CANADA

A STUDY OF THE ATHABASCA BITUMEN FROM THE ABASAND QUARRY, ALBERTA, CANADA

PART I: EARLY HISTORY, ANALYSIS OF THE BITUMINOUS SAND, AND ISOLATION AND STRUCTURAL ANALYSIS OF THE ASPHALTENE FRACTION

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DEPARTMENT OF MINES AND TECHNICAL SURVEYS, OTTAWA

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A STUDY OF THE ATHABASCA BITUMEN FROM THE ABASAND QUARRY, ALBERTA, CANADA. Part I: Early History, Analysis of the Bituminous Sand, and Isolation and Structural Analysis of the Asphaltene Fraction.

by

M. L. Boyd* and D. S. Montgomery**

ABSTRACT

A brief summary of the early history and development of the Athabasca bitumen is given as a background to the present chemical research.

The physical properties of the bituminous sand being studied are tabulated; these include elementary analysis, ash content, molecular weight, density at 20°C, the emission spectra of the ash of the bitumen, and the chemical composition, screen analysis and emission spectra of the sand.

Preliminary chromatographic experiments on the bitumen are described to illustrate the necessity for separating the asphaltene components before fractionating the remainder of the bitumen. The large-scale extraction experiments are described, in which the asphaltene fraction and the pentane extract were prepared. The following properties of the asphaltene fraction were measured: ash content, elementary analysis, molecular weight, density at 20°C, refractive index at 20°C, emission spectra of the ash, and the infra-red spectrum. A quantitative estimate of the aromaticity is made from the infra-red spectrum. The asphaltene fraction is characterized by the application of van Krevelen's structural analysis system and also by two new methods devised by the authors. The chemical structure is expressed in terms of five structural groups, and an estimate is made of the degree of condensation of the aromatic rings by determining the number of fused ring and non-fused ring junction carbon atoms.

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Direction des mines

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ÉTUDE DU BITUME DE L'ATHABASCA EN PROVENANCE DE LA CARRIÈRE ABASAND, EN ALBERTA, CANADA

Partie I: Aperçu des premiers travaux, analyse du sable bitumineux, isolement et analyse structurale de la fraction asphaltène.

par

M. L. Boyd* et D. S. Montgomery**

RÉSUMÉ

Un bref aperçu des premiers travaux d'exploration et d'expérimentation du bitume de l'Athabasca sert d'entrée en matière aux travaux de recherche chimique dont il est ici question.

Les propriétés physiques du sable bitumineux à l'étude sont indiquées sous forme de tableaux. Les auteurs y abordent successivement: analyse élémentaire, teneur en cendres, poids moléculaire, densité à 20°C, émision spectrale des cendres du bitume, composition chimique, analyse dimensionnelle et émission spectrale du sable.

On décrit les expériences chromatographiques préliminaires afin de démontrer la nécessité de séparer les composants asphaltènes avant de fractionner le reste du bitume. On y décrit les expériences d'extraction sur une grande échelle au cours desquelles la fraction asphaltène et l'extrait de pentane ont été préparés. Les propriétés suivantes de la fraction asphaltène ont été évaluées: teneur en cendres, analyse élémentaire, poids moléculaire, densité à 20°C, indice de réfraction à 20°C, émission spectrale des cendres et spectre infrarouge. On en a évalué quantitativement l'aromaticité d'après le spectre infrarouge. La fraction asphaltène est caractérisée par l'application du système d'analyse structurale de van Krevelen, ainsi que par deux nouveaux procédés mis au point par les auteurs. La structure chimique s'exprime d'après cinq groupes structuraux, et les deux chercheurs ont évalué le degré de condensation des cycles aromatiques en déterminant le nombre d'atomes de carbone de liaison des chaînes cycliques avec et sans mailles communes.

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PREFACE

Towards the end of the year 1949 the pilot-plant investigations at the fuel research laboratories of the Bureau of Mines (now Mines Branch), Ottawa, dealing with separation of bitumen from the bituminous sands of Alberta, were drawing to a close. At that time the feeling prevailed that, although much effort and money had been spent on attempts to separate the bitumen from the sand, there was comparatively little information available concerning the chemical structure of this substance that would be of assistance in the study of the refining of this material. Indeed the chemical tools required to characterize the bitumen seemed far from adequate even to give some indications of the economic possibilities of this natural resource. In the light of this, a study was initiated to secure an insight into the structure of the hydrocarbon framework; this was to be followed at a later date by studies of the functional groups and foreign atoms. Rather than examine bitumen from a wide variety of locations, a detailed study was made of the bitumen from a single source, the Abasand quarry.

This detailed study may be considered to have been made in three stages: (1) an initial separation of the bitumen on the basis of molecular weight into three broad fractions, the asphaltenes, resins, and oils; (2) further resolution of the resins and oils on the basis of chemical type; and (3) the application of modern structural analysis systems to characterize the structure of the hydrocarbon framework of all the fractions prepared under (1) and (2). This study is being presented in a series of three research reports which will describe in turn the chemical structure of the three major fractions of the bitumen: the asphaltenes, resins, and oils.

It was known from the extensive research of the American Petroleum Institute on the mid-continent crude petroleum from Ponca, Oklahoma, that oil consisted of a very large number of compounds, and it was reasonable to assume that the bitumen would resemble oil in this respect. As the average molecular weight of the Abasand bitumen, as indicated by its viscosity, was evidently higher than that of petroleum, the task of separating the bitumen into its chemical species appeared to be formidable. The more modest objective of resolving the bitumen into major types of compounds and devising schemes for characterizing these types appeared to be more in harmony with the financial and physical resources available.

As the origin of the bitumen in the McMurray area has been the object of geological speculation for a century, and since certain theories of the origin play a role in selecting promising territory for oil prospecting, the present investigation was conducted with a view to securing chemical data which might cast some light upon the origin of the bitumen and upon its relation to the area. For this reason, both the situation of the deposit and the geological theories concerning its origin have been given more extensive treatment than might otherwise be considered advisable in a purely chemical paper.

Between 1932 and 1951 Waterman and his school had developed structural analysis systems suitable for oil, and in 1950 van Krevelen was making rapid progress in developing structural analysis techniques that were particularly suitable for coal. There appeared to be a gap between these systems where neither was suitable, and it was in this area that the bitumen seemed to lie. To meet this challenge, a hydrocarbon structural analysis system was developed, for application to pure compounds, in which three chemical and two physical properties were expressed in terms of five structural groups in a form which may be solved simultaneously by modern computing equipment. Many problems arise on applying, to such broad fractions as those studied here, a system designed for and based on pure hydrocarbons. A detailed discussion of the mode of application and the interpretation of the results will form a major portion of these reports. Despite their limitations, structural analysis systems may be regarded as a means of mapping the structure of the hydrocarbon framework, even though they necessarily involve a certain amount of distortion. It will be the object of future research to confine the limits of this distortion and of the present work to compare the results with those obtained on using van Krevelen's system.

In the historical introduction of Part I a brief sketch will be given of the drilling and separating operations, so that the present work may be viewed against the background of other activities, and to provide a ready means of locating the more important references to all the various phases of development. This will be followed by a description of the primary separation of the bitumen on the basis of molecular weight. A detailed description will then be presented of the highest molecular weight fraction, commonly referred to as the asphaltenes. In Part II will be described the fractionation of the pentane-soluble portion of the bitumen by chromatography, and Part III, later, will deal with the separation of the oil fraction into numerous fractions and will summarize the interpretation of the structure of the bitumen as indicated by the results obtained up to the present time.

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M. L. Boyd
D. S. Montgomery

Ottawa, November 1961

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The chemical study of the bitumen from the Abasand quarry was undertaken to secure an insight into its chemical and physical structure. To perform this task, every effort was made to select a separation scheme that would avoid chemical transformations which might obscure the structure of the original components. This preliminary study was designed to separate the bitumen on the basis of molecular weight and chemical type, with a view to providing a guide to its economic possibilities and to establishing a basis for future separation schemes that would have as their objective the identification of individual chemical species.

EARLY HISTORY

The massive outcrops of bituminous sands along the banks of the Athabasca River in northern Alberta have been a source of great interest from the days when the early explorers in that area first noted their occurrence down to the present time.

The bituminous sand area may be defined as lying between West longitudes 111° and 112° and North latitudes 56°30' and 57° 30'. All exposures of bituminous sand in this area lie within a radius of eighty miles of McMurray, which is situated approximately 260 miles north of Edmonton, Alberta.[1]* For the most part

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* References are listed at the end of the report in the order in which they are numbered in the text.

the exposures occur along the Athabasca River and its tributaries.

In 1778 Peter Pond, one of the early fur traders, reached the Athabasca country and saw the impressive outcrops of bituminous sand on both sides of the river.[2] Since that time, many explorers passing through this area have made reference to these deposits. One of the early names associated with this area was that of David Thompson who surveyed the Lesser Slave and Athabasca Rivers in 1799.[3] In 1801, Sir Alexander Mackenzie published an account of his Voyages to the Frozen and Pacific Oceans in 1789 and 1793, in which frequent mention was made of the "tar" sands.[4] Sir John Richardson in 1823 also mentioned the occurrence of black pitch or bitumen in patches along the Slave and Mackenzie Rivers.[5]

The first systematic geological study of this area was made by the Geological Survey of Canada in the period 1875-1890. In 1875, Macoun, attached to an expedition to the Pacific Coast led by Selwyn, returned east by way of the Peace and Athabasca Rivers. He makes frequent references to the "tar conglomerate" being very abundant.[6] The existence of "tar springs" was also noted along the Clearwater River. Macoun referred to the deposit as "shale" and believed it to overlie the coral formation. In the Geological Survey reports for 1884, Bell reported on the Basin of the Athabasca River.[5] He remarked that he was especially interested in the occurrence of petroleum and asphalt. He noted

the occurrence of "petroleum-bearing sandstone" in the vicinity of Fort McMurray, and during the warm weather he observed "tar, free from any sand, oozing out of the banks". Bell assumed that this "altered petroleum contained in the soft Cretaceous sandstones of the Athabasca region" was derived from the Devonian limestones underlying them. The most complete description of this area, and one which still forms a fundamental part of our knowledge of the geology of this region, was given in 1890-91 by McConnell,[2] who issued a report on the "District of Athabasca comprising the country between Peace River and Athabasca River, North of Lesser Slave Lake"; like his predecessors, he also speculated on the origin of the "tar sands", making the following comment:

> "The tar sands must have consisted originally of almost unconsolidated sands and soft sandstone, ranging in texture from a fine silt to a coarse grit, but have been cemented into a coherent tarry mass, two hundred feet thick, by the heavy constituents of the oils which have welled up during past ages, in almost inconceivable quantities, from the underlying Devonian limestones."

He assigned them to the Dakota age.

It has already been mentioned that these early geologists regarded the bituminous sands as an indication of the existence of a large reservoir of petroleum in the underlying Devonian limestone. It is not surprising, therefore, to find that in 1894 the Federal Parliament voted seven thousand dollars for the boring for oil at Athabasca Landing.[7] Between 1894 and 1899, wells were

drilled at Athabasca Landing, at Pelican Rapids, and at Victoria on the Saskatchewan. The results of these borings were inconclusive, largely because the difficulties encountered in drilling were never successfully overcome.[8] In a series of reports from 1916 to 1919, McLearn[9] correlated, on paleontological evidence, the bituminous sands with other members of the Cretaceous series.

Notwithstanding the geological work which has been done, there is widespread disagreement at the present time, among geologists, as to the origin of the bituminous sands. Recently, Sproule has summarized the five existing theories of origin as follows:[10]

(1) "In Situ" Theory. This theory was advanced by Thompson in 1930. He held the belief that the oil was formed from organic life in the sands during the time of the deposition of the sands. This theory has been elucidated by Ball.[11]

(2) Clearwater Shale Theory. In 1917, McLearn[9] proposed the theory that the Clearwater shales were the parent rocks.

(3) McMurray Equivalent Theory. This theory, advanced by Hume,[12] considers that the McMurray oil moved laterally from marine deposits into the sands of the McMurray formation.

(4) Residual Theory. This theory was suggested by Slipper. According to this view the sands and clays of the McMurray formation are residual deposits, formed from the westward erosion of the Paleozoic limestone during the time interval between the emergence of the Paleozoic and the Lower Cretaceous rocks. This erosion took place as a wearing away of a series of receding escarpments. The Paleozoic limestones and dolomites contained horizons impregnated with bitumen, and during the recession of the escarpment this bitumen was retained in the residual sands. Subsequent submergence covered the

McMurray sands with marine Clearwater shales and the overlying members of the Cretaceous groups.

(5) Paleozoic Source Theory. This theory, originally suggested by Bell of the Geological Survey,[5] holds that the oil seeped upward along cracks in the Paleozoic formation into the overlying porous McMurray sands.

The earliest of the geological theories of the origin of the Athabasca bitumen considered the hydrocarbon material to be derived from Devonian oil. This prompted the Geological Survey of Canada to drill in the bituminous sand area. Several wells were drilled prior to 1900. In the period 1897 to 1927, Ells[13] states, some forty holes exploring for oil were put down in the McMurray area.

A new phase in the development of the bituminous sands began in 1913 when Ells of the Federal Mines Branch began topographical surveys of the bituminous sand area. By 1931, 1260 square miles had been mapped along the Athabasca River and its tributaries, locating all the major outcrops.[14] Ells took many samples by hand augering methods. In 1924 the Research Council of Alberta analyzed about 250 samples of bituminous sand; however, 45 feet was the greatest depth sampled.[15] It can readily be seen that none of the above drilling and sampling was to the bottom of deposits necessary to establish the reserves of the area.

In 1942 the Federal Government initiated the first extensive drilling program to determine the extent of the deposits[16]. From 1943 to 1947, 291 holes were put down, representing 53,918 feet of drilling. The most favourable area discovered was in the vicinity of the Mildred and Ruth Lakes, opposite the mouth of the Steepbank River. The developed reserve in the closely spaced drilled area was estimated to contain 587,824,000 tons averaging 13.4% bitumen by weight, with a ratio of bituminous sand to overburden of 2.3 to 1.[17] The total developed and inferred tonnage of the Mildred-Ruth Lakes area is 1,162,665,000 tons of bituminous sands, which is equivalent to 900 million barrels of bitumen. This program has been considerably amplified recently by a group of private companies, led by Calvan Consolidated Oil and Gas Limited and operating under the name Athabasca Oil Sands Project, who published their results in 1954.[18] In the period 1952-1954, they conducted a semi-detailed drilling program on seven oil sand permits in the McMurray area. Ninety-one holes were drilled, having a total depth of 19,402 feet. This investigation discovered six major deposits of rich oil sands, in addition to the known deposits previously outlined by the Federal Government. The total oil reserves of the new deposits were calculated to be 1,875 million barrels.

Another important phase of the bituminous sands development which precedes refining or chemical treatment of the bitumen is the separation of the bitumen from the sand. As early as 1880-1882, Hoffman[19] of the Geological Survey noted that the bitumen could be removed from the sand by boiling with water and skimming off

the bitumen. The Research Council of Alberta, since its inception in 1919-1920, has devoted considerable time to the application of the hot-water-washing method to the separation of the bitumen from the sand.[20] This work was done both on a laboratory scale and in small pilot plants. During the 1920's two pilot plants were operated in Edmonton, and a third one was located on the Clearwater River, near Waterways, in 1929-30.[21] This was followed by the erection and operation of a large pilot plant by the Alberta Government, employing the Hot Water Washing Technique, at Bitumount, Alberta, in 1949.[22]

The experience of Abasand Oils Ltd. with the Hot Water Process during World War II led them to consider the Cold Water Process to avoid large losses of heat and the excessive humidity produced in the buildings by large open tanks. After the destruction of the Abasand plant by fire, in 1945, the Cold Water Process was developed by the Federal Bureau of Mines at Ottawa. During 1949-50 this Bureau operated a pilot plant with a capacity of 200 pounds per hour of bituminous sand.[23] An alternative approach to the recovery of oil from the bituminous sands was developed at the National Research Council at Ottawa by Gishler,[24] who applied the fluidized solids technique to the study of oil recovery from the bituminous sands. By this method, yields of 85% by weight of the bitumen were recovered as distillate.[25] At the temperatures used, considerable cracking and distilling took

place, resulting in a product with properties that differed markedly from those of the original bitumen. Gishler[25] also performed some experiments using the wet crude oil produced in the water-separation processes as a starting material in his fluidized-solids pilot plant, and produced a dry, clear, coker distillate.

A considerable amount of the early work on the bituminous sand was motivated by the impression that a market existed for the untreated bituminous sand as a paving material.[26] However, most of the early workers considered the bitumen to be a potential source of commercial petroleum products.[27] Consequently, there were attempts at distilling the bituminous sands.[28] In the 1920's, samples were sent to various companies for distillation and cracking tests.[29] The following companies issued reports on these tests: Woodhall-Duckham Company, England; Universal Oil Products Company, Chicago, on the Dubbs Cracking Test; and the Kansas City Testing Laboratory, Kansas City, Missouri, on the Cross Cracking Test. Early attempts at hydrogenating the bitumen were made by the Research Council of Alberta[30] and the Federal Mines Branch.[31] More recently the Federal Mines Branch concentrated its experiments on the vapour-phase hydro-desulphurization of the coker distillates derived from the bitumen.[32] During World War II, great interest was shown in Alberta bituminous sands; the Federal Government appointed a committee to investigate the bituminous sands as a possible source of aviation

and motor gasoline and fuel oil.[33] In this connection, the Universal Oil Products Company, Chicago, was requested to determine the feasibility of producing aviation gasoline from the Athabasca bitumen. The bitumen was subjected to continuous pressure coking and fluid catalytic cracking. It was shown to be possible to produce, in low yields, aviation gasoline, motor gasoline of high sulphur content, and fuel oil, but under conditions which did not appear attractive economically.[34] These facts received some confirmation during the operation of the Abasand plant.

The end of World War II brought about some decline in interest in the recovery of petroleum products from bitumen, owing to unfavourable economic factors and the poor quality of the products. The Abasand plant was therefore never rebuilt after its destruction by fire in 1945.

On a pilot-plant scale, continued interest in the separation and preliminary refining phase was shown by the Alberta Government, which built and operated the plant at Bitumount and by the Federal Government, which constructed and operated the cold-water-separation pilot plant at Ottawa. The Alberta Government subsequently retained Blair to review the oil sand development and to make an analysis of the processing costs and the commercial value of the products.[74] This culminated in 1951 in the Alberta Government declaring its oil sands development policy.[35]

During World War II and afterwards, it was appreciated by the Bureau of Mines at Ottawa that the only way of treating the entire bitumen to produce the wide range of petroleum products meeting or exceeding the current specifications was by high pressure hydrogenation using essentially the Bergius Process. Possibly not more than one refinery of this type could be supported in the bituminous sand area, which would mean that all the operations from mining to the delivery of the finished products would have to be of commensurate size. The scale of the operation suggested the wisdom of examining on a laboratory scale the high-pressure hydrodesulphurization process. This led to the construction of the high-pressure pilot plant in Ottawa and the current research program on this phase of the refining operation.

It was also recognized that the petroleum industry could not justify the capital expenditures involved in the Bergius Process and that the development of this resource would probably take place following a cheaper refining route. This scheme involved an initial coking step to eliminate a large portion of the residual mineral matter and high molecular weight asphaltenes followed by desulphurization at 1000 psi with hydrogen to yield a refinery feed stock. Experiments were therefore performed at the Bureau of Mines to explore this route and the results of this work laid the foundation for the economic projections made by Blair[74] concerning the refining.

Against this background of activity, comparable strides in the understanding of the chemical nature of bitumen had not been made. Indeed, to many, the bitumen seemed so much like oil that it was regarded as hardly necessary to study the chemical structure. Historically, the first recorded chemical analysis of Alberta bituminous sand was made by Hoffman of the Geological Survey of Canada and reported in 1880-82.[19] This was a sample collected by Bell from the banks of the Athabasca, six miles from the Clearwater. Hoffman recorded its specific gravity at 60°F as 2.040, and its composition as 12.42% bitumen, 5.85% water, and 81.73% sand. The bitumen was insoluble in alcohol in the cold, and slightly soluble in boiling alcohol. It was readily soluble in ether, turpentine, kerosene, benzine, benzol, and carbon disulphide. The sand was reported as fine, colourless, transparent quartz, containing a few flakes of mica and feldspar; 52% passed a 90-mesh sieve. The first attempt to investigate chemically the bituminous sand was made by Krieble and Seyer in 1921.[36] They applied Marcusson's method of analysis[37] to the bitumen, resolving it into asphaltenes, resins and oily constituents. Its ultimate composition is given. In an effort to isolate constituents of the bitumen, direct distillation from the bituminous sand was attempted, but without success. The bitumen was treated with both sulphuric and nitric acids; the results were considered indicative of cyclic structures. The bitumen was

separated into four fractions, on the basis of solubility in alcohol, acetone, ether, and carbon disulphide. The oil fraction from the Marcusson analysis was distilled at a pressure of less than 1 mm, and clear, colourless oils were obtained. These distillates had molecular weights in the range 150-350.

In 1934, Katz[38] studied the composition of blown Alberta bitumen. He found that the amounts of asphaltous acids and anhydrides decreased on blowing, with an accompanying rise in fusing point of the bitumen. The amounts of oily constituents and resins also decreased, but the asphaltene content increased. During blowing, the molecular weights of the resins increased from 733 to 1012, and those of the asphaltenes from 2219 to 4690. The oxygen content was increased up to 1.88% by blowing. The oxygen was contained mostly in the resin fractions. The sulphur and nitrogen were distributed principally among the resins and the asphaltenes. He succeeded in obtaining from the Alberta bitumen, by blowing, products similar to mineral rubber.

In 1952, Waterman and Brakel published a report on Alberta bitumen.[39] Included in this report were ring analyses of the hydrogenated bitumen by the n-d-M method.[40] Hydrogenation of the crude bitumen produced an almost saturated product. The resins and the asphaltenes were not hydrogenated to completion. All substances were only partly cyclic and were paraffinic to the extent of 50%.

From the work of Rossini[41] on Ponca (Oklahoma) crude oil, it was known that petroleum contained a large number of compounds. It seemed obvious that the isolation of compounds from Alberta bitumen would be exceedingly difficult due to the much higher molecular weights than in mid-continent crude oils and also to the ease with which asphaltic substances undergo oxidation. However, it appeared to be possible to separate the bitumen, on the basis of chemical type and molecular weight, by the application of the more recently developed chromatographic techniques. So little was known of the structure of the bitumen that it was difficult to plan a suitable analytical scheme; however, every effort was made to avoid treatment with anything which might change the chemical structure, such as strong acids, bases or oxidizing agents.

ANALYSIS OF THE BITUMINOUS SAND

The bituminous sand used in this investigation was part of a 150-ton shipment obtained from Abasand Oils Ltd. in 1948. It was taken from an excavation two feet in depth and 30 by 75 feet in area, in the floor of the quarry due east of Abasand Oils Ltd. The centre of the area from which the sample was withdrawn is approximately 50 feet west of Hole #2, Section 4, drilled by the

Federal Department of Mines and Resources.* This shipment contained, on the average, 15.8% of bitumen by weight** and will be referred to in this report as "Abasand bitumen".

The properties of the bitumen are given in Table 1, and those of the sand are shown in Table 2.

TABLE 1

Properties of the Abasand Bitumen

Property	As Prepared	On Ash-free Basis
Carbon, wt %	82.6	83.1
Hydrogen, "	10.2	10.28
Nitrogen, "	0.303	0.305
Oxygen (by diff.), "	1.37	1.36
Sulphur, "	4.93	4.96
Ash, "	0.60	
Density (20°C)	1.029	
Molecular weight	800	

* This was shown in volume III of the Federal Bureau of Mines Report No. 826 (issued in 1949), on a map entitled "Exploratory Drilling Horse River Reserve, Northern Alberta, Township 89, Range 9, West of 4th Meridian".

** This figure is the average of the % bitumen figures contained in the weekly progress reports of the Bureau of Mines separation plant, which processed 75.9 tons of bituminous sand in its 1949-50 operation.

TABLE 2

Properties of the Extracted Abasand Sand

Composition of Sand[1]		Screen Analysis of Sand[2]	
	Wt %	Sieve Size (Tyler)	Wt % of Sand
SiO_2	98.4	20	0.38
Al_2O_3	0.8	40	0.58
Fe_2O_3	0.1	60	0.66
CaO	0.2	80	8.38
MgO	0.2	100	18.92
TiO_2	0.1	150	52.21
		+200	13.94
ZrO_2	trace	-200	4.92

Emission Spectra of Sand (Elements - Wt % of Sand)[3]

Si	Mn	Mg	Pb	Cr	Sr	Ni	Fe	Al	Mo	Ca	V	Ti	Cu	Zn
50	.005	.006	-	-	-	-	.07	1.5	-	.015	-	.05	.0025	-

The ash content of the bitumen was determined to be 0.60% by weight.[4] The semi-quantitative composition of this ash, as determined by its emission spectrum, is given in Table 3.

1/ On page 13 of FRL report #76, by Bowles and Booth, which is listed as No. 48 in the references of the present report.

2/ This analysis is the average of 53 screen analyses on tube mill feed composite samples for Mill Runs #1-#138 of the Bureau of Mines Separation Plant at Ottawa.

3/ Determined by the Bureau of Mines Spectrographic Laboratory.

4/ This ash determination was made on the benzene extract prepared by Soxhlet extraction.

TABLE 3

Emission Spectra of Bitumen Ash (Elements - Wt % of Ash)

Be	Si	Mn	Mg	Pb	Cr	Co	Ni	Fe	Al	Mo	Ca	V	Ti	Cu	Zr	B
.002	10	.04	1	.03	.1	.02	1	10	10	.1	.8	4	2	.1	.1	.05

A microscopic examination of the sand was made, and small woody fragments, light in colour, were observed. Since they were not coalified, it is doubtful that they were deposited at the same time as the bituminous sand. On the other hand, the microscopic examination of the Bitumount sand revealed small, coalified woody fragments.

Attention is drawn to the fact that the above properties refer to a representative sample from the Abasand shipment. It is well known that the properties of the bituminous sand vary considerably with geographic location. The bitumen content has been shown to vary from 1 or 2% up to 20%[42] and is related to the grain size of the sand, the finer-grained sands having the higher bitumen content.[43] The specific gravity of the bitumen varies from 1.00 to 1.06.[44] The sulphur content appears fairly uniform, being almost always between 4 and 5%.[45] Ward and Clark[46] have shown that the viscosity of the bitumen in the southern part of the area is one hundred times greater than that of the bitumen found in the northern part of the area. The asphaltene content of the bitumen also varies considerably with location. Pasternack and Clark[47] give figures for the asphaltene content of the bitumen from various locations.

Their results vary from 16.0 to 23.6%, the latter result representing the asphaltene content of the bitumen from the Abasand area. Ultimate analyses on a variety of samples have been published. Bowles and Booth[48] have determined these analyses for bitumen from the Abasand and Clearwater areas. Pasternack and Clark[47] have given figures for samples from four different areas. The ultimate analyses appears to remain fairly constant throughout the area.

Mines Branch results indicate the vanadium analysis of bitumen from the Clearwater area to be 0.021%. Abasand bitumen coke contained 0.08% vanadium.[49]

ISOLATION AND ANALYSIS OF THE ASPHALTENE FRACTION

Isolation of the Asphaltenes

At the outset of the experimental work, the objective was to determine whether the chromatography of the bitumen on a variety of adsorbents showed any promise of yielding a reasonably rapid and informative analytical scheme as compared with other methods of separation.[50, 51] Preliminary experiments, in which the bitumen was dissolved in a good solvent (carbon tetrachloride) and chromatographed on silica gel (48/200 mesh) at solvent/oil ratios of 6.1/1 or 18/1 and at gel/oil ratios of 5.4/1 and 16/1 respectively, resulted in poor resolutions. Flow rates were low and little separation of the dark-coloured bodies from the pale-yellow

oils was obtained. The difficulty was attributed to the presence of the high-molecular-weight components, the asphaltenes. This difficulty would not have arisen, had silica gel with pores sufficiently large to retain the asphaltenes been used. As chromatographic separation takes place on the basis of both molecular weight and chemical type, the above results indicated the desirability of narrowing the range of molecular weight distribution by removing the asphaltenes. The elimination of the high-molecular-weight asphaltenes by extraction of the bituminous sand with n-pentane* has the advantage that it is possible to analyze 77% of the bitumen by chromatography, thus giving a broader insight into the nature of the types of compounds forming this material.

It should be noted that the term asphaltenes has only been rather "loosely" defined. Asphaltenes are generally considered to be the organic fraction insoluble in petroleum ether but soluble in carbon disulphide, benzene, chloroform, and carbon tetrachloride.[52] Lack of agreement between the various methods of determining asphaltenes exists, due to the wide variety of solvents used. There are two methods for obtaining the asphaltenes. The first, due to Marcusson,[37] consists of dissolving the bitumen in benzene and then precipitating the asphaltenes with petroleum

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* Phillips "technical grade" n-pentane (95 mole % n-pentane, 4% isopentane) was used throughout this research.

ether. Katz[38] has applied this method to the Alberta bitumen. In the second method, investigators have arbitrarily adopted the difference in solubility in two solvents as a measure of the quantity of asphaltenes present.[53] The Institute of Petroleum has developed two tests for asphaltenes: in one, the asphaltenes are described as that portion insoluble in hot petroleum spirit but soluble in hot benzene;[54] in the other, cold carbon disulphide is used in place of benzene.[55]

In this investigation, the asphaltenes, except where otherwise stated, were considered to be that portion of the bitumen not extractable in a Soxhlet extractor by n-pentane but extractable with carbon tetrachloride. While this definition is not suitable from an analytical point of view, in that it does not involve thermodynamic equilibria, it is reasonably reproducible under well defined conditions. This extraction procedure, though less precise, is far more economical as far as the solvents are concerned, and more convenient. As present techniques do not permit an exact description of the asphaltene fraction, it seemed unnecessary to coin another word to describe the fraction isolated by this method.

Marcusson's method of determining the asphaltene content, as developed by Katz,[38] was applied to the Abasand bitumen to secure a more precise estimate of the quantity of this material. In this procedure, five grams of bitumen were dissolved in 25 ml benzene. This solution was then added to 300 ml n-pentane, where-

by the asphaltenes were precipitated. The precipitate was filtered and dried at 100°C. The asphaltenes prepared by this method were a blackish-brown, very finely divided, dry powder, amounting to 18.25% of the bitumen. They contained 7.9% sulphur and were found to have a molecular weight of 2135 (determined by the cryoscopic method in benzene).

From the point of view of the subsequent chromatography of the oil and resin fractions, it was found more convenient to eliminate the asphaltenes from the bitumen by the method of pentane extraction. Where only small quantities of pentane extract were required, conventional glass Soxhlet extractors were used which had a capacity of 100 grams of bituminous sand. In this type of extractor it was possible to obtain reproducible results ($\pm$ 2%). Pentane extract prepared in this manner amounted to 78.39% of the bitumen. Its molecular weight was found to be 776 (determined cryoscopically in benzene). The asphaltene content of the bitumen amounted to 21.61%, as compared with 18.25% by Katz' method.

Where larger quantities of asphaltene-free bitumen were required, a specially designed Soxhlet extractor with a capacity of 11 kilograms was employed. This apparatus is shown in Figure 1. The boiler was a 5-litre Pyrex round-bottom flask. The extractor was a brass cylinder 9 inches in diameter and 12 inches in height. The lid on this cylinder was made secure by circumferential bolts and sealed with a lead gasket. Inside the extractor, the bituminous

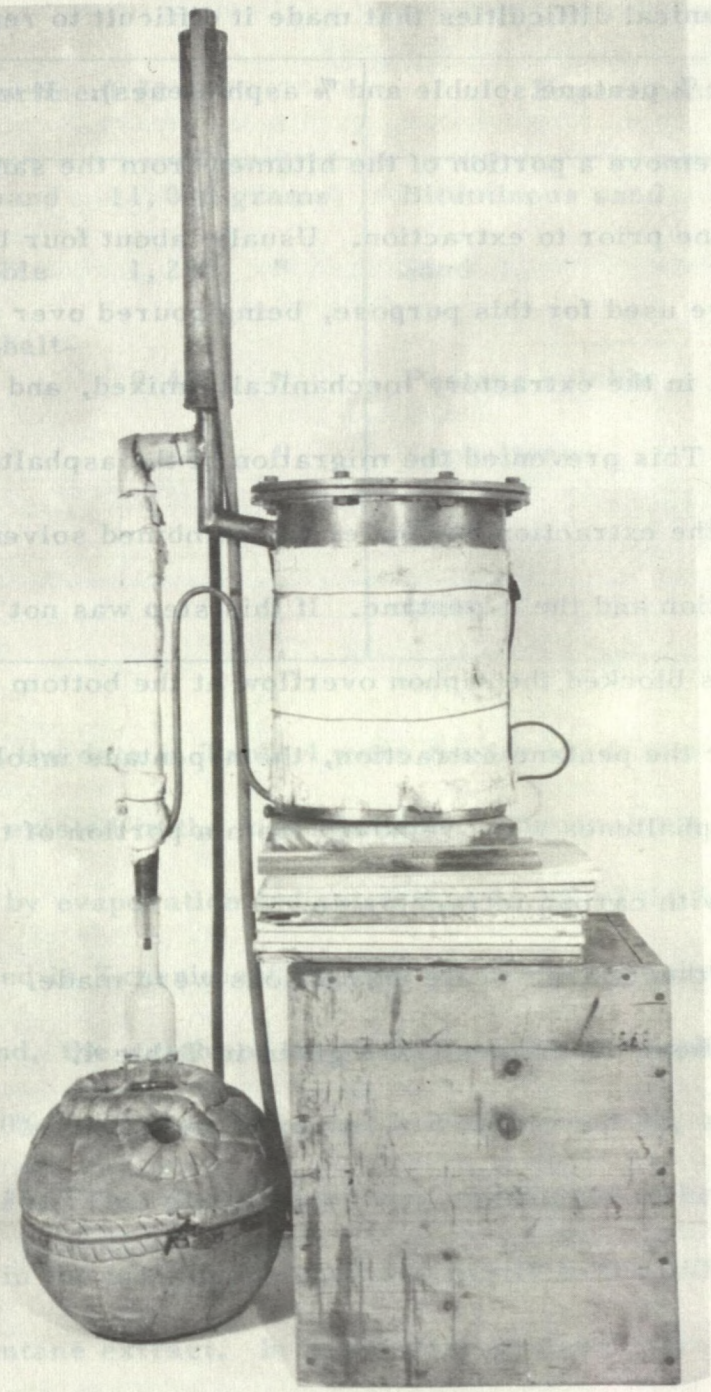

Figure 1. Large-scale extractor for the preparation of large quantities of the pentane-soluble portion of bitumen.

sand was placed in a bag made of filter cloth. The extraction with n-pentane was continued for 81 hours. In this process, there were certain mechanical difficulties that made it difficult to reproduce the results (i.e., % pentane soluble and % asphaltenes). It was found desirable to remove a portion of the bitumen from the sand by washing with pentane prior to extraction. Usually about four litres of n-pentane were used for this purpose, being poured over the bituminous sand in the extractor, mechanically mixed, and then siphoned off. This prevented the migration of the asphaltenes to the bottom of the extraction bag under the combined solvent action of the oil fraction and the n-pentane. If this step was not taken, the asphaltenes blocked the siphon overflow at the bottom of the extractor. After the pentane extraction, the n-pentane insoluble material or asphaltenes were removed from a portion of the sand by extraction with carbon tetrachloride.

Two of these large-scale extractions were made. The data secured from these experiments are given in Table 4.

TABLE 4

Results of Large-scale Solvent-Extraction Experiments

Experiment #2		Experiment #5	
Bituminous sand	11,000 grams	Bituminous sand	11,000 grams
Pentane soluble	1,290 "	Sand	9,013 "
Sand and asphaltenes	9,490 "	Pentane soluble	1,307 "
Loss	220 "	Asphaltenes	369.5 "
		Water	122.1 "
		Loss	188.4 "

When the data in Table 4 were examined, it was noted that a discrepancy existed in the mass balance. The analysis of the pentane extract by evaporation indicated that 73.8% of the bitumen had been extracted in Experiment #2, and 74.6% in Experiment #5. On the other hand, the weight of the residual sand and asphaltenes indicated that 80.0% had been extracted in Experiment #2, and 85.6% in Experiment #5. This discrepancy was considered to be due partly to moisture in the bituminous sand and partly to the difficulty of analyzing pentane extract. In heating the pentane extract sufficiently to drive off the water, some loss of the more volatile constituents also took place. All the chromatographic work to be reported in the following series of reportshas been made with the materials pre-

pared in Experiment #2, above. All calculations have been based on the assumption that 77% of the bitumen was extracted.

Ultimate Analysis of the Asphaltenes and Analytical Data for Structural Analysis

Tables 5 to 8, which follow, give in summary form the ultimate analyses of the asphaltenes, together with the values of the physical constants that are required for hydrocarbon structural analysis.

TABLE 5

Properties of the Asphaltenes (As Prepared)

Property		Asphaltenes #2	Asphaltenes #5
Carbon,	wt %	78.35	77.46
Hydrogen,	"	8.28	7.44
Nitrogen,	"	0.80	0.95
Sulphur,	"	7.64	7.75
Oxygen (by diff.),	"	0.97	3.79
Ash,	"	3.96	2.61
Density,	g/cc	-	1.17
Molecular weight		-	2492

The density of the asphaltenes given in Table 5 was determined by the helium displacement method[67, 68]. The molecular weight was determined cryoscopically in phenanthrene and calculated on the basis of "ash-free" asphaltenes.

Table 6 contains the ultimate analyses of the asphaltenes on an "ash-free" basis.

TABLE 6

Corrected Properties of Asphaltenes

Property		Asphaltenes #2	Asphaltenes #5
Carbon,	wt%	81.5	79.5
Hydrogen,	"	8.62	7.64
Nitrogen,	"	0.83	0.98
Sulphur,	"	7.96	7.96
Oxygen (by diff.),	"	1.09	3.93*

* Attention is drawn to the oxygen determinations. Since these were obtained by difference, it must be recognized that the sum of the experimental errors in the C, H, N and S values are contained in the figure given for oxygen. This accounts for the oxygen's appearing rather high in comparison with other oxygen figures for the Alberta bitumen.[38]

The composition of the asphaltene ash as determined by the emission spectrum is given in Table 7.

TABLE 7

Emission Spectra of Asphaltene Ash (Elements - Wt % of Ash)

Si	Mn	Mg	Pb	Cr	Sr	Ni	Fe	Al	Mo	Ca	V	Ti	Cu	Zn
25	.08	1.5	.07	.04	-	.35	.3	25	.01	1.5	2.8	.5	.25	.25

In order to apply the recently developed methods of structural group analysis,[56, 57] a sample of asphaltene #5 was sent to Micro-Tech Laboratories, in Chicago, to obtain an elementary analysis of suitable accuracy for these methods. In addition, the density, refractive index, and molecular weight of this sample were determined. These properties are tabulated in Table 8.

TABLE 8

Properties of the Asphaltenes Required for Structural Group Analysis

Property		As Prepared	On "Ash-free" Basis
Carbon,	Wt %	77.08	79.01
Hydrogen,	"	7.78	7.98
Nitrogen,	"	0.99	1.01
Sulphur,	"	7.87	8.07
Ash,	"	2.45	
Oxygen (by diff.),	"		3.93
Molecular weight			2492*
Density (d_4^{20})			1.158**
Refractive index (n_D^{20})			1.665***

* Determined cryoscopically in phenanthrene and calculated on basis of "ash-free" asphaltenes.

** Determined by water displacement.

*** Determined by calculation from reflectance measurements in air and water.

Application of van Krevelen's Method of Structural Analysis to the Bitumen and Asphaltenes

The presence of lignite seams within the bituminous sand in some locations[58] suggested that a comparison of the composition of the bitumen with that of bituminous coals and peat derived from lignin and cellulose might be informative. To illustrate this comparison the graphical statistical treatment developed by van Krevelen was used.[59] For this purpose the atomic ratios O/C and H/C, and the molecular weights of the bitumen and the asphaltenes, were required. The application of this method is shown in Figure 2. The location of the points in Figure 2 that define the composition of the bitumen and the asphaltene fraction indicates that either the bitumen was not derived from cellulose and lignin or a transformation has occurred which differs widely from that which takes place during coal formation. The H/C ratio for the Abasand bitumen in this investigation was determined to be 1.482. Pasternack and Clark have reported a ratio of 1.498 for natural bitumen from the Bitumount, Ells River and Mildred-Ruth Lakes areas, and 1.496 for a sample from 75 miles south of Abasand.[47] These results seem to indicate that the H/C ratio of the entire deposit varies over a rather small range.

More recently (1952-54), van Krevelen has developed methods of structural group analysis for coal which require only the elementary composition and the density.[60] These methods have been applied to the Abasand bitumen and asphaltene data. In

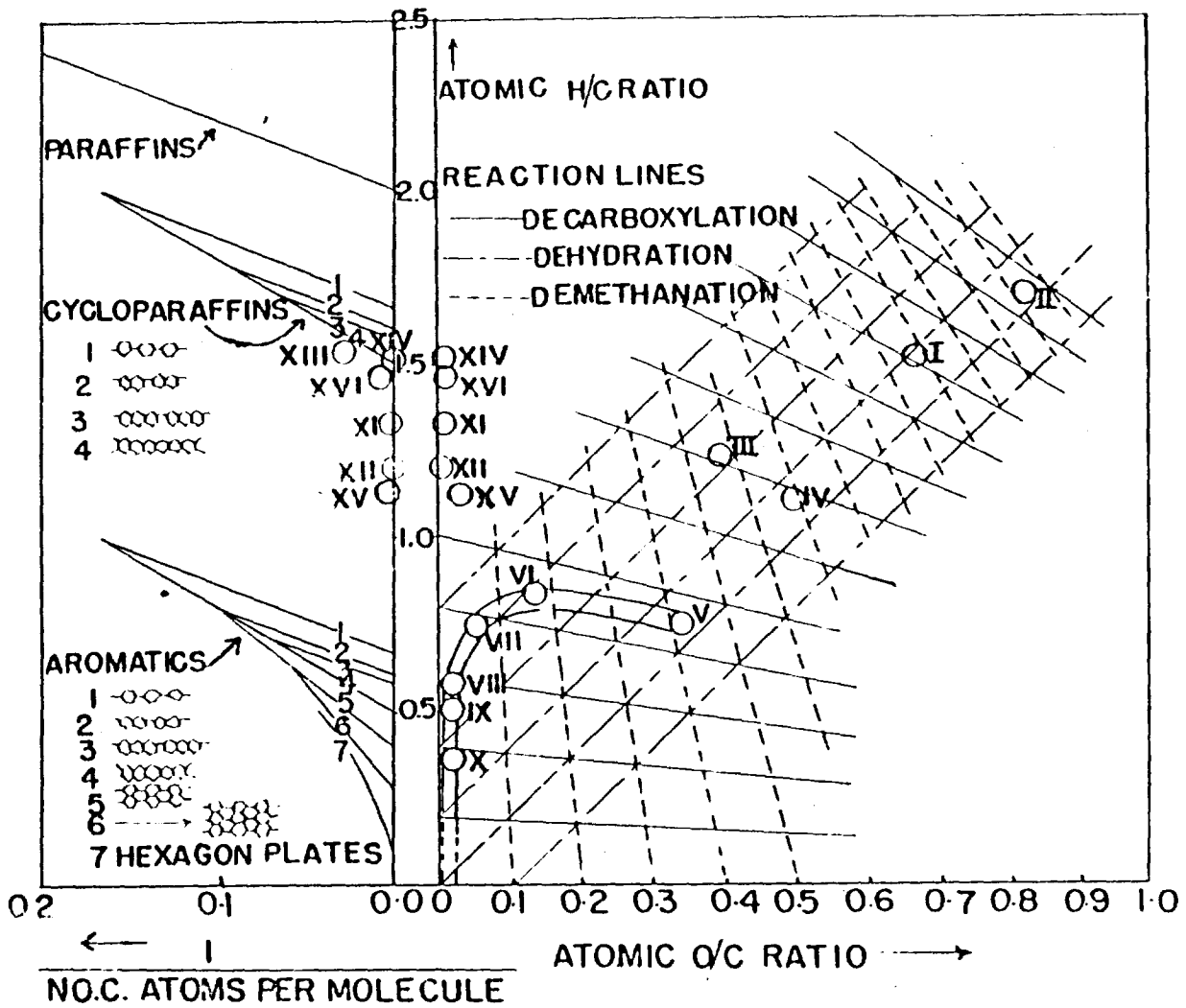

Figure 2. Van Krevelen's H/C versus O/C diagram.

I Wood; II Cellulose; III Lignin; IV Peat; V Brown Coal; VI Low Rank Bituminous Coal; VII Medium Rank Bituminous Coal; VIII High Rank Bituminous Coal; IX Semi-anthracite; X Anthracite (van Krevelen's data); XI Bitumen and Resins (Katz); XII Asphaltenes (Katz); XIII Oil Fraction (Katz); XIV Bitumen (Bowles and Booth); XV Asphaltenes (this research); XVI Bitumen (this research).

these methods, van Krevelen has described the structure in terms of two characteristics of the system, namely the ring index, which has been defined as $2R/C$ where R is the number of rings per molecule, and f_a, the fraction of aromatic carbon. Van Krevelen's methods were applied to determine the aromaticity of the bitumen and the asphaltenes. Three values for f_a were obtained in the following manner:

Method I

f_a was calculated from the following two equations,[61] which required only the density and the elementary analysis:

$$(1)\quad \frac{1}{d} = \frac{9.9 + 3.1\ H/C + 3.75\ O/C + 1.5\ N/C + 14S/C - (9.1 - 3.65\ H/C)\ R/C}{(12.01 + 1.008\ H/C + 16.0\ O/C + 14.008\ N/C + 32.06\ S/C}$$

$$(2)\quad f_a = 2 - H/C - 2R/C$$

Method II

If the experimental molecular weight is known (as it is here), then the equations in Method I become:

$$(3)\quad \frac{M}{d} = 9.9C + 3.1\ H + 3.75O + 1.5N + 14S - (9.1 - 3.65H/C)R$$

$$(4)\quad f_a = 2 - H/C - 2\left[\frac{R - 1}{C}\right]$$

Method III - Graphical Densimetric Method[62]

This method required the calculation of the following two quantities:

$$(5)\quad \frac{Mc}{d} = \frac{1}{d}\left[12.01 + 1.008\ H/C + 16.0\ O/C + 14.008\ N/C + 32.06\ S/C\right]$$

$$(6)\quad \left[\frac{Mc}{d}\right]_{corr.} = \frac{Mc}{d} - \left[8.1\ O/C + 6.4\ \frac{N}{C} + 12.5\ S/C\right]$$

f_a was then read from van Krevelen's graph of $\frac{Mc}{d}$ versus H/C.

The results of this application are tabulated in Table 9.

It should be noted that, for cases where naphthenic rings are present, this method was recommended only for those cases where f_a was greater than 0.25.[73]

TABLE 9

Results of the Application of van Krevelen's Densimetric Method

Property	Bitumen	Asphaltenes
H/C ratio	1.48	1.203
O/C "	0.0123	0.037
S/C "	0.0222	0.038
N/C "	0.00314	0.011
R/C (Method I)	0.238	0.255
R (" I)		41.88
f_a (" I)	0.0428	0.2860
R (" II)	-	41.65
f_a (" II)	-	0.30
Mc/d	14.05	13.11
(Mc/d), corrected	13.65	12.27
f_a (Method III)	0.35	0.52
R/S [Method I]	10.72	6.71

Method IV

Van Krevelen has correlated the parameters R/C, f_a and H/C in another manner.[63] This will be referred to herein as Method IV. For the purpose of studying coal, the various hydrocarbon groups were divided into four classes:

$C_1 = \frac{CH_2}{C}$ the fraction of CH_2 groups (paraffinic or naphthenic) in the molecule;

$C_2 = \frac{CH}{C}$ the fraction of carbon atoms which are junctions between fused naphthenic rings;

$C_3 = \frac{CH_a}{C}$ the fraction of aromatic CH groups; and

$C_4 = \frac{Ca}{C}$ the fraction of aromatic carbons which are junctions between fused aromatic rings.

Van Krevelen set forth the following relationships between these four types of linkages, based on the definitions of the symbols and the mass balance:

(7) $C_1 + C_2 + C_3 + C_4 = 1$

(8) $2C_1 + C_2 + C_3 = H/C$

(9) $C_2 + C_4 = 2R/C$

(10) $C_3 + C_4 = f_a$

The individual values of C_1, C_2, C_3 and C_4 could not be calculated from this set of equations, since this set did not consist of four independent equations. In fact, there are three unknowns (the fourth is known, since the sum is one) and only two independent properties, density and H/C. The right hand sides of the above set of equations are not independent, but are related to one another by the following equation, since by definition f_a and R/C are related to H/C:

(11) $f_a = 2 - H/C - 2R/C$

An algebraic rearrangement of any group of three of the set resulted in the fourth equation. Van Krevelen overcame this difficulty by developing a relationship between C_1 and H/C. This equation resulted from a statistical analysis of macromolecular model structures and expressed the probability of the occurrence of a CH_2 group as a function of the H/C ratio. Hence, van Krevelen was able to determine C_1, C_2, C_3 and C_4 from the following set of equations:

(12) $C_1 = 0.5\,(H/C)^{3/2} - 0.29\,(H/C)^{1/2}$ when $H/C > 0.6$

(13) $C_2 \approx 1 - f_a - C_1$

(14) $C_3 \approx 1 - 2R/C - C_1$

(15) $C_4 \approx 1 - H/C + C_1$

The method has been applied to the bitumen and the asphaltenes, and the results are given in Table 10.

TABLE 10

Van Krevelen's Structural Group Analysis of the Bitumen and the Asphaltenes (Method IV)

Group	Bitumen	Asphaltenes
C_1	0.549	0.34
C_2	0.408	0.37
C_3	-0.0243	0.15
C_4	0.0673	0.14

Structural Information from the Infra-red Absorption Spectrum of the Asphaltenes

To obtain additional structural information to lend support to the structural group analysis results, use has been made of the infra-red spectrum. Figure 3 is the infra-red spectrum of the asphaltenes, recorded with a Perkin-Elmer double beam infra-red spectrometer using the KBr pellet technique.

The absorption bands in this spectrum may be assigned to functional groups as follows:

Wavelength (microns)	Functional Group
2.95	Moisture in KBr pellet
3.0	N - H
3.25-3.35	Aromatic CH
3.38-3.50	Aliphatic CH
5.7 -6.0	C = O

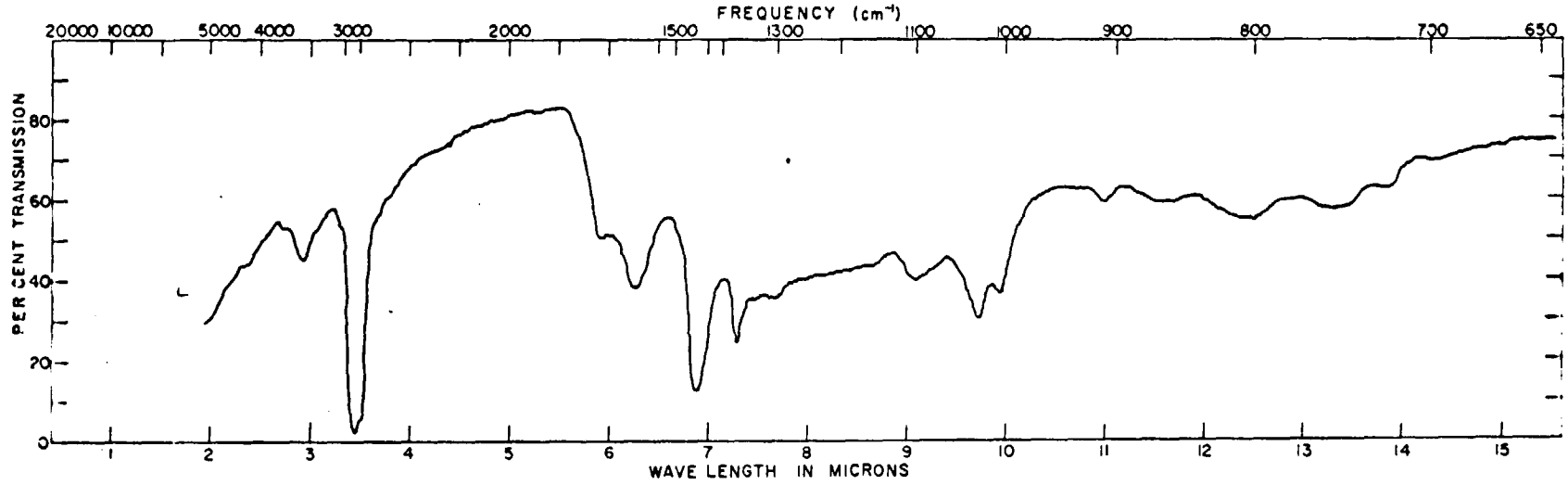

Figure 3. Infra-red spectrum of the asphaltenes.

Wavelength (cont'd)	Functional Group (cont'd)
6.25	C = C
6.8 - 6.9	CH
7.25 - 7.30	CH_3
11.0 -11.6	An isolated unsubstituted H on an aromatic ring.
11.6 -12.5	2 adjacent unsubstituted H on an aromatic ring
12.35-13.3	3 adjacent unsubstituted H on an aromatic ring
13.0 -13.6	4 adjacent unsubstituted H on an aromatic ring
13.0 -13.7) 14.08-14.5)	5 adjacent unsubstituted H on an aromatic ring
13.7 -13.9	4 or more linear - CH_2 -

Use has been made of the absorption bands at 6.25 and 7.25 microns to provide quantitative information about the amounts of aromatic carbon and methyl groups, respectively. This spectrum also indicated the presence of several other groups: carbonyl, aromatic CH, and linear CH_2. It was not possible to make use of the latter two groups quantitatively. The main concern here is the hydrocarbon skeletal structure; hence, non-hydrocarbon linkages will not be discussed.

On the basis of the absorption band at 7.25 microns it was estimated that the fraction of carbon present as CH_3 groups was 0.15.

Many investigators[64] have used the absorption band at 6.25 microns to determine the aromaticity. However, it has been found that this absorption band is affected by other structural groups present in the molecule, and that to obtain quantitative information it is necessary to select a reference compound to serve as a standard with which to compare the asphaltenes. This fact somewhat limited the use of this method as a general method of determining the amount of aromatic carbon in bituminous materials. However, it was felt that much useful information could be obtained by calculating f_a for the asphaltenes on the basis of various aromatic hydrocarbons of different types containing aliphatic and alicyclic groups. For this purpose, the spectra of 49 aromatic hydrocarbons were chosen from the spectra that had been determined in the Mines Branch, and have been roughly divided into six classes on the basis of structural differences of interest in considering the possible structure of the asphaltenes. The result of this calculation is given in Table 11.

Application of Structural Group Analysis Method (Scheme MB1) of Montgomery and Boyd to the Asphaltene Fraction

Recently, the authors have developed a new method of structural group analysis, which for convenience will be referred to as scheme MB1. In this scheme, three chemical and

TABLE 11

Calculation of f_a for the Asphaltenes on the Basis of the Absorbance of the 6.25μ Band of Pure Aromatic Hydrocarbons

Class of Compounds	No. in Class	Mean Values of f_a
1) Fused aromatics with side chains where $\frac{CH_a}{C_a} < 2.0$	4	0.75
2) Fused aromatics with side chains where $\frac{CH_a}{C_a} > 2.0$	2	0.35
3) Fused aromatics with no side chains and $\frac{CH_a}{C_a} < 2.0$	18	1.26
4) Fused aromatics containing cyclic CH_2 groups	8	1.10
5) Non-fused aromatics	5	0.65
6) Methyl naphthalenes	12	0.33
7) Brandes' method*	-	0.62

* Compare reference 65, this method calibrated against the n-d-M structural analysis method. This has been included here for comparative purposes.

two physical properties are expressed in terms of five structural groups in a form which may be simultaneously solved by modern high speed computing equipment.[57] The accuracy with which this method analyzes pure hydrocarbons has been determined.[57] This method was designed for material containing only the following types of hydrocarbon groups:

C_1 = number per molecule of CH_3, CH_2, CH and C groups in linear and branched chains.

C_2 = number per molecule of CH_2 groups in saturated rings, including the case where the hydrogen atoms may be replaced by branched or linear chains.

C_3 = number per molecule of CH groups that are junctions between fused saturated rings, as well as similarly situated groups where the hydrogen is replaced by linear or branched chains.

C_4 = number per molecule of CH groups in aromatic rings, including the case where the hydrogen may be replaced by branched or linear chains.

C_5 = number per molecule $-\overset{|}{\underset{|}{C}}-$ groups that are junctions between fused aromatic rings, as well as common junctions between saturated and aromatic rings.

It should be noted that this system of atomic groupings does not make provision for non-fused polycyclic substances. This method consisted of the simultaneous solution of the following set of five property equations:

(16) $C_1 + C_2 + C_3 + C_4 + C_5 = \Sigma C$

(17) $2C_1 + 2C_2 + C_3 + C_4 = \Sigma H$

(18) $C_4 + C_5 = \Sigma C_a$

(19) M. V. at 20° C, 1 atm. press. $= C_1 (16.38 + \frac{30.61}{\Sigma C}) + C_2 (13.20 + \frac{28.48}{\Sigma C}) +$

$C_3 (10.981 + \frac{20.679}{\Sigma C}) + C_4 (12.406 + \frac{14.042}{\Sigma C} -$

$1.96 \frac{C_1}{\Sigma C} + 10.13 \frac{C_2}{\Sigma C}) + C_5 (5.124 - \frac{5.238}{\Sigma C})$

(20) M. R. at 20° C, 1 atm. press. $= C_1 (4.623 + \frac{2.314}{\Sigma C}) + C_2 (4.468 + \frac{0.868}{\Sigma C} - 0.245 \frac{C_1}{\Sigma C}) +$

$C_3 (3.693 + \frac{0.3395}{\Sigma C}) +$

$C_4 (4.5445 - \frac{1.021}{\Sigma C} - 0.396 \frac{C_1}{\Sigma C} - 5.701 \frac{C_2}{\Sigma C}) +$

$C_5 (5.734 - \frac{14.333}{\Sigma C})$

The following properties are required for the application of this method to the asphaltenes: the total number of carbon atoms per molecule, the total number of hydrogen atoms per molecule, the total number of aromatic carbon atoms per molecule, the molar volume, and the molar refraction. The first two of these properties were calculated from the carbon and hydrogen analyses and the experimental molecular weight. Some explanation is required about the values used for the remaining three properties.

With regard to the molar volume and the molar refraction (Lorentz-Lorenz function), it was necessary to correct the values based on experimental measurements, to convert them to a "foreign-atom-free" basis, since this method is only applicable to a hydrocarbon. These corrections have been made with the use of the following two equations, which are slightly modified forms of those used by van Krevelen:[66]

(21) $M.V. = 9.9C + 3.1H + 3.75O + 1.5N + 15S - K$

(22) $M.R. = 2.558C + 1.039H + 1.65O + 2.48N + 7.64S + E.$

Equations 21 and 22 were used to determine K and E, the structural contributions to the molar volume and molar refraction, respectively. This was done by substituting the known values for M.V., calculated from the experimental molecular weight and density (20°C); that for M.R., calculated from the refractive index (n_D^{20}) and M.V.; and those for C, H, N, O, and S, calculated from the elementary analysis and the molecular weight. Using the values of K and E thus obtained, M.V. (corr.) and M.R. (corr.) were then calculated from the following equations:

(23) $M.V._{\text{corrected}} = 9.9C + 3.1H - K$

(24) $M.R._{\text{corrected}} = 2.558C + 1.039H + E.$

This method consisted essentially in "removing" the foreign atoms from the molecule without altering the structural contributions to the molar volume and molar refraction and without

altering the number of carbon and hydrogen atoms. It is rather crude in that it assumes that the foreign atoms make no contribution to K and E, but was considered adequate for this purpose as a first approximation. A number of refinements are possible, such as making some assumptions as to the structural forms in which the foreign atoms are present, or such as altering the number of hydrogen and carbon atoms to "compensate" for the removal of the foreign atoms. A number of these assumptions will be examined in the future, but to simplify the present exposition it will be assumed that the foreign atoms are removed without the addition of compensating hydrogen or carbon. Considering the small number of foreign atoms (less than 10%) involved here, and the accuracy of the structural analysis method itself, this approach seemed justified.

The most difficult chemical property to evaluate in order to apply the present structural analysis scheme is ΣC_a, the number of aromatic carbon atoms per molecule. It has already been shown (Table 11) that the infra-red spectrum of the asphaltenes does not yield a satisfactory estimate of ΣC_a. Taking into consideration the values for ΣC_a obtained from the infra-red calculation and also calculated according to van Krevelen's methods, the following strategy was adopted with regard to applying the present structural analysis scheme. Values of C_1 to C_5 were determined for arbitrary values of ΣC_a chosen to cover the entire

range of possible values. Since no reliable method exists at present for obtaining the aromaticity directly for this type of material, it was considered that certain structural information could be obtained by considering the variation of C_1, C_2, C_3, C_4 and C_5 with ΣC_a, and that certain structures could be eliminated on the basis of algebraic and chemical criteria.

The computational method used here has been altered somewhat from the original method. These changes are here summarized briefly. The original computational method has been modified to reduce the number of iterations; and the starting value in the iterative procedure has been changed from zero to ΣC, in order to eliminate cases of non-convergence and to ensure obtaining the solution between 0 and ΣC (the only physically possible one) in the iterative stage of the procedure. The program for the IBM 650 computer has been revised so that all mathematically possible solutions (between $\pm \Sigma C$) are obtained. All cases so far studied fell into two classes: (1), only one solution existed; and (2), three solutions existed. Case 1 presented no problem, but in case 2, for all substances studied, one solution was in Quadrant 1, two were in Quadrants 2 and 3, or all three were in Quadrants 2 and 3. In the cases where multiple solutions were obtained, the solution chosen for structural analysis purposes was either the solution in Quadrant 1, or, in the second case, the set of values of C_1 to C_5 having the smallest sum of negative structural groups.

A negative quantity of a structural group has, of course, no physical significance. A solution which involves numerically small negative numbers may be regarded as more plausible than one involving large negative numbers. In actual practice, no difficulty was experienced in choosing by inspection the physically possible solution in a case where multiple solutions existed.

The derived properties of the asphaltenes required for this system are summarized in Table 12 and the results of the Montgomery-Boyd analysis (MB1) are shown in Table 13.

TABLE 12

Properties of the Asphaltenes Required for the Montgomery-Boyd Analysis (MB1)

Property				
ΣC	= 163.94			
ΣH	= 197.28			
M.V. exp.	= 2151.99	ΣN	=	1.80
M.R. exp.	= 799.16	ΣS	=	6.28
M.V. corr.	= 2032.14	ΣO	=	6.12
M.R. corr.	= 736.62			
K*	= 202.44			
E*	= 112.29			

* Compare equations 21 and 22.

TABLE 13

Results of Montgomery-Boyd Analysis (MB1) of the Asphaltenes

f_a	ΣC_a	C_1	C_2	C_3	C_4	C_5
0.20	32.80	81.31	-14.89	64.68	-0.22	33.02
0.29[a]	46.88	72.44	-17.31	61.89	25.15	21.73
0.30[b]	49.35	70.55	-17.81	61.81	30.01	19.34
0.33[c]	54.10	66.51	-18.85	62.14	39.84	14.26
0.52[d]	85.20	50.94	12.21	15.55	55.45	29.75
0.60	98.34	46.14	30.18	-10.76	55.42	42.92

a - van Krevelen Method I.
b - van Krevelen Method II.
c - Infra-red 6.25μ band compared with methyl naphthalenes (12 compounds).
d - van Krevelen Method III.

These results are expressed graphically in Figure 4.

Application of Modified Montgomery-Boyd Analysis (Scheme MB2)

The original structural group analysis (MB1) developed by the authors was modified to analyze material where C_3 is zero, C_2 is small, and where both non-fused and fused aromatic rings are present. Use was made of molar volume and molar refraction equations which were developed by the authors to fit non-fused aromatic compounds.[69] This method consisted of the simultaneous solution of a second set of five equations which

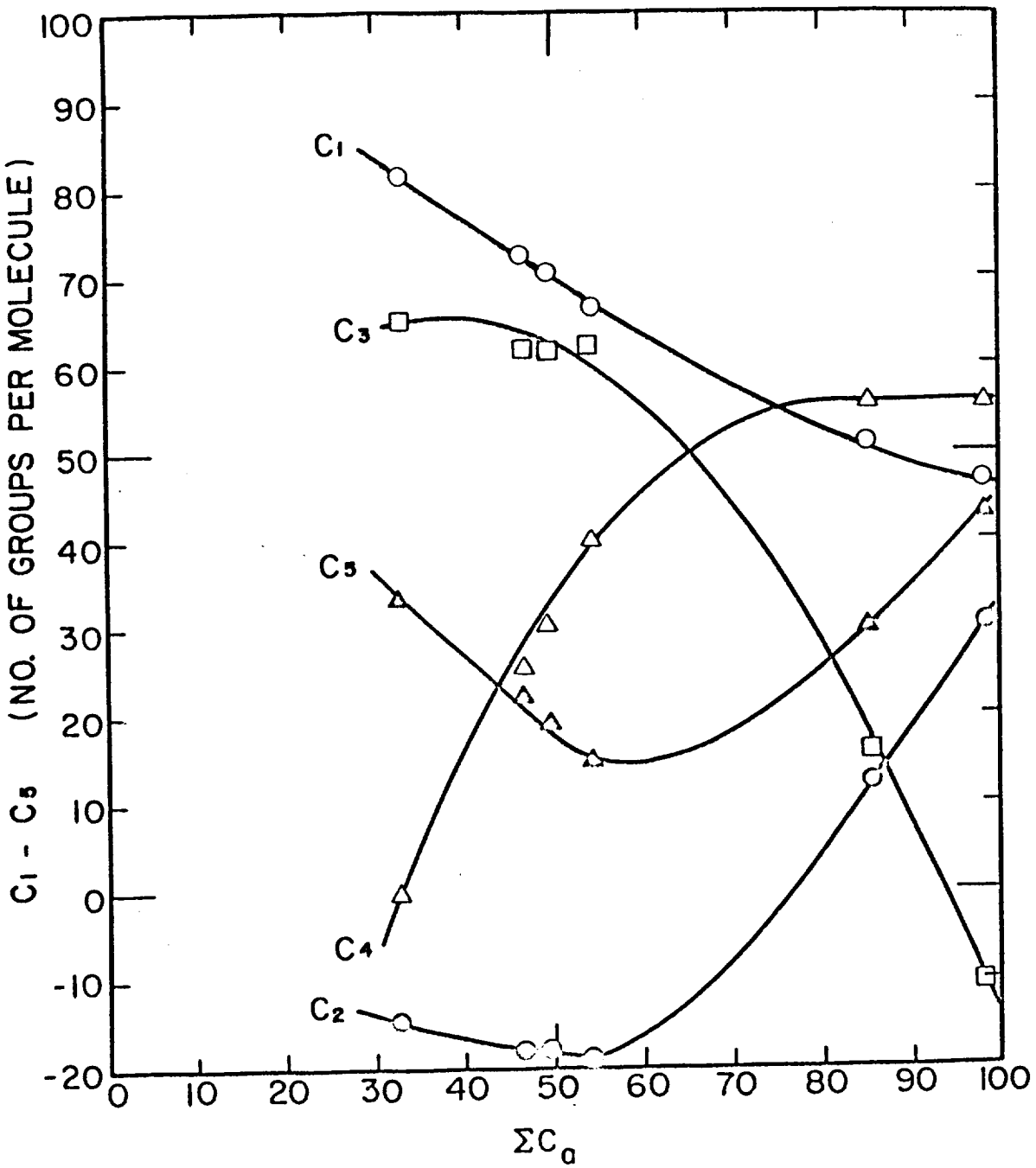

Figure 4. Results of the Montgomery-Boyd analysis (Scheme MB1) of the asphaltenes.

represented the identical properties as the first set but which were set up in terms of a second set of parameters, C_1, C_2, C_4, C_5 and C_7, where C_7 represents the number of junction carbon atoms in non-fused aromatic rings.

For convenience, this second set of five equations is tabulated below:

(25) $C_1 + C_2 + C_4 + C_5 + C_7 = \Sigma C$

(26) $2C_1 + 2C_2 + C_4 = \Sigma H$

(27) $C_4 + C_5 + C_7 = \Sigma C_a$

(28) $C_1 \left(16.38+\frac{30.61}{\Sigma C}\right) + C_2 \left(13.20+\frac{28.48}{\Sigma C}\right) + C_4\left(12.406+\frac{14.042}{\Sigma C} - 1.96 \frac{C_1}{\Sigma C}\right) + C_5 \left(5.124-\frac{5.238}{\Sigma C}\right) + C_7\left(7.04+\frac{16.53}{\Sigma C}\right) =$ M.V. at 20°C. 1 atmos. press.

(29) $C_1 \left(4.623+\frac{2.314}{\Sigma C}\right) + C_2 \left(4.468+\frac{0.868}{\Sigma C} - 0.245 \frac{C_1}{\Sigma C}\right) + C_4 \left(4.5445 -\frac{1.021}{\Sigma C} - 0.396 \frac{C_1}{\Sigma C}\right) + C_5\left(5.734 - \frac{14.333}{\Sigma C}\right) + C_7 \left(2.872 + \frac{5.405}{\Sigma C}\right) =$ M.R. at 20°C 1 atmos. press.

To obtain an estimate of how the aromatic atoms were divided between non-fused and fused rings consistent with this choice of parameters, this second analysis scheme was applied to

the asphaltenes. The value of ΣC_a used for this case was the value ($\Sigma C_a = 93.01$) corresponding to a value of zero for C_3 in the graph in Figure 4. The results of this analysis are tabulated in Table 14.

TABLE 14

Application of Modified Montgomery-Boyd Analysis (MB2) to the Asphaltenes

C_1	=	65.15
C_2	=	5.75
C_4	=	55.42
C_5	=	20.92
C_7	=	16.67

DISCUSSION OF STRUCTURAL ANALYSIS METHODS APPLIED TO THE ASPHALTENES

All the methods of structural analysis which have been applied here have two assumptions in common. First, all involved the additivity of the molar volume (and the molar refraction) in the liquid state, and, second, all double bonds present are in aromatic rings. The asphaltene fraction, although showing no signs of cold flow at room temperature, does acquire fluid properties on moderate heating which would suggest that this substance may be considered a super-cooled liquid. Regarding the nature of the unsaturation in the asphaltenes,

the infra-red spectrum did not reveal the presence of any olefinic-type linkage. There are undoubtedly small amounts of other types of unsaturation which probably account for polymerization in air and for the colour. The standard chemical tests for unsaturation yielded somewhat inconclusive results when applied to high-molecular-weight material of this type.

In van Krevelen's methods of estimating R/C and f_a, it was assumed that the density was not a function of the state of strain of the sample but was an equilibrium property of the liquid which could be expressed in terms of the sum of atomic increments and structural factors. Van Krevelen assumed that the structural factors were due solely to the rings present and could be expressed as a linear function of H/C:[61] The model substances upon which this factor was based were: cellulose, polystyrene, and graphite.

Van Krevelen's Method I gave a value of 0.29 for the fraction of aromatic carbon (f_a) for the asphaltenes. Very little difference was observed in the values for f_a obtained by this method and by Method II. This was to be expected, since the only difference between I and II was that in Method II, since the experimental molecular weight was used, it was possible to use a more accurate form of the equation relating f_a and R/C. This involved an additional term, 2/C. Method III of the van Krevelen analysis yielded a considerably higher value for f_a (0.52). This

is of particular interest here and will be referred to later in the discussion of the Montgomery-Boyd Method (MB1 system) since the van Krevelen graphical method[62] was based on the relationship between Mc/d and H/C for pure aromatic hydrocarbons. Recent controversies concerning the upper and lower ends of the f_a scale[70, 71, 72] do not affect the present case, since the asphaltenes appear to lie in the centre of the scale. Similarly, the asphaltenes would not be affected by the limitations of this method which pertain to the relative proportions of aromatic and naphthenic carbon atoms (if naphthenic groups are present, then f_a must be greater than 0.25). Since in postulating any structure for the asphaltenes the number of rings is of prime importance, it is of interest to compare the number of rings per molecule corresponding to these three values of f_a. Method I corresponded to 41.9 rings per molecule, II to 41.6, and III to 22.7. It should be pointed out that the values for R/C and f_a employed in van Krevelen's Method IV were those values obtained by Method I. Method IV indicated the following composition for the asphaltenes: 34%, CH_2 groups; 37%, naphthenic CH groups; 15%, aromatic CH groups; and 14%, aromatic C groups. However, owing to the doubtful basis of Equation 12, recognized by van Krevelen, the results cannot be given the same weight as those obtained by his other methods. This method was dependent on an expression for C_1 (Equation 12) which was derived from the

statistical analysis of a number of macro-molecular model structures and which represented the probability of the occurrence of a CH_2 group as a function of the H/C ratio.

The structural analysis method (MB1) developed by the authors will now be considered. This system consisted of five property equations that were capable of simultaneous solution. This system was designed to analyze data on pure hydrocarbons. The equations were specifically designed to fit the hydrocarbons as API Project 42, and the method was tested on pure hydrocarbons in the range of C_{10} to C_{50}. If, as is the case here, the input data fed into the system refer to a mixture of compounds, the solution obtained will be the structure of the equivalent pure compound -- i.e. the pure compound that would possess the same density, refractive index, average molecular weight, number of carbon atoms, hydrogen atoms, and aromatic carbon atoms.

As has already been explained, the MB1 analysis was applied over a wide range of ΣC_a values, because of a lack of reliable experimentally determined values. These various sets of results were critically assessed on the basis of the following criteria: (1) elimination of physically impossible solutions, i.e. negative solutions; and (2) application of van Krevelen's ring balance equation[63] which, cast in terms of our parameters, became $C_3 + C_5 = 2R - 2$ to obtain a value for R, and the subsequent calculation of the number of cyclic carbon atoms per ring (C_R/R). The values of C_R/R were compared with those of

possible model structures. This additional information is tabulated in Tables 15 and 16 and depicted graphically in Figures 5, 6, 7, 8 and 9. Table 15, which contains this analysis expressed in terms of fractions of the total carbon, was included here mainly as a convenience in comparing these results with those of the van Krevelen methods, since van Krevelen expressed all the structural parameters as a fraction of the total number of carbon atoms.

The first method of application was to determine the range of values which ΣC_a may assume without yielding negative values for any of the structural groups. This amounted to confining the aromaticity within certain limits. The figures in Table 13 indicated a considerable number of physically impossible solutions (i.e. negative values for some one of the five carbon types). An examination of Figure 4 indicated that all five carbon types would be positive only over a fairly narrow range of ΣC_a values, namely $\Sigma C_a = 77$ to $\Sigma C_a = 93$ (i.e. $f_a = 0.47$ to $f_a = 0.57$). Above an f_a value of 0.57, C_3 became negative and below a value of 0.47, C_2 became negative. The values of the five structural types corresponding to these two limiting values of ΣC_a have been tabulated in Table 17.

TABLE 15

Montgomery-Boyd Analysis of the Asphaltenes, Expressed as Fractions of the Total Carbon

f_a	$C_1/\Sigma C$	$C_2/\Sigma C$	$C_3/\Sigma C$	$C_4/\Sigma C$	$C_5/\Sigma C$
0.20	0.496	-0.0908	0.395	-0.00134	0.201
0.29[a]	0.442	-0.106	0.378	0.153	0.133
0.30[b]	0.430	-0.109	0.377	0.183	0.118
0.33[c]	0.406	-0.115	0.379	0.243	0.087
0.52[d]	0.311	0.0745	0.0949	0.338	0.182
0.60	0.282	0.184	-0.0656	0.338	0.262

a - Van Krevelen Method I.
b - Van Krevelen Method II.
c - Infra-red.
d - Van Krevelen Method III.

TABLE 16

Structural Characteristics of the Asphaltenes, Derived from the Montgomery-Boyd Analysis

ΣC_a	C_2/C_3	C_4/C_5	R	C_R/R
32.80	-0.23	-0.007	49.85	1.66
46.88[a]	-0.28	1.16	42.81	2.14
49.35[b]	-0.29	1.55	41.57	2.25
54.10[c]	-0.30	2.79	39.20	2.48
85.20[d]	0.79	1.86	23.65	4.78
98.34	-2.80	1.29	17.08	6.89

a - Van Krevelen Method I. b - Van Krevelen Method II.
c - Infra-red. d - Van Krevelen Method III.

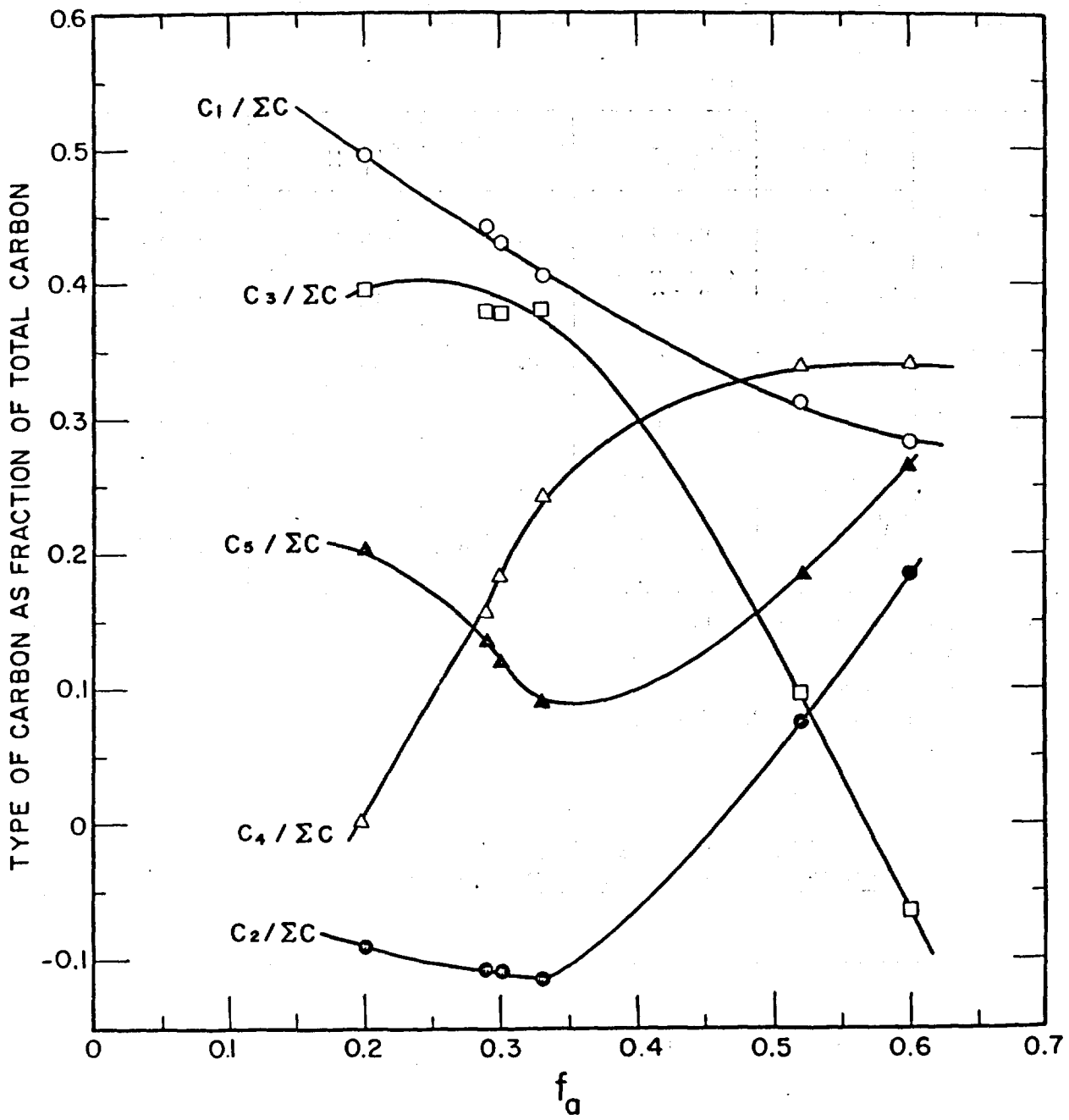

Figure 5. Results of the Montgomery-Boyd analysis (Scheme MB1) of the asphaltenes, expressed as fractions of the total carbon.

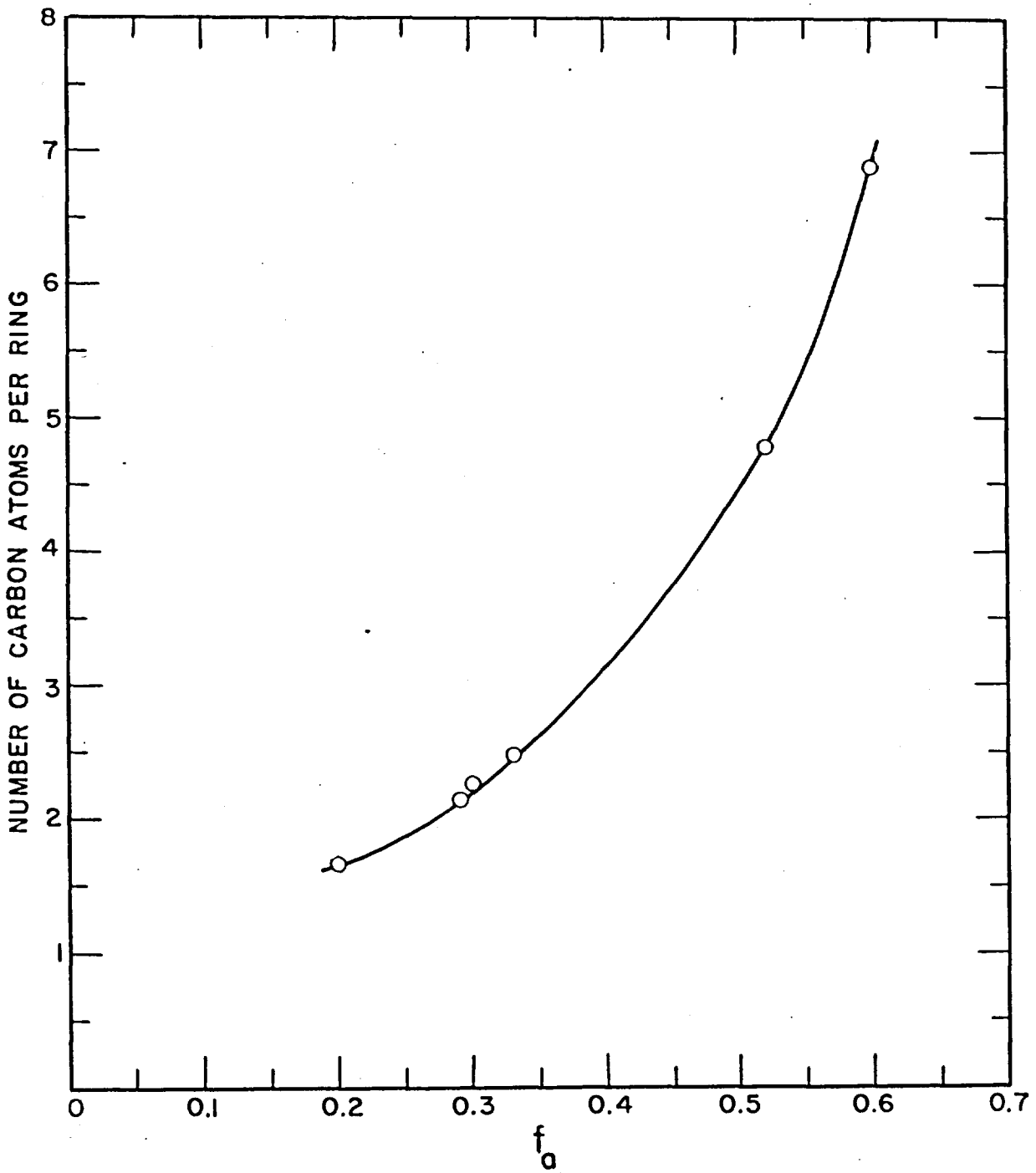

Figure 6. Number of carbon atoms per ring versus f_a for the Montgomery-Boyd analysis (Scheme MB1).

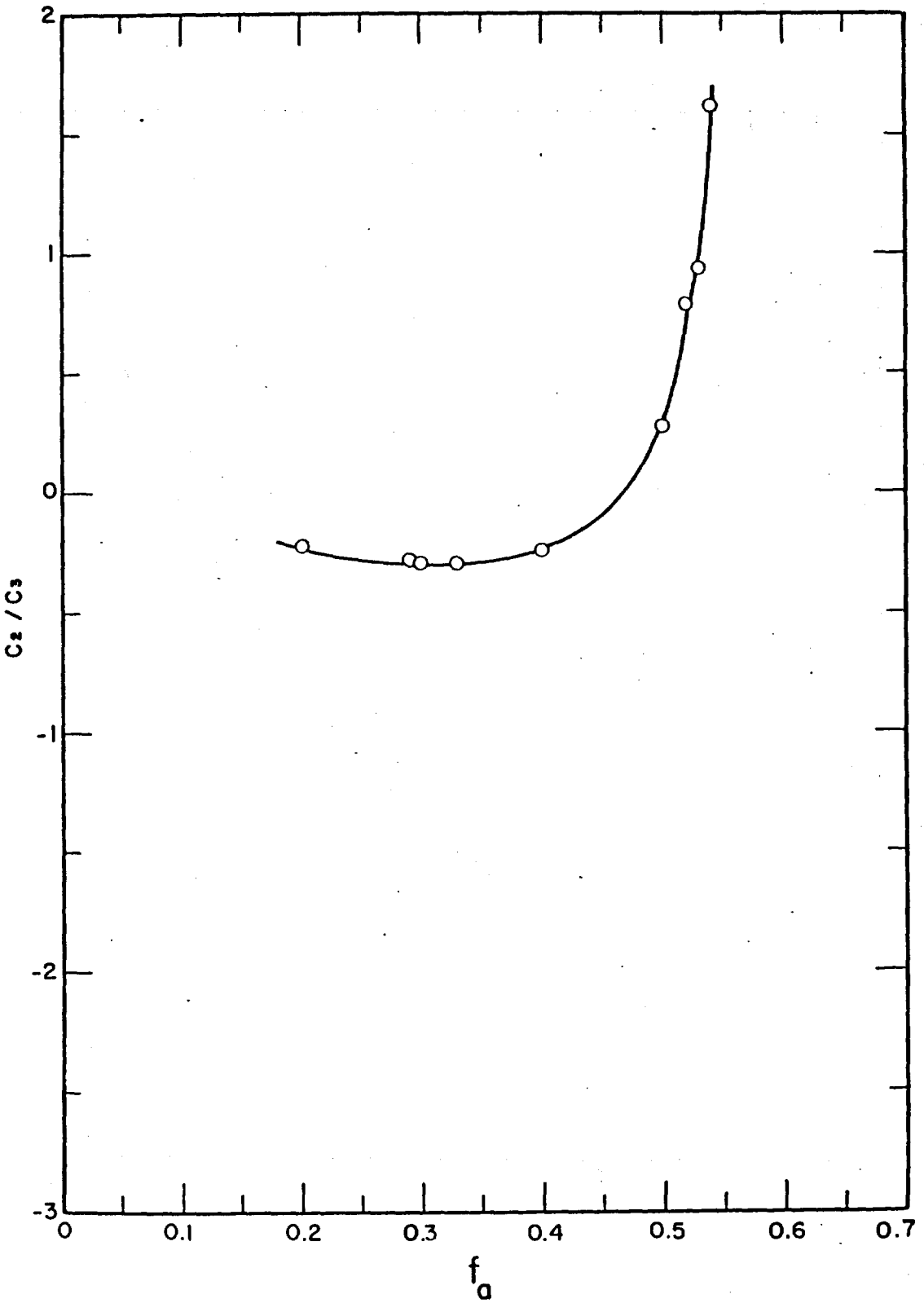

Figure 7. Variation of C_2/C_3 with f_a for the Montgomery-Boyd results (Scheme MB1).

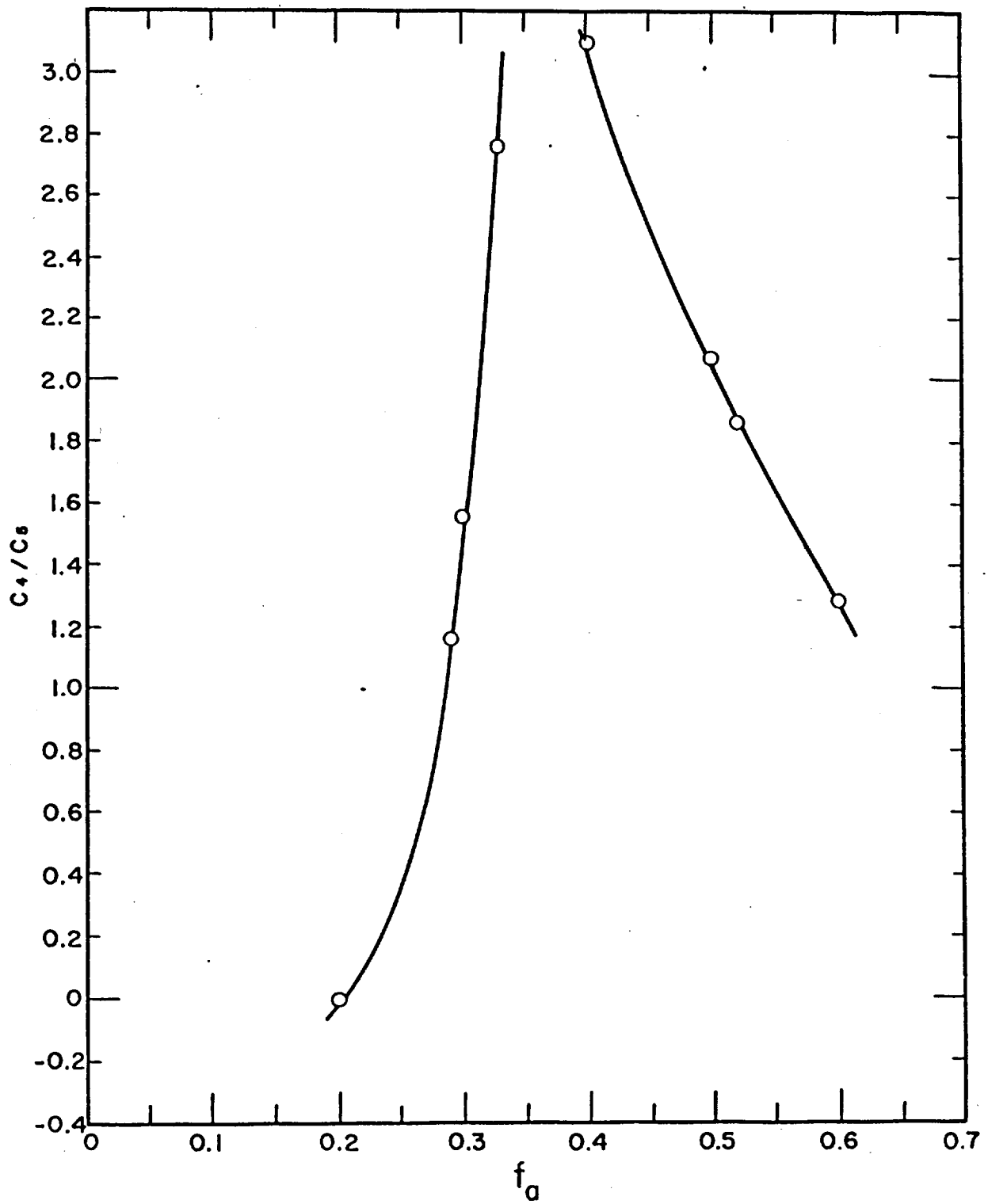

Figure 8. Variation of C_4/C_5 with f_a for the Montgomery-Boyd results (Scheme MB1).

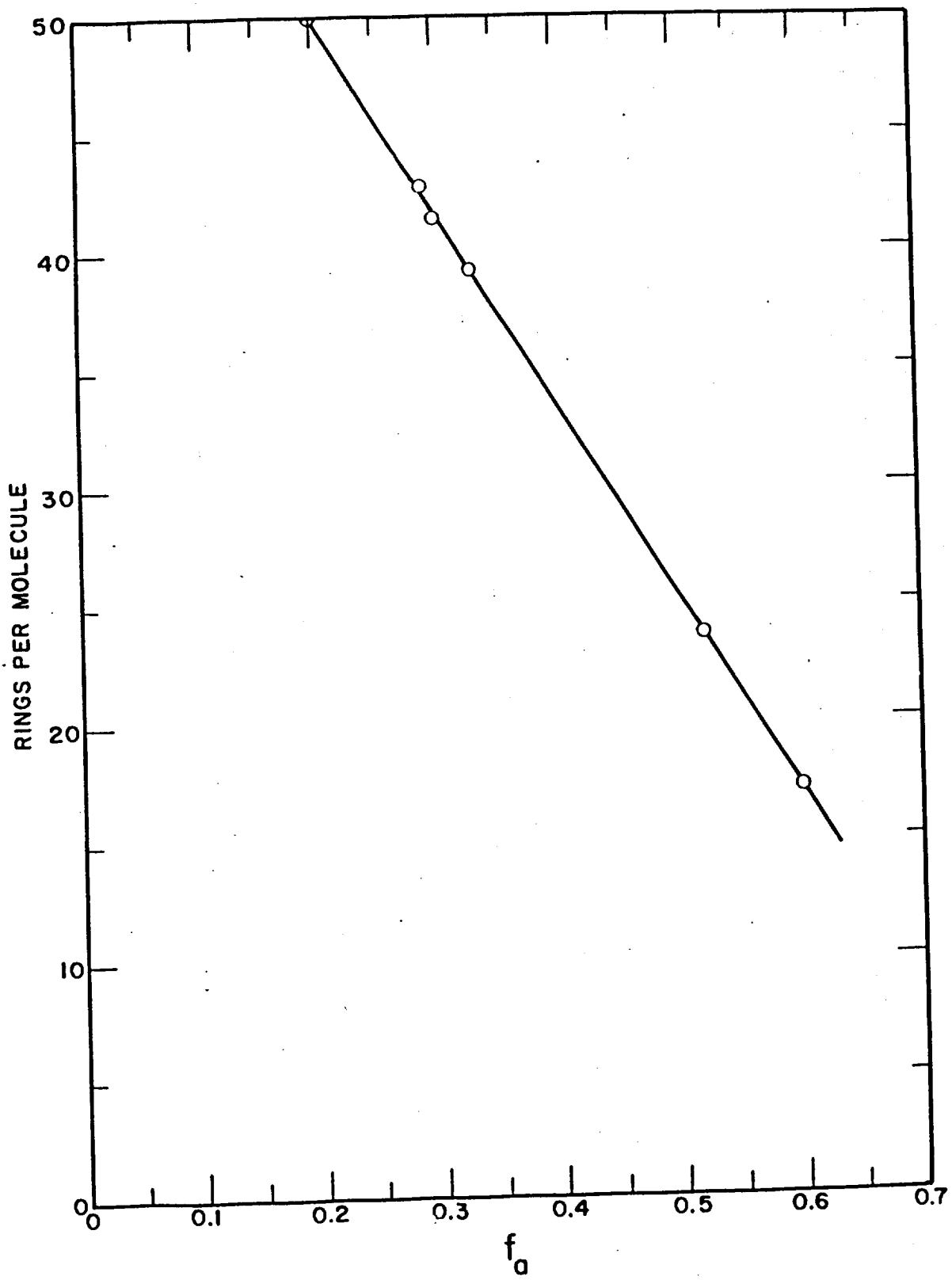

Figure 9. R versus f_a for the Montgomery-Boyd analysis (Scheme MB1).

TABLE 17

Limiting Values of the Structural Analysis of the Asphaltenes

f_a	ΣC_a	C_1	C_2	C_3	C_4	C_5
0.57	93.0	48.0	22.9	0.0	55.7	37.3
0.47	77.0	54.0	0.0	33.5	55.0	22.0

It should be noted that the f_a value, 0.52, determined by van Krevelen's graphical technique fell within the above range.

An alternative procedure, which involves more assumptions, is to assume that on the average the asphaltenes are composed of six membered rings, that the ring equation $C_3 + C_5 = 2R - 2$ is valid, and that, on the average, $C_R/R = 4.0$. This would then permit a unique solution. The significance of selecting $C_R/R = 4$ has the following basis. The limiting value with increasing molecular weight for pericondensed, six-membered rings is 3 and that for kata-condensed rings is 4, while the value corresponding to the lowest member of the kata-condensed series is 5. The value of C_R/R must lie between these extremes of 3 and 5 unless a higher degree of condensation than pericondensation is envisaged. Attention is drawn to the fact that the Waterman system of structural analysis for oils uses this assumption of kata-condensed, six-membered rings. Consequently, from Figure 6 (C_R/R vs f_a) the value of f_a was read off corresponding

to $C_R/R = 4.0$. For the asphaltenes, this gave a value for f_a of 0.47 (i.e. $\Sigma C_a = 77.0$). From Figure 4, this value of ΣC_a corresponded to the following unique set of values: $C_1 = 54.0$, $C_2 = 0.0$, $C_3 = 33.5$, $C_4 = 55.0$, and $C_5 = 22.0$; it will be observed that this analysis corresponds with that of the lower f_a limit in Table 17.

It is of interest to note the variation of the secondary structural parameters for the limiting structures whose compositions are given in Table 17. The number of rings per molecule varied from 19.5 to 27.75; C_4/C_5, from 2.3 to 1.5; C_2/C_3, from zero to infinity; and C_R/R, from 4.0 to 5.9.

Since in one of the limiting compositions of the asphaltenes C_3 was zero, this suggested that the modified Montgomery-Boyd analysis (Scheme MB2) could be applied in this case. This system considered the molecule as made up of C_1, C_2, C_4, C_5, and C_7. The qualification has been made that C_2 had to be small. This was so, since in the development of the molar volume and molar refraction equations[69] to obtain equations that fitted accurately hydrocarbons containing C_5 and C_7, a C_2 "correction term" which had been used in the equations of the original structural analysis system had to be omitted. This second structural analysis (MB2) was intended to illustrate the effects of changing the parameters of the system and to give some in-

dication of how the aromatic carbon atoms were distributed between fused and non-fused rings. The results of this second analysis (Table 14) indicated that the aromatic carbon atoms were distributed in the ratio of $C_4:C_5:C_7 = 3.3:1.2:1$. It should be noted that this second structural analysis scheme did not predict the same distribution between C_1 and C_2 as did the first scheme, MB1. The second scheme predicts a much higher proportion of C_1's. This is probably due to the inherent assumptions of the second system. At the present time, few data are available on which to test the second system.

Table 17 showed that the number of C_1 groups varied only slightly (48 to 54) over the range of limiting values. The infra-red spectrum indicated the presence of 15% terminal methyl groups, which corresponded to 24 methyl groups per molecule. This indicates that about half the paraffinic carbon atoms are terminal methyl groups.

The MB1 and MB2 methods give no specific information about the arrangement of the paraffinic carbons. The infra-red spectrum indicates the presence of chains longer than four carbon atoms, but it is impossible to give any quantitative estimate at the present time. As has already been mentioned, the estimation of CH_3 from the infra-red spectrum indicated that half the C_1 atoms are terminal methyl groups, and from this it can be concluded that, on the average, the alkyl chains are short.

Conclusions Concerning the Asphaltene Structure

1. Van Krevelen's densimetric analysis predicted the asphaltenes to have 30% aromatic carbon atoms and 41.6 rings per molecule.

2. Van Krevelen's graphical densimetric method predicted the asphaltenes to have 52% aromatic carbon atoms.

3. According to the Montgomery-Boyd five-parameter structural analysis system designed for fused-ring systems, it has been shown that the fraction of aromatic carbon must be between 47 and 57%. The carbon-type composition for this range of aromaticity varied between 29.3-32.9% paraffinic carbon, 14-zero% naphthenic CH_2, zero-20.4% naphthenic CH, 34-33.6% aromatic CH, and 22.8-13.4% aromatic $-\overset{|}{\underset{|}{C}}-$ groups.

4. If one assumes $C_R/R = 4.0$, a unique solution of the Montgomery-Boyd MB1 system is obtained, which is: 32.9% C_1, 0.0% C_2, 20.4% C_3, 33.6% C_4, and 13.4% C_5.

5. To illustrate the effect of changing the parameters, a second five-parameter system (MB2) was applied to the asphaltenes. This resulted in the following number of carbon types per molecule: $C_1 = 65.1$, $C_2 = 5.8$, $C_4 = 55.4$, $C_5 = 20.9$, and $C_7 = 16.6$.

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