

Mines Branch Information Circular IC 169

THE ATHABASCA TAR SANDS AS A SOURCE OF CRUDE OIL

by

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ABSTRACT

A general review is presented of the variable nature of the Athabasca bituminous sand resource, and the chemical composition of the bitumen is given at various stages during the refining from raw material to finished products. The research conducted at the Mines Branch on vapour-phase hydrogenation of coker distillates is described, emphasizing the effect of hydrogen pressure on the rate of catalyst deactivation. In conclusion, the quality of the hydrogenated products is described in general terms, and some observations are made on the reasons why large-scale operation is essential if an economically viable process is to be achieved.

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Direction des mines

Circulaire d'information IC 169

LES SABLES BITUMINEUX D'ATHABASCA COMME
SOURCE DE PÉTROLE

par

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RÉSUMÉ

On présente ici une revue générale de la nature variable des ressources de sable bitumineux d'Athabasca, et l'on donne la composition chimique du bitume à divers stades durant le raffinage depuis la matière première jusqu'aux produits finis. On décrit les recherches poursuivies à la Direction des Mines sur l'hydrogénation en phase vapeur de distillats de cokéfaction, en soulignant l'effet de la pression d'hydrogène sur le taux de désactivation du catalyseur. En conclusion, on décrit en termes généraux la qualité des produits hydrogénés, et l'on fait quelques observations sur les raisons pour lesquelles une exploitation à grande échelle est essentielle pour obtenir un procédé économiquement viable.

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PREFACE

In 1963 the Chemical Institute of Canada organized a Symposium on "Hydrogen and its Place in Petroleum Refining", under the chairmanship of Dr. D.J. Poynton of the Shell Oil Company of Canada. Four papers were delivered at this symposium, which was part of the 13th Chemical Engineering Conference held in Montreal on October 19-23. The first two papers in the symposium dealt with the role of hydrogen in current refining practice; the third paper discussed the production of cheap hydrogen; and the concluding paper, which is reproduced here, was intended to indicate where the future of hydrogenation lay. That future, in our opinion, lies in the refining of very heavy crude oils such as the Athabasca bitumen. In the title this substance has been referred to as the 'Athabasca Tar Sand' as a concession to popular terminology, although it is not a pyrolysis product and is therefore not strictly a tar.

Because a number of inquiries were received during the past year for additional copies of this paper, it was considered desirable to reproduce it in more permanent form; hence this information circular.

INTRODUCTION

At first sight a discussion of crude oils, including the Athabasca bitumen, might seem somewhat out of place in a symposium on "Hydrogen and its Place in Petroleum Refining". The connection, however, is that low-grade petroleum and residual oils are deficient in hydrogen and contain many "foreign atoms"--that is to say, atoms other than carbon and hydrogen--which must be removed and replaced by hydrogen in order to obtain marketable petroleum products. Of all the Canadian crude oils, the Athabasca bitumen has the largest hydrogen requirement. Inasmuch as the refining of this class of oil requires comparatively large amounts of hydrogen, and since approximately 25 per cent of the cost of refining by hydrogenation lies in the cost of producing and compressing the hydrogen, it is clear that any factor that reduces the cost of hydrogen production will have a profound influence on the economics of refining low-grade crude oils. In the light of this additional refining expense due to the hydrogen requirement, you may well ask why the refining of these low-grade oils is being considered when there is oil of higher quality in the vicinity of Edmonton--and indeed in Saskatchewan--which is closer to the major markets. This brings us to a brief consideration of the Western Canadian crude oil reserves.

Although very substantial quantities of crude oil and natural gas have been discovered in Canada since the discovery of Leduc in 1947, the annual additions of new reserves of oil have now begun to decline. What is more significant, the oil discovered per foot of wildcat drilled has steadily

decreased since 1957. Many Canadians are accustomed to thinking of Canada as a country of inexhaustible natural resources, and it may come as somewhat of a surprise to learn that the better-quality oil reserves are showing signs of depletion, and that the rate of discovery of good-quality oil is not particularly encouraging. Let me cite two facts to illustrate this point: in 1962, the exploratory wells drilled that resulted in successful oil wells made up 11.7 per cent of all the exploration wells drilled in Western Canada, and, of all the exploratory wells drilled for both oil and gas, 74.1 per cent were dry. New discoveries of oil, in contrast to gas, were rare northwest of Alberta's Swan Hills region, which is the logical direction of future exploration. Most of the oil discoveries, none major, were located in the southern half of Alberta and in southeastern Saskatchewan. Consequently, to even out the fluctuations associated with the erratic nature of oil discovery, and to meet the ever-increasing demand for low-cost petroleum products, the conventional supplies of crude oil will have to be augmented by the utilization of low-grade petroleum reserves, of which the Athabasca bitumen is a typical example.

MINES BRANCH RESEARCH

In the period following 1947, the Mines Branch considered it prudent to conduct a modest amount of research during the period of relative abundance of oil so as to prepare for the days when our high-quality crude oil reserves will be less plentiful and to make preparations for the day when more serious thought will have to be given to the efficient utilization and conservation of Canada's low-grade crude oil reserves. One aspect of this program was directed toward obtaining a better understanding of the fundamental chemical structure of the Athabasca bitumen, and the other was devoted to the study of various steps in the refining process to see what improvements might be made to reduce both the waste of the raw material and the cost of refining.

NATURE OF THE BITUMINOUS SANDS

In general terms, the Athabasca bituminous sand consists of unconsolidated clear quartz grains in which the interstitial spaces are filled with water, clay, and bitumen. When the bituminous material is extracted--with benzene, for example--the quartz, sand and clay are free-flowing and can consequently be transported in pipes with a fluidizing medium.

The bituminous sand deposits of Alberta are classified into three main groups, distinguished from one another by the stratigraphic unit and the area in which they occur. The Athabasca deposit occurs almost entirely within the Wabiskaw-McMurray unit and is located within a sixty-mile radius of McMurray, which is situated 260 miles north of Edmonton. It consists of banded structures; some zones are impregnated with bitumen,

others are not. Many of the areas within this region are of low grade; that is to say, the sands possess a bitumen content of less than 8 per cent by weight. There is, therefore, considerable variation in the potential economic value of the various areas within this region.

EXTRACTION OF THE BITUMEN FROM THE SANDS

If conventional mining forms one of the primary steps in the extraction process, it is desirable to find locations where the overburden is light, 0 to 100 ft., and where the bituminous sands are relatively thick, 150 ft., with a bitumen concentration in the range from 8 to 16 per cent by weight. The exact magnitude of the reserves that would meet these requirements is not known, but it is probably of the order of 10 billion barrels, which is quite adequate to attract commercial attention. In regions where the overburden is in excess of 150 ft., in situ methods will probably have to be developed to reduce the extraction cost.

Whatever the extraction procedure, one of the most troublesome components is the clay that occurs within the deposit. This clay may occur in some areas as beds of dense, blue, lenticular masses devoid of bitumen, but in general the clay is disseminated between the sand grains. In some areas there exists a layercake-like structure with bands of clay alternated with coarse sands impregnated with bitumen, repeating at intervals of 1/8 in. In this type of structure it is extremely difficult to cause the bitumen to flow from one layer to the next by elevating its temperature and applying an artificial gas drive. These observations suggest the importance of carefully selecting the bituminous sand structure to achieve economic extraction.

In considering the Athabasca bituminous sands as a source of crude oil, it is evident that the organic matter cannot be thought of without considering the mineral matter matrix, because the mineral matter has a profound effect on the economics of production. Table 1 shows the typical properties of the mineral matter associated with the bituminous sand at the Abasand quarry.

The refiner, on the other hand, is more concerned with the chemical character of the organic matter. The ultimate analysis of this material is shown in Table 2. From this analysis it is evident that the bitumen consists largely of carbon and hydrogen, but there is an appreciable quantity of other atoms (commonly referred to as the "foreign" atoms) that give rise to 5.0 per cent by weight of sulphur, 1.4 per cent of oxygen, and 0.3 per cent of nitrogen. In addition to this, there is a certain amount of inorganic matter that is combined with the resin and asphaltene fractions of the bitumen. In the combined form this mineral matter is capable of distilling with the hydrocarbon components, and it is therefore a considerable nuisance in vapour-phase hydrogenation or in cracking operations. The

TABLE 1

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 ₂ O ₃	0.8	40	0.58
Fe ₂ O 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	-

^{1/} Bowles, K.W. and Booth, F.L., FRL Report #76, p.13, Bureau of Mines, Canada Department of Mines and Resources, Ottawa, 1947.

^{2/} This analysis is the average of 53 screen analyses on tube mill feed composite samples for Mill Runs #1-#138 of the Mines Branch's separation plant at Ottawa.

^{3/} Determined by the Spectrographic Laboratory, Mineral Sciences Division, Mines Branch.

TABLE 2

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	

amount of this combined inorganic matter is probably slightly less than the figure of 0.6 per cent by weight shown in Table 2. The portion of the combined mineral matter that distills, and is consequently found in coker distillates, varies from 0.01 per cent to 0.1 per cent by weight of the distillate. German practice indicates that the maximum mineral matter permissible for good vapour phase operation is 0.001 per cent.

The physical properties of the bitumen vary significantly from one location to another, depending on the molecular weight and the foreign atom content. The viscosity at 60°F, for example, varies over a range from 6000 to 600,000 poises for different samples. This gives an indication of the variations in molecular weight that may be encountered.

Most of the research at the Fuels and Mining Practice Division has been done on bitumen from the Abasand quarry, which has a density of 1.029 and a number average molecular weight of the order of 800. This crude oil is somewhat more difficult to refine than the bitumen from other locations, because of its higher average molecular weight and higher asphaltene content (approximately 25 per cent).

The distillation analysis of the Abasand bitumen brings out two points. The first point is that this bitumen belongs to the Cretaceous family of crude oils, as the specific gravity of the (250 to 275°C) key cut follows Barton's depth base rule established for these crudes. The second point, which is brought out in Table 3 and is of greater commercial significance, is that the molecular weight distribution is such that a comparatively small proportion of the weight lies in the molecular weight region of the commercial products that are in greatest demand; that is to say, the bitumen contains approximately 1 per cent of natural gasoline and 18 per cent of gas oil.

As the commercial products required are essentially pure hydrocarbons of low molecular weight, it is clear that extensive cracking of the bitumen is required to reduce the molecular weight to acceptable levels. This cracking would result in the creation of large amounts of unstable olefinic hydrocarbons, unless these are stabilized by hydrogenation. It is equally important to reduce the foreign atom content to acceptable levels, and the only way to do this--resulting in a stable hydrocarbon mixture-- is also by hydrogenation.

Up to this point we have been discussing the chemical character of the bitumen in the bituminous sand. On the other hand, the refiner is more concerned with the composition of the bitumen after the primary separation, that is, after the removal of the bulk of the bitumen from the sand, since this is the material that he is actually called upon to refine. The composition of the bitumen from the hot-water process is approximately 65 per cent bitumen, 31 per cent water, and 4 per cent mineral matter. The cold-water

TABLE 3

Characteristics of Separated Athabasca Bitumen^(a)

Specific Gravity, 60/60°F	1.034
Kinematic Viscosity, c.s.	
at 210°F	1,650
at 100°F	570,000
Sulphur, wt. %	5.3
Water , wt. %	Trace
Ash , wt. %	6.6
Carbon Residue, wt. %	19.4
Distillation Summary (b)	
Gasoline (392°F E.P.), vol. %	1
Kerosene + Gas Oil, vol. %	18
Heavy Distillates, vol. %	16
Residuum, vol. %	65

(a) Cold water separation process. Bituminous sand from Abasand deposit containing approx. 15 wt. % bitumen.

(b) U.S. Bureau of Mines Method.

TABLE 4

Characteristics of the Coker Distillate
Derived from Athabasca Bitumen

Specific Gravity, 60/60°F	0.963	Sulphur, wt. %	4.1
Kinematic Viscosity, c. s.		Nitrogen, wt. %	0.24
at 100°F	66.8	Oxygen, wt. %	0.10
at 210°F	7.1	Hydrogen, wt. %	11.2
Pour Point, °F	-10	Carbon, wt. %	84.4
Molecular Weight (calc.)	393	Ash, wt. %	0.03
Carbon Residue, wt. %	4.2	Water, wt. %	nil
<u>Distillation Summary</u>			
	<u>Yield</u> <u>vol. %</u>	<u>S. G.</u> <u>60/60°F</u>	<u>Sulphur,</u> <u>wt. %</u>
Gasoline (392°F E. P.)	4.0	0.803	2.4
Kerosene + Gas Oil	21.5	0.860	2.5
Heavy Distillates	21.0	0.985	4.0
Residuum	53.5	1.012	5.5

process yields an oil of approximately the same composition when using the same type of bituminous sand. The bituminous sand is, however, very variable with respect to its separation characteristics by water, even within the same quarry, and considerable variations from this nominal froth composition may occur. The reasons for the variations are not fully understood, but clay and oxidation no doubt have a large influence on the fluctuations in froth composition, as well as on the percentage recovery of organic matter from the sand.

It is clear from these composition data that extensive removal of water and mineral matter is required. In spite of the fact that a good deal of work has been done in this field, there is still plenty of room for further research to develop cheaper and more rapid oil-purification techniques. In Russia, laboratory experiments have been recently reported on the combined use of sonic energy and surfactants, and it is possible that such methods may be profitably used to remove mineral matter and water from the Athabasca bitumen (1).

The next problems that meet the refiner are dehydration and diluent recovery. Space does not permit very much discussion of these topics here; it will suffice to say that in the Mines Branch experimental work it has been found best to heat in thin layers the bitumen containing dispersed water, to avoid the creation of excessive quantities of froth.

The next step in this sequence involves the pyrolysis of the bitumen to yield a coke that contains the bulk of the mineral matter, and a distillate that will subsequently be referred to as coker distillate. The composition of a typical coker distillate is shown in Table 4. The composition of this material does not differ greatly from that obtained by the fluidized-bed process developed by the National Research Council, with the exception that in the fluidized-bed process the density and the carbon residue were higher and there was a higher carry-over of dust in the distillate, in the form of micron-size silica and clay, which was troublesome in fixed-bed hydrogenation, and redistillation was found to be necessary.

After the pyrolysis step is completed, one has a distillate which is still not a very satisfactory synthetic crude oil, if such a term may be used, because the concentrations of sulphur and nitrogen are still too high. In the hydrogenation research conducted at the Fuels and Mining Practice Division before 1951, the principal effort was directed toward the production of a suitable feed stock for refineries that could be admitted to the pipeline system. On the experimental side, this involved the hydrogenation of the coker distillate at pressures of up to 1000 psi. This work formed the basis for some of the estimates made in the Blair report on the Alberta bituminous sands (2).

The direction of the research following this period was slightly changed. Greater emphasis was placed on the kinetics of the desulphurization reaction in fixed-bed, vapour-phase reactors. The results of this work showed that the theory of porous catalysts developed by Thiele(3), Wagner (4) and Wheeler (5) gave a qualitative description of most observations relating the functional dependence of the sulphur content upon the operating variables-- with one notable exception, the influence of the hydrogen feed rate upon the sulphur elimination. This exception suggested that a large portion of the feed was in the liquid, rather than in the vapour, state on the catalyst surface. The interpretation placed on the low activation energies for the sulphur removal was that this was a diffusion-controlled process and that the rates might be accelerated by opening up the pore system. This led to a small research program to develop alumina supports of controlled pore-size distribution.

Although techniques were developed to control the pore-size distribution of alumina and silica aluminum supports by incorporating water-soluble polymers into the gels and subsequently burning out the polymer, it was found that these supports, after impregnation with the catalyst (cobalt molybdate), resulted in improved efficiency of utilization of the catalyst but did not greatly improve the space time yield, which is the factor of principal importance.

During these experiments it was realized that one of the most troublesome aspects of vapour-phase refining was the deposition of heavy asphaltic substances on the catalyst and the consequent substantial reduction of the catalysts' activity. In 1962, in the Mines Branch, A. R. Aitken undertook a series of investigations, in association with W. H. Merrill, to determine the effect of hydrogen pressure on the rate of catalyst deactivation by the deposition of coke on the catalyst (6). Figures 1 and 2 show briefly the results of this work and indicate that if the entire coker distillate is to be processed, using a cobalt-molybdate impregnated alumina catalyst, hydrogen pressures of the order of 3000 psi are desirable to achieve stable operation with the production of good-quality diesel fuel.

At the conclusion of 1960 it was felt that the basic assumption, that the dehydrated bitumen should be destructively distilled to coke to produce a vapour-phase feed stock, should be questioned because of the relatively low quality of the distillate in terms of ash and high molecular weight residuum. It was felt that there was a good possibility that the operating performance could be improved by producing a higher-quality distillate, with a lower concentration of inorganic components and a lower asphaltene content, by conducting the pyrolytic distillation in a stream of hydrogen. The presence of hydrogen during the distillation might also reduce the amount of unusable high-sulphur-content coke produced, a result that would be more attractive from a conservation point of view.

These considerations led to the construction of a bench-scale combined liquid and vapour phase hydrogenation unit, which we hope will be in operation late in 1964. This unit closely resembles the German Bergius process, except that the vapour passes directly from the liquid-phase reactor into the vapour-phase reaction vessel without intermediate cooling and subsequent distillation. This refining scheme avoids a certain amount of polymerization that would take place in the liquid phase during the intermediate cooling operation, and it eliminates the capital expense involved in this intermediate equipment. However, to operate the plant in a stable manner considerable skill is required, as any upset in the liquid-phase system is communicated to the vapour-phase operation.

So far we have briefly reviewed some of the problems associated with the refining of Athabasca bitumen, and it would now seem appropriate to review briefly what may be said of the products obtained by refining.

THE PRODUCTS OF REFINING; GENERAL COMMENTS ON THE ECONOMIC SCALE OF OPERATION

By virtue of the fact that the Athabasca bitumen is a naphthenic-type crude oil, it makes a poor gasoline on vapour-phase hydrogenation. Extensive reforming would be necessary to make a product that is acceptable by today's standards. On the other hand, the presence of a considerable quantity of cycloparaffins in the bitumen makes this a much better feed for the production of diesel and jet fuel. The pour-point characteristics are good, and this would seem to be the best outlet for the major portion of this type of crude oil.

In general terms, the quality of the Athabasca bitumen, as compared with the majority of Western Canadian crude oils, is extremely low. It follows from this that this crude oil must be refined on a very large scale if the unit costs are to be reduced to economically attractive levels. The economic size of the refinery will vary, depending on what fraction of the bitumen is refined and what fraction is thrown away as waste coke; however, if the greater part of the bitumen is refined, it would seem that operations must be on a scale of the order of 100,000 barrels per day. This scale of operations involves very considerable financial risk and, consequently, great care must be taken to avoid technical and financial failure. Success can only be achieved by conducting the most thorough and systematic engineering work without excessive pressure to meet arbitrary deadlines. This implies that serious engineering work should be started many years before it is actually expected to get into production. The indications are, from our current estimate of the Western Canadian reserves, that the serious study of the problems associated with the recovery of commercial petroleum products from the Athabasca bitumen has started none too soon.

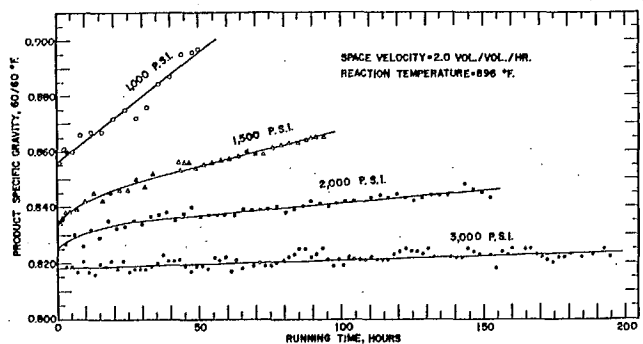


Figure 1. Effect of pressure on catalyst deactivation.

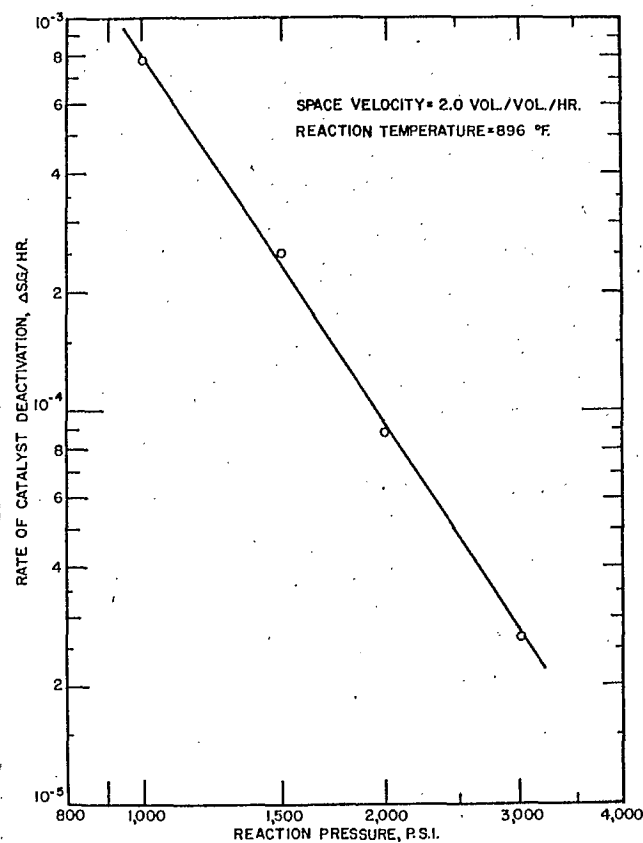


Figure 2. Correlation of rate of deactivation and pressure.

Few natural resources have attracted as much attention from the popular press as have the Athabasca bituminous sands. Endless opportunities have been provided to write up columns describing the advances made by amateur inventors in separating the bitumen from the sand. The enthusiasm in these articles usually stems from a consideration of the magnitude of the resource, but as a rule they reflect an almost complete ignorance of the quality of the natural bitumen as a source for petroleum products. It is an unfortunate fact that the quality of this oil has never been such that small-scale, simple distillation plants could produce products that were commercially acceptable, and as a result there has been no opportunity for small oil industries to take root and grow larger over a period of years through solving the usual problems associated with such development. Instead, without the benefit of work on a small scale, the oil companies are faced with having to proceed to large-scale separation and refining in order to achieve a process that will survive economically. The risks are therefore much higher than those associated with a slow and systematic growth.

In general, the problem of producing commercial products from this crude oil involves many steps, and one of the more important aspects of this problem is the production of low-cost compressed hydrogen. The relatively large contribution of the cost of hydrogen to the total refining cost of this class of crude oil means that this incremental cost cannot be ignored. Every effort must be made to secure hydrogen at the lowest possible cost, for the refined oil must be competitive with oil produced from conventional wells. It is also well to remember that the North American economy is not dependent on oil but on an abundance of low-cost oil as compared with other sources of energy.

LITERATURE CITED

1. Skripnik, Ye. I. et al., *Izvestiya Vysshikh Uchebnykh Zavedeniy, Neft i Gaz* 10, 67-70 (1962).
2. Blair, S. M., Report on the Alberta Bituminous Sands; Government of the Province of Alberta, 1950.
3. Thiele, E. W., *Ind. Eng. Chem.* 31, 916 (1939).
4. Wagner, C., *Z physik. Chem. A* 193, 1 (1943).
5. Wheeler, A., "Advances in Catalysis" (Academic Press Inc., New York, 1961), Vol. III, pp. 249-327.
6. Aitken, A. R., Merrill, W. H. and Pleet, M. P., *Can. J. Chem. Eng.* 42, 234-238 (1964).

