-xylene
5. m-xylene
6. o-xylene
7. 2-n-propyl thiophene
8. 2,3,4 - trimethyl thiophene

The amount of sulphur in the light ends increases up to a level of approximately 0.005 moles per 100 g of bitumen products and thereafter remains virtually constant with increasing hydrocracking severity, indicating a steady state between the sulphur-containing molecules cleaved from the high molecular weight components and those desulphurized to  $H_2S$ .

#### Dinuclear Aromatic Compounds

This class of compounds has been investigated to a considerable extent, especially with high resolution mass spectrometry. As far as the material that vaporized in the spectrometer was concerned (average carbon numbers for the naphthalenes were about 17.5 in the feed and about 16 in the severely cracked products),

there was little difference between the naphthalenes in the feed and products according to the mass spectra analyses. These naphthalenes were substituted by both alkyl and cycloalkyl groups with the latter predominating.

However, according to the gas chromatograms (FID), there are considerable differences between the dinuclear aromatic compounds in the feedstock and the hydrocracked products. As the products become more severely hydrocracked the molecular weight and the number of isomers decrease. This is shown in Figures 6-10. The compounds in the main diaromatic fraction of the feedstock are unresolvable by gas chromatography. In the severely hydrocracked products even the heavy oil, the main diaromatic fraction, is resolvable.

In the feedstock, alkyl and cyclo-alkyl benzothiophenes represent the sulphur compounds eluting from the liquid chromatographic column before and during the main diaromatic fraction elution. Alkyl and cyclo-alkyl dibenzothiophenes were predominant in the eluting tail of the diaromatic fraction. In the severely hydrocracked diaromatic fractions, the benzothiophenes were predominant in all fractions and small amounts of dibenzothiophenes were found only in the tail fractions. The sulphur compounds decrease in molecular weight and become more resolvable by gas chromatography with increasing hydrocracking as shown by the chromatograms in Figures 11-15.

Another aspect of the diaromatic compounds is the appearance of dibenzofurans in the tail fractions of the severely hydrocracked materials. These were not found in the feedstock and thus appear to be formed during hydrocracking.

As far as the polynuclear and polar fractions are concerned, they also become more resolvable on gas chromatography with increasing hydrocracking severity.

#### Other Changes During Hydrocracking

##### 1. Decarboxylation

In Figure 16 we see the infra-red spectra in region  $1650-1750\text{ cm}^{-1}$  of two acid fractions isolated from the bitumen. The fractions consisted of 2.7% and 0.8% of the bitumen. The infra-red spectra of the former is similar to alkyl acids and the latter to aromatic acids. In the hydrocracked material these acid fractions were virtually absent, as shown in Table 4, indicating complete decarboxylation.

##### 2. Carbazole Formation

Comparisons are made in Figure 17 of the IR spectra of various fractions obtained by chromatography on ion exchange resins of the feed, and of a severely hydrocracked heavy oil. The results of the chromatography are shown in Table 4. The absorption band at  $3460\text{ cm}^{-1}$  is considered to be due to carbazole (7). It can be seen that there is considerable increase in carbazoles during hydrocracking.

#### Sulphur Compounds in the Polynuclear and Polar Compound Classes

The amounts of sulphur compounds on a molar basis are shown in Table 5, in which it is assumed as a first approximation that each mole contains one sulphur atom. The fact that about two-thirds of the sulphur was lost in these fractions on hydrocracking indicates that a large portion of this class contains sulphur that is less thermally stable (possibly sulphides). Remaining sulphur compounds are considered to be mostly thiophenic.

TABLE 1

GROSS COMPOSITION OF ATHABASCA BITUMEN AND  
PRODUCTS OF HYDROCRACKING  
(wt % of total bitumen)

SAMPLE	PITCH CONVERSION*	GAS*	LIGHT OIL PRODUCT (LOP)		HEAVY OIL PRODUCT (HOP)	
			Below 200°C	Above 200°C	MALTENES	ASPHALTENES
FEED			1.4	(83.3% maltenes above 200°C)		15.3
LHSV-2, 435°C	59.1	3.9	7.0	10.2	65.5	13.4
LHSV-2, 445°C	68.9	4.0	11.5	10.2	62.0	12.3
LHSV-2, 455°C	77.4	5.9	13.1	10.8	59.7	10.5
LHSV-1, 445°C	80.0	6.8	13.5	25.7	47.0	7.0
LHSV-1, 460°C	91.4	9.2	18.5	34.0	35.6	2.7

(\*) Reference 1

TABLE 2

COMPOUND TYPE DISTRIBUTION (% BY WT)

SAMPLE	SATURATES	MONONUCLEAR AROMATICS	DINUCLEAR AROMATICS	POLYNUCLEAR AROMATICS	POLAR COMPOUNDS	BASIC COMPOUNDS	ASPHALTENES
FEED	21.0	7.8	11.0	20.1	19.0	5.7	15.3
LHSV-2, 435°C	33.4	9.3	10.5	14.2	12.8	2.3	13.4
LHSV-2, 445°C	36.1	10.1	10.7	12.9	11.6	2.1	12.3
LHSV-2, 455°C	38.9	10.5	11.0	11.7	9.8	1.6	10.5
LHSV-1, 445°C	42.5	10.5	10.1	11.1	10.5	1.2	7.0
LHSV-1, 460°C	47.8	11.5	9.7	9.1	8.8	0.9	2.1

TABLE 3

COMPOUND TYPE DISTRIBUTION  
WITHOUT SULFUR COMPOUNDS (MOLES/100 g)

SAMPLE	MONONUCLEAR AROMATICS	DINUCLEAR AROMATICS	POLYNUCLEAR AROMATICS	POLAR COMPOUNDS
FEED	0.017	0.012	0.004	-
LHSV-2, 435°C	0.026	0.021	0.011	0.005
LHSV-2, 445°C	0.030	0.023	0.014	0.00
LHSV-2, 455°C	0.036	0.028	0.015	0.010
LHSV-1, 445°C	0.039	0.027	0.021	0.014
LHSV-1, 460°C	0.046	0.030	0.020	0.016

TABLE 4

SEPARATION OF NITROGENOUS COMPONENTS  
ON ANION-CATION EXCHANGE RESINS

<u>ELUENT</u>	<u>DEASPHALTED FEED</u> (MALTENES)		<u>DEASPHALTED HOP</u> (MALTENES)	
	<u>wt % Eluate</u>	<u>% N</u>	<u>wt % Eluate</u>	<u>% N</u>
n-Pentane	73.0	0.02	82.7	0.02
Cyclohexane	5.4	0.46	2.4	0.70
<u>Anion Exchange Resin A-29</u>				
Benzene	7.8	1.26	7.2	5.29
Benzene-Methanol	2.4	1.28	1.2	5.57
Benzene-Methanol-CO <sub>2</sub>	2.7	0.34	0.2	--
Benzene-Acetic Acid <sup>2</sup>	0.8	2.95	0.1	--
<u>Cation Exchange Resin A-15</u>				
Benzene	4.5	0.64	2.0	2.07
Benzene-Methanol	1.8	0.92	0.4	--
Benzene-Methanol-Isopropylamine	1.6	2.14	1.9	7.32

TABLE 5

SULPHUR CONTENT DISTRIBUTION  
(MOLES/100 g)

<u>SAMPLE</u>	<u>MONONUCLEAR</u> <u>AROMATICS</u>	<u>DINUCLEAR</u> <u>AROMATICS</u>	<u>POLYNUCLEAR</u> <u>AROMATICS</u>	<u>POLAR COMPOUNDS</u>
FEED	0.005	0.016	0.043	0.040
LHSV-2, 435°C	0.010	0.015	0.030	0.025
LHSV-2, 445°C	0.011	0.015	0.026	0.022
LHSV-2, 455°C	0.010	0.015	0.024	0.018
LHSV-1, 445°C	0.080	0.013	0.014	0.018
LHSV-1, 460°C	0.080	0.013	0.015	0.013

#### ACKNOWLEDGEMENT

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#### REFERENCES

1. George, A.E., Banerjee, R.C., Smiley, G.T. and Sawatzky, H. Am. Chem. Soc. Fuel Preprints 21, no. 6, p 174; 1976.
2. Merrill, W.H., Logie, R.B. and Denis, J.M. Pilot scale investigation of thermal hydrocracking of Athabasca bitumen; Mines Branch Report R-281; 1973.
3. Pruden, B.B. and Denis, J.M. Heat of reaction and vaporization of feed and product in the thermal hydrocracking of Athabasca bitumen; CANMET Laboratory Report ERP/ERL 76-66 (R); 1976.
4. Hirsch, D.E., Hopkins, R.L., Coleman, H.J., Cotton, F.O. and Thompson, C.J., ACS Preprints, Div. of Petrol. Chem., p A65; 1972.
5. Sawatzky, H., George, A.E., Smiley, G.T. and Montgomery, D.S.; Fuel; v 55, p 16; 1976.
6. Siegfriedt, R.K., Wiberley, J.S. and Moore, R.W.; Analytical Chemistry; v 23, no. 7, p 1008; 1951.
7. Haines, W.E. Extension of the U.S. BM-API scheme for the characterization of heavy oils; *Erganzungsbend der Zeitschuft Erdol und Kohle Erdgas, Petrochemie, Compendium 75/76*, S.521-533 and references cited therein.
8. Sawatzky, H., Ahmed, S.M., Smiley, G.T. and George, A.E. Separation of nitrogenous materials from bitumen and heavy oils (pending publication).
9. Yen, T.F.; Energy Sources; v 1, p 447; 1974.
10. Carlson, C.S., Langer, A.W., Stewart, J. and Hill, R.M.; Industrial and Engineering Chemistry; v 50, no. 7, p 1067; 1958.
11. Doyle, G. Desulfurization via hydrogen donor reactions; A.C.S. Petrol. Preprints, 21, no. 1, p 165; 1976.

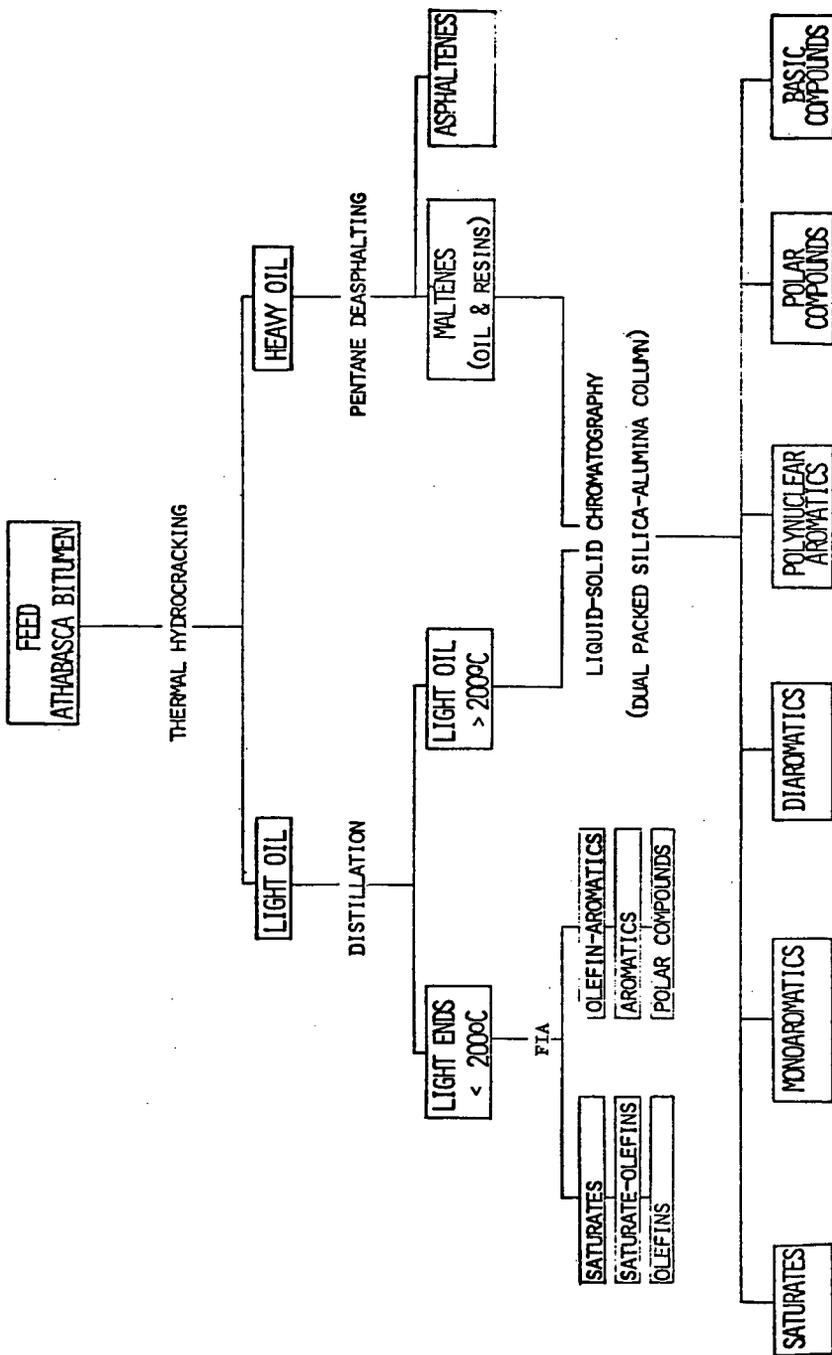
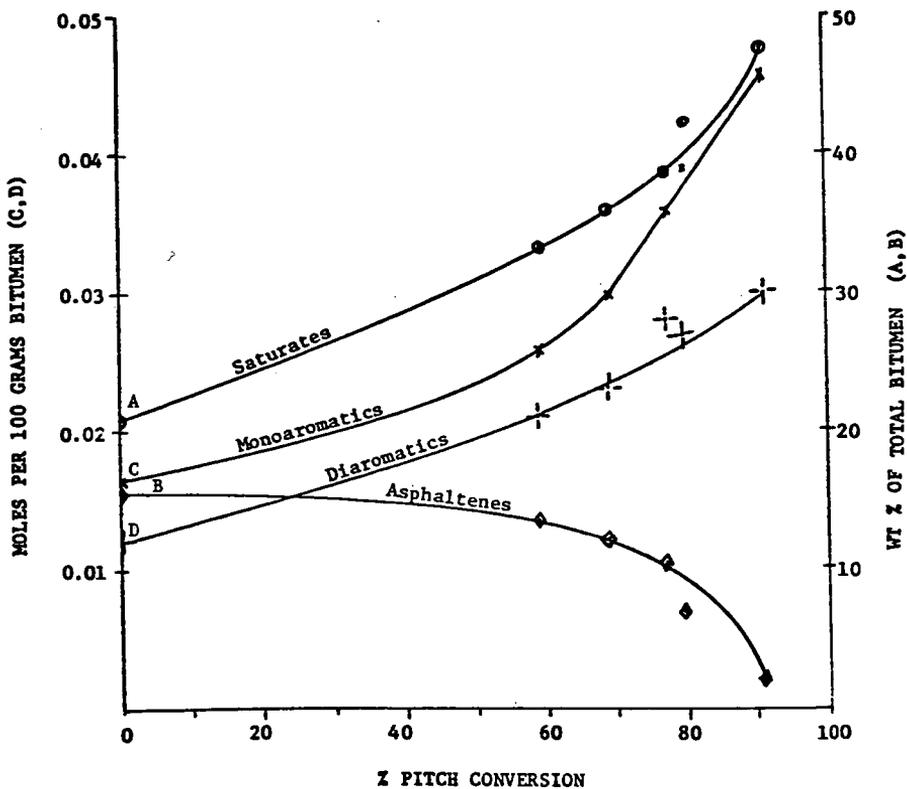


FIGURE 1 - HYDROCRACKING AND SEPARATION SCHEMATIC



The Effect of Hydrocracking on Saturate, Monoaromatic and Asphaltene Contents in Athabasca Bitumen

FIGURE 2

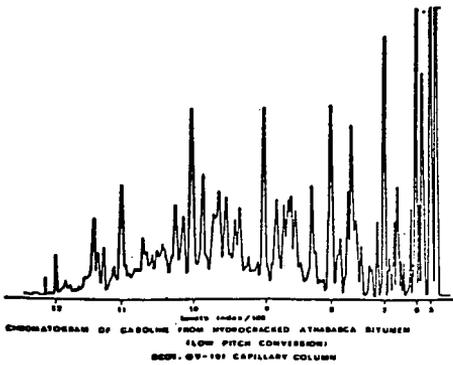


FIGURE 3

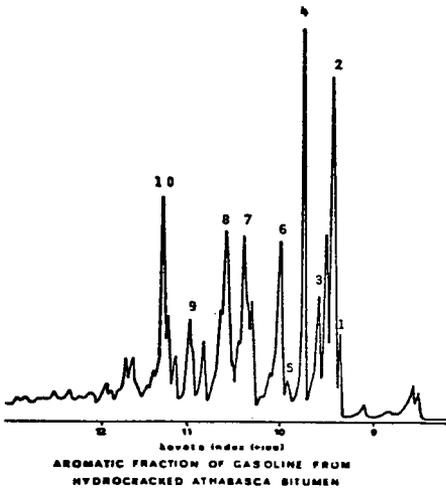


FIGURE 4

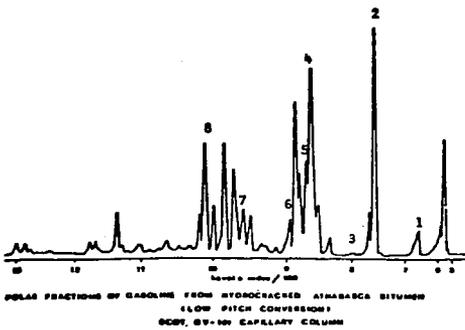


FIGURE 5

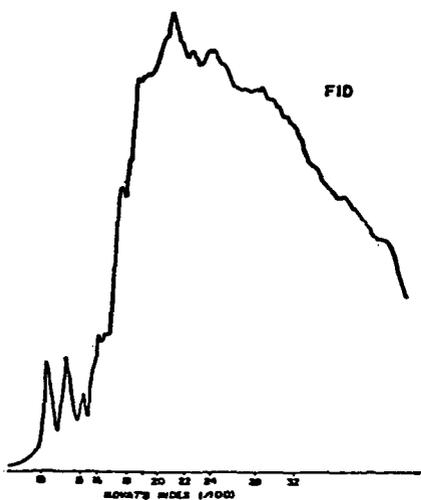


FIGURE 6  
DIAROMATICS OF ATHABASCA FEEDSTOCK  
Light Oil Product (above 200°C)  
OV-1 on Chromosorb W, a.w., 60-80 m

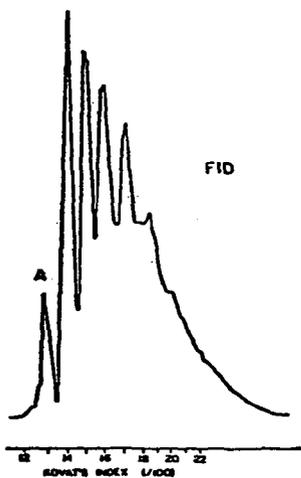


FIGURE 7  
DIAROMATICS OF HYDROCRACKED ATHABASCA  
(435°C, LHSV-2)  
Light Oil Product (above 200°C)  
OV-1 on Chromosorb W, a.w., 60-80 m

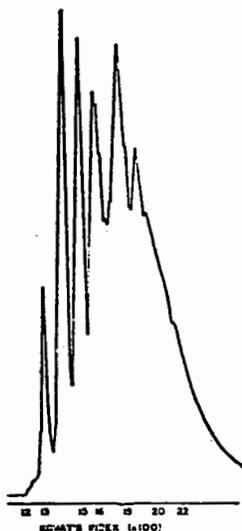


FIGURE 8

DIATOMICS OF HYDROCRACKED ATHABASCA  
 (460°C, LHSV-1)  
 Light Oil Product (above 200°C)  
 OV-1 on Chromosorb W, a.w., 60-80 m

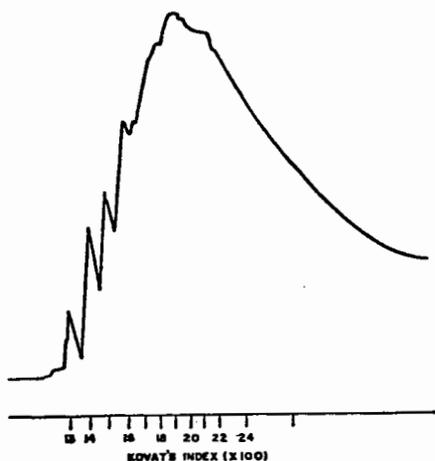


FIGURE 9

DIATOMICS OF HYDROCRACKED ATHABASCA  
 (435°C, LHSV-2)  
 Heavy Oil Product (deasphalted)  
 OV-1 on Chromosorb W, a.w., 60-80 m

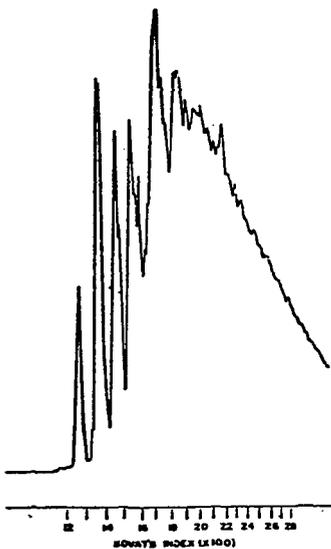


FIGURE 10

DIAROMATICS OF HYDROCRACKED ATHABASCA  
 (460°C, LESV-1)  
 Heavy Oil Product (deasphalted)  
 OV-1 on Chromosorb W, a.w., 60-80 m

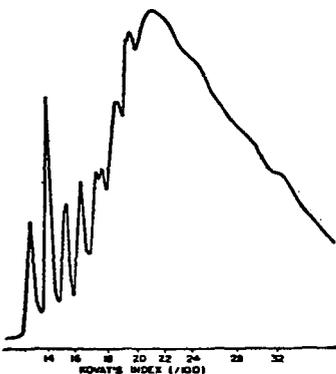


FIGURE 11

DIAROMATIC SULPHUR OF ATHABASCA FEEDSTOCK  
 Light Oil Product (above 200°C)  
 OV-1 on Chromosorb W, a.w., 60-80 m

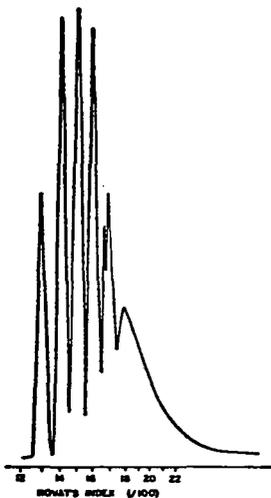


FIGURE 12

DIAROMATIC SULPHUR OF HYDROCRACKED  
 ATHABASCA (435°C, LHSV-2)  
 Light Oil Product (above 200°C)  
 OV-1 on Chromosorb W, a.w., 60-80 m

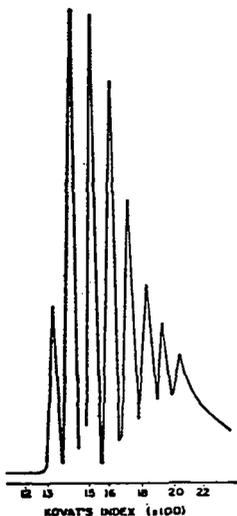


FIGURE 13

DIAROMATIC SULPHUR OF HYDROCRACKED  
 ATHABASCA (460°C, LHSV-1)  
 Light Oil Product (above 200°C)  
 OV-1 on Chromosorb W, a.w., 60-80 m

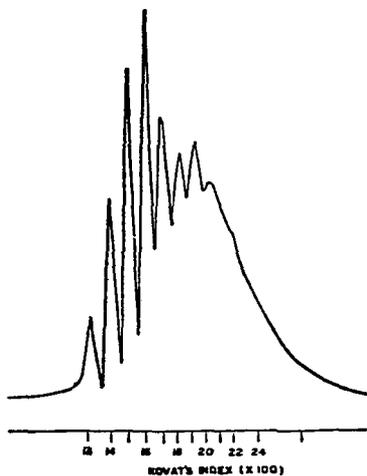


FIGURE 14

DIAROMATIC SULPHUR OF HYDROCRACKED  
 ATHABASCA (435°C, LHSV-2)  
 Heavy Oil Product (deasphalted)  
 OV-1 on Chromosorb W, a.w., 60-80 m

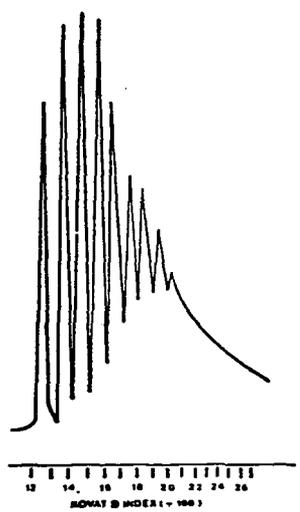


FIGURE 15

DIAROMATIC SULPHUR OF HYDROCRACKED  
 ATHABASCA (460°C, LHSV-1)  
 Heavy Oil Product (deasphalted)  
 OV-1 on Chromosorb W, a.w., 60-80 m

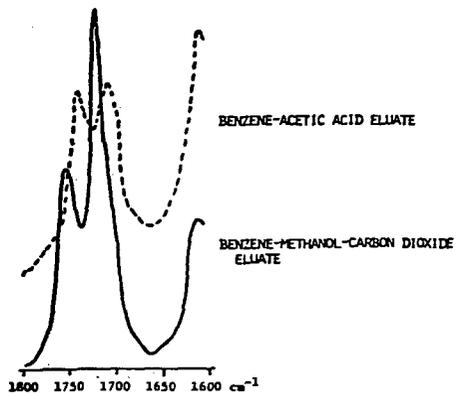


FIGURE 16

INFRA-RED SPECTRA OF ATHASASCA BITUMEN ACIDS.

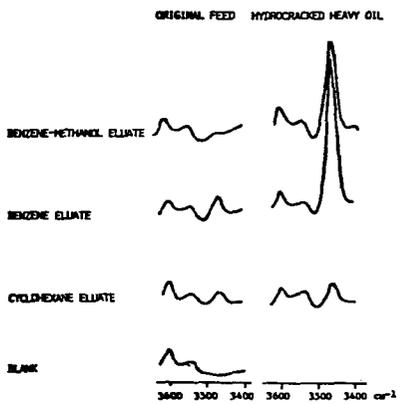


FIGURE 17

ATHASASCA BITUMEN; INFRA-RED SPECTRA OF ELLIATE FROM ANION EXCHANGE RESIN

## FIREFLOODING CHANGES IN ATHABASCA BITUMEN AND WATER PROPERTIES

D.W. Bennion, L. Vorndran, J.K. Donnelly & R.G. Moore

Department of Chemical Engineering, University of Calgary  
2920 - 24 Avenue N.W., Calgary, Alberta, T2N 1N4

### INTRODUCTION

Fireflooding is the process of igniting the hydrocarbons in the formation at the site of an injection well; this is followed by propagation of the combustion front through the reservoir to producing wells. Combustion is maintained by the injection of air and as the fire-front moves through the reservoir, it vaporizes oil and the formation water. These are moved ahead of the front in a gas phase, then condensed in cooler portions of the reservoir and eventually produced from a production well. The fuel for combustion is supplied by the heavy residual material which is not vaporized by the fire-front. This material is generally referred to as coke and is deposited on the rock matrix.

Combustion can proceed in two directions: in the most commonly used process, the combustion zone advances in the same direction as the air flow and is known as "forward combustion"; in the second method, the combustion front advances in the direction opposite to the flow of air and is called "reverse combustion". Forward combustion burns the least desirable fraction of the oil, leaves a clean formation behind and is an efficient heat generating process. Its main drawback is that there must be sufficient mobility for the vaporized oil and water to be produced after they have condensed ahead of the firefront. In reverse combustion, the produced liquids are produced through the heated portion of the reservoir. The fuel for this process is an intermediate fraction of the original oil and the coke remains in the matrix. The process also produces crude oil which contains more oxygen compounds than crude produced with forward combustion. Because spontaneous ignition can occur the process is difficult to control.

In the forward combustion process, water has been injected with the air to remove heat from the hot rocks and to reduce the amount of air required. A number of investigations of different types of wet combustion have been made (1-3). These investigators have classifications for this process according to the amount of water being injected. In this paper we will use Burger and Sahuguet's (1) nomenclature. They classified the types of wet combustion into normal, incomplete and super wet. In normal wet combustion the water evaporation front is behind the firefront and all the coke is burned. In incomplete combustion the water evaporation front is behind the combustion zone but not all the coke is burned. In both of these processes superheated steam passes through the firefront. Super wet combustion takes place when enough water enters the combustion zone to cause the disappearance of the peak combustion temperature.

The object of this study is to present the data from the analysis of the effluent of a dry combustion test and a wet combustion test performed on oil sands from the Athabasca Oil Sands deposit. The paper gives a brief description of the apparatus used to run the tests, as well as a description of the analytical methods used to do the effluent analysis and a discussion of the results obtained.

### EXPERIMENTAL APPARATUS

A schematic diagram of the combustion tube is shown in Figure 1. The combustion tube is constructed from a 1.83 meter length of 10.2 cm diameter 600 Inconel tubing of 1.067 mm wall thickness. The combustion tube, which is designed to withstand temperatures as high as 1150°C is equipped with heaters and thermocouples; the

heaters are controlled so the tube is able to approach adiabatic conditions. The adiabatic tube is placed in a pressure jacket with a pressure rating of 6,895 kPa.

The following variables are measured throughout a run: pressure drop, temperature along the tube, volume of injected air and water, composition of produced gas, and volumes of produced gas, oil and water. A complete description of the equipment can be found in two other sources (4-5).

#### EXPERIMENTAL PROCEDURE

A sample of Athabasca oil sands was manually tamped into the tube. Samples were removed every 7.5 to 15.25 cm to determine fluid saturation. After the tube was packed, it was placed in the jacket and brought up to the desired pressure. In order to get the oil to flow it was necessary to pack samples with high water saturation or to heat the combustion tube to about 100°C. After communication through the tube was obtained, the air injection end was heated to about 300°C while flowing nitrogen through the pack. When the ignition temperature was reached, the nitrogen flow was switched to air and the first zone allowed to reach its peak temperature. From this time on, air and water were injected. During the run all of the variables previously mentioned were recorded. The tube was allowed to cool at the end of the run and was then depressured. The tube was removed and unpacked in 7.5 to 15.25 cm sections. Each sample removed was analyzed for fluid saturation and coke content.

#### GAS ANALYSIS

The produced gas was analyzed on a Hewlett-Packard 5830 three column, dual TC, FID detector gas chromatograph. The gas was analyzed for the following components: oxygen, nitrogen, carbon monoxide, carbon dioxide, hydrogen, methane, ethylene, ethane, propylene, propane, iso-butane, normal butane, iso-pentane, normal pentane, normal hexane, hydrogen sulfide, carbonyl sulfide, and sulfur dioxide.

#### OIL ANALYSIS

The produced oil and water samples were separated by heating and high speed centrifuging. Samples were heated to 80°C, then centrifuged at speeds of up to 19,500 rpm; heating the sample increased the density difference between the oil and water. Once the oil was separated from the water, the following measurements were performed: weight percent carbon, hydrogen, nitrogen and sulfur; viscosity and density of the oil; weight percent asphaltenes; and a vacuum distillation on the asphaltene free oil.

The weight percent carbon, hydrogen and nitrogen were measured using a Hewlett-Packard Model 185, C, H, N-analyzer. The analyzer oxidized C, H<sub>2</sub>, and N<sub>2</sub> and measured the concentration of these compounds using a thermal conductivity detector. The weight percent sulfur was determined using a Horiba Model SLFA 200 total sulfur analyzer which employs x-ray absorption to measure the sulfur concentration.

Viscosity was measured using a Wells-Brookfield microviscometer which relates shear stress to the torque over a conical surface. Density was measured with a PAAR digital density meter which determines density by measuring the variations of the natural frequency of a hollow oscillator when liquids or gas were introduced into it.

The asphaltene content was determined by taking approximately 10 gms of oil sample, adding 100 ml of pentane and mixing the two at 20°C. The precipitated asphaltenes were filtered out and dried at 100°C. The pentane soluble portion was then distilled into three fractions. First, the pentane and light oil were removed at room temperature by reducing the pressure to 1.2 mm of Hg. The sample was then heated to 200°C at a pressure of 1.2 mm of Hg. The portion distilled off was defined as the middle oil and the residue was defined as the heavy oil. Since many

of the samples were small, it was necessary to develop a special distillation apparatus in which to do the distillations. Figure 2 is a photograph of the device used. A complete description of the procedure and equipment is in a paper by Hayashitani et al. (6). A simulated distillation curve was then obtained on the middle oil using the ASTM-D2887 procedure.

In addition to oil samples obtained from the effluent, samples were obtained from the initial material placed in the combustion tube and from the tube after the burn was completed. The oil was extracted from the sand using the Dean Stark method (7). Following the extraction, toluene was removed by heating the sample to 100°C under a pressure of 280 mm of Hg. The type of tests on these samples depended on the amount of sample obtained from the extraction.

#### WATER ANALYSIS

The water separated from the produced oil was filtered using 20 micron filter paper to remove most of the suspended solids. The following tests were then performed: pH; total organic carbon; potassium, calcium, sodium, magnesium, barium, iron, sulfate, chloride, carbonate and bicarbonate concentrations.

The pH was determined using a Brinkmann Model 104 meter. Total organic carbon was determined using a Beckmann Model 915A total organic carbon analyzer. Operation of the instrument involves injection of aqueous samples into two different combustion tubes using air as the carrier gas. In the total carbon channel, a high temperature (950°C) furnace heats a combustion tube packed with a cobalt oxide-impregnated asbestos fiber. The oxygen in the carrier, the elevated temperature, and the catalytic effect of the packing result in oxidation of both organic and inorganic carbonaceous material to CO<sub>2</sub> and steam.

In the inorganic carbon channel, a low temperature (150°C) furnace heats a combustion tube containing quartz chips wetted with 85% phosphoric acid. The acid liberates CO<sub>2</sub> and steam from inorganic carbonates. Operation temperature is sufficiently high for the desired reaction, but is substantially below that required to oxidize organic matter.

The effluent from each combustion tube passes through the associated condenser for removal of condensed steam, and flows to the Sample Select Valve. This valve directs the effluent from a selected channel through a filter to the Model 215A Infrared Analyzer. Here the CO<sub>2</sub> formed during passage of the sample through the combustion tube registers a transient peak on the meter and the recorder chart.

The metal ions concentration was measured using a Perkin Elmer model 303 atomic absorption spectrophotometer, which is equipped to do both flame and flameless analysis.

Sulfates were measured with a standard turbidimetric method. The concentration was determined with a Bausch and Lomb Spectronic 710. Chloride, carbonate, and bicarbonate concentrations were determined by titration. A silver nitrate titration using an Orion solid state chloride specific ion electrode was used for chlorides. The amounts of carbonates and bicarbonates were obtained by titrating 0.02 N, H<sub>2</sub>SO<sub>4</sub> to a pH end point of between 4.2 to 4.5.

#### DISCUSSION OF RESULTS

This paper presents the results of two combustion tube experiments. In the first test referred to as Run 1, 1.14 meters of the 1.83 meter tube were burned, and then the tube was cooled. The material was then removed and the oil extracted using the Dean Stark method. In the second run (Run 2) the tube was completely burned through,

and the analysis of the effluent was reported. Tables 1 and 2 present the properties of the material in the combustion tube for these two runs. Table 3 presents the average properties and run conditions. Run 1 was dry while Run 2 was a wet test in the super wet region. Run 1 had a high bitumen saturation so that there would be sufficient oil ahead of the fire-front for the analysis. Run 2 contained a lower concentration for ease of operations with wet combustion. Tables 4 and 5 present the oil analysis data from the two runs. Table 6 and 7 present the simulated distillation data on Runs 1 and 2.

In Run 1 the residual oil analysis data shows a reduction of the light ends, an increase in the asphaltene content of the oil, and an increase in coke content as the fire-front is approached from the production end of the tube. When the fire flood was stopped the front was 1.14 m along the tube. Figure 3 shows the temperature profile at this time. The coke content at this point was 1.84 weight percent. At temperatures above 450°C the oil was all vaporized. Coke started to form at temperatures in the range of 200°C. Ahead of the fire-front the amount of oil gradually increased to a maximum value of 10.25 weight percent at 1.562 m. The data shows that the oxygen content of the crude oil increases significantly in front of the fire front. Some of the low temperature oxidation reactions could have occurred after the fire stopped burning. During the bleed down the air in the tube was passed through this heated oil. The data shows all the oil in the tube had been significantly changed from the initial bitumen. The sulfur content of oil directly ahead of the fire front was reduced.

The analysis of the produced oil from Run 2 shows that the production was gradually upgraded. The weight percent asphaltenes decreased from 20.0 to 5.6 weight percent. The distillable portion increased from 8.6 to 43.7 weight percent. The residue fraction decreased from 71.4 to 50.7 weight percent. The H/C atomic ratio increased from 1.54 to 1.94. The sulfur content decreased from 4.62 to 2.429 weight percent. The viscosity decreased from 400 to 5.5 cp at 80°C. The density decreased from 1.0155 to 0.9342 gm/cm<sup>3</sup> at 25°C. The simulated distillation data shows that while the amount of the distillable fraction increased with time, the amount distillable at any temperature decreased with time.

Table 8 presents the water analysis data. The pH showed an initial increase from 4.63 to 7.09, then decreased to a low of 1.15. Sodium decreased from 690 to 90 mg/l. Potassium increased from 56 to 270, then decreased to 20 mg/l. Calcium increased from 220 to 340 and then decreased to 26 mg/l before a slight increase. Magnesium decreased from 92 to 18 mg/l. Iron increased from 50 to 1,200 then decreased to 180 and rose to 290 mg/l at the end of the run. Chloride increased from about 180 to 3,500, then decreased for the remainder of the run. Sulfate concentration appeared to increase significantly with a pH below 2. It started out at a value of 3,720, decreased to 230, and then increased to a high of 14,000 mg/l. The pH of the water for most of the run indicated that carbonates and bicarbonates were not present. We believe that the low pH values are caused by Sulfur and CO<sub>2</sub> reactions plus the formation of some organic acids. Sulfate concentration increases indicate that sulfur is reacting to form sulfuric acid. The amount of inorganic carbon from the TOC analysis indicates that there is a possibility of some carbonic acid being present.

The TOC analysis shows hydrocarbon concentrations as high as 7,200 mg/l. We have made no effort to identify the types of hydrocarbon which are dissolved in the produced water. The total dissolved solids ranged from a low of 0.58 to a high of 3.01 weight percent. This curve follows the sulfate curve very closely.

Table 9 presents the average gas analysis for the two runs. Both of these runs show that the only sulfur gas produced was H<sub>2</sub>S. Run 2 data indicate that with the injection of water hydrogen was generated.

## CONCLUSIONS

From the results of the analysis of the products from these two runs it was concluded that thermal cracking, combustion gas reactions, and hydrogenation caused the following:

1. A reduction in the sulfur content of the produced oil.
2. An upgraded oil with a higher H/C ratio, lower density, lower viscosity, and lower asphaltene content.
3. The sulfur removed from the oil is mainly produced as acid, water, and a small amount of H<sub>2</sub>S.
4. The produced water contains up to 7,200 mg/l of dissolved organic carbon.

## REFERENCES

1. Burger, J.C. and Sahuquet, B.C., "Laboratory Research on Wet Combustion", J. Tech., (Oct. 1973) 25, 10, p. 1137.
2. Dietz, D.N. and Weijdenra, J., "Wet and Partially Quenched Combustion", J. Petrol. Tech. (April 1968) 20, 4, p. 411.
3. Parrish, D.R. and Craig, F.F., Jr., "Laboratory Study of a Combination Forward Combustion and Waterflooding - The COFCAW Process", J. Petrol. Tech. (June 1969) 21, 6, p. 753.
4. Harding, T.G., Moore, R.G., Bennion, D.W., and Donnelly, J.K., "Adiabatic Combustion Tube Evaluation of In Situ Processes For Oil Sands", Proceeding of the Symposium on Tar Sands, 26th Canadian Chemical Engineering Conference, Toronto, Ontario, October 3-6, 1976.
5. Harding, T.G., "A Combustion Tube for Investigation of In Situ Oil Recovery", M.Sc. Thesis, The University of Calgary, 1976, 217 pp.
6. Hayashitani, M., Bennion, D.W., Donnelly, J.K. and Moore, R.G., "Thermal Cracking of Athabasca Bitumen", Proceeding of the Canada-Venezuela Oil Sands Symposium 77, Edmonton, Alberta, Canada, May 27-June 4, 1977.
7. "API Recommended Practice for Core-Analysis Procedure", American Petroleum Institute, New York, N.Y., (1960).

TABLE 1

Initial Sand Pack Properties  
Run 1

Sample No.	Mid Point Depth cm.	Weight gms.	Wt. % H <sub>2</sub> O	Wt. % Bitumen	Wt. H <sub>2</sub> O gms.	Wt. Bitumen gms.
coarse sand	8.89	3,172.5	6.30	0.0	200.0	0.0
1	24.93	1,475.0	2.20	13.43	32.5	198.1
2	38.58	2,078.0	1.54	12.44	32.0	258.5
3	51.12	1,830.2	2.85	12.86	52.2	235.3
4	62.71	1,619.1	1.15	12.46	18.6	201.7
5	74.22	1,936.0	2.20	12.66	42.6	245.1
6	86.36	1,893.0	1.11	13.11	21.0	248.2
7	99.22	2,110.9	2.90	11.98	61.2	252.9
8	112.72	1,927.3	1.04	11.96	20.0	230.5
9	126.69	1,859.1	1.18	12.86	21.9	239.1
10	139.70	1,760.6	1.57	12.70	27.6	223.6
11	152.88	1,922.8	2.83	11.91	54.4	229.0
12	167.64	2,241.2	2.17	12.17	48.6	272.8
13	178.28	831.0	0.98	12.96	8.1	107.7
coarse sand	181.85	438.6	6.30	0.00	27.6	0.0
TOTAL					668.3	2,743.0

TABLE 2

Initial Sand Pack Properties  
Run 2

Sample No.	Mid Point Depth cm.	Weight gms.	Wt. % H <sub>2</sub> O	Wt. % Bitumen	Wt. H <sub>2</sub> O gms.	Wt. Bitumen gms.
coarse sand	8.26	2,492	11.0	0.0	274.1	0.0
1	21.12	1,553	8.0	6.5	136.7	100.9
2	30.64	1,504.5	9.8	7.0	147.4	105.3
3	40.96	1,611	8.7	6.9	140.2	111.2
4	51.12	1,514	11.7	6.2	177.1	93.9
5	60.17	1,550	10.3	6.7	159.7	103.9
6	79.22	1,539	9.8	6.5	150.8	100.0
7	79.06	1,542	8.9	6.5	137.2	100.2
8	88.43	1,516	10.0	6.9	151.6	104.6
9	98.43	1,553	10.6	7.3	164.6	113.4
10	109.22	1,543	9.7	8.5	149.7	131.2
11	119.38	1,493	9.6	6.1	143.3	91.1
12	129.86	1,538	9.5	6.6	146.1	101.5
13	140.97	1,518	9.4	6.6	142.7	100.2
14	152.08	1,554	9.0	5.5	139.9	85.5
15	164.78	2,054	10.0	6.9	205.4	141.7
16	173.83	498	10.0	6.9	49.8	34.4
coarse sand	179.23	1,425	4.0	0.0	57.0	0.0
TOTAL					2,673.3	1,619.0

TABLE 3

## Average Properties and Run Conditions

	Run 1	Run 2
Weight of coarse sand - gms.	3,611.1	3,917
Weight of water in coarse sand - gms.	227.6	331.1
Weight of oil sands - gms.	23,484.2	24,080.5
Weight of bitumen in oil sands - gms.	2,743.0	1,619.0
Weight of water in oil sands - gms.	668.3	2,673.3
Weight percent bitumen in oil sands - %	11.68	6.7
Weight percent water in oil sands - %	2.85	11.1
Porosity - %	39.23	39.22
Water Saturation - %	11.7	52.6
Bitumen Saturation - %	48.0	28.3
Run Pressure - K Pa	5,860	5,860
Air Flux - $m^3/m^2\text{-sec}$	$5.95 \times 10^{-3}$	$9.36 \times 10^{-3}$
Water air ratio $m^3/m^3$	Dry	$3.37 \times 10^{-3}$
Initial Properties of Bitumen:		
Density at 25°C $gm/cm^3$	1.0135	1.0135
Viscosity at 85°C cp	400.00	4,000
Weight percent Carbon	82.91	82.91
Weight percent Hydrogen	10.66	10.66
Weight percent Sulfur	4.62	4.62
Weight percent Nitrogen	0.57	0.57
Weight percent Oxygen by Difference	1.24	1.24
Weight percent Asphaltenes	20.0	20.0
Weight percent Distilled	8.6	8.6
Weight percent Residue	71.4	71.4

## Simulated Distillation of Distilled Fraction

Temperature °C	Percent Distilled	
203	0.22	0.22
232	1.54	1.54
245	5.33	5.33
277	16.51	16.51
300	41.95	41.95
323	69.46	69.46
345	84.57	84.57
368	92.61	92.61
391	97.41	97.41
414	100.00	100.00

TABLE 4  
Summary of Residual Oil Analysis  
Run 1

Position # In Tube (ft)	Wt-% Coke	Wt-% H <sub>2</sub> O	Wt-% Bitumen	Wt-% C	Wt-% H <sub>2</sub>	Wt-% N	Wt-% S	Wt-% Asphaltenes	Wt-% Distilled	Wt-% Residue	Density g/cc 25°C	Max. Temp. Zone Reached (°C)	Wt-% Oxygen by difference
1.791	0.0	4.87	7.91	82.90	11.5	< 0.4	4.144	16.2	17.2	66.6	0.9843	136	1.06
1.715	0.0	7.00	9.37	83.66	11.3	< 0.3	3.725	18.2	17.3	64.5	0.9915	140	1.02
1.638	0.0	5.99	9.05	83.32	11.6	< 0.5	3.481	21.6	17.8	60.6	1.0064	155	1.10
1.562	2.43	2.00	10.25	78.9	10.7	< 0.3	2.921	27.6	16.1	57.3	1.0610	195	7.48
1.486	5.90	0.69	5.42	71.9	9.6	< 0.3	1.872	41.8	2.9	55.3	1.1102	278	16.63
1.410	3.60	0.69	6.85	77.3	10.3	< 0.3	2.227	35.6	5.6	58.8	1.0894	332	10.17
1.334	4.12	0.57	4.01	82.0	11.0	< 0.3	2.597				1.0339	437	4.40
1.238	4.00		0.4										
1.137	1.84												
1.054	1.03												

• Measured from air injection end

TABLE 5  
Summary of Oil Analysis  
Run 2

Time hrs.	Density g/cm <sup>3</sup> (25°C)	Viscosity cps (80°C)	Wt-% C	Wt-% H	Wt-% N	Wt-% S	Wt-% Asphaltene	Wt-% Distilled	Wt-% Residue
5.50	0.9543	39.6	82.94	11.6	0.3	4.052			
6.00	0.9754	47.2	82.51	12.1	0.3	3.966	14.8	17.2	68.0
6.50	0.9831	133.6	82.20	12.1	0.3	4.253			
7.25	0.9825	98.6				4.078	16.7	13.8	69.5
8.00	0.9858	112.6				INS.S.			
8.25	0.9689	60.95	82.06	12.3	0.5	4.039	15.1	17.0	67.9
8.50	0.9566	14.8				3.426	11.7	17.3	71.0
9.08	0.9560	19.0	82.92	12.2	0.3	3.432	10.9	26.9	62.2
9.58	0.9564	15.3				3.213			
10.08	0.9571	17.9				3.359			
10.50	0.9546	16.7				3.257			
10.92	0.9511		82.60	13.0	0.3	2.991	9.4	33.4	57.2
11.58	0.9494	12.3				2.967			
12.00	0.9464		82.99	12.5	0.3	3.081	9.1	31.2	59.7
12.25	0.9462	12.0				3.010			
12.95	0.9422					2.718			
13.45	0.9402	8.2	82.60	13.3	0.3	2.664	8.1	27.3	64.6
13.95	0.9340		82.71	13.4	0.3	2.462	5.6	43.7	50.7
14.47	0.9396	8.6				2.774			
14.85	0.9342	5.7				2.429			
15.47	INSUFF.	5.9				INS.S.			
15.92	SAMPLES	5.5							
16.50	"								
17.20	"								
17.47	"								

TABLE 6

Simulated Distillation Data  
Percent Distilled  
Run 1

Temp. °C	Position in Tube * (m)					
	1.791	1.715	1.638	1.562	1.486	1.410
203	1.99	1.17	0.92	0.44	0.40	0.72
232	11.67	8.95	6.77	3.46	5.74	4.67
245	29.36	25.47	21.49	13.34	20.58	15.95
277	53.48	50.73	44.70	32.97	42.95	37.04
305	75.01	74.39	68.41	59.61	68.35	61.97
323	89.41	89.59	86.12	82.54	86.61	81.77
345	96.16	96.40	95.33	94.34	95.09	93.05
368	99.06	99.15	99.16	98.87	98.77	98.25
391	100.00	100.00	100.00	100.00	100.00	100.00
414	100.00	100.00	100.00	100.00	100.00	100.00

\*Measured from air injection end.

TABLE 7

Simulated Distillation Data  
Percent Distilled  
Run 2

Temp. °C	Production Time (Hours)								
	6.0	7.25	8.0	8.5	9.08	10.92	12.0	12.95	13.24
203	4.74	3.17	2.75	3.48	1.05	1.13	0.79	0.32	0.38
232	18.56	15.66	14.24	14.90	9.03	8.33	6.59	5.55	4.09
245	13.67	38.06	34.26	33.47	25.38	22.84	20.06	19.01	14.01
277	63.36	67.47	59.19	58.00	49.56	44.69	41.74	41.42	30.68
300	81.47	86.67	78.62	79.97	73.47	68.98	66.48	65.93	54.68
323	92.16	95.15	90.81	92.41	89.07	86.95	85.50	84.47	79.08
345	97.13	98.22	96.80	97.47	96.34	95.89	95.27	94.57	93.53
368	99.26	99.82	99.20	99.37	99.05	99.24	98.89	98.52	98.19
391	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
414	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

TABLE 8

## Summary of Water Analysis - Run 2

Time	pH	Na mg/l	K mg/l	Ca mg/l	Mg mg/l	Ba mg/l	Fe mg/l	Cl mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	CO <sub>3</sub> <sup>2-</sup> mg/l	HCO <sub>3</sub> <sup>-</sup> mg/l	TOC		Total Solids %
												Total Carbon	Organic Carbon	
1.10	4.63	690	56	220	92	< 1	180	230	3,720			15	3,735	0.72
2.20	6.87	610	56	220	85	< 1	50	180	2,880					0.61
2.95	7.09	530	60	200	77	< 1	42	15	2,600			12	428	0.58
3.92	4.10	410	81	220	80	< 1	250	300	2,000					0.67
4.28	3.51	350	95	230	87	< 1	330	770	1,520					0.68
4.67	3.39	200	110	240	67	< 1	480	1,100	780					0.71
5.00	3.51	130	100	200	62	< 1	500	1,000	540					0.58
5.50	3.54	120	130	230	70	< 1	670	1,300	500					0.58
6.00	3.20	130	160	290	78	< 1	790	2,000	480					0.84
6.50	2.93	100	160	340	92	< 1	1,100	2,900	420					1.05
7.25	2.24	80	230	300	78	< 1	1,200	3,700	270					1.07
8.00	1.66	66	260	250	61	< 1	1,100	4,700	230			18	2,882	1.14
8.25	1.69	64	220	200	50	< 1	900	3,500	330					0.99
8.50	1.73	53	230	160	38	< 1	720	3,100	320					0.84
9.08	1.54	43	270	93	32	< 1	540	2,500	1,220					0.96
9.58	1.49							2,400	2,770					1.16
10.08	1.45							2,100	3,610			17	5,133	1.33
10.50	1.43							1,700	4,560					1.48
10.92	1.49	48	160	30	30	< 1	250	1,500	4,180					1.33
11.58	1.49							1,300	4,480					1.27
12.00	1.48							400	4,980					1.35
12.25	1.45							260	5,920					1.48
12.95	1.41							610	6,180					1.51
13.45	1.41	11	62	26	28	< 1	180	400	6,460					1.48
13.95	1.13	17	68	56	63	< 1	430	260	14,000					3.01
14.47	1.17							1,100	10,700					2.44
14.85	1.15							110	12,300					2.69
15.47	1.20							< 15	9,850					2.14
15.92	1.30	11	53	35	20	< 1	290	< 15	7,100			18	7,232	1.60
16.50	1.26							< 15	8,280					1.94
17.20	1.43	10	32	40	19	< 1	290	< 15	6,860					1.51
17.47	1.64	13	23	43	18	< 1	220	< 15	5,370					1.10
18.08	1.76	20	22	44	18	< 1	240	< 15	4,870					1.00
21.35	2.03							< 15	3,400			12	1,938	0.82

TABLE 9

## Gas Analysis

	Run 1 Mole-%	Run 2 Mole-%
Nitrogen	86.5	87.06
Oxygen	0.0	0.08
Carbon Dioxide	10.60	11.47
Carbon Monoxide	1.93	1.34
Methane	0.62	0.02
Ethane	0.05	0.00
Ethylene	0.05	0.00
Propane	0.02	0.00
Propylene	0.01	0.00
C <sub>4</sub> <sup>+</sup>	0.20	0.00
Hydrogen Sulfide	0.02	0.01
Hydrogen	0.00	0.02

Key to Figure 3.1

1. High Pressure Air and H<sub>2</sub> Cylinders
2. Compressor
3. Recycle Flow Control Valve
4. Compressor Suction Pressure Control Valve
5. Fluoride Meter
6. Fluoride Controller
7. Gas Feed Rotameter
8. Water Storage Cylinders
9. Water Pump
10. Combustion Tube
11. Pressure Jacket
12. High Pressure Nitrogen Cylinder
13. Differential Pressure Controller
14. Annulus Vent Control Valve
15. Annulus Pressure Gauge
16. Bias System Isolation Valve
17. Back Pressure Gauge
18. Back Pressure Controller
19. Differential Pressure Controller
20. Bitumen Collector
21. High Pressure Separator
22. Back Pressure Control Valve - Gas
23. Back Pressure Control Valve - Liquid
24. Temperature Controlled Low Pressure Separator
25. Condenser
26. Gas Sampling Valve
27. Process Gas Chromatograph
28. Wet Test Meter

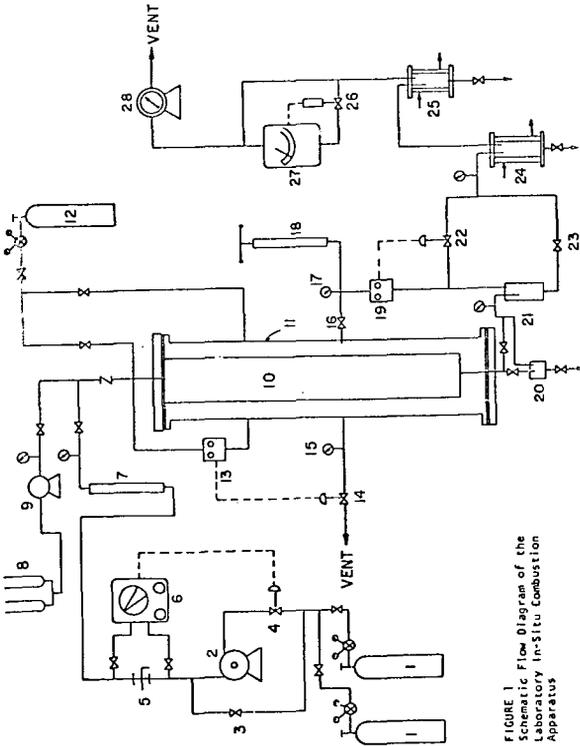
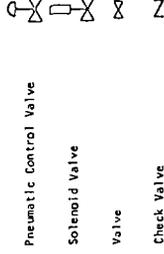


FIGURE 1  
Schematic Flow Diagram of the  
Laboratory In-Situ Combustion  
Apparatus

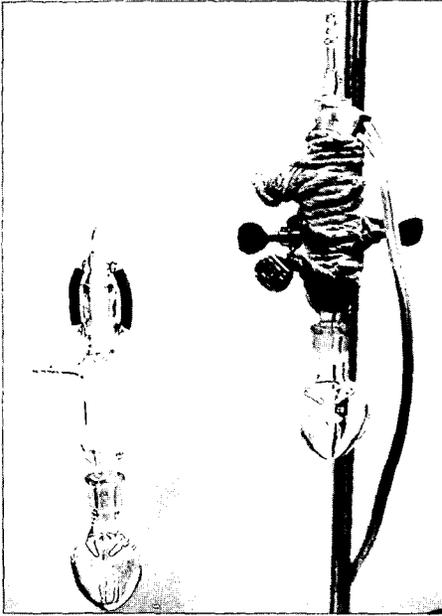


FIGURE 2  
Distillation Apparatus

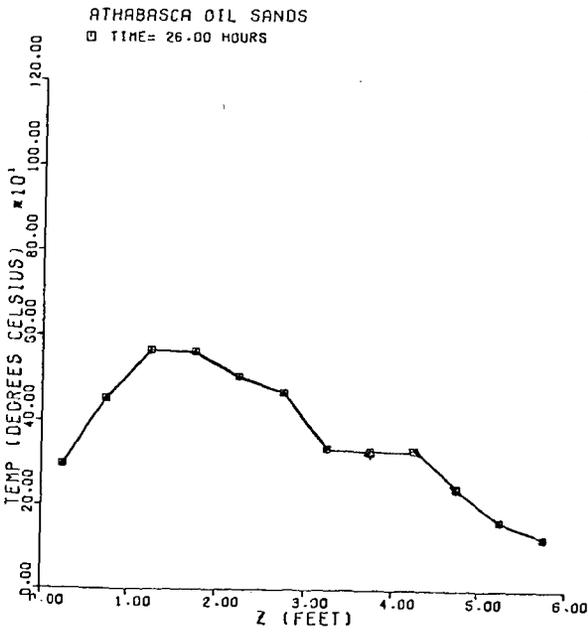


FIGURE 3  
Temperature Profile

## The Chemistry of the Alberta Oil Sand Bitumen

O.P. Strausz

Hydrocarbon Research Center, Department of Chemistry  
University of Alberta, Edmonton, Alberta, Canada  
T6G 2G2

Bitumen chemistry is a complex field and poses a considerable challenge to the chemist. Bitumens are known to be comprised of an exceedingly large number of organic molecules which, in the case of the Alberta oil sand bitumen (AOSB), range from the simplest organic molecule, methane, to large polymeric molecules having molecular weights in excess of 15,000. In the AOSB hundreds of organic molecules representing paraffinic, olefinic, aromatic and heterocyclic structures with various functional groups have been identified. Most of these molecules are neutral but some have acidic or basic functions and are capable of salt formation. Others, by virtue of their skeletal or functional reactivity, may form  $\pi$ -bonded, hydrogen bonded or charge transfer complexes. While most of the constituent molecules are stable, some are relatively unstable and can undergo thermal decomposition even well below room temperature. Indeed, it has been demonstrated in recent studies that slow thermal processes are taking place in some of the major Alberta oil sand formations. These reactions are accelerated by the catalytic effect of the mineral matter present in the bitumen.

What distinguishes bitumen from conventional petroleum is the small concentration of low molecular weight hydrocarbons present and the abundance of high molecular weight polymeric materials. The latter are amorphous solids which are dissolved in colloidal form in the lower molecular weight liquid constituents, endowing the bitumen with a viscous, syrupy consistency. The high molecular weight solids are soluble in liquid aromatics such as benzene or toluene and insoluble in low molecular weight paraffins and therefore can be separated from the bitumen by *n*-pentane precipitation from a benzene solution of the bitumen. The solid precipitated this way is called asphaltene. It is evident that such an operational definition of the asphaltene based entirely on solubility may group together a large number of structurally unrelated molecules. Current studies provide clear evidence that the polymeric framework of the asphaltene molecules derived from various sources may be quite different.

Most asphaltenes are rich in heteroatoms, oxygen, nitrogen and especially sulfur. The asphaltene content of the AOSB is in the 16-25% range and the asphaltene contains ~80%C; 8.0%H; 8-9%S, 2.5%O; and 1.0%N.

The main difficulty associated with underground recovery of the AOSB is the consequence of the extremely high viscosity of the bitumen for which the asphaltene is mainly responsible. Therefore, in order to develop a rational approach to the conceptual understanding and practical resolution of the problem one must start with the study of asphaltene itself. The molecular structure of this material has not yet been fully understood and is still the subject of some conjecture. Apart from its pertinence to *in situ* recovery technology, knowledge of the molecular structure of asphaltene is the key to its possible future commercial utilization, to the elucidation of its origin and diagenetic history, and may conceivably shed some light on the history of the bitumen formations.

The chemical composition of the deasphalted bitumen, the maltene, is also of interest from both a practical and conceptual point of view. This fraction represents the bulk of the bitumen and is one of the major factors which determine the commercial value of the separated bitumen. Detailed

knowledge of the chemical composition of this fraction in conjunction with geological and microbiological data will ultimately lead to the unravelling of the mystery of the source and origin of the bitumen formations of Alberta, the relation between the various major oil sand deposits and their interrelation with conventional oil accumulations of the region.

#### The Thermal Maturation Process.

The realization that a slow, thermal maturation is presently occurring in the bitumen formations of Northern Alberta was the ultimate conclusion of a recent kinetic study of the low temperature thermal behaviour of the oil sand [1-4].

The oil sand in its natural state was shown to contain small quantities of volatile hydrocarbons, methane, propane, propylene and, curiously, neopentane, together with some acetaldehyde. The latter molecule is too reactive to survive long periods of time in the oil sand and must have been formed relatively recently. Heating of the oil sand under controlled conditions resulted in the production of additional amounts of the volatiles present originally in the sand and also some new products. The amounts of gases in question are small, in the ppb-ppm range, nonetheless they can be measured with reasonable accuracy. Thus, measurements of gas evolution at moderately high temperatures provided a key to the detection and monitoring of chemical changes which take place in the oil sand. In the course of the measurements it was found that the rate of evolution of gases, hydrocarbons, acetaldehyde, CO<sub>2</sub>, CO, H<sub>2</sub>S, COS, CS<sub>2</sub>, SO<sub>2</sub>, etc., obeyed Arrhenius' law which made it possible to determine the activation energy and preexponential factor for the production of each gas. The activation energies were all low, 5-23 kcal/mole, and the preexponential factors high. From these Arrhenius parameters it was then possible to determine the rate constant for the evolution of each gas in the formation at the formation temperature, 5°C. This in turn made it possible to estimate the time interval required for the accumulation of the quantity of gases present. The results indicate time periods from several days to several months and therefore we are forced to conclude that a slow thermal maturation is taking place presently in the Athabasca oil sand formation and the measured concentration of gases represent a steady state distribution governed by the rate of formation and rate of loss by chemical reactions and/or diffusion. The role of microbial degradation as compared to the thermal processes appears to be negligible.

The total amount of gases released is small and even at 210°C comprises only a few tenths of one percent of the bitumen. But because the volatilized fragment represents a relatively small proportion of the molecules affected by the decomposition, the fractional amount of bitumen still capable of undergoing maturation would be much higher, probably in the order of several percent.

Similar studies on the separated bitumen, asphaltene and maltene, have indicated that the mineral matter present in the oil sands acts as a catalyst for decomposition and that maltene and asphaltene behave in a similar manner but the activation energies associated with their decomposition are significantly higher than those of the whole oil sand. For a better understanding of this maturation process it will be necessary to extend these studies to all major oil sand deposits, examine the relation between reactivity and depth, identify reactive precursors such as those of neopentane and acetaldehyde and to improve the reproducibility and accuracy of the experimental techniques employed.

At present virtually no information exists on the magnitude or composition of the gas accumulations in the oil sand although this would be extremely important in order to understand what is transpiring in the formations.

The results of current similar studies on the Cold Lake formation indicate an analogous thermal behaviour for the bitumen. The total amounts of volatile hydrocarbons produced in the formations are difficult to estimate, but may be in the range of  $10^5$ - $10^6$  tons annually. A fraction of this would undoubtedly escape into the atmosphere and influence the air quality of the region.

The Chemical Composition of the Maltene.

The composition of maltene, the deasphalted bitumen, has been investigated by the API-60 procedure, a somewhat simplified version thereof and also by microanalytical procedures developed in organic geochemical studies [5-7].

The elemental compositions of Peace River, Wabasca, Athabasca and Cold Lake bitumens are given in Table I, and Table II gives their gross composition according to classes.

TABLE I  
Overall Composition of Alberta Oil Sand Bitumens [5-7]

Fraction	Source*	%					H/C	mw
		C	H	N	O	S		
Whole Bitumen	A	83.98	10.22	0.65	1.97	4.57	1.46	620
	P	81.68	9.98	0.14	2.08	5.60	1.46	520
	C	83.93	10.46	0.23	0.94	4.70	1.49	490
	W	82.44	10.32	0.42	0.82	5.51	1.49	600
Asphaltenes	A	81.31	7.88	1.06	2.79	7.53	1.16	5,920
	P	79.87	8.15	0.78	2.08	8.82	1.21	3,500
	C	80.54	7.39	1.15	1.78	6.51	1.10	8,140
	W	80.46	8.20	0.99	1.16	8.40	1.21	5,760
Deasphalted Oil	A	84.38	10.63	0.07	0.87	3.91	1.51	435
	P	82.89	10.61	0.08	1.27	5.41	1.53	440
	C	84.19	11.01	0.27	0.61	3.89	1.54	430
	W	82.99	10.74	0.28	1.04	5.25	1.54	530

\* A=Athabasca, P=Peace River, C=Cold Lake, W=Wabasco bitumen.

TABLE II  
Gross Composition of Alberta Oil Sand Bitumens [5-7]  
% of whole bitumen\*

	Cold Lake	Athabasca	Peace River	Wabasca
Asphaltenes	15.3	16.9	19.8	18.6
Deasphalted oil	84	83.1	80.0	81.2
Acids	15.2	13.69	12.0	10.3
Bases	6.38	6.5	6.8	6.38
neutral N-compounds	1.15	1.35	1.41	2.67
Saturates	21.3	18.3	15.15	14.60
Monoaromatics	8.3	8.1	8.57	7.61
Diaromatics	3.6	3.8		
Polyaromatics+ non-defined polar compounds	24.35	23.8		
Thiopheno-aromatics from mono- and diaromatic fractions	0.8	0.88		

\*Bitumen = 100%

As indicated by these data and the results of computerized gc-ms multiple ion cross scans [8] and matrix analyses, the bulk and fingerprint composition of these bitumens are quite similar and the minor differences which appear seem to signify some subtle trends in diagenetic history.

The similarity in chemical composition points to a common origin for the four major oil sand deposits. The distribution pattern of steranes (C<sub>26</sub>, 5%; C<sub>27</sub>, 44%; C<sub>28</sub>, 33%; C<sub>29</sub>, 17%; C<sub>30</sub>, 1%) is reminiscent of the ratio obtained from the reduction of marine sterol mixtures and therefore suggests a marine origin. From microbiological model studies it can be concluded that AOSB is a microbiologically degraded residue. Microbiological simulation experiments showed that the end product of the microbiological degradation of a conventional oil is a bitumen-like material, low in paraffins and small ring, less alkylated aromatics and rich in polycondensed polyalkylated aromatics and polar materials, including asphaltene.

The Peace River and Athabasca bitumens seem to represent the end product of biodegradation. The Cold Lake bitumen contains slightly more paraffins, including small amounts of *n*-alkanes, and less asphaltene, and the Lloydminster heavy crude which is the least biodegraded material contains more paraffins and even less asphaltene.

The *n*-paraffins of the Cold Lake bitumen range from C<sub>13</sub> to C<sub>33</sub> with a maximum at C<sub>19</sub> and a carbon preference index of 1.0. The isoprenoid fraction contains both pristane and phytane along with lower and higher mw homologues of the series.

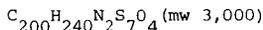
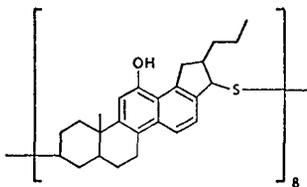
The gc-ms fingerprint spectra of the hopane series in all the oil sand bitumens showed the presence of the 17 $\alpha$ (H), 21 $\beta$  isomer of C<sub>27</sub>, C<sub>29</sub>-C<sub>35</sub> hopanes with a maximum at C<sub>30</sub>. Both C<sub>22</sub> diastereoisomers were present in approximately equal quantities. Living organisms synthesize the 17 $\beta$ (H), 21 $\beta$  isomer and the high conversion to the 17 $\alpha$ (H), 21 $\beta$  isomer is indicative of some geothermal history of the oil sand, although the role of the mineral matter as a catalyst for the isomerization cannot be readily assessed.

Steranes and hopanes comprise only a small fraction of the saturates, the bulk of which still has not been identified. The compositions of the other separated fractions, the acids, bases, neutral nitrogen compounds, olefins, mono, di and polycycloaromatics, etc., are not well established either at present, although recent gc-ms multiple cross scan and matrix analyses have yielded valuable estimates.

As was pointed out above, the combined microbiological simulation and chemical analytical studies leave little doubt as to the severity of microbial degradation which the oil sand bitumen has suffered, nonetheless the question of whether the oil sand bitumen is a primary degraded kerogen without a significant thermal history, similar in character to the precursors of conventional oils, or whether it is the microbiological end product of a conventional oil has not been settled unambiguously.

#### The Chemistry of Bitumen Asphaltene.

The asphaltene fraction of the Athabasca bitumen has recently been subjected to detailed chemical studies for the elucidation of its molecular structure [9]. Here the essential question was to establish the role of sulfur in the polymeric framework of the asphaltene molecule. It was possible to show that in the Athabasca asphaltene the sulfur is present largely in the form of sulfides holding together dicycloaromatic carbon units of average molecular formula



Two of these molecules are joined together by hydrogen bonding. In reality, asphaltene is a complex mixture of molecules with a broad distribution of molecular weight and with significant deviations in the structures of monomeric units from the average dicycloaromatic unit above.

Esr studies of the Athabasca asphaltene showed the presence of paramagnetic species, approximately one free spin per 80-90 molecules and most of the molecules carrying free spin appear to carry more than one [10-12]. The resonance at  $g=2.0036$  is thought to be associated with polycycloaromatic doublet radicals and singlet and triplet state diradicals. The relative distribution of these radicals can be influenced by temperature, the addition of paramagnetic gases such as  $O_2$  and  $NO$ , and by other means. The effects are reversible. Since the minimum degree of condensation required in a cycloaromatic system for the formation of stable free radicals is about six, it seems that at least 1.1% of the asphaltene molecules contain at least one hexacycloaromatic sheet.

After completion of the initial phase of these studies on the molecular structure of the Athabasca asphaltene, current research has been extended in three directions:

a) It appeared to be desirable to compare the elemental composition, mw and the number of sulfide linkages in the polymeric framework of various asphaltenes from different sources. The results suggest that Athabasca asphaltene contains the highest percentage of bridged sulfur, as will be shown in a separate article [13,14].

b) More precise information on the chemical nature of the monomeric units liberated in the reductive cleavage of the sulfur-carbon bonds or in the mild thermolysis of the asphaltene will be obtained using a combination of hplc, gel permeation chromatography and organic geochemical microanalytical techniques.

c) Taking the synthetic approach, the feasibility of making asphaltene-like materials from simple or complex organic base materials by treatment with sulfur has been explored. In this way it was possible to prepare asphaltene-like materials with molecular weights approaching those of natural asphaltene in which the carbon monomeric units are joined together with sulfide linkages. Details of these studies will be given in another article [15].

#### Acknowledgements.

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#### References.

1. O.P. Strausz, K.N. Jha and D.S. Montgomery, Fuel, in press.
2. R.G. Draper and A. Yates, Fuels and Mining Practice Division, Ottawa Divisional Report FD 67/87-PGA, June, 1967.
3. T. Ignasiak, H. Sawatsky and D.S. Montgomery, Fuel Research Center, Ottawa, Mines Branch Investigation Report IR 69-42, April, 1969.
4. K.N. Jha and O.P. Strausz, Preprints, Symposium on Tar Sand and Oil Shale, Fuel Division, A.C.S., Meeting of A.C.S.-C.I.C., Montreal, May 29-June 2, 1977.
5. M.L. Selucky, Y. Chu, T. Ruo and O.P. Strausz, Fuel, in press.
6. M.L. Selucky, Y. Chu, T. Ruo and O.P. Strausz, Fuel, in press.
7. Y. Chu, M.L. Selucky and O.P. Strausz, to be published.
8. I. Rubinstein, O.P. Strausz, C. Spyckerelle, R.J. Crawford and D.W.S. Westlake, Geochim. and Cosmochim. Acta, in press.
9. T. Ignasiak, A.V. Kemp-Jones and O.P. Strausz, J. Org. Chem., 42, 312, (1977).
10. T.F. Yen and D.K. Young, Carbon, 11, 33 (1973).
11. S. Niizuma, C.T. Steele, H.E. Gunning and O.P. Strausz, Fuel, in press.
12. S. Niizuma, H.E. Gunning and O.P. Strausz, to be published.
13. T. Ignasiak, O.P. Strausz and D.S. Montgomery, Fuel, in press.
14. T. Ignasiak, A.V. Kemp-Jones and O.P. Strausz, Preprints, Symposium on Tar Sands and Oil Shale, Fuel Division, A.C.S., Meeting of A.C.S.-C.I.C., Montreal, May 29 - June 2, 1977.
15. A.V. Kemp-Jones and O.P. Strausz, *ibid.*

RECENT ADVANCES IN THE STUDY OF POTENTIAL KEROGEN  
PRECURSORS FROM RECENTLY-DEPOSITED ALGAL-MATS

R. P. PHILIP

Dept. of Chemistry and Laboratory of Chemical Biodynamics  
University of California, Berkeley, Cal. 94720

INTRODUCTION

The most abundant form of organic carbon on Earth is kerogen. It is commonly defined as the residual organic material remaining after minerals have been removed from a sample of shale or sediment with hydrochloric and hydrofluoric acids, after humic material has been removed with base, and after the soluble organic material has been removed by exhaustive extraction with organic solvents. It has been estimated that there are  $1.3 \times 10^{18}$  tons of kerogen on the Earth compared with  $1.5 \times 10^{15}$  tons of coal (1). Kerogen is generally found in sedimentary rocks in the form of oil shales. The best known, and most widely studied shale, the Green River oil shale, has been estimated to contain 8,000 billion barrels of oil currently in the form of kerogen (2). But in spite of its vast abundance, relatively little is known about the origin, structure, or method of formation of any type of kerogen. Tissot has classified kerogens into three general categories, i.e., a) humic-type kerogens, derived from higher plant material and generally aromatic in structure; b) algal-type kerogens derived from algae and generally aliphatic in structure; and c) kerogens which are intermediate between these two and are a mixture of algal- and humic-type materials (3).

Many attempts have been made to obtain structural information on kerogens using various chemical degradation techniques. These have included chromic acid and alkaline potassium permanganate oxidation, saponification with methanolic potassium hydroxide, reduction with lithium aluminum hydride, hydrogen bromide treatment and ozonolysis (4). Another widely-used technique in this type of study is pyrolysis. However, the major problems associated with all of these studies include: a) the lack of reactivity of kerogen with most reagents due to the fact that the degradation reactions are generally heterogeneous; b) the random nature of the degradation by some of these reagents; and c) the fact that some products are secondary degradation products. As a result of these problems any information obtained is usually not very structurally specific and only gives general information on whether a kerogen is aliphatic or aromatic in nature.

To say that there is one common solution to all of these problems is very misleading. However, valuable structural information could be obtained if: a) specific reagents for cleaving only one type of bond were used; or b) information was first obtained on the structure of potential kerogen precursors and the ways in which the precursors are involved in the formation of kerogen.

In an attempt to examine this latter line of approach and to get more structural information on algal-type kerogens, an investigation has been made into the structure of the insoluble organic residues isolable from recently-deposited algal ooze and from some pure cultures of green and blue-green algae. The major aim of the study was to determine whether or not there was any kerogen-like material in the sample of algal ooze; if so, what was its structure, and can it react to form the more complex kerogen moiety found in ancient shales and sediments; and finally if there was kerogen-like material in the algal ooze, can it be said that the basic "building blocks" of kerogens are actually in the organisms themselves prior to being deposited in the sedimentary environment?

To try and provide answers to some of these questions, a series of degradation

experiments, previously performed on ancient kerogens, were repeated on the insoluble organic residues from an algal ooze and some pure algal cultures. The sample of algal ooze for this study was obtained from Laguna Mormona, Baja California, in an environment where the sources of organic matter are well documented. The environment at Laguna Mormona is characterized by extreme local variations in sedimentological, geochemical, and biological properties (5). Semi-arid climatic conditions and restricted water movement from the ocean have combined to produce an evaporite flat and hyper-saline marsh environment. Large quantities of organic matter are slowly accumulating because of the high salinity which inhibits organisms that normally consume and degrade the organic material. The intertidal algal mats examined at Laguna Mormona are characterized by the blue-green algae *Microcoleus chthonoplastes* and *Lyngbya aestuarii*. Pure cultures of the blue-green algae *Phormidium luridium* and *Anacystis nidulans* were obtained from an earlier study by Han and McCarthy on the soluble lipid components of the same organisms (6).

This paper will describe results obtained from the degradation of the insoluble organic residue from the algal ooze using saponification, oxidation and pyrolysis. It will also summarize the results obtained from alkaline potassium permanganate oxidation of the pure cultures of the blue-green algae. As described above, these degradations were performed in an attempt to determine whether there were any apparent structural similarities between the algal ooze, the organisms and algal kerogens. The paper will also attempt to illustrate some of the major potential problems involved in trying to make molecular structure determinations of kerogens using these types of chemical degradations.

#### EXPERIMENTAL

The kerogen fraction was isolated from the sample of algal ooze in the same way as kerogen would be isolated from an ancient shale or sediment. This involved removal of carbonates and silicates by treatment with 6N HCl and 48% HF respectively, followed by exhaustive extraction of the remaining residue with toluene/methanol (1:1). No attempt was made to remove any pyrite from the residue with concentrated HNO<sub>3</sub> since this generally leads to the alteration of certain structural features of the kerogens. The residues from the pure cultures of algae were obtained by acid treatment of the cultures with 6N HCl followed by removal of the soluble organic material by extraction with toluene/methanol (1:1).

##### (i) Saponification.

The algal ooze residue was refluxed for three days with 0.5% KOH/MeOH. After termination of the reaction, the methanolic solution was decanted, acidified, and extracted with heptane and ethyl acetate. The extracts were combined, evaporated and subsequently methylated with BF<sub>3</sub>/MeOH (13% w/v). The methylated extracts were fractionated into normal and branched/cyclic fractions by urea adduction prior to analysis by gas chromatography (GC) and computerized-gas chromatography-mass spectrometry (C-GC-MS).

##### (ii) Oxidation.

a) Oxidative degradation of the algal ooze residue was performed using alkaline potassium permanganate and a method similar to that previously described by Ogner (7). The residue was subjected to three four-hour periods of oxidation, a total of twelve hours oxidation. After each oxidation, the reaction mixture was acidified and excess MnO<sub>2</sub> solubilized by addition of sodium bisulphite. The clear reaction mixture was extracted with heptane and ethyl acetate, the extracts combined and methylated using BF<sub>3</sub>/MeOH (13% w/v). The methylated extracts were fractionated into normal and branched and cyclic fractions by urea adduction prior to analysis by GC and C-GC-MS.

b) The residues from the algal cultures were oxidized in the same manner as described in (a) except that only one four-hour oxidation period was required to

totally degrade the residue.

(iii) Pyrolysis.

The pyrolysis experiment was performed by initially heating the algal ooze residue in a quartz tube for 5 min. at 200°C to remove any unbound soluble lipid material, and then increasing the temperature to 600°C for 30 mins. The pyrolysate was collected in a U-tube using a liquid nitrogen trap. When the reaction had been terminated, the products were dissolved in ethyl acetate and transferred from the U-tube to a small vial, the solvent removed and the crude pyrolysate weighed. The pyrolysate was subsequently filtered through an alumina column and fractionated into a non-polar (heptane eluate) and a polar fraction (ethyl acetate eluate). The heptane fraction was further purified by thin-layer chromatography and urea adduction prior to analysis by GC and C-GC-MS.

(iv) Analytical Procedures.

GC analyses of the various degradation products were performed on a Varian 2700 GC equipped with a flame ionization detector and a 15' x 0.03" i.d. glass column packed with Dexsil 300 coated on Gas-Chrom Q. Helium was used as carrier gas with a flow rate of 12 ml/min and temperature conditions were: oven temperature 70 to 280°C, programmed at 6°/min; injector temperature 280°C and detector temperature 250°C.

C-GC-MS analyses were performed using a DuPont 491-2 double-focussing mass spectrometer coupled directly to a Varian Aerograph 204 gas chromatograph. A glass capillary column, 22' x 0.03" i.d., packed with Dexsil 300 coated on Gas-Chrom Q was used for the analyses; oven temperature: 90 to 280°C, programmed at 6°/min. Data were continually acquired during the C-GC-MS analyses using a DuPont 21-094 data system.

#### RESULTS AND DISCUSSION

Saponification of the algal ooze residue provided some specific information on the types of compounds attached to the residue as esters. The normal fraction was dominated by the n-C<sub>16</sub>, n-C<sub>18</sub> and C<sub>18</sub>:1 carboxylic acids with the latter two in a 1:1 ratio. Other normal acids were present in the C<sub>12</sub>-C<sub>32</sub> range in relatively minor proportions. The branched and cyclic fraction was dominated by a cyclopropyl-C<sub>19</sub> acid, and phytanic and pristanic acids. The distribution of these fatty acids is similar to that observed in the soluble lipid fractions from other samples of these algal-mats and oozes which have been examined and also other Recent sediments (8,9, 10). However, there is not a great deal of similarity between these products and those obtainable from saponification of ancient kerogens. One plausible explanation for this is that, with increasing time, additional lipid material becomes complexed to the insoluble residue. Alternatively, the material already linked to the residue can undergo structural alteration by either bacterial or geochemical effects during maturation.

Oxidation of the algal ooze residue, when performed in a stepwise fashion, produced mainly normal carboxylic acids and isoprenoid acids in the first step, but with increasing time gave rise to increasing amounts of  $\alpha,\omega$ -dicarboxylic acids and only small amounts of isoprenoid components as summarized in Table I. These results suggest that the normal and isoprenoid components are attached to the outer part of the kerogen nucleus and the  $\alpha,\omega$ -dicarboxylic acids result from degradation of a highly cross-linked nucleus in a similar manner to the degradation of ancient kerogens (11). Alternatively these degradation products may not be truly representative of the original kerogen structure at all but are formed by secondary degradation of the initial oxidation products. However, until more specific and less severe oxidizing reagents are found for use in this type of study, the above problem will never be completely eliminated. It is also noteworthy that the time taken to completely degrade the kerogen-like material from the algal ooze was only twelve hours compared to the ninety

Table I  
DISTRIBUTION OF OXIDATION PRODUCTS OBTAINED FROM DEGRADATION OF RESIDUE A

Oxidation Step	ADDUCTED PRODUCTS						NON-ADDUCTED PRODUCTS
	$\alpha, \omega$ -Dicarboxylics		n-Carboxylics		Monomethyl-Carboxylics		
	Range <sup>1</sup>	Max.	Range	Max.	Range	Max.	
Step 1	9-16	11	11-31	16	13-19	15	Isoprenoid Acids <sup>2</sup>  C <sub>20</sub> , C <sub>16</sub> , C <sub>19</sub> , C <sub>17</sub> , C <sub>15</sub> , C <sub>13</sub>
Step 2	8-14	11	10-28	16, 18	12-18	15	
Step 3	6-15	8	14-20	Minor amounts only	-	-	

<sup>1</sup>Carbon number range

<sup>2</sup>Arranged in decreasing order of abundance

hours required to completely degrade the kerogen from the Green River oil shale (11). This again illustrates the less complex nature of this immature kerogen-like material compared to that from ancient kerogens.

Pyrolytic degradation of the insoluble organic residues from the algal oozes and ancient kerogens is of little use in obtaining specific structural information on the residues. It is of use in classifying kerogens as algal or humic depending on whether aliphatic or aromatic compounds respectively are the dominant products of pyrolysis. The hydrocarbons obtained from the pyrolysis of the algal ooze residue used in this work were predominantly aliphatic, confirming that algal kerogen-precursors have an aliphatic type of structure. The major products were homologous series of n-alkanes and n-alkenes in the range C<sub>15</sub>-C<sub>34</sub> with a C.P.I. =1, and one isomer of pristene (C<sub>19</sub>H<sub>38</sub>) plus three phytene isomers (C<sub>20</sub>H<sub>40</sub>) and minor amounts of phytadiene (C<sub>20</sub>H<sub>38</sub>). The distributions of the products were similar to those obtainable from the pyrolysis of mature kerogens which again supports the theory that there are structural similarities between these kerogen-precursors and ancient algal kerogens.

In work published elsewhere, results from the comparative pyrolytic degradations of several different algal residues has been reported (12). In that study significant differences between the distributions of the cyclic hydrocarbons from the various residues were observed. Pyrolysis coupled with microscopic examination of the residues, should be a valuable technique for correlating source material with structural information.

It is clear from these three degradation studies that there are structural similarities between the algal ooze residue and ancient algal kerogens. The oxidation studies on the insoluble organic residues from the blue-green algae produced results which enable this statement to be extended to say that there are structural similarities between the organisms, the algal ooze residue and the ancient algal kerogens. This is based on the fact that the major oxidation products from the Phormidium luri-dium residue were  $\alpha,\omega$ -dicarboxylic acids (range C<sub>7</sub>-C<sub>10</sub>; max. C<sub>9</sub>) with minor amounts of n-carboxylic acids (range C<sub>11</sub>-C<sub>16</sub>; max. C<sub>12</sub>), and from the Anacystis nidulans residue,  $\alpha,\omega$ -dicarboxylic acids (range C<sub>7</sub>-C<sub>12</sub>; max. C<sub>9</sub>) and equal amounts of n-carboxylic acids (range C<sub>11</sub>-C<sub>18</sub>; max. C<sub>14</sub>).

#### CONCLUSIONS

The work described above has shown by various chemical degradation techniques that there are structural similarities between the insoluble organic residues from blue-green algae, algal oozes, and ancient algal-type kerogens. The conclusion is based on similarities between the degradation products obtained from the insoluble organic residues. Further work is now required using the insoluble organic residues from the algal oozes to explore new and specific types of degradation reagents. More emphasis needs to be placed on using reagents which are known to cleave specific linkages, such as ether linkages, to obtain larger molecular fragments from the degradation. These larger fragments, although less volatile, could be examined initially using high pressure liquid chromatography, gel permeation chromatography, ultra-violet, or infra-red spectroscopy, which should give valuable information as to their structure. After this initial examination the fragments could be mildly and specifically degraded, again, to give compounds more readily identifiable by GC and GC-MS.

It is clear that although these studies have demonstrated the presence of kerogen precursors in algae and algal-oozes, a great deal of work remains to be done in order to determine the exact origin of kerogen and the way in which it attains the degree of molecular complexity found in ancient sediments.

#### ACKNOWLEDGMENTS

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#### REFERENCES

- (1) Hunt, J. M., Bull. Am. Assoc. Petrol. Geol., 56, 2273, (1972).
- (2) Yen, T. F., In: Science and Technology of Oil Shale (T. F. Yen, ed.) pp. 1, Ann Arbor Science, Michigan, 1976.
- (3) Tissot, B., Durand, B., Espitalie, J., Combaz, A., Bull. Am. Assoc. Petrol. Geol., 58, 499, (1974)
- (4) Robinson, W. E., In: Organic Geochemistry, Methods and Results (G. Eglinton and M. Murphy, eds.), p. 629, Springer-Verlag, Berlin, 1969.
- (5) Vonder Haar, S. P., Geol. Soc. Amer. Abs., 5, 117, (1973).
- (6) Han, J., Calvin, M., Proc. Nat. Acad. Sci., 64, 436, (1969).
- (7) Ogner, J. G., Acta Chem. Scand., 27, 1601, (1973).
- (8) Cardoso, J., Brooks, P., Eglinton, G., Goodfellow, R., Maxwell, J. R., Philp, R. P., In: Environmental Biogeochemistry (J. O. Nriagu, ed.), pp. 149, Ann Arbor Science, Michigan, 1976.
- (9) Crarwell, P. A., Chem. Geol., 11, 307, (1973).
- (10) Eglinton, G., Maxwell, J. R., Philp, R. P., In: Advances in Organic Geochemistry, 1973 (B. Tissot and F. Bienner, eds.), pp. 941, Editions Technip, Paris, 1973.
- (11) Burlingame, A. L., Haug, P. A., Schnoes, H. K., Simoneit, B. R., In: Advances in Organic Geochemistry 1968 (P. A. Schenck and I. Havenaar, eds.), pp. 85, Pergamon Press, Oxford, 1968.
- (12) Philp, R. P., Calvin, M., Nature, 262, 134, (1976).

# THE OIL SANDS DEPOSITS OF ALBERTA: THEIR ORIGIN AND GEOCHEMICAL HISTORY

G. Deroo

Institute Français du Pétrole, 1 et 4 Avenue de Bois-Preau, Rueil Malmaison, France

T.G. Powell

Institute of Sedimentary and Petroleum Geology,  
3303-33rd Street N.W., Calgary, Alberta, T2L 2A7

## INTRODUCTION

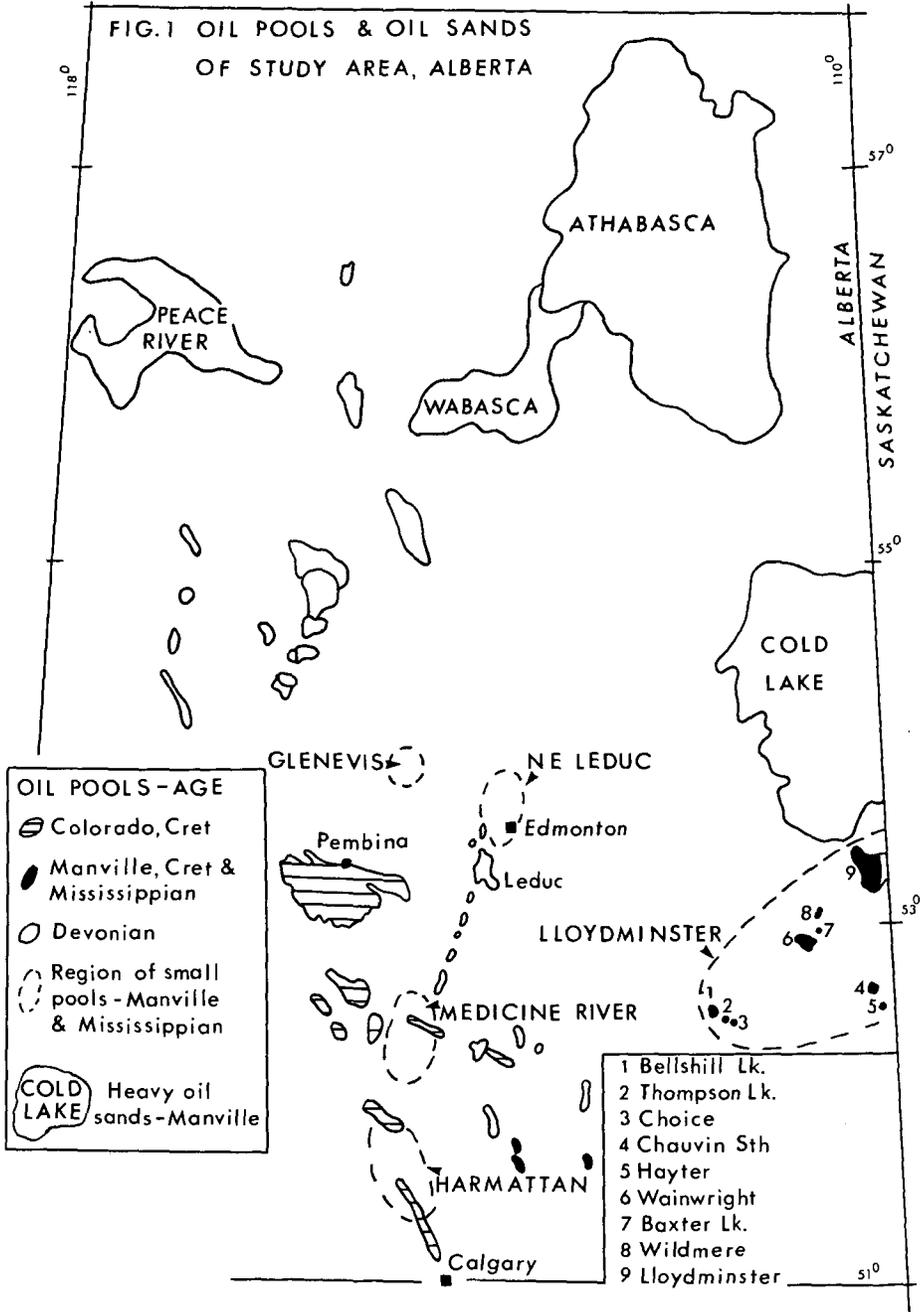
The heavy oil deposits and heavy conventional oils of eastern Alberta (Fig. 1) occur in various reservoirs within the Mannville Group of Lower Cretaceous age. The Mannville Group is separated from underlying rocks by a profound angular unconformity which allows strata of different ages to underlie the Mannville Group in different parts of the Alberta syncline. At Peace River the underlying rocks are of Mississippian, Permian and Jurassic age whilst at Athabasca, Cold Lake and Lloydminster the underlying rocks are various formations of Devonian age. Montgomery *et al.* (1) have summarized the various theories that pertain to the origin of heavy oil deposits of eastern Alberta. Briefly these theories are:

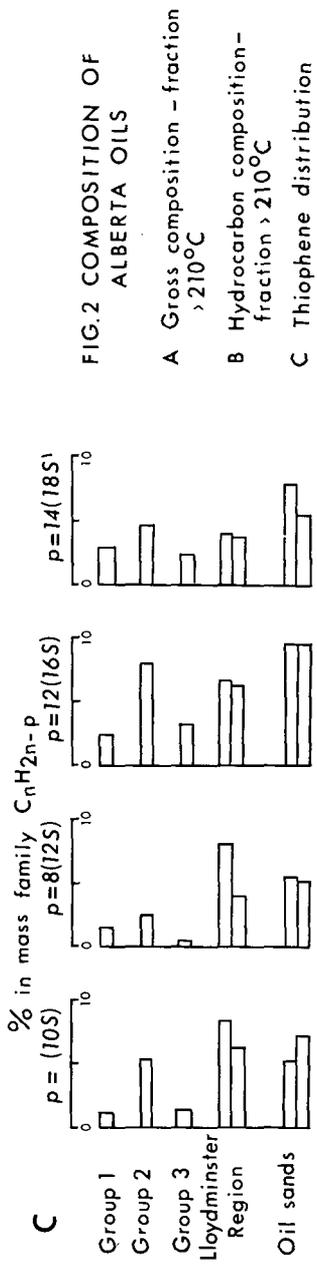
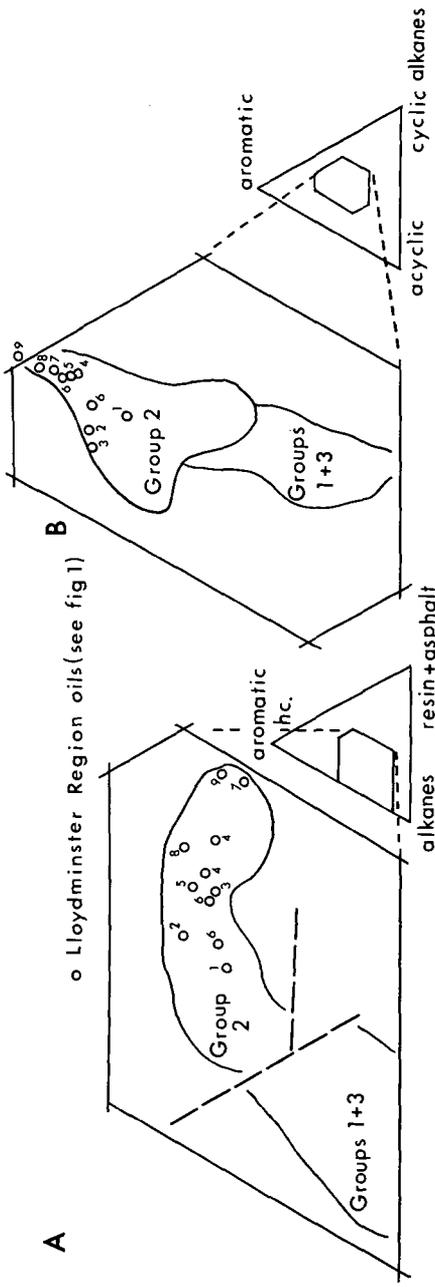
1. The heavy oils are conventional oils which have become altered by biodegradation and associated phenomena. They could have either a Devonian or a Lower Cretaceous source.
2. The heavy oils are young immature unaltered oils.
3. The heavy oils are derived from organic matter which was deposited *in situ* with the host sands.

In this report, evidence will be presented to show the chemical similarity of the heavy oils of the Lloydminster area and the heavy oil deposits, to conventional oils occurring in the central part of the Alberta syncline. Secondly the effects of alteration, particularly biodegradation, will be demonstrated for both the conventional oils and the heavy oil deposits. Finally the geochemical processes which lead to the formation of heavy oils and oil sands will be examined by detailed comparison of the composition of normal and secondarily altered oils at various levels of thermal maturation. The techniques and samples employed in this study have been summarized by Deroo *et al.* (2, 3). Saturated hydrocarbons obtained from rock extracts and oils were examined by capillary gas chromatography and mass spectrometry. The distribution of monoaromatics, diaromatics, polyaromatics and thiophenic compounds were determined by capillary gas chromatography using both flame ionisation and flame photometric detectors and by mass spectrometry at a low ionisation potential (10eV).

## HEAVY OILS OF THE LLOYDMINSTER REGION

In the central part of the basin, oils (Group 2) reservoired in the Mannville Group (Lower Cretaceous) Jurassic and Mississippian are readily distinguished from the oils occurring in the Devonian (Group 3) and the Colorado Group (Lower to Upper Cretaceous) (Group 1) on the basis of their gross composition (Fig. 2). The oils occurring in the Mannville, Jurassic and Mississippian are richer in sulphur, aromatic hydrocarbons, resins and asphaltenes than either Groups 1 or 3 (Fig. 2). The high sulphur contents are reflected in the large amounts of benzothiophenes and dibenzothiophenes in the oils (Fig. 2) and the dibenzothiophenes have a characteristically wide distribution by carbon number (range C<sub>21</sub> to C<sub>30</sub>) (2, 3). Detailed analysis of rock extracts has shown that the Group 2 oils have their source in the fine-grained sediments of the Mannville Group. This correlation is based on the





distribution of the various mass families in the aromatic fractions and in particular the distribution of benzothiophenes and dibenzothiophenes (3).

The oils from the Lloydminster region which are reservoirized within the Mannville Group, have similar sulphur contents (above 2%) and are similar in composition to the Group 2 oils (Fig. 2). They are however, slightly richer in aromatic hydrocarbons, resins and asphaltenes than the majority of the oils and form a discrete group at the limit of the field of composition of the Group 2 oils. However, within the Lloydminster region there is considerable variation in the distribution of the saturated hydrocarbons. Gas chromatographic analysis reveals that a number of samples have undergone biodegradation i.e. the n-alkanes have been partially or completely removed by bacterial activity. This can be appreciated by comparison of the ratio of pristane and phytane to the C<sub>17</sub> and C<sub>18</sub> normal alkanes in the different oils. The oils with ratios below 0.60 are unaltered, namely Bellshill Lake, Thompson Lake, Choice and Wainwright (Lloydminster Fm.). Those with ratios between 0.60 and 1.00 have had some n-alkanes removed, namely Wainwright (Wainwright Fm.). A ratio of 1.00 corresponds to the type a stage of biodegradation previously defined (2) for the heavy oil extracts (Fig. 3). Ratios between 1.00 and 2.00 (Baxter Lake, Chauvin South - Sparky Fm.) demonstrate the progressive renewal of n-alkanes. Finally in the Wildmere and Lloydminster samples only the isoprenoids remain and are equivalent to the type b level of biodegradation in the heavy oil extracts (Fig. 3).

Biodegradation of the saturated hydrocarbons has occurred in the Mannville oils between the Wainwright, David and Lloydminster pools but it has not affected those from Bellshill Lake, Thompson Lake and Choice lying to the southwest (Fig. 1). The alternate theory (1) that an immature unaltered oil (Lloydminster) has undergone cracking reactions to yield oils with n-alkanes (Thompson Lake, Bellshill Lake and Choice) is untenable for the following reasons.

- (1) The oils lie at closely similar depths 2500 ± 500 feet which is insufficient for any marked maturation difference.
- (2) Independent indicators of thermal maturation such as moisture contents and vitrinite reflectance values of coals indicate little maturation variation (4).
- (3) The progressive change in n-alkane content relative to isoprenoids is explained on the basis of biodegradation but is not explained by a thermal maturation theory.

Mass spectrometric evidence from two oils (Choice and Lloydminster) indicates a close similarity to the Group 2 oils but they contain a higher proportion of monoaromatic steroids and triterpenoids than the oils from the central part of the basin.

#### HEAVY OIL DEPOSITS

Evidence showing the progressive biodegradation of the heavy oil extracts between Bellshill Lake and the heavy oil deposits at Athabasca has been presented previously (2). The stages in the transformation are illustrated in Figure 3 with type examples. Type a is illustrated by the Edgerton sample in which there is a decrease in the n-alkane content with an apparent increase in the proportion of isoprenoid compounds. Type b oils are those in which the n-alkanes have disappeared totally but pristane and phytas are relatively unaffected. Type c extracts contain no normals or isoprenoids. The coincidence of alteration with the occurrence of relatively fresh water in the reservoirs and the selective removal of first the n-alkanes and then the isoprenoids support the biodegradation theory.

It is evident from the distribution of the cyclo-alkanes that the heavy oil deposits resemble the Group 2 oils (2). The same conclusions have been reached

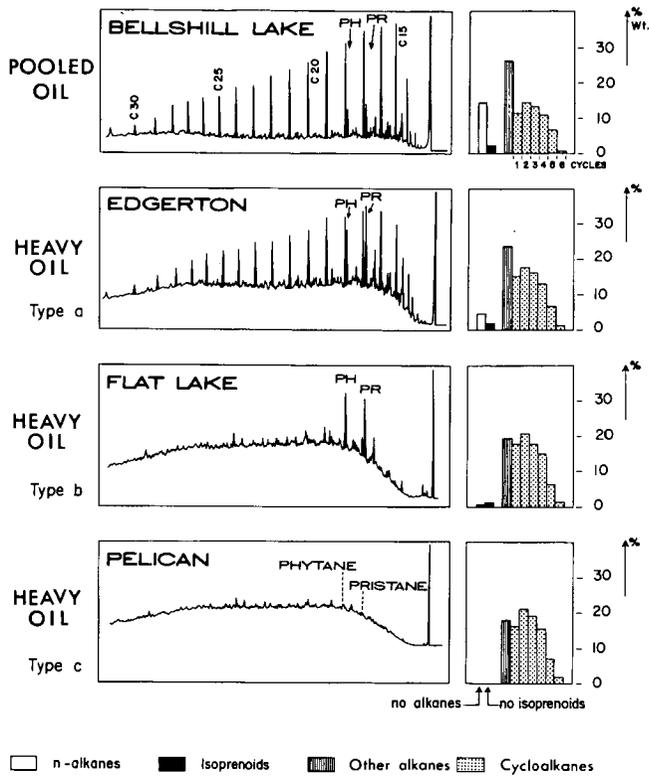


FIG 3 EFFECTS OF BIODEGRADATION ON NORMAL AND ISOPRENOID ALKANES IN OIL SANDS

when one considers the distribution of aromatic hydrocarbons and sulphur compounds as determined by capillary gas chromatography (2) and mass spectrometry (Fig. 3). The characteristic features are the importance of the thiophenes particularly the dibenzothiophenes in the range  $C_{21}$  to  $C_{35}$  in the mass families  $C_nH_{2n-16}S$  and  $C_nH_{2n-18}S$  and the higher concentration of these families than the phenanthrene family ( $C_nH_{2n-18}$ ) is the polyaromatic fraction.

#### PROCESSES LEADING TO THE FORMATION OF HEAVY OIL DEPOSITS

On the basis of the foregoing discussion one would suppose that the higher sulphur, resin and asphaltene contents of oils in the Lloydminster region might be solely a consequence of concentration brought about by alteration processes. This is not exclusively the case since the unaltered oils in this region (Wainwright, Thompson Lake, Choice and Bellshill Lake) have resin and asphaltene contents which are higher than many unaltered oils in the Mannville from the central part of the basin (Fig. 2). The question is put in perspective if we examine the distribution of reserves of Group 2 oils against an independent measure of maturity such as vitrinite reflectance (Fig. 4).

It is evident that the Lloydminster oils occur at a relatively low maturation level compared with the remainder of the oils in the central part of the basin. In addition in the Lloydminster region the content of steroids and triterpenoids ( $C_{25}$  and above) in the mass families  $C_nH_{2n-12}$  and  $C_nH_{2n-14}$  is higher than in the unaltered oils to the west and is indicative of a maturation trend across the basin. In Figure 5 the maturation trend across the basin is illustrated by variations in gross composition of oils which occur in the Mannville Group. There is a progressive decrease in resin, asphaltene and aromatic hydrocarbon content towards the west. However, at each stage of maturation there is an enrichment in resins and asphaltenes in certain oils. In the Lloydminster region this is attributed at least in part to biodegradation whereas in the central part of the basin it occurs where oil from the Mannville crosses the pre-Cretaceous unconformity into underlying formations (Mississippian or Devonian).

In order to distinguish the effects of alteration relative to thermal maturation, it is necessary to examine these effects in restricted areas within which variations in maturation levels are minimal. For this purpose detailed examination of the aromatic fractions of a series of oils has been undertaken in areas where the geothermal gradient is relatively constant. The relative stages of maturation within these areas can be distinguished by consideration of the maximum depth of burial.

The effects of alteration on the aromatic fraction can be summarized as follows:

1. In the mass family  $C_nH_{2n-8}$  there is a shift in the mode to higher carbon numbers.
2. In the mass families  $C_nH_{2n-12}$  and  $C_nH_{2n-14}$  there is an overall enrichment, particularly in the range above  $C_{20}$  or  $C_{25}$  in the former family.
3. In the diaromatics of the families  $C_nH_{2n-12}$  and  $C_nH_{2n-14}$  there is
  - (a) a decrease in the total percentage
  - (b) a decrease in the mode or/and
  - (c) a displacement of the mode to higher carbon numbers
4. In the thiophene families  $C_nH_{2n-10}S$ ,  $C_nH_{2n-12}S$  and  $C_nH_{2n-18}S$  there is
  - (a) an increase in their concentration
  - (b) an enrichment in the higher carbon number ranges ( $C_{20}$  and above) accompanied by/or -
  - (c) a decrease in the concentration of compounds in below  $C_{20}$ .

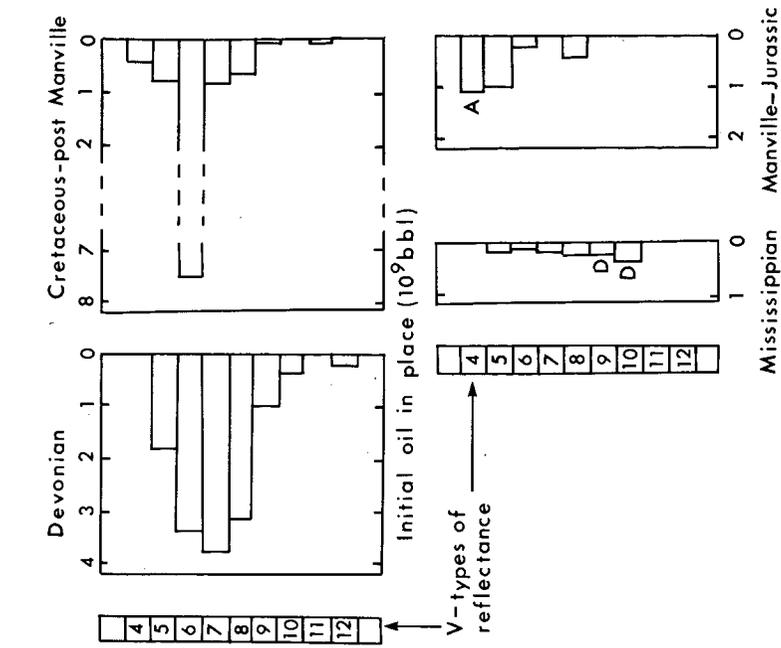


FIG. 4 RELATION BETWEEN OIL DISTRIBUTION AND MATURATION LEVEL (after Hacquebard)

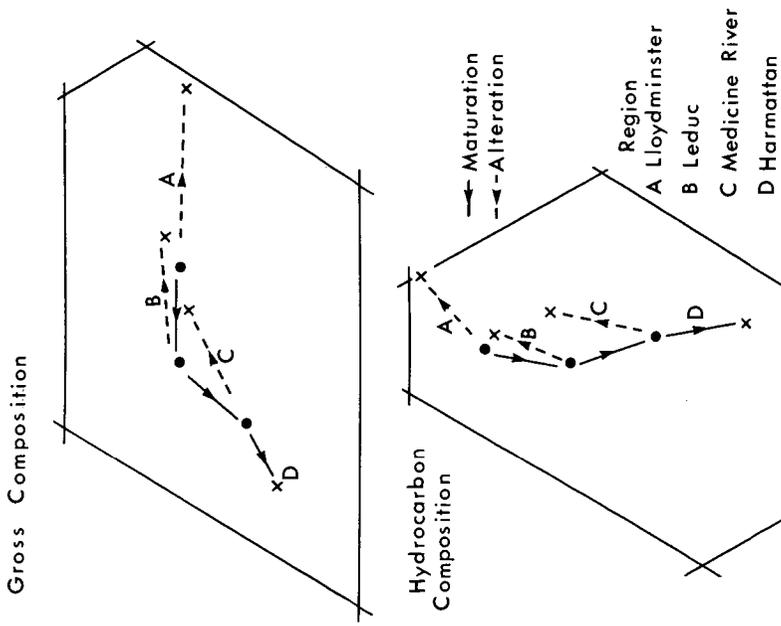


FIG. 5 EFFECTS OF MATURATION AND ALTERATION ON OIL COMPOSITION (GROUP 2) (see fig 2 for key)

In this context the term alteration is used to designate both the consequences of secondary migration and bacterial degradation, water washing and inorganic oxidation. These processes are examined in successive maturation zones.

Zone 1 Geothermal Gradient 30°C per 1000 m. This zone includes the oil pools adjacent to the Foothills and the Glenevis region. In the Medicine River region the Jurassic and Mississippian oils have a shallower depth of burial than the from the Mannville because of the structural position of the pools. They have variations 1, 3a and b, in comparison with the Mannville oil and they have a higher content of benzothiophenes (Fig. 6A). The Mississippian and Jurassic oils at Medicine River are in reservoirs of similar depths of burial and have similar gas to oil ratios (GOR) which are lower than that for the Mannville reservoir. The observed variations are considered to be due to secondary migration of the more mobile compounds. The oils in the Jurassic and Mississippian are trapped beneath the pre-Cretaceous unconformity. Leakage of light components along the unconformity would explain the observed phenomena.

The Mississippian oils from Harmattan to the southwest of the Medicine River pools are clearly more deeply buried. The high distillate content, overall composition, (Fig. 5) distribution of n-alkanes, cyclic-alkanes and aromatic compounds (Fig. 5) indicate a higher degree of maturation than the Medicine River oil. However, as well as being richer in non-aromatics (Fig. 6A) than the previous oils it also shows variations 1, 3a and b for the mass families  $C_nH_{2n-12}$ . This anomaly can be explained by secondary migration of the more mobile components to higher reservoirs. In the Harmattan East field the oils in the Mannville reservoirs have a higher GOR than that in the underlying Mississippian.

The Mississippian oil from the Glenevis region lying to the north of the oils discussed above has been the least buried of oils from this zone. It shows variations 1, 2, 3a and b in the mass families  $C_nH_{2n-14}$ , a relative increase in the concentration of dibenzothiophenes beyond  $C_{10}$  and a lower maturation state than the Medicine River oils. Thus within this zone the oils of the Glenevis region have undergone least maturation whilst that from Harmattan East has suffered the most maturation. This conclusion is consistent with the palaeotemperatures derived from coal rank studies (4). The estimated palaeotemperature of pools in the Glenevis region is 76°C whilst those at Medicine River and Harmattan East are 111°C and 127°C respectively. Oils occurring in Mississippian and Jurassic reservoirs have been affected by secondary migration; the lighter hydrocarbons have probably escaped from the reservoirs along the unconformity leaving in place the less mobile components.

Zone 2 Geothermal Gradient 40°C per 1000m. This zone includes most of the oils in production and contains altered oils such as Lloydminster or unaltered oils as at Leduc and Pembina. It also includes heavy oil extracts which may be altered or unaltered.

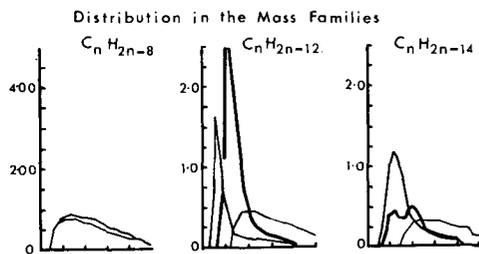
The Pembina sample (Fig. 6B) which has been buried the deepest of this group, has characteristics similar to the Mannville sample from Medicine River. The latter is more deeply buried but occurs in a zone with a lower geothermal gradient. An oil from Leduc-Woodbend occurs in the Wabamun (Devonian) directly under the pre-Cretaceous unconformity. It shows varieties 1, 3a and b in the aromatic compounds and variation 4a in the thiophenic compounds (Fig. 6B). The oil occurring in the Wabamun Formation has a lower GOR than oils in the reservoirs above the unconformity in the same field. Here again, the variations can be attributed to secondary migration.

Impregnations consisting of concentrations of heavy fractures could be residues from migration, a product of alteration processes or could be an original unaltered oil. A heavy oil extract from the Wabamun at Golden Spike (adjacent to the Leduc

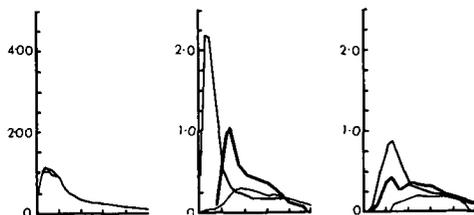
MEDICINE RIVER-HARMATTAN REGION

Geothermal Gradient 30°C/km

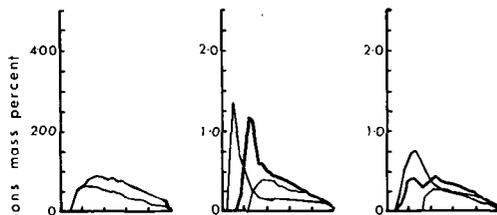
Pool; Harmattan East  
Age; Mississippian



Pool; Medicine River  
Age; Mannville, L. Cret.

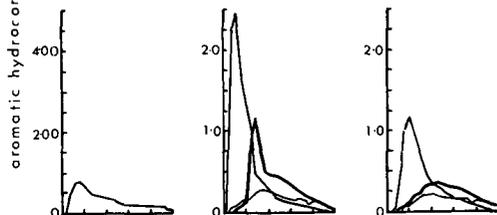


Pool; Medicine River  
Age; Mississippian



PEMBINA-LEDUC REGION  
Geothermal Gradient 40°C/km

Pool; Pembina  
Age; Manville, L. Cret.



Pool; Leduc Woodbend  
Age; Wabomun, U. Devonian

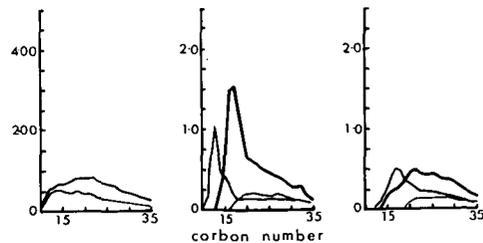
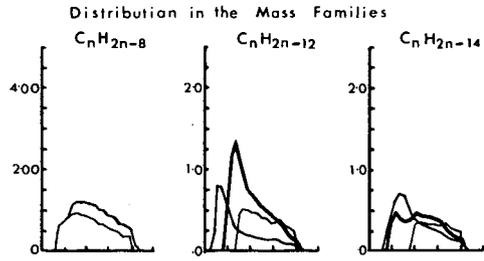


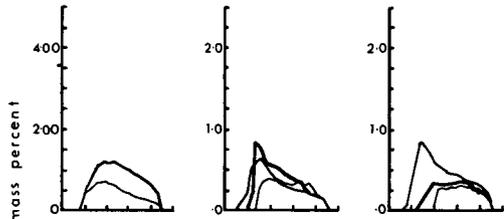
FIG 6 DISTRIBUTION OF AROMATICS IN GROUP 2 OILS AT VARIOUS MATURATION LEVELS

LLOYDMINSTER REGION  
 Geothermal Gradient 40°C/km

Oil sand; Edgerton  
 Age; Mannville, L. Cret.

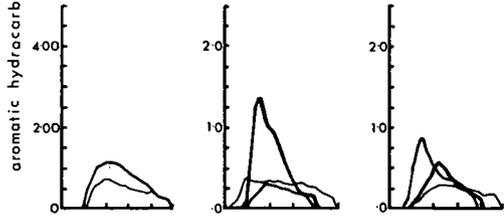


Pool; Lloydminster  
 Age; Mannville, L. Cret.

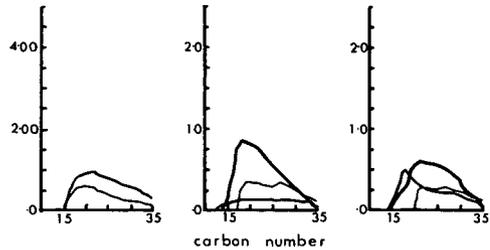


ATHABASCA REGION  
 Geothermal Gradient unknown

Oil sand; Marten Hills  
 Age; Mannville, L. Cret.



Oil sand; GCOS Plant  
 Age; Mannville, L. Cret.



— monoaromatics    — diaromatics    — polyaromatics

FIG 6 continued

field) is very similar to the Wabamun oil at Leduc Woodbend discussed above. It is considered to be a residue left from secondary migration. A heavy oil extract from Edgerton (Mannville) Figure 6C closely resembles the Golden Spike extract. Although less deeply buried, the Edgerton sample can only be  $C_nH_{2n-8}$  distinguished from the Golden Spike sample by its higher content of monoaromatic (mass families  $C_nH_{2n-12}$  and  $C_nH_{2n-14}$ ) particularly the steroid and triterpenoid compounds above  $C_{25}$ . The difference can be attributed to the lower degree of maturation of the former. The Edgerton and Golden Spike samples tend to contain few light monoaromatic compounds ( $<C_{20}$ ) in the mass family  $C_nH_{2n-8}$  and even less in the families  $C_nH_{2n-12}$  and  $C_nH_{2n-4}$ ; this is probably the result of secondary migration.

The heavy oil from the Lloydminster pool is in its turn compared with the Edgerton sample (Fig. 6C) since the geothermal gradient and depths of burial are similar. The relative importance of the monoaromatics beyond  $C_{25}$  in the mass families  $C_nH_{2n-12}$  and  $C_nH_{2n-14}$  can be interpreted as due to a low degree of maturation, but the effect of concentration due to alteration must be considered. The effects of alteration are shown in the aromatic and thiophenic compounds by variations 1, 3c, 4b and c. These changes are greater than those attributed solely to secondary migration. A certain degree of alteration of the aromatic fraction accompanies the bacterial removal of n-alkanes in the saturate fraction (Type b). This alteration is attributed to water washing of the relatively soluble aromatic compounds, to inorganic oxidation of weakly soluble or insoluble compounds and/or possibly the biodegradation of some benzothiophenes.

Zone 3 Unknown Geothermal Gradient. This part concerns the heavy oil deposits in the most northerly part of the study area (Fig. 1). The present geothermal gradients are unknown but the burial depths are estimated to be equivalent to those of the preceding samples; this assumption is supported by the parallel significance of the heavy monoaromatics ( $C_{25+}$ ) in the families  $C_nH_{2n-12}$  and  $C_nH_{2n-14}$  (Fig. 6D).

The aromatics from the Marten Hills sample (type b biodegradation) show the same alteration effects observed in the Lloydminster oil and are attributed to water washing and inorganic oxidation. The sample from the GCOS Plant has the most degraded saturated hydrocarbons (type c). The same changes occur with regard to the aromatics as were observed in the Marten Hills and Lloydminster oils but variation 3c is particularly significant. This sample represents the most advanced stage of alteration of the aromatics by water washing and inorganic oxidation.

### Summary

The heavy oil deposits and the heavy conventional oils of eastern Alberta resemble the conventional oils reservoir in Lower Cretaceous (Mannville) sediments in the central part of the basin and as such differ in origin from the Devonian oils. They are, however, relatively less mature than the contemporaneous oils to the west. Although their relative immaturity can partially account for their heavy character, secondary processes such as biodegradation, water washing, secondary migration of light components and possibly some inorganic oxidation results in the concentration of heavy ends with the ultimate formation of solid bitumen.

Comparative analyses of the aromatic hydrocarbons of the Group 2 oils allows the relative significance of maturation and alteration to be assessed as follows:

1. In the main oil field area, all oils located beneath the unconformity (Jurassic, Mississippian or Devonian) are altered as a result of secondary migration of the lightest components from the reservoir to vertically or laterally higher reservoirs. The geochemically defined

maturation state of the oils in zones with comparable geothermal gradients correspond well to their respective depths of burial.

2. In the heavy oil zone, to the north of the main field area, all oils have undergone less maturation than the preceding oils. In addition to the effects of secondary migration, the aromatics from these oils have undergone degradation by water washing and inorganic oxidation which are associated with the biodegradation of the alkanes. These effects are at a maximum in the reservoirs closest to the Cretaceous unconformity even if the biodegradation of the normal alkanes has not reached the most advanced stage. In all probability, the unconformity corresponds to an aquifer and controls the distribution and alteration of hydrocarbons in its vicinity.

#### LITERATURE CITED

1. Montgomery, D.S., Clugston, D.M., George, A.E., Smiley, G.T. and Sawatzky, H., Can. Soc. Petroleum Geol. Mem. 3, 168 (1974).
2. Deroo, G., Tissot, B., McCrossan, R.G. and Der, F., Can. Soc. Petroleum Geol. Mem. 3, 148 (1974).
3. Deroo, G., Powell, T.G., Tissot, B. and McCrossan, R.G., Geol. Surv. Can. Bull. 262 in press.
4. Hacquebard, P.A., Geol. Surv. Can. Bull. 262 in press.

## MICROBIAL EXTRACTION OF BITUMEN FROM ATHABASCA OIL SAND

BY

J. E. Zajic and D. F. Gerson  
Biochemical Engineering  
The University of Western Ontario  
London Canada

### INTRODUCTION

In the 1950's the Department of Mines and Technical Surveys in Canada (now Energy, Mines and Resources or EMR) undertook a variety of investigations pertaining to the recovery of bituminous values from Athabasca tar sand using a cold water, solvent-surfactant approach. In addition to a pilot plant operation (1), studies were made by Montgomery and co-workers (2) on the effects of approximately 60 wetting agents in a laboratory scale cold-water, solvent-surfactant extraction of bitumen from Athabasca tar sand. One conclusion from these studies was that surfactants with HLB (hydrophilic-lipophylic balance) values (3) of 6-8 were most useful in terms of producing a bituminous extract which was free of water and clay while also resulting in a high overall yield. The cold-water, solvent-surfactant process for tar sand extraction has several potential advantages over present hot-water extraction technology. These include a reduction in the dispersion of clay particles (with a concomitant reduction in effluent disposal problems), and a reduction in the energy required for the extraction step (although the total energy budget of an extraction plant depends on the final design of all components.

Microbes (bacteria, fungi) are known to utilize hydrocarbon substrates such as kerosene or components of crude oil as a primary source of carbon for growth and metabolism. The solubility of most hydrocarbons in water or microbial growth media is usually negligible, and it appears that many hydrocarbonoclastic microorganisms overcome this limitation to the availability of their primary foodstuff by producing extracellular materials which adsorb, emulsify or wet the hydrocarbon phase, in order to increase contact area and to produce sub-micron droplets which can be phagocytized (4). Certain microorganisms produce surface active materials in the absence of hydrocarbons, such as *Bacillus subtilis* which produces subtilysin and of course, many biological lipids are surface active.

Recently, we have been studying the production of surface active agents by hydrocarbonoclastic microbes (5,6,7,8) and the utility of these agents in the cold-water extraction of Athabasca tar sand (9). In these studies, approximately 80 microbial cultures which were isolated from a variety of natural environments and which are capable of utilizing hydrocarbons as their primary carbon source were screened for growth rate, genetic stability and surfactant production.

Crude preparations of microbial surfactant were tested for their ability to stimulate the separation of bitumen from the mineral matter in a variety of samples of Athabasca tar sand. Within the scope of the test system which has been developed, microbial surfactants act as successful tar sand separation agents and are comparable in effectiveness with synthetic surfactants while holding the promise of reduced production costs through continuous production from a hydrocarbon feedstock in a single processing step.

## EXPERIMENTAL

### Microbiological and Chemical

Pure strains of microbes were cultivated in a mineral salts medium (pH 7.0) containing  $\text{NaNO}_3$  (2%),  $\text{K}_2\text{HPO}_4$  (1%),  $\text{KH}_2\text{PO}_4$  (0.5%),  $\text{KCl}$  (0.1%),  $\text{MgSO}_4$  (0.05%),  $\text{CaCl}_2$  (0.01%),  $\text{FeSO}_4$  (0.01%), ethylenediamine tetraacetic acid (0.001%), kerosene (Imperial Oil Number 9 refined oil (4%)) plus vitamins and minerals as needed by the various strains. Growth was studied either in 50 ml of the above medium in 500 ml shake flasks (rotated at 200 rpm with a 1.5" eccentricity) or in a New Brunswick 28 litre fermentor. Plate counts were used to determine viable cell number and biomass was considered to be that material which was retained by a 0.22 $\mu$  pore diameter Millipore filter. Certain bacteriological identification tests were performed using the API-20 and API-50 test systems. (API Laboratory Products, 4008 Cote Vertu, St. Laurent, P.Q. H4R 1V4 ).

The surface tension of fermentation broth or solutions of crude surfactant was measured with a Fisher surface tensiometer (Autotensiomat) and is taken as the maximum of the stress-strain curve. Critical micelle concentrations (CMC) were measured and are expressed as follows: the surface tensions of a serial dilution series were measured and plotted as a function of the log of the concentration expressed as a percent of the original (%V/V). The concentration at which saturation occurs is the CMC. Critical micelle concentrations expressed in this way are an inverse measure of the concentration of surfactant in the fermentation broth or crude extract and have proven to be highly useful in the optimization of surfactant production. Emulsification was tested by violently mixing equal volumes of an aqueous surfactant solution and a liquid hydrocarbon, allowing the mixture to settle for 24 hours and recording the percent of the total volume occupied by emulsion. Droplet size has not been studied at this time.

### Tar Sand Extraction Test

In order to maximize the differentiation between the effects of various surfactants, tar sand was tested for extraction in a low shear test system. In this test, 5.0 g tar sand was placed in a 500 ml flask with 50 ml of the aqueous surfactant solution to be tested. This mixture was shaken as described above for 48 hours and quantitatively analyzed for bitumen separation from sand. The shaking procedure resulted in the fractionation of bitumen into 4 fractions (Figure 1): 1. Surface oil fraction, which was collected by mopping the surface with a siliconized (Siliclad, Clay-Adam) glass fibre filter paper; 2. Residual tar sand balls, which were collected on a 40 mesh screen; 3. Sand + Clay fraction, which was collected on Whatman # 41 filter paper; and 4. Emulsified bitumen which was extracted from the filtrate with toluene. The bitumen content

of each fraction was determined by extraction with toluene and taking the O.D. at 700 nm and referring to a standard curve. A summary of the bitumen distributed in control (no surfactant) tests is given in Table 1 (+ standard error of the mean of 10 observations).

TABLE 1

SUMMARY OF BITUMEN DISTRIBUTION FOLLOWING LOW SHEAR AQUEOUS  
EXTRACTION IN THE ABSENCE OF SURFACTANTS (Control values)

<u>FRACTION</u>	<u>TAR SAND SAMPLE 1</u>	<u>TAR SAND SAMPLE 2</u>
Original bitumen content	7.8 ± 0.3	10.2 ± 1.0
(%w/w) percent of total		
Bitumen in:		
(a) surface fraction (1) *	18.6 ± 0.3	0.6 ± 0.2
(b) residual fraction (2)	54.0 ± 5.0	97.7 ± 0.7
(c) sand + clay fraction	27.1 ± 3.8	1.3 ± 0.6
(3)		
(d) emulsified fraction	0.3 ± 0.2	0.4 ± 0.1
(4)		
Bitumen concentration in:		
(a) surface fraction (1)	100	100
(b) residual fraction (2)	30 ± 4.6	12 ± 1.8
(c) sand + clay fraction	3 ± 0.5	1 ± 0.3
(3)		

\* Numbers refer to fractions of Figure 1.

RESULTS AND DISCUSSION

Surfactant Production

Table 2 gives the surface tension and CMC of whole fermentation broth for 5 selected microbial cultures which utilize kerosene for growth. Surfactant production in both shake-flask and batch fermentations reaches a sharp peak early in the growth cycle for cultures 1 and 2

TABLE 2

<u>MICROBE</u>	<u>STRAIN</u>	<u>MINIMUM SURFACE TENSION (dynes/cm)</u>	<u>CMC (% OF WHOLE BROTH)</u>
1. <i>Corynebacterium</i> sp	OSGB1	28	0.05%
2. <i>Pseudomonas</i> , sp	Aspha 1	31	6%
3. <i>Candida lipolytica</i>	GA	33	90%
4. <i>Vibrio</i> , sp.	Chry-B	65	100%
5. <i>Corynebacterium</i> , sp	CD1	32	0.5%

The most generally useful technique for recovering the surface active components has been extraction by exhaustive emulsification. In this method, whole fermentation broth is first centrifuged (10,000 Xg, 15 min.) to remove cells and is then mixed with an equal volume of kerosene or hexadecane and shaken violently. The resulting mixture separates into aqueous phase, an emulsion phase and a kerosene phase (certain cultures require dilution with distilled water). The emulsion is separated and mixed with more hydrocarbon and distilled water and the extraction is repeated; in addition, the aqueous phase is extracted with more hydrocarbon and the emulsion fractions are pooled. Following a triple extraction, the emulsion is lyophilized to give the crude product. Biochemical fractionation of this crude surfactant mixture is underway and indicates that there are several surface active components. Table 3 gives the CMC and surface tensions ( $\gamma$ ), interfacial tensions ( $\gamma_H$ , kerosene) spreading tensions ( $\gamma_S$ ) and Gibbs surface excess ( $\Gamma$ ) for 5 selected crude microbial surfactants. Spreading tension is directly related to HLB, although no attempt has been made to determine the HLB by other means. Emulsification as a function of the chain length of the emulsified hydrocarbon is given in Figure 2 for one of the microbial surfactants.

TABLE 3  
SURFACIAL PROPERTIES OF MICROBIAL SURFACTANTS AT THE CRITICAL  
MICELLE CONCENTRATION

MICROBE	CMC (% w/v)	$\gamma$ (dynes/cm)	$\gamma_H$ (dynes/cm)	$\gamma_S$ (dynes/cm)	$\Gamma$ (pMoles/cm <sup>2</sup> )
1	0.015	49	9	22	845
2	0.02	55	20	1	256
5	0.2	34	25	-15	673

Large scale (20 litre) production of microbial surfactant has been studied for Culture 1 and the results are given in Figure 3. The most remarkable feature of the fermentation is that surfactant concentration in the broth increases 100-fold over an approximately 5 hour period and then drops off to lower values. The meaning of this in terms of microbial growth is uncertain at this time, but it is correlated with maximum oxygen consumption, carbon dioxide formation, the formation of a yellow compound and the movement of the microorganisms from the aqueous to the hydrocarbon phase.

Crude microbial surfactants have been tested for toxicity using the *Daphnia magna* test system (10) and some of the results are given in Table 4. Microbial surfactants have in general proven to be a source of nutrition to the *Daphnia* and death rates in the absence of surfactant exceed those with surfactant, demonstrating a complete lack of toxicity at the concentrations tested (all are near the CMC). Results for several synthetic surfactants are included for comparative purposes.

TABLE 4

SURFACTANT	CONCENTRATION (ppm)	% MORTALITY ABOVE CONTROLS, 48hrs.
1	100	-10*
2	200	-4*
5	2000	65
Petrostep-A-50	900	100
Standamid	1050	100
Unamide JJ-35	100	100

\* Greater survival rate than controls

#### Tar Sand Extraction

Table 5 gives the tar sand distribution results for 5 selected cultures. In these tests, tar sand was treated with a 0.02% solution of whole microbial broth for 48 hours. Two effects predominate: either (1) the microbial surfactant induces the release and flotation of bitumen as a surface slick or floating droplets, or (2) the microbial surfactant enhances the ablation of clean sand and clay particles from the tar sand balls, resulting in tar balls of increased bitumen concentration. The latter effect was noted and studied by Imperial Oil (11) and their process, which lacked surfactants, is termed sand reduction. The flotation of bitumen is given as the percent of total bitumen in the surface fraction and the effect of sand reduction is given as the bitumen concentration in the residual tar sand. All of these microbial surfactants compare favourably with the synthetic surfactants, especially if one considers that the synthetic surfactants are pure, while the microbial surfactants are present only as a small percentage of the total crude extract.

TABLE 5  
TAR SAND SEPARATION BY 0.02% (v/v) WHOLE FERMENTATION BROTH CONTAINING  
MICROBIAL SURFACTANTS

MICROBE	BITUMEN DISTRIBUTION FOLLOWING LOW SHEAR TREATMENT OF TAR SAND (SAMPLE 2)				BITUMEN CONCENTRATION IN 4
	1	2	3	4	
1	0.6	96.9	2.1	0.4	17.9
2	3.7	85.9	10.1	0.3	17.0
3	3.6	95.7	0.6	0.1	34.9
4	2.7	94.5	2.5	0.3	18.4
5	1.3	97.5	0.9	0.3	25.7
Petrostep-A-50	0.0	93.0	0.0	7.0	15.7

#### CONCLUSIONS

Microbial surfactants provided by hydrocarbon fermentations are effective in tar sand separation by a cold-water process, and compare well with synthetic surfactants in their ability either to cause flotation of the bitumen or to cause ablation of sand and clay from the bitumen. The usefulness of these surfactants in a solvent-surfactant, cold-water extraction process is under study and

preliminary results indicate that these surfactants cause increased yield in a laboratory-scale extraction process. The surfactants have a high affinity for kerosene-water mixtures, which may result from biological selection for growth in such mixtures.

#### ACKNOWLEDGEMENTS

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#### LITERATURE CITED

1. Djingheuzian, L.E. and T. E. Warren, *Can. J. Res.*, 29, 170 (1951).
2. Montgomery, D.S. and M.P. Pleet, Canada Dept. of Mines and Technical Surveys, Mines Branch Report IR58-41 pp 24, (1958).
3. Griffin, W.C. *IN* Kirk-Othmer, "Encyclopedia of Chemical Technology", 5 709 (1950).
4. Kaeppli, O. and A. Fiechter, *Biotech. Bioeng.* 18, 967 (1976).
5. Zajic, J.E. and E. Knettig, U.S. Patent 3,997,398 (1976)
6. Zajic, J.E., H. Guignard, and D. F. Gerson, *Biotechn. Bioeng.* In Press.
7. Zajic, J.E., H. Guignard, and D. F. Gerson, *Biotechn. Bioeng.* In Press.
8. Zajic, J.E., and C. J. Panchal, *CRC. Crit. Rev. Bioeng.* 5, p 39-66 (1976).
9. Gerson, D.F., J.E. Zajic and A. Margaritis, "Microbial Separation of Bitumen from Athabasca Tar Sand", Univ. Western Ontario, pp 240 (1976).
10. Behie, L.A., J.E. Zajic, D. Berk, J. Ho, R.J.P. Brouzes and V.A. Naish, Twelfth Can. Symp. on Water Pollution Research, Toronto Feb 17, 1977.
11. Bichard, J.A., C.W. Bowman, R.M. Butler and J.L. Tiedje, "The K.A. Clark Volume", Information Series # 45, Research Council of Alberta, p. 171 (1963).

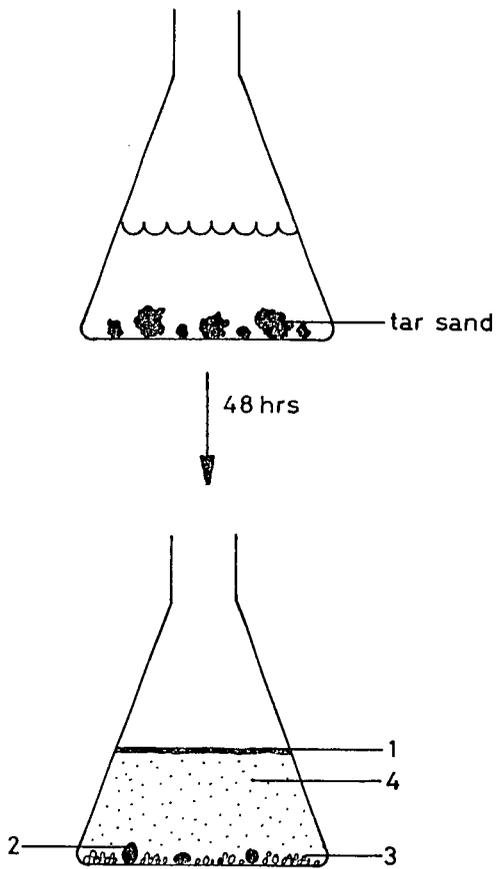


Figure 1

Emulsification with  
crude surfactant from  
1. Corynebacterium sp.  
(aqueous conc., 0.25mg/ml)

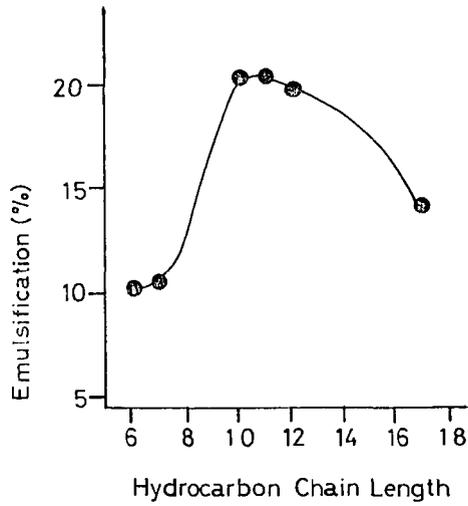


Figure 2

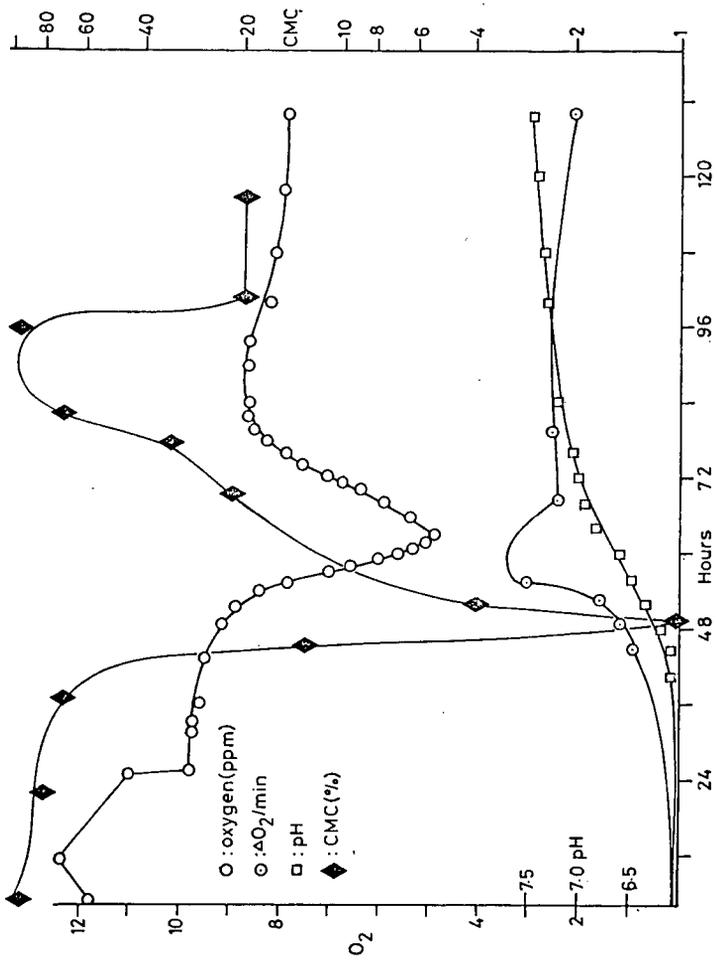


Figure 3

## BIODEGRADATION OF OIL RESERVOIRS

Robert J. Crawford, Christian Spyckerelle  
and Donald W.S. Westlake

Departments of Chemistry and Microbiology,  
The University of Alberta, Edmonton, Alberta,  
Canada, T6G 2G2

The origin and history of the Athabasca and associated oil sands formation is concerned with the possibility that the oil sand bitumen is the microbiologically degraded residue of conventional crude oils rather than the alternative an abnormal diagenetic history not involving microbial degradation. Microbial degradation of the oil sand bitumen should be minimal if it is in fact the end product of the degradation of conventional crude oils. For comparative purposes we have studied the effect of microbiological degradation on several conventional pooled oil reservoirs and on oil sand bitumens.

The model systems employed a typical conventional crude oil from Prudhoe Bay, and samples from the Kumak well in the MacKenzie delta. The Kumak samples are of particular interest since production occurs from three zones at A (1353 m., 49°C), B (2148 m., 62°C) and C (2306 m., 67°C), geologically these samples are believed to be of common

origin, but the change in physical properties are believed to be due to biodegradation (1).

The microorganisms were grown using minimal salts media in a gyratory shaker under aerobic conditions at 30°C. 0.2 g to 1 g of oil was incubated. The cultures were obtained from an enrichment of Shell Lake (NWT) soil using either Normal Wells or Kumak (A, B or C) crude oils. From Norman Wells enrichment the mixed culture contained six different species based on the type of colony produced. The mixture consisted of approximately 90% Gram-negative rods and 10% Gram-positive coryneform type rod. The pure culture obtained was the Gram-positive coryneform isolated from the mixed culture. From the different Kumak enrichments the cultures obtained were characterized by an abundance of pseudomonas type rods.

The principal analytical method used was a gas chromatography-mass spectrometry computer system employing multiple ion cross scans (MICS). Visual comparisons between MICS of various samples gives an immediate graphic indication of similarities and differences. The oil was extracted from the culture medium with chloroform, filtered, and separated into three major components by absorption chromatography on Silica Gel (2).

Table 1 reports some of the data on the Kumak samples along with our analysis of the percentage of saturated, aromatic and polar components contained in the bitumens. The

Table 1. The effect of biodegradation upon fractions from three production zones of KUMAK J-06, MacKenzie Delta.

Sample	Culture Method	Sat.	Fraction Arom.	Polar	Recovery	Pour Point °C
KUMAK A	media washed	48%	48%	5%	-	-34
	SLK C*	47	46	7	92%	-
	SLK B	48	44	7	97	-
KUMAK B	SLK A	46	50	4	100	-
	media washed	46	50	4	-	+8
	SLK C	37	57	6	97	+6
KUMAK C	SLK B	39	56	5	75	+4
	SLK A	54	41	5	75	-
	media washed	51	45	4	-	+13
KUMAK C	SLK C	40	55	4	71	-37
	SLK A	51	45	4	-	-
	UREA**	35	61	4	86	-47

\* Shell Lake culture grown on KUMAK C then transferred to sample. \*\* Non-adduct of urea clathration of crude oil.

removal of n-alkanes from KUMAK C converts it to a sample much like that of KUMAK A in terms of its physical properties. This supports the hypothesis of Burns et al. (1) that the oil from the shallowest zone has been subjected to biodegradation. The gc-ms patterns for the samples of biodegraded material from the deeper zones (KUMAK B and C) strongly resembled those for A.

We then examined samples of a Prudhoe Bay (PB) crude for comparison with Lower Cretaceous pooled oils such as Bellshill Lake (BH) and Lloydminster (Ll) along with oil sand bitumens from the Cold Lake (CL), Peace River (PR) and Athabasca oil sands. The analytical data from these samples are presented graphically in Figure 1.

The gc-ms reveal close similarities between the biodegradation products of the oil from Prudhoe Bay and the oil sands and heavy oils of Alberta. We are not postulating a common source for all of these oils, although they probably share a similar origin and diagenetic history. These results do not give a direct indication as to the maturity and thermal history of the Alberta oil sands but they do support the hypothesis that the oil sands, and some conventional crude oils found in the reservoirs of the Lower Cretaceous formation of Alberta share a common origin and are related by their degrees of biodegradation.

1. B.J. Burns, J.T.C. Hogarth and C.W.D. Milner, Bull. Can. Pet. Geol., 23, 295 (1975).
2. I. Rubinstein, O.P. Strausz, C. Spyckerelle, R.J. Crawford and D.W.S. Westlake, to be published.

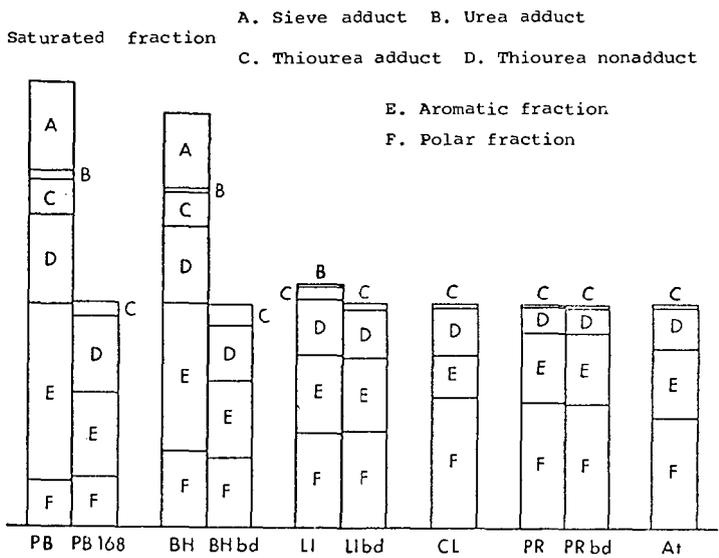


Figure 1. Gravimetric analyses of the Prudhoe Bay oils and the Alberta oils and bitumens.

AROMATIC HYDROCARBONS: DEGRADATION BY BACTERIA AND FUNGI.

Carl E. Cerniglia

and

David T. Gibson

Department of Microbiology  
The University of Texas at Austin  
Austin, Texas 78712

The decline in the supply of natural oil and gas reserves over the past 10 years has caused the Western Hemisphere to import huge volumes of petroleum and petroleum products. If the Western Hemisphere persists in maintaining a petroleum based industrial economy alternative sources of energy will have to be found and developed.

Oil Shale

One alternative source of energy is the extraction of the organic components of oil shale to yield oil and gas. Numerous organic rich shale deposits occur throughout the United States. The release of the energy yielding organic fraction from oil shale has been brought about by retorting the oil shale at temperatures above 500° C and distilling the organic material. This pyrolytic process also generates solid waste in the form of spent oil shale ash. A part of this oil shale ash consists of polycyclic aromatic hydrocarbon derivatives such as benzo[a]-anthracene, dibenzo[a,h]anthracene, benzo[a]pyrene and 3-methylcholanthrene. These aromatic hydrocarbons can be metabolized by mammals and have been implicated in chemical carcinogenesis.

It is known that aromatic hydrocarbons are formed by pyrolytic processes. The types of compounds that are produced depends on the temperature of formation. Thus, the low temperatures that are associated with petroleum formation produce a diverse array of aromatic structures. A

predominant feature of this group of compounds is the presence of alkyl substituents. In contrast, pyrolysis at high temperatures leads to the formation of unsubstituted aromatic hydrocarbons.

#### Fate in the Environment

Crude petroleum is introduced into the environment by natural means (oil seeps) or by the activities of man. Factors that affect the oil include evaporation of volatile components, dissolution, photochemical and biological degradation. The latter process has been amply demonstrated with respect to the linear and branched alkane components of petroleum.

For many years it has been tacitly assumed that crude petroleum in the reservoirs is immune to microbial attack. However, recent studies have shown that under appropriate conditions extensive degradation can occur. It is possible that microbial activities play a significant role in the formation of tar sands.

Little is known about the microbial degradation of the aromatic constituents of petroleum. This is not surprising in light of the immense numbers of different structures that are known to be present. Nevertheless, studies with relatively simple aromatic hydrocarbons have revealed general features of biodegradation that may be used to predict the fate of more complex molecules.

#### Microbial Degradation

Oil pollutants are recycled in nature by the metabolic activities of microorganisms. The environment contains a wide range of different bacterial species, filamentous fungi and yeasts that degrade hydrocarbons. The rate of degradation of crude oil is markedly influenced by a range

of environmental conditions. Some of the more significant factors are organism availability, nutrient availability, oxygen, temperature, and type of petroleum.

There is a specificity of the utilization of individual hydrocarbons by different microorganisms depending upon the enzyme repertoire of the organisms involved and the molecular conjugation of the hydrocarbon. It has been demonstrated that hydrocarbon-utilizing bacteria have a preference for long chain aliphatic hydrocarbons. Straight chain n-alkanes containing 10-18 carbon atoms are assimilated with the greatest frequency and rapidity. Branched chain alkanes, monocyclic substrates and aromatic compounds are utilized least frequently.

Crude oil contains thousands of aromatic hydrocarbons and related compounds. Relatively few of these molecules have been studied in terms of metabolism by microorganisms and higher forms of life. Nevertheless it now appears that certain general features of degradation have emerged which distinguish the mechanisms used by procaryotes and eucaryotes to degrade the benzenoid nucleus.

#### Mammalian Metabolism

It has been well documented that mammals metabolize aromatic hydrocarbons via the oxidative formation of arene oxides. This reaction is catalyzed by a monooxygenase and is characterized by the incorporation of one atom of molecular oxygen into the hydrocarbon substrate. The enzyme system involved in this hydroxylation is membrane bound and functions as a multicomponent electron transport system for a variety of endogenous substrates. It has an absolute requirement for NADPH and molecular oxygen and is also known as microsomal hydroxylase, or a mixed function oxidase.

Mammals metabolize naphthalene to form naphthalene 1,2-oxide. The 1,2-naphthalene oxide formed can spontaneously isomerize to 1-naphthol by a reaction that has been termed the NIH shift. Alternatively, the 1,2-naphthalene oxide can undergo enzymatic hydration by the enzyme epoxide hydrase to yield *trans*-1,2-dihydroxy-1,2-dihydronaphthalene (*trans* naphthalene dihydrodiol). Another reaction of the naphthalene oxide is conjugation both spontaneously and by enzymatic catalysis with glutathione which leads to the formation of mercapturic acids.

#### Bacterial Metabolism

Until recently bacteria were thought to metabolize aromatic hydrocarbons through *trans*-dihydrodiols. Investigations in our laboratory implicated *cis*-3,5-cyclohexadiene-1,2-diol (*cis*-benzene diol) as an intermediate in the oxidation of benzene by *Pseudomonas putida*. Bacteria incorporate two atoms of molecular oxygen into aromatic hydrocarbons to form *cis*-dihydrodiols. *cis*-Dihydrodiols have now been implicated as intermediates in the bacterial metabolism of a variety of aromatic hydrocarbons and related compounds. Further oxidation yields catechols which are the substrates for enzymatic fission of the aromatic ring. *Pseudomonas putida* and *Pseudomonas* species NCIB 9318 form *cis*-1,2-dihydroxy-1,2-dihydronaphthalene (*cis*-naphthalene dihydrodiol) when grown in the presence of naphthalene. This reaction is a prerequisite for subsequent fission of the aromatic nucleus.

#### Fungal Metabolism

There have been several studies on the metabolism of aromatic hydrocarbons by fungi. These investigations suggest a biochemical relatedness between fungal and mammalian liver microsomes towards the monooxygenation of aromatic substrates.

The fungi used in this study were isolated by enrichment culture technique. Soil and water samples were obtained from littoral areas along the coast of North Carolina and placed in a crystallization dish. Crude oil was added to the water surface and the dishes were incubated for 3-4 weeks at 25° C. After this incubation period, samples were removed and streaked on well plates. The well plate procedure was developed as a method for adding hydrophobic substrates to agar plates in a way that growth could readily be observed. Fungal growth predominated and several different genera of fungi were isolated.

The fungus used throughout this report was identified and characterized as *Cunninghamella elegans*, a terrestrial phycomycete.

This organism can utilize a wide variety of paraffinic and mixed base crude oil as sole source of carbon and energy. In addition, *C. elegans* can utilize naphthalene, all alkanes tested from C<sub>3</sub> through C<sub>32</sub>, a wide variety of long chain alkenes, ketones and fatty acids as sole source of carbon and energy.

Cells of *Cunninghamella elegans* were incubated with naphthalene for 24 hours. After 24 hours the mycelia was filtered and the culture filtrate extracted with three volumes of ethyl acetate. Thin layer chromatographic analysis of the culture filtrate revealed the presence of six transformation products. Each product absorbed ultraviolet light and gave a characteristic color with Gibb's reagent. In order to ascertain that the products were indeed derived from naphthalene the experiment was repeated with <sup>14</sup>C-naphthalene. Six radioactive products were observed that corresponded to the metabolites located on thin layer chromatograms by Gibb's reagent.

To isolate the transformation products *C. elegans* was grown in the presence of 4 liters of dextrose broth in the presence of 2 grams of naphthalene. After 24 hours the culture filtrate was extracted with ethyl acetate. Removal of the solvent gave 1.54 grams of a brown solid that was applied to a deactivated silica gel column (20% water). The column was eluted with chloroform and 20 ml fractions were collected. After 30 fractions had been collected the eluting solvent was changed to chloroform:methanol (99:1). Products eluting from the column were detected by thin layer chromatography in solvent A (chloroform:acetone 80:20).

The residue obtained from fractions 5-8 was recrystallized to leave 37 mg of yellow needles. Preparative thin layer chromatography of the mixture gave 15 mg of pure 1,4-naphthoquinone and approximately 1 mg of 1,2-naphthoquinone. The isolated 1,4-naphthoquinone gave identical melting point, infrared, proton magnetic resonance, mass and ultraviolet spectra to those given by a freshly sublimed sample of synthetic 1,4-naphthoquinone. The isolated 1,2-naphthoquinone gave an identical absorption spectrum and melting point to that given by authentic 1,2-naphthoquinone. The residue from fractions 9-17 was sublimed under vacuum at 50° C for 4 hours. The sublimed product (776 mg) was obtained in the form of needle-shaped white crystals that melted at 96-98° C. This melting point was not depressed on admixture with a pure sample of synthetic 1-naphthol. Also 2-naphthol was obtained in pure form by preparative thin layer chromatography.

In order to ascertain the ratio of 1- to 2-naphthol produced by *C. elegans* a crude sample of the transformation products was treated with trifluoroacetic anhydride and analyzed by gas chromatography. The ratio was found to be 96:4 (1-naphthol:2-naphthol).

Fractions 18-27 were pooled and the solvent removed to leave 297 mg of a yellow oil. The oil was dissolved in a small volume of chloroform and applied to a column of neutral alumina. The column was eluted with chloroform and 5 ml fractions were collected. Fractions 3-10 were pooled and removal of solvent gave 265 mg of a yellow oil. This material was chromatographed and showed the presence of a single compound ( $R_f$ , 0.38). The infrared, proton magnetic resonance, mass and ultraviolet spectra established the structure of the compound as 4-hydroxy-1-tetralone. Additional evidence was provided by treating this compound with chromic acid. The resulting oxidation product gave an identical ultraviolet absorption spectrum and was chromatographically identical to synthetic 1,4-naphthoquinone.

The residue obtained from fractions 45-64 was recrystallized from petroleum ether. Two recrystallizations gave 63 mg of white needles that melted at 104-105° C. This melting point was not depressed on admixture with a pure sample of synthetic *trans*-1,2-dihydroxy-1,2-dihydronaphthalene. In addition acid catalyzed dehydration (6N HCl, 100° C, 15 min) of the dihydrodiol produced material with the ultraviolet spectrum and chromatographic properties of 1-naphthol.

High pressure liquid chromatography was employed to separate and quantitate each metabolite produced from naphthalene by *C. elegans*. The major metabolites were 1-naphthol (67.9%) and 4-hydroxy-1-tetralone (16.7%). Minor products isolated were 1,4-naphthoquinone (2.8%), 1,2-naphthoquinone (0.2%), 2-naphthol (6.3%) and *trans*-1,2-dihydroxy-1,2-dihydronaphthalene (5.3%).

Centrifugation studies on mycelia extracts of *C. elegans* indicated that naphthalene hydroxylase activity was located in the 10,000 x g supernatant fraction. High speed centrifugation (100,000 x g for 1 hr)

of the 10,000 x g supernatant yielded a pellet with 95% of the naphthalene hydroxylase activity. The metabolites formed from the microsomal hydroxylation of naphthalene were *trans*-1,2-dihydroxy-1,2-dihydronaphthalene, 1-naphthol and 2-naphthol. The amount of naphthalene hydroxylase activity remaining in the 100,000 x g supernatant varied from 1-5% but was generally very low. The microsomal hydroxylation of naphthalene by *C. elegans* was found to specifically require NADPH. When NADH was substituted as a source of reducing power no activity was observed. The enzyme system was inhibited by carbon monoxide, SKF-525A, and metapyrone implicating that naphthalene hydroxylation in *C. elegans* may involve a factor similar to cytochrome P-450. These results were further supported by the lack of inhibition when treated with cyanide ions.

The data presented in this paper indicates that the fungus *C. elegans* metabolizes naphthalene similar to monooxygenases of hepatic microsomes. There is relatively little information on the microbial degradation of aromatic hydrocarbons when the molecules are present as constituents of crude oil. Nevertheless it is possible that the types of reactions described do occur when microorganisms interact with oil in the environment.

## TOTAL YIELDS FROM HEATED OIL SANDS

P. C. Stangeby and P. L. Sears

University of Toronto  
Institute for Aerospace Studies  
4925 Dufferin St.  
Downsview, Ontario  
M3H 5T6

There is at present considerable interest in dry processes for the extraction of bitumen from the Athabasca oil sands. The Lurgi Ruhrgas process is perhaps the best known example of this general technique.

In order to investigate the yield of volatile material from tar sand samples under a variety of conditions, a heated electrical grid apparatus was constructed, basically similar to that used elsewhere<sup>1</sup> for work with coal samples. This permits the heating of small (ca. 20 mg.) samples of oil sand to 900°C at rates up to 10<sup>4</sup> K/sec. The pressure of the surrounding gas is variable between 10 microns Hg and 100 atm. Samples are supported and contained by fine stainless steel mesh, which is heated by a low voltage D.C. circuit. The temperature is measured with a thermocouple in contact with the mesh. Temperature/time profiles are recorded with a high speed chart recorder.

### EXPERIMENTAL

Gravimetric measurement of sample weight changes entailed the weighing of the sample with its supporting mesh. Hence it was important to ensure that this did not change in weight on heating. Trial runs in the absence of a sample indicated that hydrogen and helium atmospheres were consistent with this condition, but that carbon dioxide and air were not. The latter exclusion unfortunately precluded gravimetric measurement of the burning of bitumen from the oil sand, which would have provided a valuable comparison with pyrolysis and analytical results.

Further errors in measurements could arise from two phenomena concerning the oil sand itself. The first of these - the oxidation of bitumen by oxygen impurity in the gas, was avoided by the use of ultra high purity gases (hydrogen and helium). The second - "sputtering" of the heated sample through the mesh of its support was eliminated by using stainless steel foil as the support. Total weight loss was not affected by this change, although no solid or liquid material could escape. The use of two folds of mesh was found to contain solids and liquids, while allowing comparatively free transit of gases.

### SLOW PYROLYSIS

After the checks described above, a series of heating runs was made on samples of oil sand. A prior analysis of this oil sand, by its supplying laboratory, had indicated 13.8% bitumen, 1.8% water (84.4% sand).

Temperatures up to a maximum of 660°C were reached in this series of runs. One minute was taken to reach the maximum temperature in any given runs, which was held for a further two minutes. The surrounding gas was helium at one atmosphere.

Figure 1 shows the results of 37 such runs. It may be seen that the relationship between temperature and weight loss is approximately linear, though with considerable scatter, up to a temperature of about 500°C, where a maximum is approached. This maximum is about 13%, which may be compared with the nominal total bitumen

and water content of 15.6% by analysis.

A straight line which represents a least squares fit to the 27 data points for which T is less than 500°C has been drawn in Figure 1. This is used for comparison with data from other experiments.

#### EFFECT OF HEATING RATE

Series of experiments were carried out for heating rates of 50 K/sec and 1000 K/sec. These were under the same gas conditions as the slow pyrolysis experiment, and also had the same residence time at the maximum temperature (2 minutes). Figure 2 shows the results of these runs, compared with the straight line fit for Figure 1.

It may be seen that these data are not significantly different from those in Figure 1.

#### EFFECT OF REDUCED PRESSURE

A number of runs were carried out in helium at lower than atmospheric pressure. Pressures of 400 torr, 200 torr and 7.6 torr were used, without any appreciable effect on the amount of sample volatilized.

#### EFFECT OF VERY HIGH TEMPERATURES AND OF TIME AT MAXIMUM TEMPERATURE

A small number of runs were carried out in which the samples were rapidly (1000 K/sec.) heated to temperatures well above those used in previous runs.

<u>T<sub>-max</sub></u>	<u>% Weight Loss</u>
760°C	12.9
910°C	12.8
950°C	12.8

These are all within experimental error of the loss attained at about 500°C.

A series of experiments at 510°C, in which the time the sample spent at 510°C was varied showed that reaction was at least 90% complete at 1 second, and approaching completion by 15 seconds. Heating for several minutes beyond this had no effect.

#### PYROLYSIS IN HYDROGEN

Pyrolysis of the oil sand in a hydrogen atmosphere was carried out at pressures of 1, 30 and 100 atm. No great difference from the results in helium at 1 atm were noted, except in the case of 100 atm pressure. Here the weight loss of the sample was increased by about 1 - 1-1/2% over the slow pyrolysis case. As elsewhere, the rate of heating appeared to be irrelevant to weight loss.

The quantity of high purity hydrogen required for each run at 100 atm unfortunately precluded extensive investigation of reaction at this pressure.

#### HELIUM AT HIGH PRESSURE

Helium, at pressures up to 100 atm was also used for a number of runs. In this case, the pressure had a distinct lowering effect on the weight loss of the sample. Again, rate of heating showed no appreciable effect.

Figure 3 shows the data for both hydrogen and helium high pressure work. All

runs were to 500°C.

#### COMPOSITION OF VOLATILIZED MATERIAL

The experimental work described here provided little opportunity to investigate the products of reaction. However, evacuation of the reaction vessel to 100 microns before heating the sample allowed measurement of the gas pressure resulting from reaction. Pressure increases of the order of 100 microns were recorded, but these were consistently higher for slower than for faster heating rates. This implies that the material volatilized has a greater liquid/gas ratio when rapid heating is used.

#### SUMMARY

About 12.9% of the weight of the supplied oil sand is volatilized by heating to 500°C. Rapid heating, higher temperatures, and prolonged heating have little effect on this figure. If the original analysis figures are to be trusted, this implies about 80% yield of bitumen as oil and gas. The oil/gas ratio is probably greater for higher heating rates.

High pressures of inert gas reduce the yield, while high pressure hydrogen increases it. Work in hand on this system includes carbon analyses on the pyrolyzed residues to provide a check on the fate of the bitumen which is not volatilized. A gas chromatographic study of the volatilized material is in the preparatory stages.

#### REFERENCE

1. D. B. Anthony, J. B. Howard, H. P. Meissner and H. C. Hottel, Rev. Sci. Instrum. 45 (1974), 992.

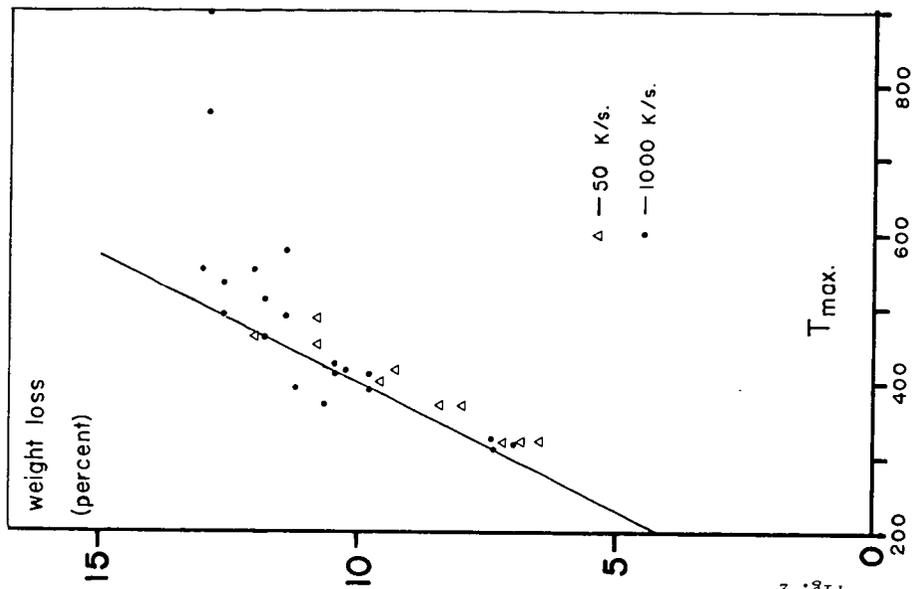


Fig. 2

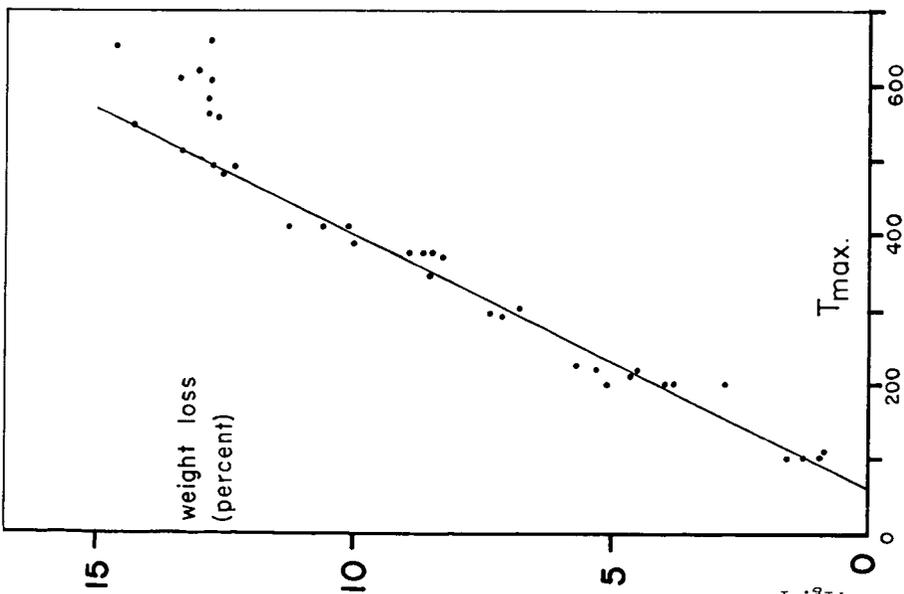


Fig. 1

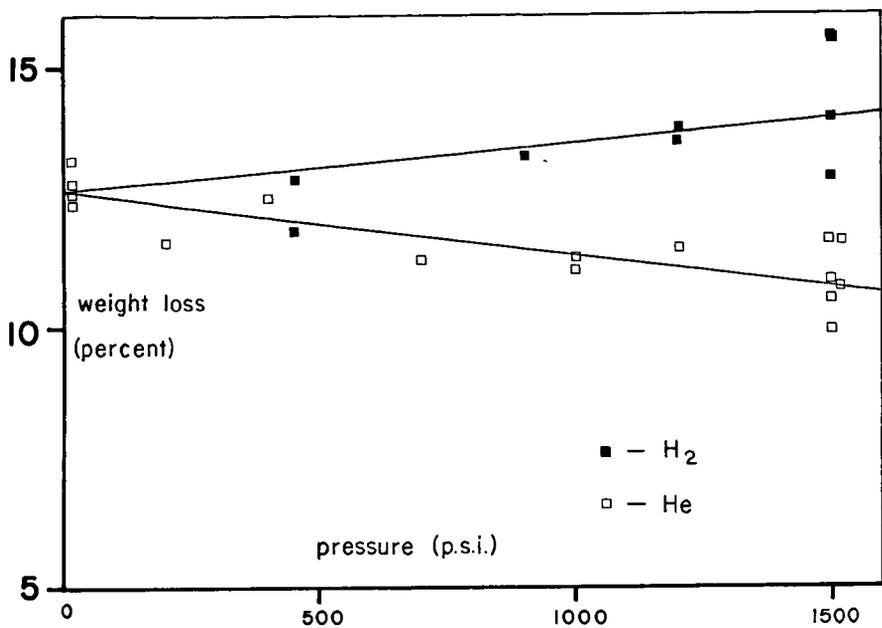


Fig. 3