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ARPA WORKSHOP ON NEEDS OF THE DEPARTMENT OF DEFENSE FOR CATALYSIS

VOLUME II - PROCEEDINGS

NOVEMBER 5-6, 1973

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Volume II contains the proceedings of the workshop on "Needs of the Department of Defense for Catalysis," held at R&D Associates, November 5-6, 1973, consisting of talks given by 26 research scientists in industry and the universities, and discussions following the talks.

PREFACE

The ARPA Workshop on Needs of the U.S. Department of Defense for Catalysis took place in Santa Monica on November 5 and 6, 1973. The Workshop was conducted by R&D Associates, under contract for the Defense Advanced Research Projects Agency. This volume contains papers presented at the Workshop and transcriptions of the informal remarks of participants during discussions. The transcriptions are close to verbatim; however, the editor has taken occasional liberties in making the verbatim transcriptions of the talks and discussions more readable, and hopes in the process not to have perturbed the intent and meaning of the speakers. The opinions expressed in these proceedings do not necessarily represent those of the editor, R&D Associates, ARPA, nor the U.S. Government.

An Executive Summary of the findings of the Workshop is in preparation and will be issued soon as Volume I of this report, RDA-TR-3501-001.

Leona Marshall Libby, Editor
Santa Monica, California
December 14, 1973

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ARPA Workshop on the Needs of the Department of Defense for Catalysis

I. INTRODUCTION: A SURVEY OF HETEROGENEOUS CATALYSIS

Some chemical reactions proceed spontaneously and rapidly at room temperature merely by bringing the reactants together; for example, sodium and water form sodium hydroxide and hydrogen.

$$2Na + 2H_2O = 2NaOH + H_2$$

Many reactions are slow even though the occurrence of the reaction would lead to a more stable system. Some of these attain a substantial rate upon elevating the temperature, such as the reaction between hydrogen and oxygen, viz.

$$2H_2 + O_2 = 2H_2O$$

In still other cases, there is <u>no</u> temperature at which the reaction can be effected usefully. An example of this is the synthesis of ammonia.

$$N_2 + 3H_2 = 2NH_3$$

Ammonia is more stable than nitrogen plus hydrogen at temperatures below about 400°C, but the rate of its formation is negligible at these temperatures. At very high temperatures the rate becomes substantial, but the stability relations change with temperature and, at temperatures that give substantial rates, the position of stability has changed far in the direction of nitrogen plus hydrogen. Thus, there is no temperature at which ammonia can be synthesized from nitrogen plus hydrogen.

In the early 1900's, sodium nitrate from the beds of Chilian saltpetre was the only substantial source of nitric acid (HNO_3) used in making all explosives of military interest at the time. The government of Germany, recognizing that a British blockade could eliminate its supply of Chilian saltpetre and prevent the German government from engaging in a war of any duration, supported research to provide an alternate source of nitric acid. The German chemist Haber discovered a catalytic process to synthesize ammonia. He found that nitrogen and hydrogen would react on the surface of iron at about 400°C to form ammonia at useful rates, that is, iron is a catalyst for ammonia synthesis.

Nitrogen and hydrogen adsorb on the surface of the iron to form chemisorbed intermediates which react to form adsorbed ammonia which upon desorption frees the surface of the iron for further catalytic action. The adsorption of nitrogen and hydrogen is chemisorption and involves formation of surface chemical compounds of iron with nitrogen and hydrogen. These react to form adsorbed NH_2 which reacts with H(ads) to form ammonia. Desorption of ammonia regenerates the original surface of the iron. Thus, myriads of molecules of ammonia can be formed on each element of the surface of iron. In modern ammonia plants, a charge of iron catalyst can be used for years with only slight loss in catalytic activity. Because of this and because of the high level of development of the modern Haber process, ammonia is the second cheapest manufactured chemical. (Sulfuric acid, also made catalytically, is the cheapest.)

The invention of the Haber process solved the nitric acid problem because it was already known that ammonia could be converted into nitric acid by the following reactions

$$4NH_3 + 5O_2 = 4NO + 6H_2O$$

$$4NO + 3O_2 + 2H_2O = 4HNO_3$$

Conversion of NO to HNO_3 proceeds without a catalyst, but the first reaction requires a catalyst. Although ammonia can be burned in air without a catalyst, the products of reaction are nitrogen and water, which are not the desired products. If, however, nitrogen and oxygen are passed very rapidly over a platinum-rhodium alloy at about 1000°C, about 97% of the ammonia is converted to NO; that is, the catalyst is very selective in catalysing

$$4NH_3 + 5O_2 = \underline{4NO} + 6H_2O$$

rather than

$$4HN_3 + 3O_2 = \underline{2N_2} + 6H_2O$$

Many years of development were required to obtain the modern process for oxidizing ammonia to NO at such very high selectivity.

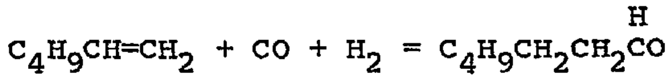
Selectivity is a dominant feature in catalysis. In most reaction mixtures, two or more reactions are possible, but one usually desires only a single reaction. It may take much work to find a catalyst and operating conditions highly selective for the desired reaction. That was true for the oxidation of ammonia to nitric acid since most other catalysts lead to the formation of much more nitrogen.

Reaction of carbon monoxide (CO) with hydrogen provides a good example of selectivity. By suitable choice of the catalyst and conditions, one can effect many different reactions of which just three appear below.

$CO + 2H_2 = CH_3OH$	Synthesis of methyl alcohol
$CO + 3H_2 = CH_4 + H_2O$	Methanation
$6CO + 13H_2 = n\text{-}C_6H_{14} + 6H_2O$	Fischer-Tropsch reaction

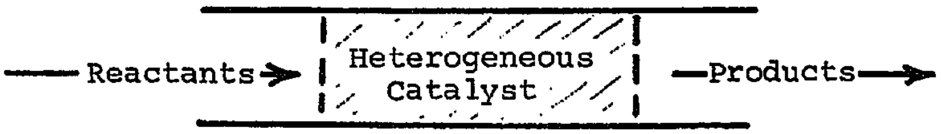
The first reaction is run on a large scale commercially on a zinc chromite catalyst. The methanation reaction proceeds on various nickel-based catalysts and is currently of considerable interest because it is essential to the manufacture of "synthetic natural gas" from coal. The Fischer-Tropsch reaction occurs on a cobalt-thoria-silica catalyst and leads to a mixture of a large number of hydrocarbons rather than just to hexane shown as an example. The Fischer-Tropsch reaction supplied a large share of the German gasoline during World War II.

All of the examples of catalysis instanced above involve <u>heterogeneous</u> catalysis. The catalyst is a solid, and the reactants disappear from and the products appear in a gas phase. In <u>homogeneous</u> catalysis, the catalyst is dispersed as molecules in the same phase, gas or liquid, as the reactants and products. A technically important example is the hydrocarbonylation of olefins which is catalysed by $HCo(CO)_4$ dissolved in liquid hydrocarbon. A particular example follows:



$$C_4H_9CH{=}CH_2 + CO + H_2 = C_4H_9CH_2CH_2\overset{H}{C}O$$

Homogeneous catalysis is of considerable scientific interest, and there are other technically important examples; however, heterogeneous catalysis is of much greater technological importance and is apt to remain so. Heterogeneous catalysis lends itself particularly well to efficient, large-scale manufacturing processes for the following reasons. The catalyst is placed in a reactor chamber provided with a means to add or remove heat as appropriate. The reactants, usually gaseous, are passed over it as shown below.



The reactants pass continuously over the catalyst, and the products issue from the reactor. Since the catalyst remains in place, no step is required to separate it from the products as in homogeneous catalysis. The simplicity of operation, and the ease in controlling the determining variables of pressure, temperature and flow rate, make heterogeneous catalytic processes very cheap and efficient. At present, there is considerable activity aimed at "heterogenizing homogeneous catalysts", that is, in attaching homogeneous catalysts to solid supports so that they can be used in reactors of the type described above.

Some heterogeneous catalysts are in forms with a small area/mass ratio. The platinum-rhodium alloy used in the oxidation of ammonia to nitric acid is of this form. However, in general the rate of heterogeneous catalytic reaction is proportional to the surface area of the catalytic ingredient, and one usually wishes to make the (area/mass) for the catalytic ingredient as large as possible. Further, one wishes to pack the reactor chamber with particles large enough (a few mm in diameter in most commercial reactors) so that the pressure drop through the reactor at desired flow rates is not too large. Finally, one often wishes to protect the catalytic material against sintering with accompanying loss of catalytic activity. The objectives are commonly achieved by starting with a porous support of very high internal area (of the order of 100 to 500 square meters per gram) in pellets of the desired diameter. The material usually has a porosity like that of a loose gravel bed where the "gravel" particles have a diameter of about 15 nm (150 Å). The catalytically active ingredient is deposited throughout the pore volume as small crystallites whose diameter may be in the range of 2 nm. As a result of this small size, of the order of 50% of the catalytic ingredient may be on the surface, and the isolation of the tiny crystallites from one another greatly reduces their rate of sintering. Alumina and silica are commonly used supports. Alumina may also contribute catalytic activity. The catalytically active ingredient is often a metal like platinum, palladium or nickel, or an oxide or mixture of oxides like chromium oxide or cobalt oxide-molybdenum oxide.

As already mentioned, heterogeneous catalytic processes are particularly suited for industrial applications, and they permit manufacturing many products which are available in no other way. Their use is particularly dominant in conversion reactions involved in the manufacture of fuels. Heterogeneous catalysis is equally dominant in all projected processes for the manufacture and conversion of fuels from coal, oil shale, and from hydrogen generated from nuclear reactors.

The following heterogeneous catalytic reactions are examples of those used in petroleum refining.

a) Catalytic cracking (the conversion of large molecules in petroleum to smaller ones in the gasoline or kerosine range).
b) Hydrocracking (another process giving the results of cracking).
c) Catalytic reforming (conversion of gasolines of low octane number to gasolines of high octane number).
d) Isomerization (another process leading to improved octane number).
e) Desulfurization (reaction of sulfur compounds in gasoline, jet fuel, heavy oil, etc., with hydrogen to form hydrogen sulfide gas).

Myriads of reactions are possible in such complicated mixtures of hydrocarbons, and highly selective catalysts are needed.

The greater part of a barrel of petroleum now passes over at least one catalyst, and with demands for reduced emissions of sulfur dioxide, even more catalytic processing will be required in the future.

It is clear that the production and conversion of fuels from coal, oil shale, and nuclear power will be completely dominated by heterogeneous catalytic processes.

Heterogeneous catalytic processes also dominate the petrochemical industry and much of the chemical industry. It is probable that many types of heterogeneous catalytic reactions remain to be discovered and exploited since many possible kinds of reactions have been little investigated.

II. SUMMARY OF MEETING

A. Composition of Delegates

The panel included a representative cross section of highly knowledgeable chemists, physicists, and chemical engineers currently doing research in heterogeneous catalysis. The delegates came from industry, universities, government, and research institutions. Several made brief presentations that could be classified under one of the general topics relating to fuel production, pollution control, special techniques, specific applications, or the role of various organizations in catalysis. Also in attendance were representatives from Advanced Research Projects Agency, Mobility Equipment Research and Development Center, Naval Research Laboratory, U.S. Fuels and Lubricants Center, and members of the Department of Defense.

B. Statement of Problem

In the recent past an increasing majority of new chemical processes of technological interest have involved catalysis, and the great majority of these have involved heterogeneous catalysis. In addition, heterogeneous catalysis is involved in other ways than in the preparation of chemicals, for example in the production and transformation of fuels, in the control of pollution, and in fuel cells.

Thus, heterogeneous catalysis is of major importance to the Department of Defense. But, of course, many areas of science and technology are also of major importance, and not all need special attention by the Department. This report addresses itself to the following questions:

1) Is research in heterogeneous catalysis in the United States in an adequate state of health?
2) If not, does any weakness in the current state of heterogeneous catalysis endanger important interests of the Department of Defense?
3) If important interests are endangered, what should be done?

C. Historical Perspective, Comparison with Other Countries

For almost twenty years, much of the long-range research in catalysis was performed in industry. Success can be assessed by the number of new catalytic processes which were developed by teams associated with the names of U.S. industrial chemists and chemical engineers engaged in fundamental studies: Beeck, Ciapetta, Clark, Farkas, Greensfelder, Hall, Hirschler, Jenkins, Low, McIver, Mills, Neikam, Oblad, Ritchie, Voge, Wei, Weller, and others. Because of untimely death, early retirement, retirement, transfer to administrative or academic work, none of the above is currently still doing the basic work for which he became known. But what is significant is that these men have not been replaced in number or quality so that the ranks of basic researchers in industrial catalysis have been severely depleted.

At the same time, the number of faculty appointments in catalysis has remained quite small in American chemistry departments. While a spectacular increase in such appointments in chemical engineering has taken place during the past ten years, a substantial fraction of the catalytic research carried out in university departments of chemical engineering is oriented toward phenomenological rather than molecular aspects of the field.

By contrast, basic research in the molecular aspects of catalysis has grown enormously abroad, especially in Japan, the USSR, France, and the Netherlands. Logically, this is where the basic knowledge required to develop the new processes needed by the changing energy technologies is likely to be generated. The result will be a dangerous dependence on foreign technology in a period of acute technological needs and unfavorable balance of trade.

The challenge to DOD is that new technology is needed now to assure economical interconversion of available fossil energy sources to produce needed liquid and gaseous fuels for uses in eventual combat, to permit the use of lower grade oil and to develop quiet power plants such as fuel cells or liquid fuel plants aboard nuclear aircraft carriers for refueling of conventional ships at sea. The basic knowledge required to reach these objectives is either not available or when available, must be brought to fruition by additional engineering research.

The primary overall goal of the DOD is for self sufficiency in energy supplies.

III. RECOMMENDATIONS

The recommendations arrived at during the ARPA Workshop were collated and clarified directly after its termination by Professors Joe Hightower, W. Keith Hall, Michel Boudart, R.L. Burwell, Jr., and James T. Richardson.

There is room for improvement in almost all commercially important heterogeneous catalytic processes, and research in each should ultimately lead to enhanced activity, greater selectivity, longer life, and more efficient use of raw materials. While some improvements may be effected through more sophisticated engineering design, others can only be expected through development of a basic understanding of the individual steps in a catalytic sequence. The most productive approach to developing or improving catalysts involves simultaneous studies of specific processes and the fundamental aspects of catalysis. Since it is, of course, impossible for the DOD to become involved in all commercial processes, the panel of experts has divided the recommendations into three areas: those aimed at improving the fundamental understanding of catalysis, a few specific processes that appear to have a direct bearing on the mission of the DOD, and the formation of a panel to search for new areas where applications of catalysis might have a positive influence on the DOD. These should not be considered as limiting but should serve only as examples of projects that merit DOD support.

A. RESEARCH TO EXTEND GENERAL UNDERSTANDING OF CATALYSTS

1. Surface Physics and Instrumental Techniques

The growing list of spectroscopic and diffraction techniques developed for the study of composition, structure, and electronic states of well-defined surfaces presents new challanges and promises in catalytic research (See Nagel's Table, Appendix B).

In the past, adaptation of a new physical technique to the examination of catalytic materials has taken ten to fifteen years. This is far too long. Attempts to use a new technique directly, without proper adaptations, have frequently led to early disenchantment, with incomplete information. This can be avoided by the support of co-operative efforts between chemical physicists and catalytic chemists. Finally, while methods of surface analysis well suited to the examination of catalytic materials *in vacuo* are of great interest, priority should be given to those methods which permit the observation of catalytic surfaces at pressures and temperatures used in catalytic processes. The ultimate goal is the determination of composition, structure, and bonding of the surface intermediates propagating the catalytic sequence of elementary processes. Close collaboration between physicists, surface chemists, and materials scientists on the one hand and physical chemists and chemical engineers on the other hand is a necessary condition for swift and successful transfer as advocated here.

2. Kinetics, Mechanisms

One of the largest present weaknesses in the theory and practice of catalysis is the lack of knowledge concerning the elementary processes that occur inside the catalytic reactor. Such mechanistic knowledge is frequently essential for process control, trouble-shooting, improving catalysts, or discovering alternatives to existing catalytic routes. Regretably, a knowledge of mechanisms cannot generally be derived from kinetic studies alone, that is, by studies only investigating how the reaction rate (or selectivity) changes with concentration of the reactants, temperature, and time reactants spend in the reactor. These must be supported (and sometimes guided) by much auxilliary data, including work with isotopically labeled tracers, model compounds,and sometimes studies of the chemisorption of various gases. In the latter connection, the use of some of these as selective poisons may result in improvement in selectivity, which is the key feature of practical catalysis. Knowledge of this kind is currently badly needed in the areas of coal gasification and hydrodesulfurization.

A central feature of mechanism is a knowledge of the intermediates formed on the catalyst surface. Special techniques have been developed to examine these intermediates which play a key role in the reaction mechanism. A reasonably complete picture of the chemistry of the catalytic process results when such information about intermediates is combined with data from kinetic studies. Such multifaceted approaches should be encouraged.

3. Physical Properties, Transport Effects

Most catalysts are porous, spongelike solid materials. Their effectiveness frequently is limited not by their intrinsic catalytic activity but by the rate of entry and exit of reactants and products from the pores. When this is the case, physical properties of the solids have overriding effects on their performance as catalysts. Such factors as particle size, pore size and distribution, and thermal conductivity influence the transport properties of reactants that affect reaction rates, selectivities, kinetics, temperature dependencies, catalyst strengths, and poisoning susceptibilities. It is possible to modify these physical characteristics and thereby to synthesize materials with properties controlled in such a way as to maximize performance for the desired reactions. Detailed investigations of the relationship between physical properties and performance are necessary in order to optimize the system. It is recommended that in any system of catalytic interest, the role of physical properties be investigated in order to optimize its performance. This will necessarily involve synthesis of catalysts in which the parameters have been systematically varied for testing.

4. Activation, De-activation, Poisoning

In use, catalysts suffer decline in activity. Such loss in activity appears to result from the presence in the reactants of poisons that adsorb permanently and prevent reaction at the active sites, from change in the area, in the structure of the surface or in the chemical identity of the bulk of the catalyst, and from deposition of by-products on the surface of the catalyst. Such factors substantially influence the efficiency of technical catalytic processes, and they are poorly understood in general. In particular, many catalysts consist of active ingredients such as Pt or Cr_2O_3 deposited on a porous, high area support like Al_2O_3 or SiO_2. The crystallites of Pt, for example, are initially very small (a few nanometers in diameter) with 50% or more of the atoms of Pt often being in the surface of the tiny Pt crystallites. With use, the Pt crystallites grow, the catalytic activity falls, and the selectivity may change. Furthermore, reactivation of a "poisoned" catalyst may result in further enlargement of the crystallites, thus leaving even a smaller fraction of the active atoms on the crystallite surface where they are useful.

Almost no understanding of just what happens during these processes exists, and it is important that additional work be done in this area which is a pervasive problem in heterogeneous catalysis. The other aspects of deactivation are apt to be specific to a particular catalyst and reaction. Work which is imaginative and likely to be of practical use in these other areas is worthy of support. For example, success of a process frequently depends on the ability to re-activate catalysts without causing them to sinter.

B. Research to Support Specific Applications of Catalysis

1. Development of catalysts for the optimal conversion of non-petroleum feeds (coal, shale, tar sands, etc.) into usable hydrocarbon fuels.

2. Improve catalytic methods for hydrogen production, a fuel to be used in fuel cells for quiet power generation, for deep-sea recovery vessels, and as a heat source to drive turbines.

3. Investigate catalysts for hydrogenation, methanation, and Fischer-Tropsch synthesis of fuels.

4. Study non-noble metal catalysts for inexpensive, reliable fuel cells that operate on fuels other than hydrogen and oxygen.

5. Investigate the mechanism of catalytic removal of sulfur, oxygen, and nitrogen from fuels.

6. Explore the novel catalytic requirements that would be involved in building small, mobile, ship-board, refineries, to produce hydrocarbon fuels on nuclear powered ships, from coal and oil.

7. Explore the interfacial and catalytic factors involved in decomposition of solid phase propellants and explosives.

8. Investigate any possible catalytic effects involved in the ablation of heat shield materials from missiles or re-entry vehicles.

C. Commission Panel to Investigate DOD's Needs for Catalysis

In general, the panel found it difficult to make specific recommendations that would be unique to the DOD's needs. This was largely due to uncertainties on the part of the members as to exactly what the needs are. Most of the areas discussed (e.g. fuels, chemicals, pollution control, etc.) are common both to DOD and civilian uses, and considerable research has already been expended in these areas by the civilian sector. It is therefore recommended that a somewhat smaller panel (perhaps 10 people) be commissioned to visit various DOD centers and to itemize areas where research in catalysis might be expected to have a unique and positive effect on the DOD's mission, and on DOD self sufficiency for its energy needs.

INTRODUCTORY REMARKS

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Welcome to the ARPA Workshop on Catalytic Needs of the DOD and welcome to R&D Associates.

The purpose of the Workshop is to discuss the present state of catalytic processes important to the DOD and to recommend a program of researches in catalysis to be considered for support by the DOD. These recommendations will be attributed to the Workshop itself and not to any individual or corporation. We do not want to discuss any proprietary information and hope that you will not do so. But if we encroach in proprietarial areas, please warn us off so that the discussions do not go up blind alleys.

Professor Joe Hightower and his panel will collate and clarify the recommendations from this Workshop.

The talks and ensuing discussions will be recorded, and typed and will be sent to the speakers for correction. The proceedings will be edited and published as an ARPA document. Each attendee will have a copy of his own. Dr. Joe Hightower is our chairman.

INTRODUCTORY REMARKS

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I am delighted with the response each of you has given to the call for input to this meeting. In view of the worldwide energy crisis, the public concern about pollution control, and the fear that U.S. leadership in technology is in jeopardy, the time seems appropriate for the Department of Defense to consider more direct involvement in heterogeneous catalysis, a branch of science and engineering that can have an enormous impact in all these areas.

We have assembled here today a representative group of proven researchers in the field...people who have demonstrated their expertise and who wield considerable influence on the direction catalytic research will take in the U.S. during the next few years. It is hoped that through our discussions, areas will be pin-pointed where catalysis can make an impact on the needs and objectives of the DOD.

In order not to take up too much time, I have summarized my introductory remarks on three slides. Figure 1 describes the objectives and format of the meeting, Figure 2 lists some areas where catalysis is used, and Figure 3 shows the program. I hope each person will feel free to discuss openly, amplify on, or challenge any of the statements made during the next two days.

A group of five members attending this meeting will remain an extra day to summarize the findings and draw up a set of recommendations to ARPA. These people include Drs. Boudart, Burwell, Hall, Hightower, and Richardson. Their report will be circulated to each delegate for additional comments before it is attached to the printed proceedings.

If there are no questions or comments, let's proceed with the scheduled agenda.

FIGURE 1

ARPA WORKSHOP

Composition of Workshop

- Speakers - Industries, Universities, Governmental Agencies, Research Institutes.
- DOD Representatives
- Observers
- W.F. Libby
- Richard J. Kokes

Objectives

- Identify areas where catalysis affects DOD
- Predict research areas where improvements can be reasonably expected
- Show locations where catalysis research is carried out today
- List current funding sources for catalysis research

Each Speaker Asked to:

- Discuss briefly use of catalysis in his area
- Show relevence to mission of DOD
- Mention anticipated advances through research
- Talk only 15 minutes!

Each Observer Encouraged to:

- Fill in missing information during discussion
- Provide facts on omitted areas
- Question speakers
- Help make recommendations
- DOD - show where catalysis projects are now being funded

FIGURE 2

IMPORTANCE OF CATALYSIS

Importance of Catalysis Today

- Products worth $100 billion/year mfg. goods
- Defense technology
- Industrial productivity
- Energy sources
- Space program
- Environmental quality
- Food supplies

Projected Results of Advances in Catalysis

- Formation of new industries
- Improved efficiency of established industries
- More economical generation of electricity
- Expand supply of synthetic natural gas
- Pollution-free transportation
- Less costly conventional explosives
- Corrosion inhibition

National Goals of 93rd Congress - Catalysis Can Help!

- Improving environmental quality
- Maintaining U.S. Leadership in science and technology
- Strengthening national economy
- Solving energy crisis

Taken in part from "Catalysis"

Rothberg, Lib. of Congr.
Congressional Res. Service
Report T-175-US, April, 1973

FIGURE 3

PROGRAM

- Keynote Address
- Catalysis in petroleum refining
- Catalysis in fuel production from unconventional sources
- Catalysts in pollution control from stationery sources
- Some special techniques in catalysis
- Miscellaneous Topics
    - Rubber
    - Fuel cells
    - Power plants
- Role of some non-industrial organizations in catalysis
- Expected advances in catalytic processes through research

Hightower (Continued)

Our first speaker, Dr. Val Haensel, is from Universal Oil Products in Des Plaines, Illinois. For a number of years he was director of Research. He is now Vice President for Science and Technology at UOP. He has been active in catalysis societies and was Chairman of the Fifth International Congress on Catalysis in 1972. He is Director of US-USSR joint technology exchange program and he has recently been awarded the Presidential National Medal of Science Award. Our program does not have anyone speaking specifically on reforming catalysts which play an important role in petroleum refining. This is partly intentional because Dr. Haensel is the father of modern day reforming. In his keynote address, I am sure he will mention reforming, a subject of considerable importance to fuel supplies for the DOD.

IMPORTANCE OF CATALYSIS TO DOD

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I know very little about the importance of catalysis to the DOD and I am sure there are others that feel likewise. The reason for it, I think, is this: we know the general areas where catalysis is important but catalysis is only a means by which certain supplies are provided. For example, catalysis provides for interconversion from the less useful forms of energy to more useful forms. This means gasoline and jet fuel from crude oil and eventually from coal, shale, tar sands, etc., but it also may mean electrical energy from natural gas or hydrogen or eventually from crude oil by means of a fuel cell. In any event, I want to emphasize that after all catalysis is a means, a way of doing things, but it is not really the supplier and if I know anything about what the DOD needs, it is to have the energy readily available, to have energy available on the spot, and interconversion facilities available. I hope in this meeting we will get some clarification with respect to these particular conversion systems. In other words, we would like to know what does the DOD really need? We have found that unless we know the existence of a problem, there is very little we can do, and it is amazing that once you know the problem how many different answers and how many solutions can be found. I hope out of this conference there will come a cooperative communications system, which will tell us what the country needs and if catalysis can play a part in this, it would be a successful cooperative venture.

Northwestern is running a series of lectures on catalysis as part of their yearly symposium and I notice that in the flier, there is a quote from Berzelius dating from 1835 and it says, "This is a new power to produce chemical activity belonging to both inorganic and organic nature which is surely more widespread than we have hitherto believed and the nature of which is still concealed from us." Now, I hate to admit it, but what was said in 1835 is just as applicable today. The nature of catalysis is still concealed from us. We have learned a great deal, but we don't understand it. We have lots of facts, we have reproducible experiments, but the true nature still escapes us. I do hope that this Workshop will give us a little better view as to the areas where we can work.

As Joe Hightower pointed out, catalysis contributes to more than $100 billion worth of goods manufactured in the USA, but the average consumer has no realization what catalysis means and what it does for him. He does know in part, that most of the crude oil conversion processes are done through catalysis. He should know that most of the synthetic products that we wear, and so on, are created by catalysis. And great strides have been made in homogeneous catalysis. Right now homogeneous catalysis and heterogeneous catalysis are undergoing some sort of a merger, a marriage or whatever you want to call it, wherein the homogeneous people would like to have a heterogeneous catalyst and some of the heterogeneous people would like to have their catalysts behave like homogeneous catalysts. There is getting to be some sort of understanding between these two concepts.

Now I have been wondering what I should say about where we go from here. The DOD should realize that those of us who work in catalysis are not very many. The DOD should also realize that catalysis is a tremendously versatile tool. That, to me, is the most fascinating part of catalysis, the tremendous versatility of a system: as you vary it, you get completely different results, so that a system can be affected either from external sources or from internal sources. I would like to talk about how you can change a chemical reaction by introducing small amounts of impurities into the feed system, into the charging stock, and also what you can do if you change the composition of the catalyst. I would like to use as an example, the versatility of a catalyst which, for example, has little to do with the needs of the DOD per se. We have been involved for many years in the catalytic conversion of petroleum naphtha, to a point, now, where essentially all of the naphtha is being processed certainly in the United States, by a platinum containing catalyst, to convert it to high-octane gasoline. The only reason this process has taken hold is because it has been able, more efficiently, to produce octane numbers that were higher than before and that is the only reason for it.

Right now, in the United States, we are processing probably something in the order of 4 million barrels a day over platinum-containing catalysts. That is a tremendous amount, and in terms of energy it represents a very substantial investment on the part of the oil industry.

What we are interested in is the conversion of cyclohexane into benzene by the catalytic reforming process. The rate of conversion is a function of reciprocal space velocity. Let us define space velocity as follows: if I have a container which has 100cc of catalyst in it and 200cc of liquid material is passed through per hour, the resulting space velocity is two reciprocal hours. Thus, space velocity can be defined as the volume of reactant per hour per volume of catalyst. So the unit of space velocity is reciprocal hours, and therefore reciprocal space velocity is an effective time of conversion and all of catalysis can be described in this way: in infinitely short contact time you will have essentially no conversion and at very long contact times, you will have essentially equilibrium conversion. All of catalysis depends on knowing the shape of this curve for specific catalysts. In between zero conversion and equilibrium conversion the curve is rising and our work is right in here in the region of the steep slope. You will be amazed at how much catalytic investigation is being done at the wrong conditions, that is close to equilibrium, rather than where the slope is steep. Where you want to work is where the catalyst has to work hardest and this is at the highest possible space velocity. This slide shows the conversion of cyclohexane to benzene plus hydrogen over a platinum-alumina catalyst under conditions of very high space velocities, that means a thousand liters of charging stock per liter of catalyst per hour. The normal commercial refining practice may be anywhere from one to five space velocity. So we are working in this lower range here to try to determine where does a catalyst do its job most efficiently.

At a thousand space velocity with 32% conversion of cyclohexane itself, the bulk of the material goes to benzene. At extremely high space velocity, conversion will be reduced, the maximum amount of benzene is still being produced, but we are making more and more cyclohexene suggesting that very likely cyclohexane goes through a cyclohexene intermediate on the way to benzene.

Now what happens if this reaction is poisoned. In a sequence you have cyclohexane going to cyclohexene going to benzene. If the two rates for the first step and the second step were affected by poison in a different manner, more or less of the intermediate would be created depending on which step is poisoned.

Incidentally, it is extremely difficult to run experiments like this until you develop a good knowledge of chemical engineering principles of reactions at very high space velocities. In this example, with the same experimental conditions we put in 50 ppm of sulfur as an impurity. With sulfur present, instead of getting all benzene, we form less benzene as we increase the space velocity, but, instead, we are forming methylcyclopentane and methylcyclopentene as the major products. Very likely, in the presence of the poison, the sequence is to go from cyclohexane to cyclohexene and then to methylcyclopentene and then methylcyclopentane, but no benzene. So, this is a very good example of being able to control the reaction by means of outside poisons, namely by feed additives.

The catalyst business is a cooperative venture between organic chemists, physical chemists, inorganic chemists, and of course people that understand surfaces. This may be an example of materials science. The organic chemists say that the carbon-carbon bond opens and then closes in a different orientation to form a methylcyclopentene structure. This operation must be acid catalyzed. Then a basic impurity, in other words, an alkali may stop this reaction from taking place, or perhaps pyridine, a base. So we introduce pyridine into the feed stock, to the extent of 10ppm, in addition to the 50ppm of sulfur already present. And now the methylcyclopentene and methylcyclopentane have disappeared. We have stopped their production from occurring, by the introduction of the basic impurity and the reaction moves back in the direction of benzene except that there is also produced a little bit more cyclohexene. We have shown the important ability to control catalytic reactions by means of additives.

With respect to the conversion of cyclohexane on an absolute basis, we have had to use widely different space velocities in order to obtain similar conversions, because we are poisoning everything, but we are poisoning some reactions more than others. This is the whole point. In absence of any poison, we produce mostly benzene and a little methylcyclopentene, and a small amount of cyclohexene. In the presence of sulfur we form tremendous amounts of methylcyclopentane and methylcyclopentene, and an intermediate amount of cyclohexene. With both nitrogen and sulfur as a poison, we need a lower space velocity to reach the same conversion: we form again benzene, and cyclohexene as a major product. Now suppose we want to make only cyclohexene, and not benzene. Here is a way to control this system to be able to do that. If cyclohexene is a valuable raw material, there is some paydirt in these concepts.

We have been speaking of control of reactions by external factors. We may next ask if control can also be accomplished by internal factors. Let's look at the conversion of normal paraffins to normal olefins, much like the production of cyclohexene from cyclohexane as an intermediate without production of materials which are much more likely to form. Consider $C_{11}H_{24}$ going to $C_{11}H_{22}$, an olefin, after which it can change into anything it wants. A normal paraffin can be converted to a normal olefin, from which detergents and other products can be derived. But how do you stop the reaction with formation of the intermediate olefin?

Think of the myriad of reactions that may occur in the system. From the olefin the reaction can proceed to cracked products, and to isoparaffins, and from the cracked products to iso-olefins; from the normal olefin, the olefin may tend to go to a diene, then to a triene or aromatic; the cyclo-paraffin can form directly going to cyclo-olefins. The chances of an olefin reacting on the catalyst are much greater than the chances of the paraffin reacting on the catalyst. So the problem is to get the olefin off the catalyst before secondary reactions occur.

Let's cut out all of the acid acting portions of the catalyst, by adding alkali to the catalyst. If we increase the alkali we find that the non-normal production is more drastically reduced than the production of the desired olefin, so we have not sacrificed too much. The conversion to the normal olefin is desired but the production of the undesirable material is reduced to a much greater extent. There are always tradeoffs in catalysis and compromises.

Here is another good example; 2, 2-4 trimethylpentane can be converted to a naphthene with the same total number of carbon atoms using a platinum catalyst containing alkali. We now add arsenic to it as an additional poison; we would like to call it an attenuator. When it is arsenic modified, there is 8.5% cyclization; when it is unmodified there is 47%. In other words, by means of arsenic addition this reaction path is blocked very effectively.

The next slide shows dehydrogenation of C^{11} to C^{14} normal paraffins at a certain temperature range. Up to 10% conversion, the selectivity is about

95% to the olefin, which is pretty good considering the high reactivity of the olefins. Beyond 10%, nothing else can happen except degradation of the product.

The next slide shows the actual temperature requirement for a certain conversion to the olefin versus the number of carbon atoms of the paraffin. As the number of carbon atoms in the molecule is reduced, a higher and higher temperature is required. Thus, for a mixed feed of paraffins, one must choose very carefully the optimum temperature and optimum conditions, for the dehydrogenation of the mix as compared to dehydrogenating a single species of hydrocarbon is a more difficult reaction.

The next slide shows that with increasing molecular weight, the activation energy drops. Herein lies an indication for diffusion control of the reaction. At low molecular weight there is certainly none, but at high molecular weight there is the tendency to keep high boiling material on the catalyst. Modification of catalysts both by external and by internal forces is being done almost all the time in catalysis. Sometimes we are doing this without realizing it, and sometimes it is deliberate and specific. For example, instead of converting cyclohexene to benzene it is possible to convert benzene to cyclohexane by hydrogenation for use in nylon manufacture, etc. But some methylcyclopentane is also formed if there are acid sites on the catalyst. Addition of alkali stops the side reactions from taking place and increases the purity of cyclohexane. Thus, the main trick in catalysis is to stop the side reactions without too much slow-down of the reaction that is wanted.

Now, may I return to some of the problems that we have faced in connection with catalysis. Catalysis is interdisciplinary, we certainly found that out in the work on the emission control systems, so that it is very difficult to carry catalysis research to a successful conclusion at the university level, and we have considerable difficulties even at the industrial level. Among the participants in a problem of catalysis, there are physical chemists, organic chemists, analytical chemists, chemical engineers, and, for understanding of surfaces, we hope for contributions from solid-state scientists. Now, we have a frequent problem, those of us who work in industry, in that company XYZ calls us and says, we are studying this reaction and we know you are active in catalysis. Would you send us a couple of representative catalysts. So I ask: "Representative of what?", "Oh, you know, catalysts, you know." Now, this kills me. A more sophisticated guy will call and he will say I need a little information on catalysis; could you give me a telephone description of catalysis for a proposal I am writing, whether for DOD or not. But, to me, that is ridiculous and insulting to people that have been spending their lifetime working in catalysis, to be confronted by the fact that most people have no concept of the magnitude of the field of catalysis. It really is very unfortunate. Now to the DOD we say that we wish to know what are your problems. This is what I said in the beginning. We have a great many experts in catalysis; we certainly don't know the fundamentals, but as is true in so many other areas where we don't know the fundamentals either, we seem to get along fairly well. We would like to know the fundamentals and we would like to have some theories from which we can work. And this is really all we ask for. In order to gain fundamental understanding, a great deal more efficient effort can be carried on by both government and industry as well as at the university level and there is a great need to establish better communications among all these parties. Thank you very much.

Worley: I am puzzled, why you don't see any cyclohexadiene in that first reaction.

Haensel: The reason we do not see cyclohexadiene, and we have looked for it, is that in order to detect it, we will probably have to operate at a space velocity maybe another order of magnitude higher than where we have detected cyclohexene and we only found that when we went to very high space velocities. We are pretty sure that it may be a product, but in very low concentrations, because it is drained off faster than it is produced. Only when you chop off the drain, are you able to show its presence.

Worley: You are not sure that the cyclohexadiene is even needed as an intermediate?

Haensel: No, I'm not at all certain, but I think this could be an intermediate.

Heinemann: Just to continue on that question, Val, what about methylcyclopentadiene in coke. When you poison and you push the direction of the reaction into the MCP area, now you should form methylcyclopentadiene which cannot readily re-isomerize, you should go to coke. What does the coke look like?

Haensel: We find that methylcyclopentene by itself undergoes a reaction to form dimethylnaphthalene, which in turn could be the precursor for the coke. In other words, you don't even have to go to the diene. I think that the diene would certainly be an end product. This thing here is quite well established as a product. The coke is normally reduced as we poison, because poisoning reduces acid catalyst reactions, and that is the reason for the longer lives in these catalysts.

Holliday: You commented that research in catalysis is in the interdisciplinary area. What are your views on how the proprietary nature in much of catalysis research in the world has affected the development of the theory.

Haensel: I think the development of the theory has not been hurt in any way by the proprietary nature of catalysis. We have been very free in disclosing what we believe is a mechanism of the reaction which in effect is a theory. We have not been free to disclose the nature of the catalyst itself or the way we make it, because we do not believe in giving away our bread and butter. We sell it. As far as theory development, we have published very freely in these areas because we gain something in return by having comments from interested industrial and academic circles. The theory is more readily given away than actual physical quantities and what do you care whether a catalyst is made out of platinum or palladium or metal mixtures. Until you come to the final commercial application it is not critical, and the concept remains the same.

Hightower: You use, of course, platinum in your reforming most of the time, and you said it really doesn't make too much difference what the catalyst was.

Haensel: For theoretical implications.

Hightower: For practical implications, it can make quite a difference.

Haensel: It makes a tremendous difference.

Hightower: Especially when we have very little platinum in this country to go around.

Haensel: That's right, and maybe that's what Dr. Burwell was referring to. We have certainly had a revolution in catalytic reforming. We have gone almost completely from the single metal, from platinum, to the bi-metallics, of which platinum-rhenium is a very good example. It makes the operation more efficient, that is gives more yield from a given feed stock and so makes a more selective reaction.

Hightower: Do you foresee non-platinum catalysts being developed for reforming?

Haensel: Joe, you are the editor of the report that we issued sponsored by the National Academy, and Bill Bailey is the co-chairman of that committee dealing with catalytic reforming, so you should know as well as I do. We do not foresee at the present time, a replacement of the platinum catalyst nor the platinum attenuated catalyst by another metal system.

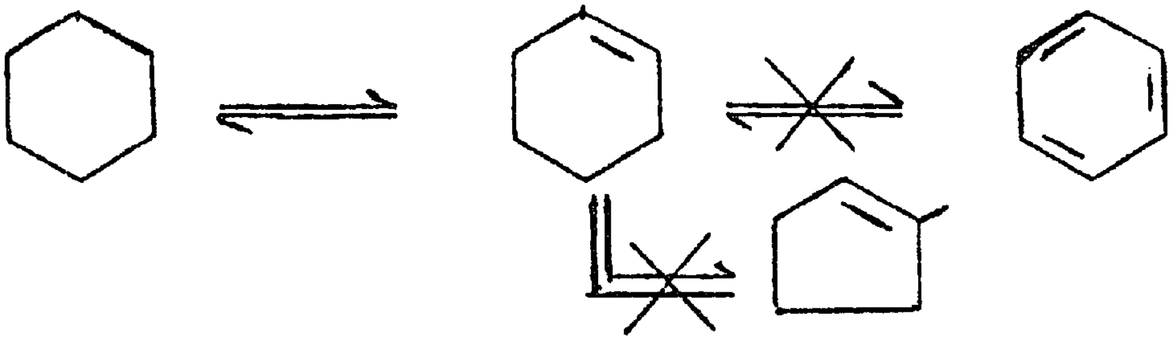
Hightower: Of course, but since that report came out there have been reports by Professor Boudart and others who have claimed that this may be a possibility, and I wonder if there is any comment. . .

Haensel: We would love to hear about it.

Boudart: Everything is in print.

Haensel: You see, he is holding out. This is the University academic circle holding out.

Hightower: It is obvious from Val's talk that any thermodynamically possible chemical reaction can be made to go more selectively and under milder conditions by use of the proper catalyst. There is a tremendous area here for research. Certainly reforming is a classic example. Thank you very much, Val.

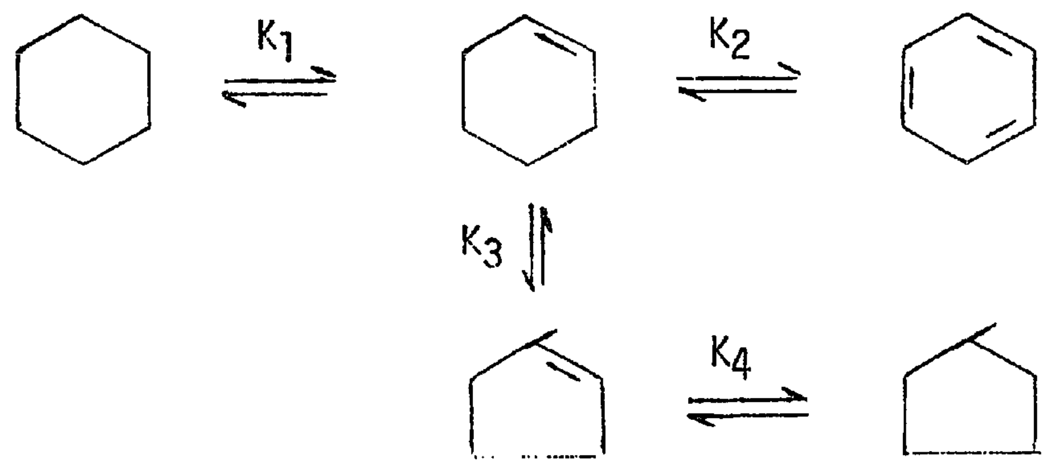


1

Conversion of CH over Pt-Al_2O_3 catalysts.
General conditions: 300 psig, 520°C, 6:1 mol ratio H_2/charge,
charge stock, 50:50 mol % CH:Bz.

2

LHSV	CH reacted, (Mol % of CH charge)	Conversion of CH to products (Mol % of CH reacted)				Ratio [$CH^=$/Δ Bz] x 10^3
		$CH^=$	Bz	MCP	Paraffins	
1 000	32.0	0.1	99.4	0.5	0.0	1
2 000	27.5	0.7	98.7	0.6	0.0	7
4 000	18.0	1.7	97.3	1.0	0.0	17
8 000	9.1	2.3	96.8	0.9	0.0	24
16 000	5.5	2.7	96.2	1.1	0.0	28
32 000	2.9	2.8	95.8	1.4	0.0	29
∞ (blank)	0.0	0.0	0.0	0.0	0.0	-



3

The unpoisoned relative rates are:

$$K_2 \gg K_1 \gg K_3 < K_4$$

4

LHSV	wt ppm in charge S	N	CH reacted mol % of CH charge	Conv. of CH to products (mol % of CH reacted) $CH^=$	Bz	MCP	$MCP^=$	Paraf.	Ratio $[CH^=/\Delta Bz] \times 10^3$
16,000	0	0	5.5	2.7	96.2	1.1	0	0	28
4,000	50	0	4.4	4.2	27	45	24	0	155
2,400	50	10	6	17	82	1	0.2	0	207

Conversion of CH over Pt-Al_2O_3 catalyst.
General conditions: 300 psig, 520°C, 6:1 mol ratio H_2/charge,
charge stock, 50:50 mol % CH: Bz.

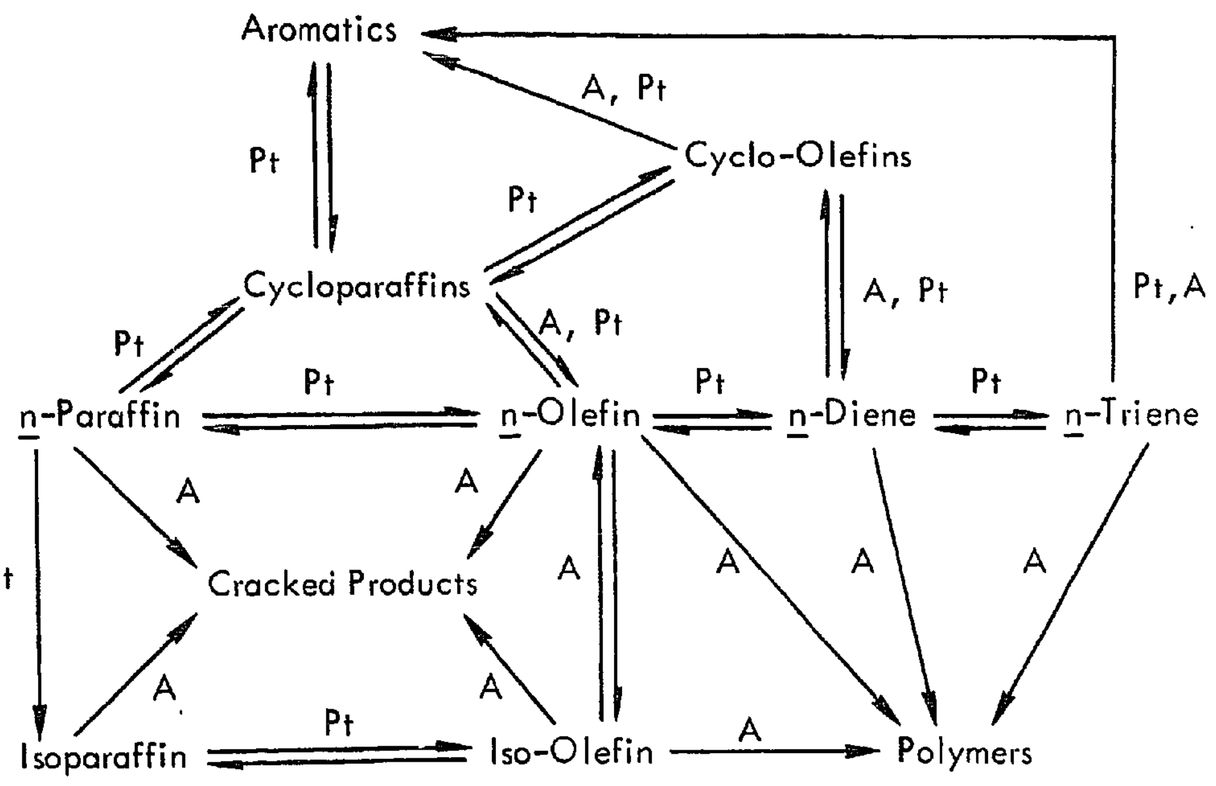
5

LHSV	Wt.-ppm in charge		CH reacted (Mol % of CH charge)	Conversion of CH to products (Mol % of CH reacted)					Ratio $[CH^=/\Delta Bz]$ x 10^3
	S	N		$CH^=$	Bz	MCP	$MCP^=$	Paraffins	
200	50	0	72	0.7	65	32	1.0	1.5	11
800	50	0	47	0.9	57	37	5.0	Trace	16
1 600	50	0	19	1.5	48	42	8.7	0	31
4 000	50	0	4.4	4.2	27	45	24	0	155
8 000	50	0	1.0	18	(-)	44	38	0	∞
8000	0	0	9.1	2.3	97	0.9	0	0	24

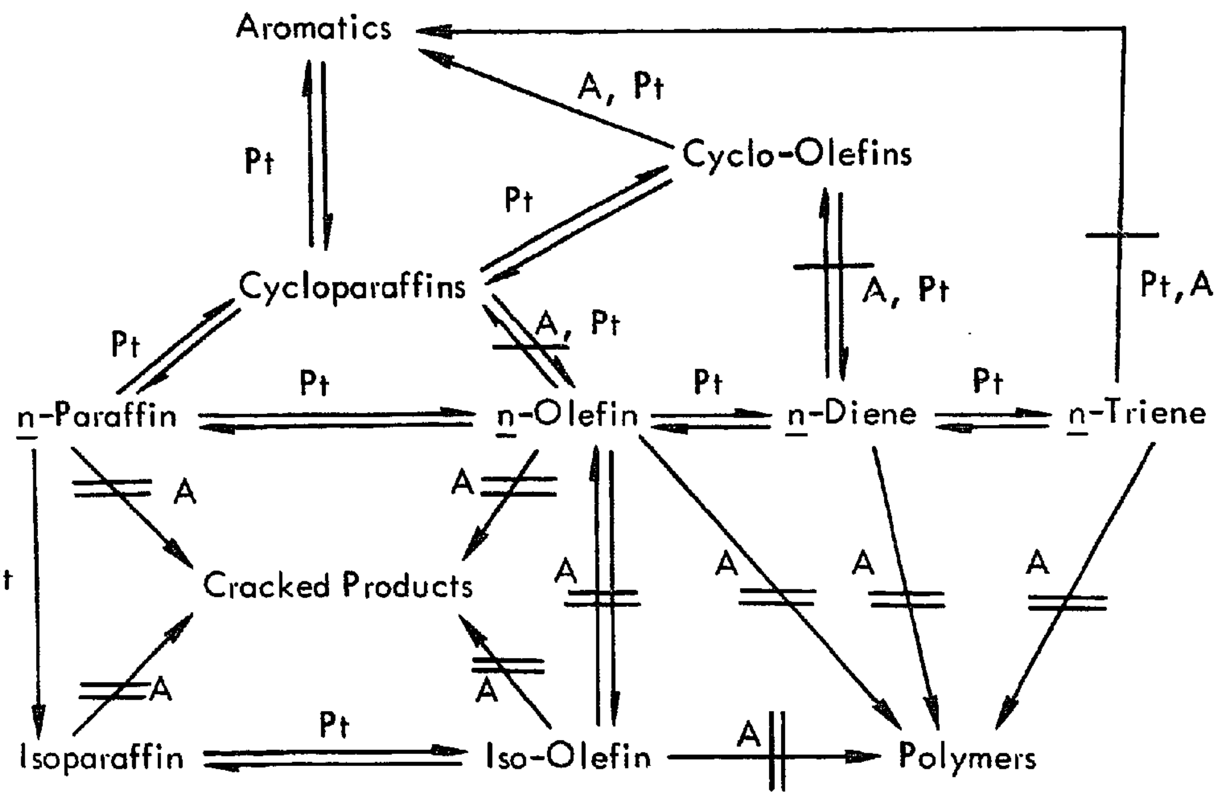
Conversion of CH over Pt-Al_2O_3 catalyst.
General conditions: 300 psig, 520°C, 6:1 mol ratio H_2/charge,
charge stock, 50:50 mol %.CH:Bz.

6

LHSV	Wt.-ppm in charge		CH reacted (Mol % of CH charge)	Conversion of CH to products (Mol % of CH reacted)					Ratio $[CH^=/\Delta Bz]$ x 10^3
	S	N		$CH^=$	Bz	MCP	$MCP^=$	Paraffins	
800	50	10	21	6	92	2	0.3	0	65
1 600	50	10	10	12	84	3	0.8	0	143
2 400	50	10	6	17	82	1	0.2	0	207


Aromatics
Pt
A, Pt
Cyclo-Olefins
Pt
Cycloparaffins
A, Pt
Pt,A
Pt
A, Pt
n-Paraffin
Pt
n-Olefin
Pt
n-Diene
Pt
n-Triene
A
A
Pt
Cracked Products
A
A
A
A
A
A
Pt
Isoparaffin
Iso-Olefin
A
Polymers

7


Aromatics
Pt
A, Pt
Cyclo-Olefins
Pt
Cycloparaffins
A, Pt
Pt,A
Pt
A, Pt
n-Paraffin
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n-Olefin
Pt
n-Diene
Pt
n-Triene
A
A
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Cracked Products
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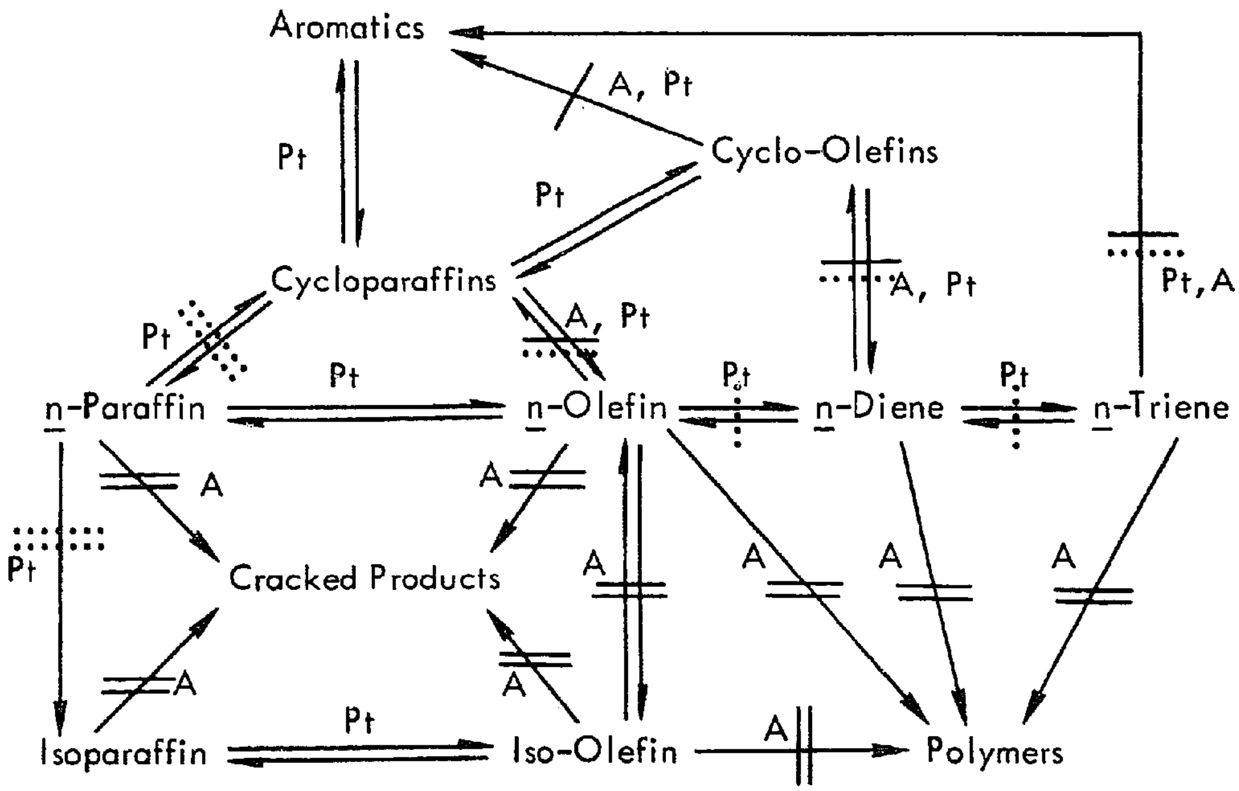
A
A
A
Pt
Isoparaffin
Iso-Olefin
A
Polymers

8



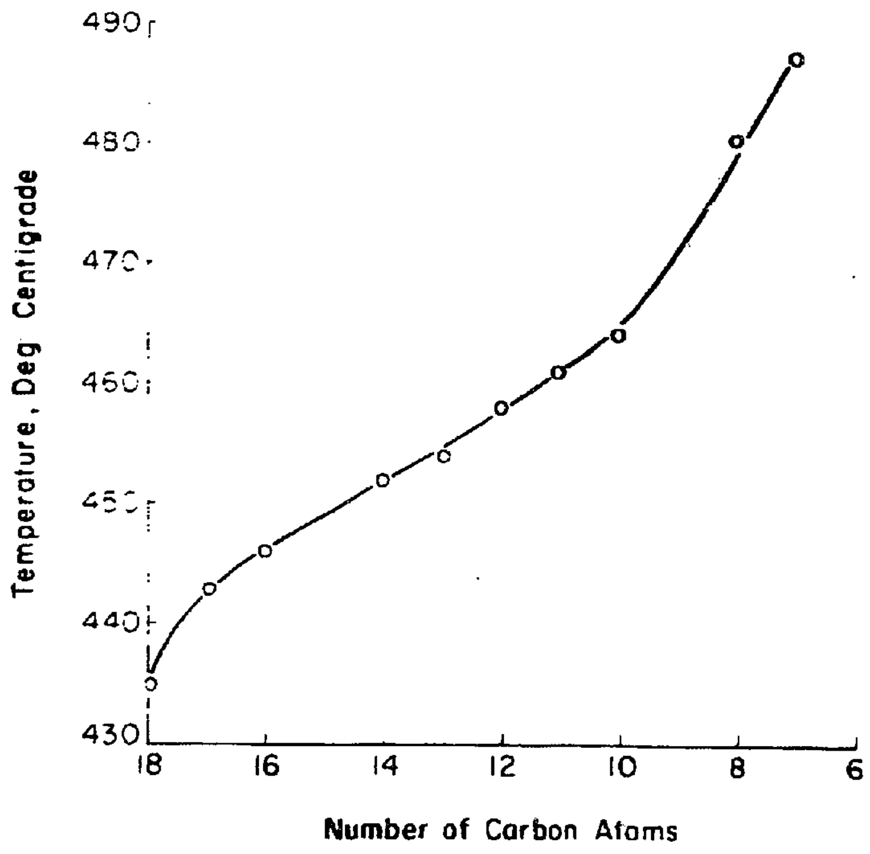
9

CYCLIZATION OF 2,2,4-TRIMETHYLPENTANE

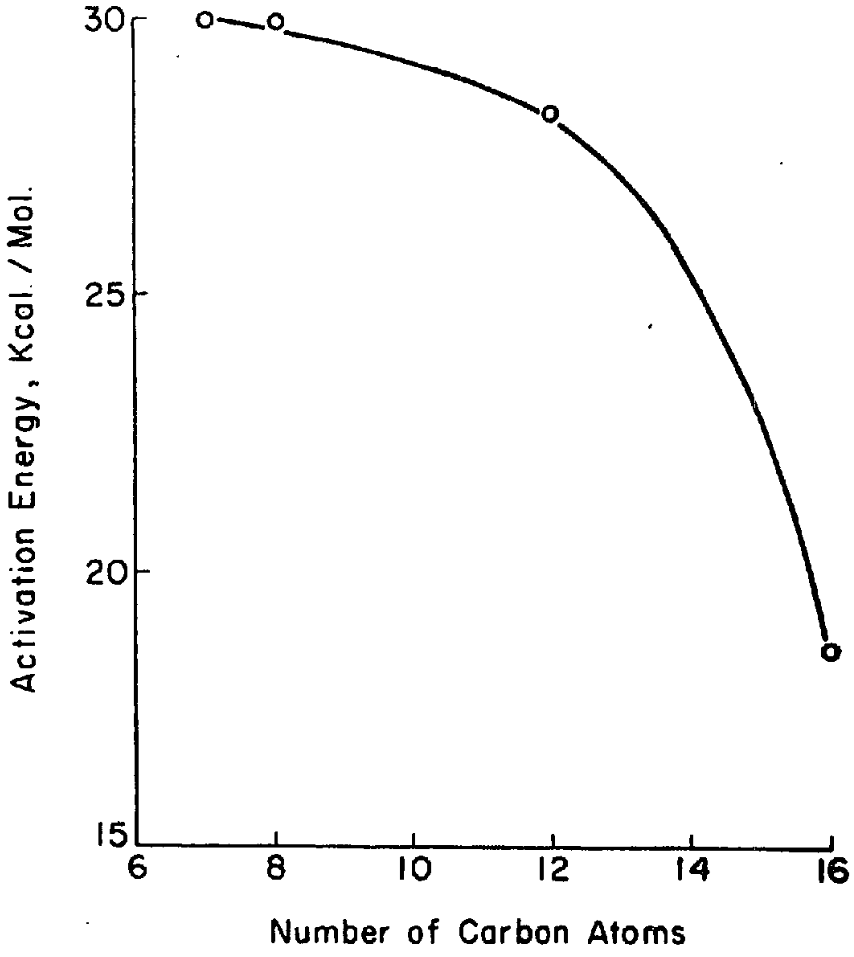
(371°C, 50 psig, 2 LHSV, 4 H_2/Hc)

10

	As-Modified Pt	Unmodified Pt
Percent Conversion To		
1,1,3-Trimethylcyclopentane	8.5	47

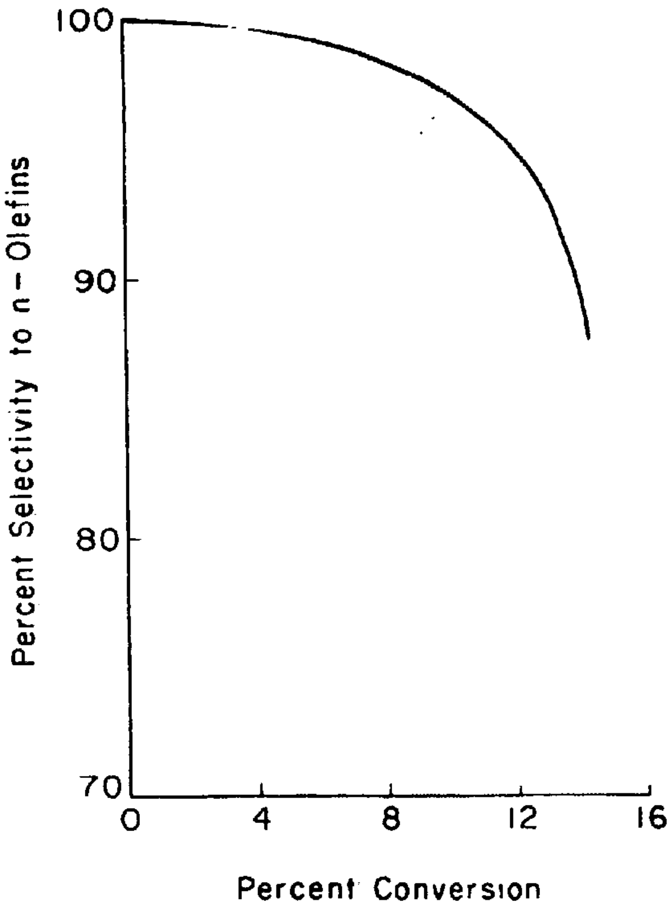

Dehydrogenation of n-Paraffins
(Temperature For 11.5% Conversion)

11


Dehydrogenation of n-Paraffins

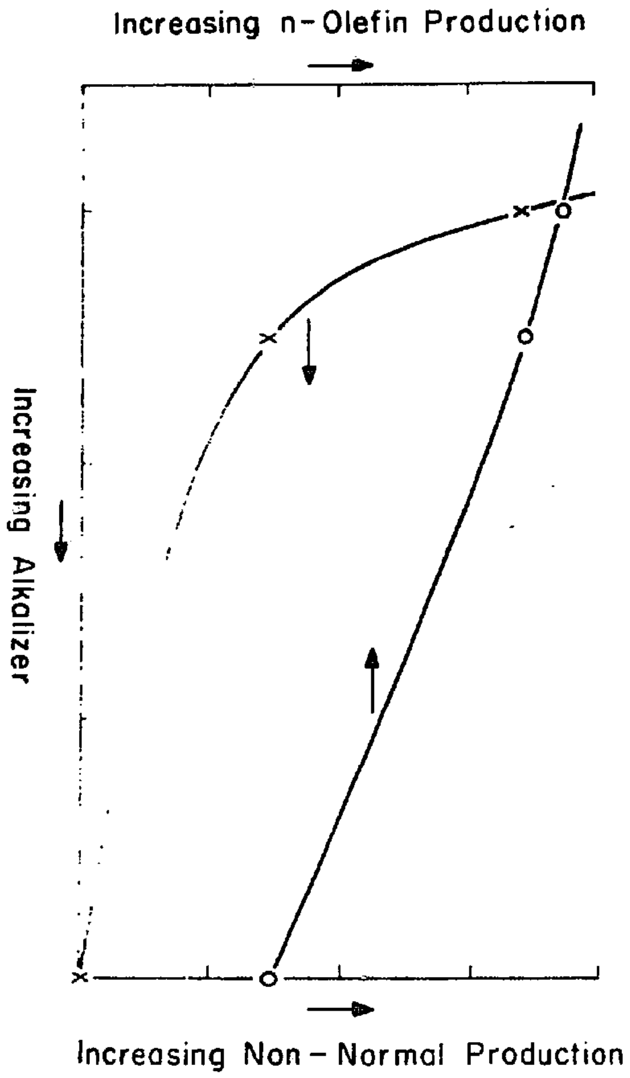
12

Dehydrogenation of $C_{11}-C_{14}$ n-Paraffins
(460 - 475° C)



13

$C_{11}-C_{14}$ Feed



14

THE USES AND POTENTIAL OF ZEOLITE CATALYSTS IN REFINING

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It is the purpose of our discussion to find the relevance and the focus of the interests of the DOD. I do not know what are the fields of interest of the DOD, so I hope very much, with Val, that in the course of these two days we are going to establish some form of communication and learn the problems of the DOD, so we can respond. In my quick little review here, I am going to describe a general problem and then discuss one item in a little bit of detail. I can't do much in 15 minutes.

Zeolites are porous crystals. Here are some electron micrographs. At this magnification showing a few thousand of these crystals, they look like ordinary white powders, like any other white powder. At a higher magnification of the electron microscope looking at a crystallite of about 1 micron in size, the face of a single crystal of a zeolite is seen to be porous. At seven million magnification, it suddenly appears that this face of the crystal has holes in it, in a very regular manner, and uniform, as must be since this is a crystal. The ports are cavities or holes going all the way through the crystallite. Those holes here are man-made, uniform and defined all the way through the crystallite and because of the uniform size of those holes and cavities they can absorb anything that's smaller than they are, reject everything that is bigger than the port. For this reason they are called molecular sieves.

This slide shows the framework structure of Y,X, and faujasite crystallites, showing holes. Behind this port there is a cavity. Zeolites are porous crystals, and have specific properties. Zeolite minerals have been known for a hundred years. They have a tremendous tenacity to adsorb polar molecules, like water, very tenaciously, but will desorb when heated up. It is also known that they adsorb only certain things like water and don't absorb other things. Before X-ray crystallography there was no way to determine the size of these pores or their uniformity. The recent advance in this area has begun with the development of synthetic varities of these minerals, some similar to natural minerals, others quite different. Some are known in nature to have pores large enough to admit molecules of interest in industry, in chemistry, in fuel and petroleum technology. Most interesting are those with pores able to admit hydrocarbons in petroleum.

This slide lists the prime properties of these porous crystals. I'll talk about those having large pores which can admit those molecules of interest in petroleum technology, of more than 7, 8, 9 Ångstroms in diameter. They can freely admit paraffins, naphthenes, aromatics, and affect them chemically. The fact that zeolites are crystalline means that they have large uniform surface areas. The crystal's outside surface area is very small, of a few tenths of a square meter per gram. The inner surface is big, hundreds and hundreds of square meters per gram, up to 800 square meters per gram. So outside area is not very important. What goes on within the crystallite on the inside surfaces is all important in catalysis. Some of the crystal cations are exchangeable, namely can be removed if something else is substituted for it. Sodium can replace calcium, calcium can replace sodium, and so forth so that one can form a great variety of chemical compositions and polarities and absorption properties. This slide shows these properties. First is absorption and the blue underlining lines show which properties are important for absorption. Polarity is important. Intra-crystalline pore and cavity systems are very important because they can accept, in a very specific manner, lots of atoms, ions, salts. Host lattices we call them because they accept guest compounds. The next important property is structure stability. In petroleum refining where temperatures of about 500 degrees C are used, materials of interest must be stable at those conditions. Outstanding catalysts are very thermo-stable, some up to 1000 degrees C and even beyond, and also chemically stable. Some of them are even stable in concentrated acid. Instead of absorption I focus on two areas, catalysis and surface chemistry. The interest in zeolite catalysts has changed rapidly from being a laboratory curiosity into having gigantic applications in industry. Probably all large refinery cracking units use zeolite catalysts. Catalytic cracking increases the gasoline yield from petroleum feed stock as compared with distillation. Another area is hydrocracking which increases the yield of gasoline from high boiling petroleum distillates by hydrogenation and cracking. Zeolites have important applications as hydrocracking catalysts. Selectoforming cracks out of the gasoline those components of low octane number. Zeolites of small pore size crack normal parafins of low octane number producing a gasoline with higher octane number. All these processes result through the action of zeolites. Isomerization increases the octane number of the gasoline, and in this process the molecular sieve property as well as other properties of zeolites is dominant. A most recent industrial application has to do with benzene alkylation, important in the chemical industry, and in this field it is important that zeolites have the molecular sieve property and the property of acidity. Beyond these industrial applications, there are many others maturing at various stages of research and development, for example iso-parafin alkylation, xylene isomerization and toluene disproportionation. The greatest present day technical benefits are from increased gasoline yield, and increased octane number, high yields of gasoline and better quality of gasoline. To best show what zeolites do in petroleum refining, in catalytic cracking, let's take this example. Zeolites as catalysts have a higher activity by orders of magnitude than the previously used silica-alumina type catalysts. Because of that they can process more feed stock in a single pass through the reactor than the previously used silica-alumina catalyst. Furthermore there is more gasoline yield with the zeolite and more yield of butane, and propane. On the other hand, there is less of light gases and less coke. In summary there are more of the desirable products, and less of the undesirable ones by use of zeolites in cracking.

I quote here estimates of the economic value of zeolites in petroleum refining published in 1966. "When it is applied to the whole industry, to the whole amount of catalytic cracking feedstock, the savings because of the better yields of gasoline product were estimated at $250, million per year. It was anticipated that this increase will be bigger in the time to come."

A similar, most recent review was given by a distinguished researcher in the field, Paul Weisz, who estimated that zeolites produce 7% more gasoline from the same feedstock as the silca-alumina catalyst. These raw material savings means a savings of 200 million barrels of crude per year, of value anywhere up to a billion dollars.

What makes zeolites such outstanding catalysts in so many fields of petroleum processing? In the case of selective forming, which seeks out normal paraffins and destroys them, eliminating them from the gasoline, it is the molecular sieve property of zeolite that allows only the normal paraffin to enter and be destroyed. Now, how about catalytic cracking and hydrocracking. The important property is the very strong acid behavior. Zeolites have a tremendous number of acidic hydroxy groups within those pores. The molecules absorbed within the zeolite are subjected to its crystal field. They become part of the crystal, subjected to the forces of the crystal molecular. Finally zeolites have a higher action capacity for the molecules occurring in petroleum than does silica-alumina. These are the principle features that are agreed to that differentiate zeolite catalysts from other catalysts. Well, you may ask, if catalysis is so important to our industry why don't we know more about it. Well, I think the answer is that catalysis is a very complex interdisciplinary field with as yet no real firm basis of predictability. By the way there is a Supreme Court decision, stating that catalytic, phenomena are not predictable. They are right.

The first significant publication on zeolite catalysis was printed in 1960. Since then there have been several thousand publications on zeolites, and more than 1000 issued U.S. patents, in a little over a decade. The research effort, quite big, has introduced new thoughts, new concepts, and an influx of scientists from different fields including physicists and surface chemists. I have made a review in 1966 of the Russian literature and found 200 Russian scientists publishing on zeolites, whereas there were few before 1960. Their effort has not been different from ours; they mainly repeated and expanded our work in the United States.

There is an area well researched which has not been applied as yet, namely surface chemistry. Zeolites introduce a type of new surface chemistry for the simple reason that the zeolite surface within the crystal is different, because it is within the crystal and is subject to the crystal field, and so provides phenomena different from those observed on ordinary crystal surfaces. They are much more close to the phenomena observed in solid state chemistry within the crystal. There is a big difference, though. The zeolite inner surface is accessible. If the pore size is large you can put all kinds of molecules within those crystals. Among those phenomena that have been found in these crystal fields are unusual subvalent states of cations, such as Na^+, Pd^+, and metal atoms like palladium trapped in small cavities; there are electrons trapped in large orbitals up to ten Ångstrom diameter, and the phenomena such as Na_4^{+3} and Na_6^{+5} clusters. You can trap salts in a very specific manner or ionize them within those crystals. These phenomena distinguish the internal surface chemistry of the zeolites from those found on ordinary crystal surfaces.

It was a very big effort and took the patient investment of our industry in research of a fundamental kind, requiring millions of dollars and many years, at our company and at many petroleum companies, to develop this field and to find applications. It took many more millions of dollars after the phenomena had been found to develop applications. I certainly agree that catalysis is a very complex, interdisciplinary field and makes technology more efficient in the fields of chemistry, fuel technology, and biochemistry, important for general areas of economy as well as for human life, and deserving of more attention of a basic kind than what has occurred so far.

I would like to say a few words about what areas might be of interest to DOD. One of the areas where zeolites can be used is in conservation of energy resources. They can be absorbants for undesirable gases, for example, in submarines. They are oxidation catalysts, and have the capability of releasing and accepting molecules. For example, they can release something that might aid or control the reaction rates in oxidation of rocket fuel. This new type of surface chemistry in missiles may also find wide applications in the future.

Bailey: I must take exception to your statement that there is a conservation of energy resources here. You remarked about high yields of gasoline; that is, of course, quite true, and if gasoline were the only product we were going to make it would definitely be a conservation of energy resources. However, you are shifting one potential energy resource to another and therefore it is certainly true that zeolites allow such a shift very satisfactorily. But I see no conservation of energy resources.

Rabo: I agree, you are quite right. Zeolites only focus on the gasoline.

Hall: You mentioned coke. Is this significant?

Rabo: Haensel will make the comment on coke.

Haensel: On coke, no. But in connection with what Bill had to say, two things. Number one, you indicate a higher gasoline yield. That is correct. At the same time, the zeolite catalyst produces less olefins in both butene and propylene. As a result, there is less output feedstock which in turn makes gasoline. So we have to look at the total picture of the refinery output.

Rabo: There is a further refinement to the overall effect of zeolites on the petroleum technology and fuel conservation. It optimizes on gasoline but there are more sophisticated aspects of this such as recycling of olefins and other paraffins into the gasoline stream.

Haensel: Number two, for normal C_{11} paraffins going to normal C_{11} olefins, we separate the normal C_{11} paraffins from kerosene by means of zeolitic systems on a continuous basis. In addition to that we obtain 12% by zeolitic systems. We use another absorbent system in order to separate the olefin from the paraffin so we can recycle the paraffins. So I think the

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Haensel (Continued)

contributions of the zeolitic concept have been extremely valuable in developing processes that now utilize that principle.

Rabo: Right. I decided not to comment on adsorbents because how do we do all that so quickly.

Mills: A most interesting point is that we are arguing about conservation of resources. I agree with Weisz this is a saving of 200 million barrels because with non-zeolite catalysts you have to struggle harder to make that gasoline. The number was 200 million barrels a year and since we use 5 billion barrels per year in the United States, this is 4%. Four percent is about the amount of oil that we are importing from the Arab nations. (No, you're wrong...) Well 6% is sufficient, from the near east. So 6% to 12% is the rate depending what countries you count. One further comment: while in the past dollars were the criteria by which we judged, now the new coin can be resources. We should measure catalytic contributions in terms of the conservation contributions.

Rabo: I agree with all of your three comments. There should be a new, more detailed, assessment in terms of ultimate fuel economy to reevaluate the function of zeolite catalysts. I have no particular bias either way.

Burwell: The last two speakers spoke of the deep, dark, mystery of heterogeneous catalysis and how we didn't know anything about it and they are certainly correct. However, the basic phenomenon of catalysis involves a series of elementary processes in no way different from the chemistry of any other kind of reaction. In homogeneous catalysis all of these steps are those of ordinary chemistry. In heterogeneous catalysis the elementary

Burwell (Continued)

processes are surface processes and any given catalyst may present more than one kind of surface site. So several reactions may be going on but basically each is no different from other chemistry. When people say they don't understand catalysis they must be saying they cannot give a detailed picture of the elementary steps. But for what reactions can one? Perhaps a hydrogen atom reacting with a deuterium molecule to make HD plus D is about the only reaction we have understood. How many reactions more complicated or involving macrorganic molecules have been predicted a priori? Essentially none. How many new homogeneous catalysts? If this were so easy why didn't somebody invent homogeneous hydrogenation catalysts instead of happening upon them. Heterogeneous catalysis is more difficult to understand and we have made little progress but it too is fundamentally chemistry.

Rabo: We are not as depressed as you might think. But I agree.

McCormack: The conservation question is certainly important to us and to optimize the different components is important. But looking at the objectives which affect the nation as well as DOD, we are going to both need fuel to drive us to work and the feedstock to run the plants. The plants are shutting down currently.

Wise: In the areas of catalysis would you project the future? Do you believe that the research will be increased or decreased, and will there be a shift from the fossil fuel economy to a hydrocarbon economy?

Rabo: Any new item has a certain lifetime and any catalyst will be superceded some day by a better one. We are going to learn one day enough about zeolite

Rabo (Continued)

catalysis and make some other system that might work better. Or we might make catalysis of zeolite types that are better than the ones we have right now. On the other hand there is a tremendous potential in using the presently existing porous crystals in the general area of fuel conservation more broadly than is current. That may give an added impetus in the future interest for further research and exploitation.

Libby: Even though perhaps it is not perhaps approved to consider dollar values, have you an estimate of the R&D dollars that were put into zeolite research since 1960?

Rabo: In our organization all I could say on this point, it has been a multimulti-million dollar effort. At the beginning of the 50's our particular organization decided to make a long range commitment of more than dollar value because it meant that our research effort was limited to one area. For many years a substantial fraction of our research has been directed to this one particular area. It takes a very large commitment; it is a high risk with little predictability of specific use. Pores which are just the size of a molecule may or may not be of tremendous industrial use. So this was a tremendous high risk for industry to engage in. The stakes were enormous. In our case we had a great interest in crystals and in technology of solids. But I don't know what has been the total investment.

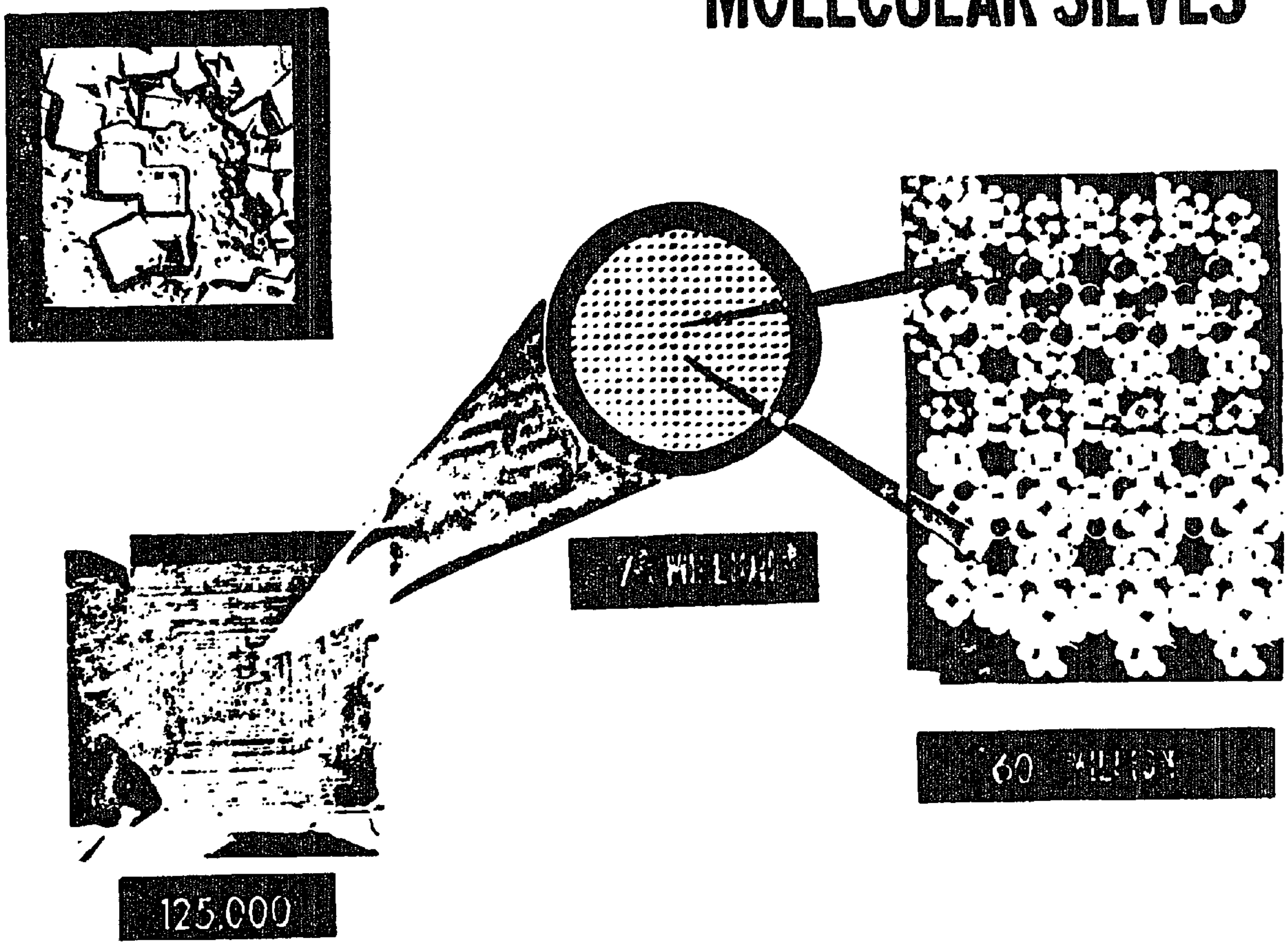
Heinemann: Just a comment to Dr. Libby. I have no figure on the cost of industrial research on zeolite but I have an estimate on research, not development, on zeolites for one purpose only, and that is catalytic cracking, of the order of $25 million dollars in industry alone.

Rabo: I could add that in Russia the effort is quite substantial. But I don't know of any new direction or idea that differs from what we found so far. Of course, we know only those things that are published.

Hall: About the potential future of catalysis: First, one does not use pure zeolite in many of these processes, but instead mixed with other components like silica-aluminum for the cracking reaction, creating a new dual function catalyst which helps moderate behavior in a complex reaction. In such dual functioning systems, there are vast areas for potential improvement. Just as an example of this, Dr. Hansford of Union Oil Corporation has pointed out that by making proper modification of a zeolite-type catalyst -- I believe this was for hydroisomerization - they had been able to simply dump a reactor, which contained a previous catalyst, and put this new catalyst into it and save building an additional reactor. In this way they doubled the capacity of the plant. I believe there will be in the future perhaps a tailing off in the amount of research. But there is a great potential left for future economic development in this area.

Rabo: That's quite true. And, of course, a new catalyst affects the technology of catalytic cracking as well as the other processes, all aimed at improved economy, which leads ultimately to conservation of fuel.

MOLECULAR SIEVES



ADSORPTION: ______
CATALYSIS: ______
NEW SURFACE CHEMISTRY _____

ZEOLITES

PROPERTIES

CRYSTALLINITY:

- LARGE AND UNIFORM SURFACE
- CRYSTAL SURFACE ~0.5 M^2/G, INTRACRYSTALLINE SURFACE ~500-800 M^2/G.
- UNIFORM PORES
- IT IS A MOLECULAR SIEVE

EXCHANGEABLE CATIONS:

- VARIABLE CHEMICAL COMPOSITION
- POLARITY

INTRACRYSTALLINE PORE AND CAVITY SYSTEM

- HOST LATTICE

STRUCTURAL STABILITY

- STABLE UP TO 1000°C

CHEMICAL STABILITY

- MODIFIED STRUCTURES
- ACID STABLE STRUCTURES

ZEOLITE ADSORBENTS

PROCESS	TECHNOLOGICAL BENEFITS
SEPARATION BY MOLECULAR SIZE	INCREASE GASOLINE OCTANE NUMBER
SEPARATE POLAR COMPONENTS FROM GAS MIXTURES	HIGH SELECTIVITY AND CAPACITY
REMOVE ACID GASES	ENVIRONMENTAL CONTROL

ZEOLITE CATALYSTS

COMMERCIAL PROCESSES	TECHNICAL BENEFITS
CATALYTIC CRACKING	INCREASED GASOLINE YIELD
HYDROCRACKING	HIGH YIELD AND RESISTANCE TO N-BASES
SELECTOFORMING	INCREASE OCTANE NUMBERS
ISOMERIZATION	INCREASE OCTANE NUMBER
BENZENE ALKYLATION	USE OF PETROLEUM IN PETROCHEMICAL INDUSTRY.

POTENTIAL PROCESSES

ISOPARAFFIN ALKYLATION

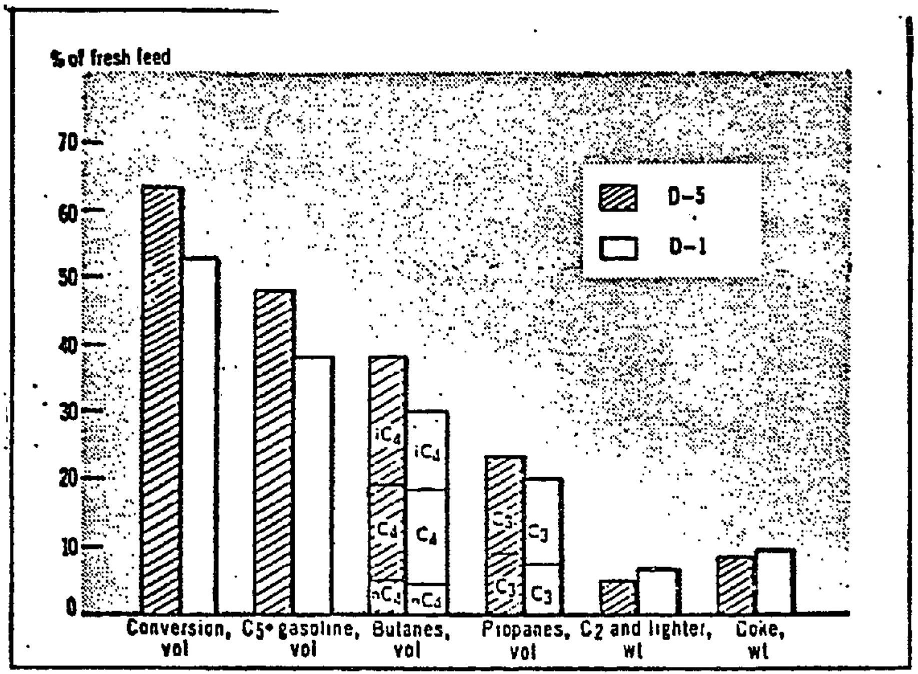
XYLENE ISOMERIZATION

TOLUENE DISPROPORTIONATION

BENEFITS PROVIDED BY SIEVE CATALYSTS

			HIGH ALUMINA	ZEOLITIC CATALYST	
REFINER A	%	CONVERSION	71	72	(FEED INCREASED BY 25%
		GASOLINE ON FRESH FEED	47	56	OVER HIGH ALUMINA RUN).
REFINER B	%	CONVERSION	63	76	(AT SAME FEED RATE AS
		GASOLINE ON FRESH FEED	43	56	HIGH ALUMINA RUN).

R. H. EBEL, OIL AND GAS JOURNAL



DURABEAD 5 increases gasoline yield substantially. Chart shows average yields from three cat crackers when operating at maximum throughput. Fig. 1.

L. P. EVANS, ET AL, OIL AND GAS JOURNAL,
PG. 113, SEPT. 9, 1963.

6

Laboratory results with conventional and new catalyst

Table 1

Catalyst	Kao-spheres*	HZ-1†
Cat-D:		
Conversion, wt %	54.8	77.9
Gasoline, vol %	37.6	60.8
Coke, wt %	4.0	4.2
Gas, wt %	17.7	20.2
Gas gravity	1.42	1.67
Ball mill, 6-hr	44.0	90.0
Bulk density	0.81	0.92

*Equilibrium Kao-spheres from plant 7 days before HZ-1 addition.
†Typical of shipments to plant.

R. E. ASHWILL, ET AL., OIL AND GAS JOURNAL,
PG. 114, JULY 1966.

7

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E. J. DEMMEL, ET AL

HYDROCARBON PROCESSING, 45:5, MAY 1966.

"WHEN APPLIED TO THE INDUSTRY'S 3,500,000 BPD OF CATALYTIC CRACKING FRESH FEED, THE SAVINGS BECOME $250,000,000 PER YEAR. THESE SAVINGS WILL BE INCREASED SUBSTANTIALLY IN THE FUTURE."

8

PAUL B. WEISZ

CHEMTECH, P. 498, AUGUST 1973

"IN 1967 IT WAS ESTIMATED (15) THAT, IN NORTH AMERICA ALONE, EACH INCREASE OF GASOLINE PRODUCTIVITY BY 1% WOULD ALLOW A SAVING OF 27 MILLION BARRELS PER YEAR OF CRUDE OIL RESOURCES TO PRODUCE THE EXISTING GASOLINE DEMAND. AN INCREASE OF 7%,WHICH WAS MORE CHARACTERISTIC OF ZEOLITE CATALYSTS THEN MADE, SAVED NEARLY 200 MILLION BARRELS PER YEAR. SINCE THEN FURTHER IMPROVEMENTS HAVE EXCEEDED SUCH PERFORMANCE.

9

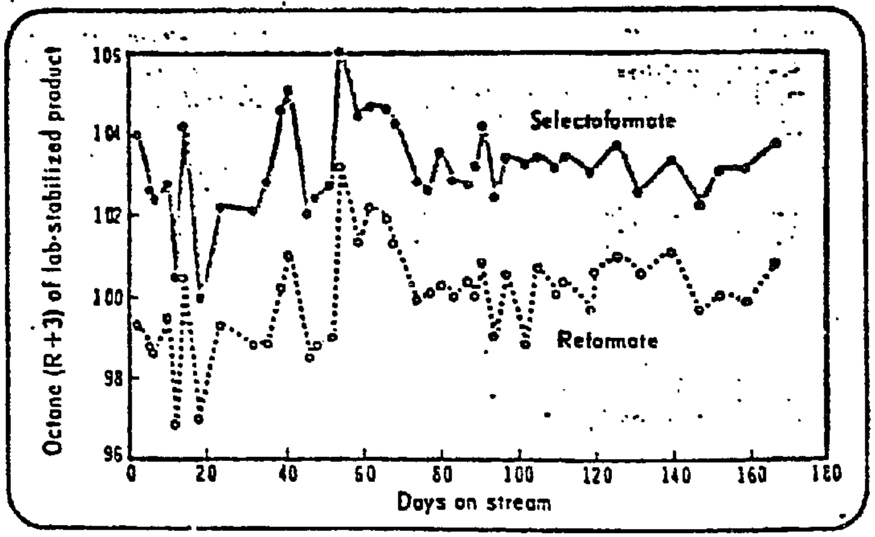
Comparison of Catalysts - FCC

Commercial Plant- Constant Carbon

	Sieve	High Alumina
Conversion, %	73	65.6
Coke, wt % F.F.	7.4	7.3
$C_1 + C_2$ "	2.9	3.0
Total C_3 vol. % F.F.	7.7	8.4
C_3= "	5.5	6.2
Total C_4 "	15.9	12.6
C_4= "	7.8	6.7
C_5+ Gasoline "	55.4	50.5
Octanes- RON- Cl.	91.2	92.4
+ 3 cc	97.3	97.3
MON- Cl	77.6	77.7
+ 3 cc	83.4	82.2

10

Selectoforming produces high-octane gasoline



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NOT REPRODUCIBLE

N. Y. CHEN, ET AL, OIL AND GAS JOURNAL,
PG. 157, NOV. 18, 1968.

NEW SURFACE PHENOMENA

INTRACRYSTALLINE ZEOLITE SURFACE IS QUITE DIFFERENT FROM ORDINARY CRYSTAL SURFACES. THE PORES AND CAVITIES ARE PART OF THE ZEOLITE CRYSTAL MATRIX AND THEY ARE SUBJECT TO ITS CRYSTAL FIELD. AS A RESULT, IN THE PAST DECADE A WHOLE HOST OF CHEMICAL PROPERTIES WERE DISCOVERED WHICH ARE NOT FOUND ON EXTERNAL CRYSTAL SURFACES - ORDINARY SURFACES. SEVERAL OF THESE NEW SURFACE PHENOMENA IN ZEOLITES ARE SIMILAR TO THOSE FOUND WITHIN SOLID MATRICES.

SURFACE PHENOMENA IN ZEOLITES:

UNUSUAL SUBVALENT STATE OF CATIONS: NI^+, PD^+ 12

TRAPPED METAL ATOMS: PD^0

ELECTRON TRAPPED IN LARGE, OPEN CAVITIES: NA_4^{3+}, NA_6^{5+}

IONIZATION AND TRAPPING OF SALT MOLECULES.

WHAT MAKES ZEOLITES OUTSTANDING CATALYSTS IN PETROLEUM PROCESSING?

1. IN CASE OF SELECTOFORMING IT IS ITS PROPERTY AS MOLECULAR SIEVE.
2. IN THE OTHER CASES? VERY STRONG ACID BEHAVIOR.

BUT WHY? THE ANSWER IS SUBTLE RATHER THAN OBVIOUS. 13

THE MAIN CONTRIBUTING FACTORS ARE:

LARGE NUMBER OF ACIDIC OH GROUPS.

ADSORBED MOLECULES ARE SUBJECT TO THE ZEOLITE CRYSTAL FIELD.

HIGHER ADSORPTION CAPACITY AT HIGHER TEMPERATURE.

POTENTIAL AREAS OF INTEREST TO DOD

CONSERVATION OF ENERGY RESOURCES

SPECIAL ADSORBENTS FOR UNDESIRABLE GASES

OXIDATION CATALYSTS

REACTION RATE CONTROL THROUGH ADSORPTION OR RELEASE OF REACTANTS.

NEW SOLID STATE APPLICATIONS

SELECTIVITY IN GASOLINE PRODUCTION

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Ladies and gentlemen, Jules Rabo did a beautiful job of saying some of the things that I was going to say and so gave me a little more time. I have chosen to talk about some work at the Mobil Laboratories that has been going on over the last thirteen years but is restricted to a very narrow area -- namely, cracking of hydrocarbons with zeolites. I want to show the evolution that has occurred in the selectivity obtained with zeolites and how one can expect further changes of this kind in the future.

The second is the conservation of equipment. Increased selectivity can increase the through-put of a given piece of equipment. When the new zeolite catalysts in catalytic cracking were first introduced, industry for a period of five years or so did not have to install new cracking capacity even though demand for gasoline continued to rise at the old rate. The reason was that because of the better selectivity the same equipment could produce larger quantities of gasoline.

The third is a potential contribution to pollution control. The first slide shows that when zeolite cracking catalysts were introduced, they proved to be more active and produce a hexane conversion greater than that of the old standard catalyst, which was silica alumina.

Zeolite catalysts are as much as ten thousand times as active as silica alumina, but this did not help so much in commercial cracking, because the heat transfer problems were such that you couldn't really take advantage of these great activities. What was exploited was the selectivity.

Heinemann (Continued)

The next slide shows that with silica alumina catalyst the product distribution showed relatively few paraffins, a lot of olefins, and an appreciable amount of aromatics. With zeolite, the shift is away from olefins to paraffins and a somewhat greater production of aromatics, and this occurs for a number of feed stocks. Now, the reason for this increased selectivity and this decreased coke content, is the hydrogen transfer activity of the zeolite. Normally, oil is cracked to gasoline and gasoline to gas.

With zeolites, where there is a hydrogen transfer activity, we catch the intermediates, which are largely olefins, and by hydrogen transfer, stabilize them before they go all the way down to gas. As the zeolite technology improved, we went from X to Y zeolites, and the product distribution changed. For the feed stock on this slide which is particularly hard to crack, the coke fraction becomes smaller when Y zeolite is used, instead of X, the gasoline yield becomes bigger, compared to the distribution obtained with silica-alumina. In other words, the product distribution changes in a specific direction, and the explanation of this change perhaps lies in the increased silica-alumina ratio which controls the concentration of active sites in the zeolite.

Now all this is old, really. From catalytic cracking, we have gone to Selectoforming which embodies catalyst shape selectivity. In other words, the zeolite pore mouths admit only certain shapes of molecules and reject others.

The next slide shows such selectivity simplified, from a synthetic charge stock of normal hexane, 2-methylpentane, and benzene; all of the hexane is cracked

<u>Heinemann</u> (Continued)

at the higher temperature. We hardly touch the branched chain paraffin, and we do not convert the aromatic at all. This catalyst is now completely shape selective to normal paraffin. It can make high octane gasoline, from a reformate, by cracking the low octane component of normal paraffins without touching the branched chain paraffin of high octane number or the aromatics of high octane number.

Alternatively, reforming at more severe conditions increases the octane number, but then hydrocracking takes over and cracks out branched chain paraffins as well as normal paraffins. With Selectoforming, you can reduce the severity of reforming operation. In other words, you do not have to go to a high octane number in the reforming step, and that permits an increase in the capacity of the existing reformer; you add on the Selectoformer to crack out the normal paraffins and get the high octane number desired.

Now, let me go to the third objective. How can we provide a high octane number without lead in gasoline. Of course, we all know that emissions from an internal combustion engine decrease if the gasoline contains lower mass hydrocarbons and, perhaps, even hydrogen. We have considered, putting a small catalytic cracking unit in front of the internal combustion engine, in place of the carburetor in which to crack the low octane components of gasoline or naptha, such as normal paraffins, converting them to molecules of low molecular weight which have extremely high octane numbers. Methane and propane have octane numbers of one hundred to one hundred and fifty.

Heinemann (Continued)

But a cracker ahead of an internal combustion engine causes other constraints that do not normally occur. For instance, high space velocities are needed. The normal engine at full throttle consumes up to ten cc's of gasoline per second. At a space velocity of 1 or 2, this requires a ten gallon reactor, which obviously cannot be carried in a car; but if the catalytic activity is increased by a factor of a hundred, the reactor can be of reasonable size. Cracking, normally, creates a lot of coke as a patent to Gray points out, about two percent of coke, so that after operation for six minutes the catalyst has to be regenerated and you can't do that easily in a car. A recent catalyst development permits operation at space velocities of approximately one hundred to one hundred twenty. Using a very shape selective zeolite, one obtains a feed of high octane number, and, at the same time, no coke, so it is possible to run approximately one thousand miles or so before having to regenerate the catalyst.

This slide shows the motor octane number (because it's more closely related to road performance than is the research octane number) versus on-stream time. This non-coking, highly shape selective zeolite performs on a feed of approximately eighty octane number, and gives a motor octane number improvement of about five octane numbers after many hours on stream, whereas the ordinary zeolite cracking catalyst gives very little improvement, because by the time you measure its performance, it's already deactivated and essentially dead, and one observes only thermal conversion.

The same thing is shown in the next slide for a naptha feed to the engine instead of a gasoline, and again, it performs at a relatively stable level.

Heinemann (Continued)

The other commercial cracking catalyst cokes too fast, and doesn't perform much better than a thermal reaction.

So there is the possibility of running an engine on very mildly reformed or cracked naphthas. But much work remains to be done on a catalyst chamber to precede the engine, and the catalyst may have to be regenerated about once every thousand miles.

There are problems, of course, in getting the right temperature and space velocities in the reactor, but the high activity of the catalyst allows use of small volumes of catalysts, and most important of all, as propane, butane, ethane, methane are added to the hydrocarbon feed, the octane number increases and the engine can be run at lean fuel-to-air ratios with a minimum of emissions. Thank you.

Klimisch: Generally, when one gets a hundredfold increase in activity, one has difficulty realizing it because of mass transfer reasons. Have you taken that into account?

Heinemann: The greater problem would be if this were a very endothermic or exothermic reaction with heat transfer problems, which fortunately is not the case. The mass transfer problems can be solved in this case, by using

Heinemann (Continued)

the right catalyst size and the right kind of feed introduction. I recognize the problem. I do not yet have a practical process here, but there is a lot of on-going work, for example in Germany, and there is a group in Massachusetts, -- International Materials, I think, working on this. There is also work by the Propulsion Laboratory of NASA mixing hydrogen with gasoline, and they all face essentially the same problem.

Bett: Can you be more specific at this stage about the properties of the zeolite which enables you to operate without carbon formation in the reactor?

Heinemann: No.

Cohn: You are putting a miniature chemical refinery in each car. You couldn't prepare the fuel in a big refinery and make use of the by-products otherwise? I think it is impractical to put a small refinery in each car, and burn all the by-products in the engine. A central refinery makes the fuel, and uses the by-products otherwise.

Heinemann: I would agree with you, Dr. Cohn. I do not propose that we have a small refinery in every car. I wanted to use this example as one of an evolution of selectivity in catalytic cracking, which changes from catalytic cracking, to a Selectoforming where you crack only certain molecules, to one which essentially eliminates all coke formation.

Boudart: May I see your first slide again, Heinz. It's really quite important, to compare the activity of the material containing silica-alumina, oxygen and hydrogen, to one of the same chemical compositions, but with long range crystaline alumina silicas, and you see a difference of activity like this.

Boudart (Continued)

Now, that's a very difficult thing to explain. Jule Rabo said it was settled. I think it's extremely settled, because I don't understand it. And it has been in the open literature for ten years.

Heinemann: This Table has been in the open literature for about two years and is taken from the paper of the World Petroleum Congress in 1971.

Voice: It's a basic scientific question which to my knowledge has received no satisfactory explanation.

Ogle: I thought I ought to ask a question. I am not sure I am asking it of the speaker or chairman but it has to do with the purpose of the meeting. I ought to add that I know nothing about catalysts, but it seems to me the purpose of this meeting has something to do with the development of the Dept. of Defense use of catalysts. What I'm hearing mostly has to do with gasoline, which is a big national product. With respect to the Department of Defense, some other things ought to be mentioned.

The gasoline the Department of Defense burns is probably the same as anybody else's gasoline, and they also burn a lot of kerosene. But the DOD also has some comparatively unique needs. They propel missiles on liquid fuels and solid fuels. They use high explosives. Now, I guess my question is: Do catalysts fit in those fields at all? Because they may be things which are unique to the Department of Defense where you could really help them. My own feeling is that gasoline is going to get a lot of attention anyway for civilian needs.

Heinemann: Possibly the very next presentation will cover a different area. It so happens that we started out with gasoline.

Hightower: We will have some papers on catalysis in rubber production and in production of other chemicals. The big question that all of us have asked in putting the program together is: What are the needs of the DOD, and I don't know.

Ogle: The reason I brought this up is that the speakers might comment on these other uses in addition to what they are talking about.

Hightower: Excellent point, and I hope that people will speak to that in the next day and a half.

Emmett: Apropos of the remark Dr. Beuther made, a factor of thirty to fifty is about as much increase in activity as we get for a sieve compared to silica alumina. A few years ago, 1967, one of your men from Mobil gave a paper in Florida on Cetane cracking in which he announced an increase of tenfold for the sieve compared to the silica alumina.

I asked him whether this was the same type of catalyst in which a figure of ten thousand was reported for heptane. He said we get a factor of ten which sort of confuses the situation as to whether it varies with the molecular weight of hydrocarbon that much or whether the hexane value that you quoted here might be a first shot on a fresh catalyst but would not obtain after regenerating the catalyst.

Heinemann: We better discuss this privately, because time won't permit it here. It's important to remember that the activity is of major importance only for noncoking catalysts. Because coking catalysts, such as used for normal catalytic cracking are limited by the need for regeneration and by the rate of heat transfer, and only if these factors do not play a role, does activity become important. Selectivity is important throughout, but activity is an illusory term.

Hightower: Is ten thousand a steady state value?

Heinemann: Yes.

Burwell: What is to come of this meeting? We have had some very nice presentations on the role of catalysis in producing gasoline, and I imagine that the Department of Defense burns gasoline. But is the petroleum industry doing all that's necessary here? Are there areas in which there should be Department of Defense funding? What are the recommendations? None of the speakers yet have addressed themselves to this question and it a key question.

Haensel: None of the speakers have addressed themselves, because they don't know what the problems are, and that's exactly what they're saying.

Burwell: There are sure to be special needs in the Department of Defense for some specific products. But with regard to the shortage of petroleum and the restriction of energy supply by the Arabs, should the Department of Defense, which must have gasoline and jet fuel, assume that the present industrial setup will produce it in the best possible way, or should the DOD interest itself in the matter? That is a key question.

Ogle: It occurs to me that the Department of Defense does have an unusual problem. They need gasoline, but I think they need gasoline that won't burn. (Laughter.)

Mills: Recently I attended a meeting organized by Commander Paul Petrich of the Navy in which were outlined the needs of the Department of Defense, particularly the Navy, and these are, of course, aviation gasoline, diesel fuels, and jet fuels.

Those needs varied from civilian needs. For example, the Navy, has a great

Mills: (Continued)

increased need of fuels for gas turbines. They have a greater conviction that hydrogen will be a fuel of the future, and this is noticeably different than in the civilian economy.

Another thing which was news to me is that the Department of Defense uses about four per cent of all petroleum fuels directly plus an additional amount because of manufacture for the DOD.

Furthermore four per cent of all fuels is really a much larger percentage of transportation fuels because transportation fuels are about twenty-five per cent, so, four twenty-fifths is 20% of all transportation fuels, a significant fraction. So, the concern of the DOD was, as presented at that meeting, how to produce vast amounts of conventional fuels and, secondly, how to produce hydrogen and fuels of the future.

Now I am not the Department of Defense's spokesman. I'd be glad to be corrected or changed.

Heinemann: In the period of a fossile fuel shortage, the Department of Defense as well as the civilian economy will be forced to make better use of whatever fuels are available. I don't think they will be able to increase their percentage in a major way at the expense of the civilian economy. Probably everybody will be cutting back equally. So, better utilization of the available fuels in which catalysis can play a major role is a very important item for the Department of Defense.

Quillian: I worked for the Department of Defense, specifically the Army, for a number of years, although I'm a contractor. And I propose that you go ahead with your agenda, Joe, as it is, because it seems to me the Department

Quillian (Continued)

of Defense has adequate interest in this kind of agenda. It seems to me that the DOD has three areas of interest relative to energy. One of these is interest in the national effort to become self-sufficient in energy again, because a healthy economic security in this country is essential and prerequisite to a healthy defense security.

The second area of interest that DOD appears to have is conservation as a contribution to the national effort, and this conservation area would involve their own bases and vehicles with which they're obliged to operate as economically as possible.

The third area of interest, which Dr. Ogle mentioned, is their prime responsibility, to assure the availability of combat fuels under war time conditions.

We're talking about all three of these areas. They're all important, and your agenda is very good.

Hightower: Thank you. There are two philosophies that we have adopted. One is to have the DOD tell us what they need. The other approach is to say here is what we can do and what we're doing. How can you use us. That is the approach we have adopted at this meeting.

Ogle: While I agree with what you said, I'm still left slightly confused, because I thought the question was not the proper use of energy by the Department of Defense, but how could they benefit by the technology of catalysts.

Quillian: Yes, I will mention this tomorrow.

APPROXIMATE TEMPERATURE FOR OBTAINING APPRECIABLE (~5% TO 20%) *n*-HEXANE CONVERSION

Catalyst material		*Major cations in exchange solution*	*Analysis of product (wt %)*					*Temperature (°C)*	*Alpha*
Sample	*Crystal structure*		SiO_2	Al_2O_3	*Na*	*Ca*	*RE*		
1	Amorphous $SiO_2{\cdot}Al_2O$	(Standard catalyst)						540	1·0
2	Faujasite	Ca	47·8	31·5	7·7	12·3	—	530	1·1
3	Faujasite	NH_4	75·7	23·1	0·4	—	—	350	6400
4	Faujasite	La	—	—	0·4	—	29·0	270	7000
5	Faujasite	RE	—	—	0·39	—	28·8	<70	>10000
6	Faujasite	RE, NH_4	40·0	33·0	0·22	—	26·5	<270	>10000
7	Faujasite	RE, NH_4	—	—	—	—	—	420	26
8	Zeolite A	Ca	42·5	37·4	7·85	13·0	—	560	0·6
9	Zeolite ZK5	—	—	—	—	—	—	400	38
10	Zeolite ZK5	H	76·8	23·1	0·47	—	—	340	450
11	Mordenite	Ca	(~ 77)	—	1·01	—	—	520	1·8
12	Mordenite	Ca, H	82·0	14·0	0·4	—	—	360 to 400	40–200
13	Mordenite	NH_4	—	—	—	—	—	<270	>10000
14	Mordenite	H	80·1	13·4	0·3	1·54	—	300	2500
15	Mordenite	NH_4	—	—	0·1	—	—	<270	>10000
16	Gmelinite	NH_4	—	—	—	—	—	<270(~200)	>10000
17	Chabazite	NH_4	—	—	—	—	—	<270	>10000
18	Stilbite	NH_4		—	—	—	—	370	120
19	Offretite	NH_4		—	—	—	—	<270	>10000

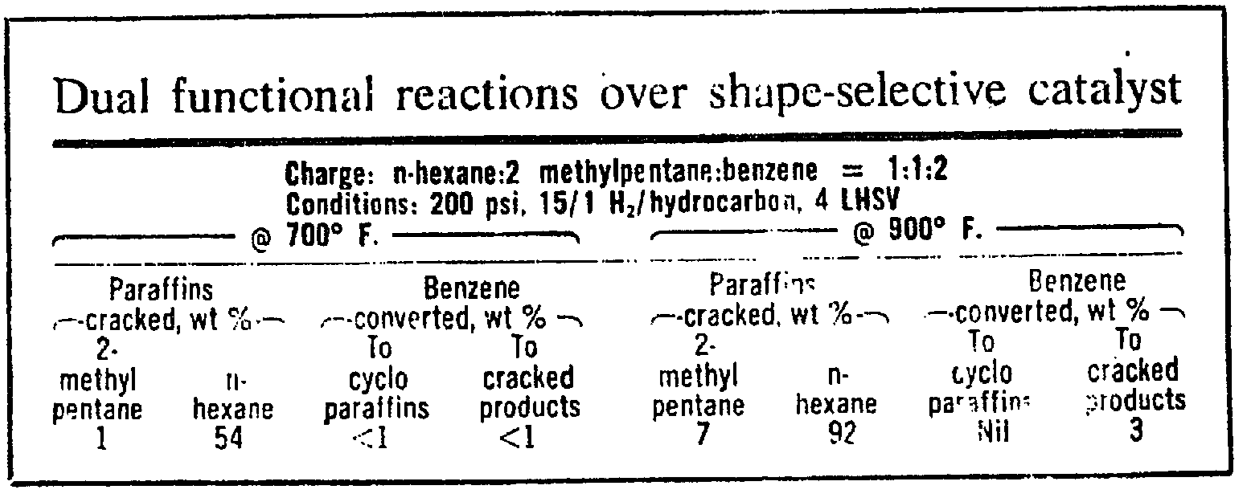
COMPARISON OF GASOLINE COMPOSITIONS FROM SIEVE VS. CONVENTIONAL CRACKING CATALYSTS

Feed:	*Calif. virgin gas-oil*		*Calif. coker gas-oil*		*Gachsaran gas-oil*	
Catalyst, Durabead Gasoline	5	1	5	1	5	1
%Paraffins	21·0	8·7	21·8	12·0	31·9	21·2
%Cycloparaffins	19·3	10·4	13·4	9·5	14·3	15·7
%Olefins	14·6	43·7	19·0	42·8	16·3	30·2
%Aromatics	45·0	37·3	45·9	35·8	37·4	33·1

Durabead 1 = silica-alumina
Durabead 5 = zeolite

NOT REPRODUCIBLE

$$\begin{tikzcd}
\text{oil} \arrow[r, "k_a"] & \text{gasoline, incl. olefins} \arrow[r, "k_c"] \arrow[d, "k_h"] & \text{gas} \\
& \text{stabilized gasoline.} &
\end{tikzcd}$$ 3



4

Dual functional reactions over shape-selective catalyst

Charge: n-hexane:2 methylpentane:benzene = 1:1:2
Conditions: 200 psi, 15/1 H_2/hydrocarbon, 4 LHSV

@ 700° F.				@ 900° F.			
Paraffins cracked, wt %		Benzene converted, wt %		Paraffins cracked, wt %		Benzene converted, wt %	
2-methyl pentane	n-hexane	To cyclo paraffins	To cracked products	2-methyl pentane	n-hexane	To cyclo paraffins	To cracked products
1	54	<1	<1	7	92	Nil	3

Selective cracking for propane and Selectoformate

Case Yields, wt %	1 Charge	 Products	2 Charge	 Products
C_1, C_2, H_2	7.0	8.7	13.6	16.6
C_3	5.3	15.3	10.8	15.5
C_4	5.9	6.3	10.8	8.9
i-C_5	6.4	7.6	8.7	8.0
n-C_5	6.1	1.6	7.0	3.9
C_6 + n-paraffins	8.9	1.8	2.6	1.3
C_6+iso's+aromatics	60.4	58.7	46.5	45.8
Octane Numbers	**Reformate**	**Selectoformate**	**Reformate**	**Selectoformate**
C_5+, RON + 0	86.1	93.3	96.5	99.5
C_5+, RON + 3	96.3	100.8	102.5	104.7
C_5+, DON + 3*	93.0	98.5	100.2	103.9
C_6+, RON + 0	87.3	94.3	102.9	104.7
C_6+, RON + 3	97.1	101.3	106.3	107.6

*Distribution Octane Number; a measure of front-end octane quality

5

NOT REPRODUCIBLE

YIELDS OF PRODUCTS FROM CYCLE STOCKS [illegible]ACKED OVER DURABEAD 5 AND DURABEAD 7 COMPARED WITH Si/Al

	Si/Al *Yields*	*Durabead 5*[1] *Yields*	 *Delta Si/Al*	*Durabead 7*[2] *Yields*	 *Delta Si/Al*
			Augusta catalytic light fuel oil[3]		
Conversion, Vol %	35·6	35·6	—	35·6	—
C_5 + Gasoline, Vol %	22·1	25·9	+3·8	29·2	+7·1
Total C_4's, Vol %	8·7	7·9	−0·8	6·2	−2·5
Dry Gas, Wt %	5·2	4·1	−1·1	3·5	−1·8
Coke, Wt %	4·3	2·2	−2·1	1·4	−2·9
			Beaumont heavy catalytic fuel oil[4]		
Conversion, Vol %	42·5	42·5	—	42·5	—
C_5 + Gasoline, Vol %	24·5	26·3	+1·8	30·6	+6·1
Total C_4's, Vol %	9·4	9·4	0	8·2	−1·2
Dry Gas, Wt %	6·5	5·2	−1·0	4·7	−1·5
Coke, Wt %	8·7	7·8	−0·9	4·9	−3·8

6

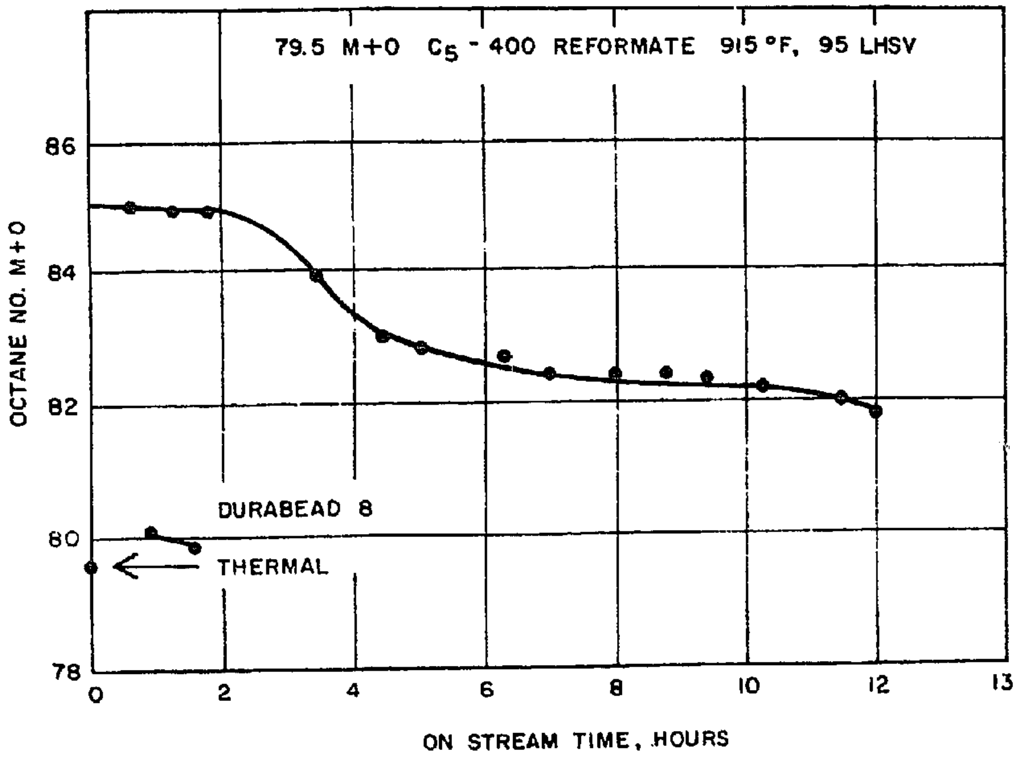
[1] Contains REHX in silica-alumina.

[2] Contains REHY in silica-alumina.

[3] Properties—27·3°API, Aniline No. = 139·5°F, ASTM boiling range = 516°–666°F.

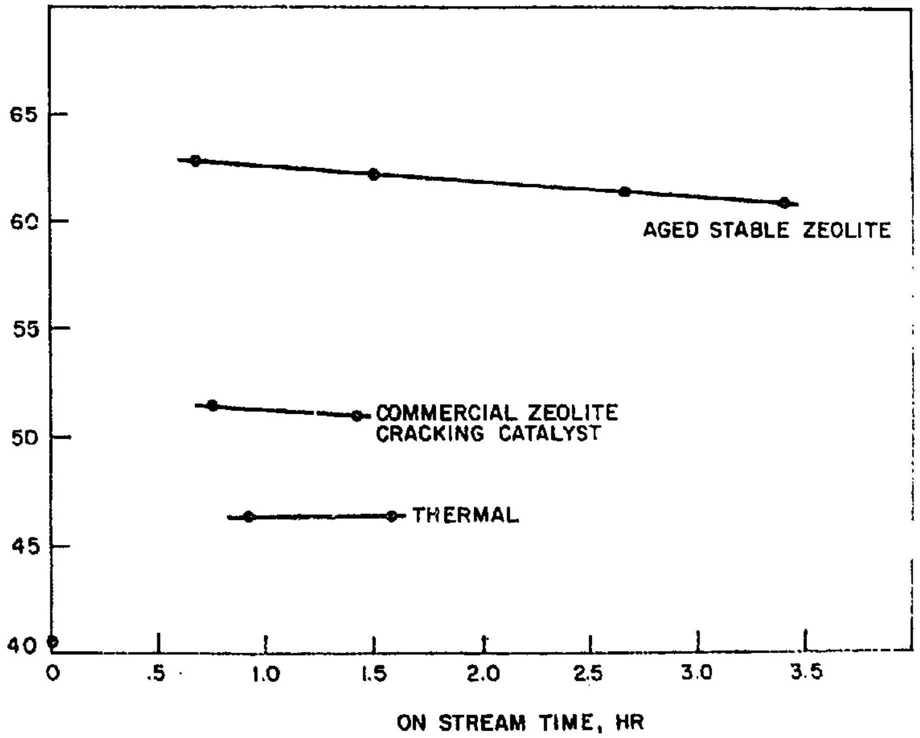
[4] Properties—19·5°API, Aniline No. = 157·5°F, ASTM boiling range = 410°–760°F.

EFFECT OF ON STREAM TIME
ON OCTANE RATING — KNOCK TEST ENGINE



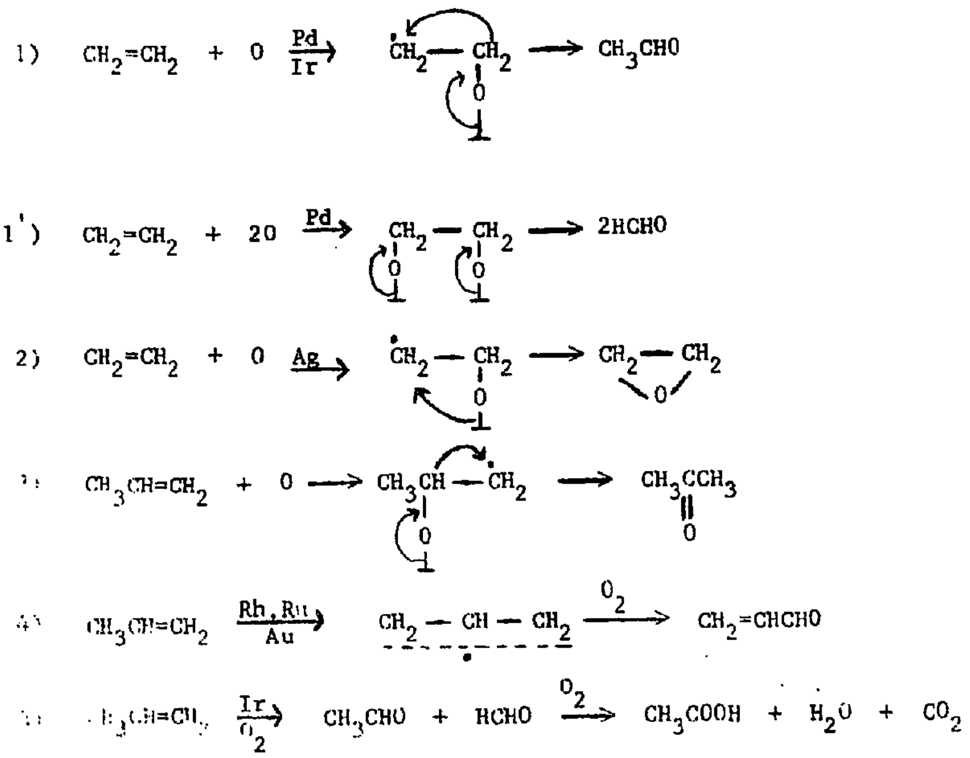
7

EFFECT OF ON STREAM TIME ON OCTANE RATING
405 M+O KUWAIT NAPHTHA
915°F 95 LHSV

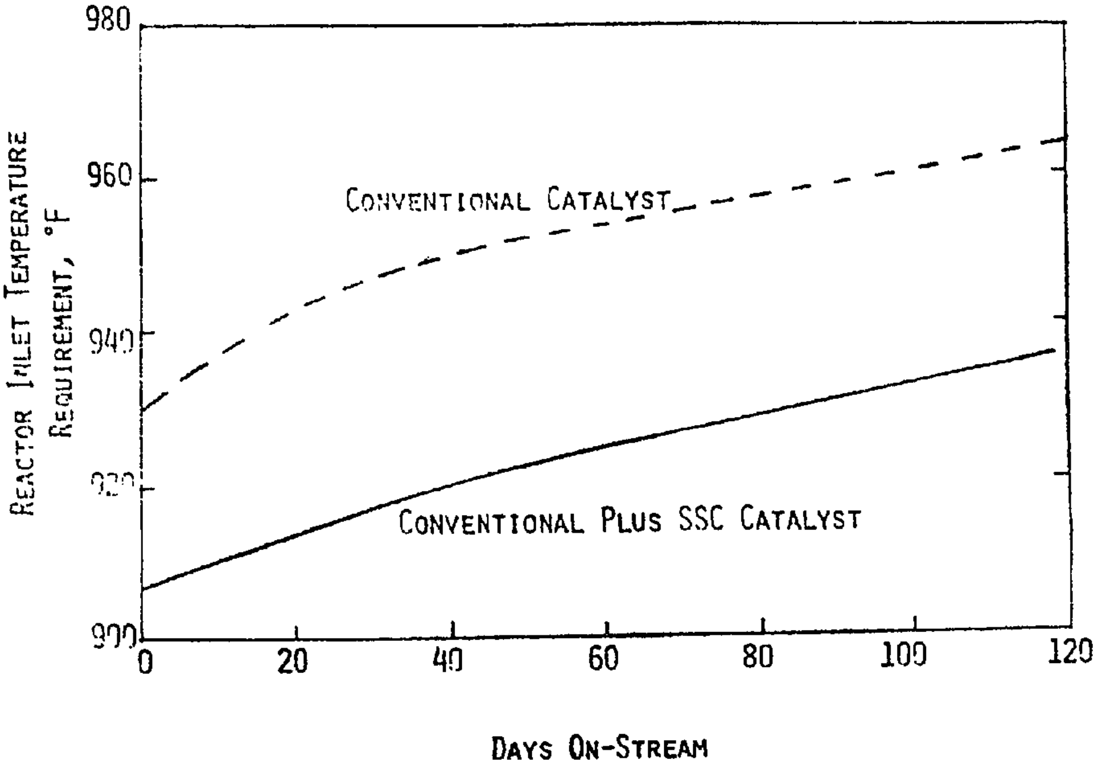


8

Partial Oxidation Chemistry Characterized by Tracers



PILOT PLANT TEMPERATURE AGING RESULTS



1

REMOVAL OF SULFUR FROM PETROLEUM FEEDSTOCKS

by

Harold Beuther

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For the past 20 years the removal of sulfur from distillate petroleum stocks has been carried out effectively throughout the world. Technology has been developed to the point where any degree of sulfur removal can be obtained and distillate fuel oils of very low sulfur content are produced at a reasonable cost. The removal of sulfur from residual oils, however, has been much more difficult. It has only been in the past 5 to 6 years that the desulfurization of residual oils has been carried out commercially. These operations, mostly in the Far East, have been imminently successful; yet they are more expensive than we would like, they have not demonstrated conversions to very low sulfur contents (0.1% S and less) and they have avoided residual feedstocks of high metal contents.

The above-mentioned deficiencies in the desulfurization of residual oils can be overcome by the development of more active, more selective and in general better catalysts. The factors which limit the desulfurization of residual oils and increase its cost are (1) steric hindrance (the difficulty of sulfur atoms in large molecules to contact the catalyst surface), (2) the large size of residual oil molecules (making transport to the center of the catalyst pellet more difficult), and (3) excessive deposits of coke and nickel plus vanadium on catalysts (deposits which cover active catalyst surfaces). Before discussing these areas where catalysts can improve desulfurization to make residual fuel oils, a brief discussion of the mechanism of desulfurization will be given. A simplified and schematic approach to this mechanism is shown in Figure 1. This figure gives diagrammatically the steps in catalytic desulfurization. On the top of the figure is a schematic sketch of a molybdenum-sulfur catalyst surface. On this surface hydrogen is absorbed and dissociates. A sulfur-containing molecule also adsorbs, is activated and gives its sulfur atom to the surface vacancy. The sulfur-free molecule is hydrogenated and desorbs. Finally, the surface again reaches equilibrium by losing the sulfur atom it gained from the sulfur-containing hydrocarbon as H_2S.

All sulfur-containing molecules, however, do not behave in such an ideal manner. In Figure 2, the nonhindered molecule at the top has been shown to react one hundred times faster than the molecule with an additional carbon atom on each aromatic ring. For simulated residual oil molecules shown on the bottom of the figure, the structure on the left should be easy to desulfurize while the one on the right would be quite difficult. This latter molecule would probably require cracking into smaller molecules to make the sulfur atom available to the catalyst surface.

A second deficiency in residual oil desulfurization is the formation of coke deposits that fill catalyst pores and make the catalyst surface less available for desulfurization. Coke deposits are high because of the aromatic nature and size of the residual oil molecules and the type of catalyst surface normally used. In a sense, desulfurization catalysts are dual-functional catalysts in that they must effect desulfurization as well as hydrogenation in hydrocracking. Figure 3 is a diagrammatical simplification of the behavior of a dual-functional catalyst. This figure shows a decalin molecule that is first dehydrogenated to an olefin; the olefin is then adsorbed and activated. In this activated state it readily isomerizes and hydrocracks. The fragments from hydrocracking which are too far from the hydrogenation component have a lesser tendency to react with hydrogen atoms and soon combine with other reactive fragments to form larger adsorbed molecules which eventually convert to coke. Thus, in the desulfurization of residual oils, an important function of the metal catalyst is to keep the catalyst surface clean and free from coke.

The sequence of events that result in coke formation when desulfurizing residual oils is simplified and shown on Figure 4. Initially, a mono-layer of adsorbed molecules covers the surface. Some molecules are retained too long and lose hydrogen. They then become reactive and more aromatic-like and as such are more strongly adsorbed because of greater flatness of the aromatic structure. These then serve as building blocks for aromatic groups which in time stack upon the layer of aromatics existing on the surface. Bonding of these stacks occurs and the resultant "coke" becomes irreversibly bound to the surface. Coke produced by this principal is the main problem in the deactivation of catalysts for residual oil desulfurization. High hydrogen pressures are used to minimize this deactivating influence.

In the catalytic processing of residual oils, organometallics contained in the oil also deposit on the catalyst and reduce catalyst activity. Oils from Venezuela are particularly high in metals. These metal compounds are reduced at high hydrogen partial pressures and in the presence of a catalyst. In a poorly designed catalyst, the metal portion of the molecule will deposit preferentially on the periphery of the catalyst pellet causing clogging of the pores at the surface. Figure 5 shows the distribution of vanadium in a normal catalyst pellet and how improved designs can allow these deposits to be more evenly distributed throughout the catalyst pellet. The bottom lefthand figure depicts profiles of a good, a poor and an average catalyst pellet.

Vanadium deposits are maldistributed because of the general structure and large size of the vanadium-containing molecules. Since vanadium must be bound coordinately to nitrogen, a large molecule with a minimum size of 14 Å results (Figure 6). Realistically, most molecules found in crude oil are much larger because other molecular groups are generally attached to this basic molecule. Such a large molecule travels more slowly through the catalyst pores and is probably more strongly adsorbed because of its structure. Thus, it is more apt to react, decompose and deposit the vanadium near the pellet edge. The presence of vanadium not only clogs the catalyst pores but also makes regeneration (oxidation of coke) difficult. During regeneration SO_2 is produced from oxidation of the sulfided catalyst metal. The SO_2 is then catalytically converted to SO_3 by vanadium deposits. SO_3 reacts with the alumina catalyst support and causes a breakdown of the catalyst structure. Figure 7 shows relative effects of vanadium and coke in the plugging of pores of a typical catalyst pellet. The plot shows a pellet at "end of run" conditions with the percentage of pores filled with deposits versus distance of the deposit from the center of the catalyst pellet. For this pellet the pores at the surface were 90% filled, while the pores in the center contained relatively few deposits. An ideal catalyst would have a constant distribution of coke and vanadium from edge to center and could be used for a much longer time.

The fact that these deficiencies exist in residual oil desulfurization suggests that much still remains to be done in the development of catalysts to produce residual fuel oils of low sulfur contents and at reduced costs. Such catalyst developments must be pursued if we are to utilize the large volumes of high sulfur Middle East crudes and moderate sulfur, high vanadium Venezuela crudes to satisfy our energy demands and maintain or improve the quality of our environment.

Figure 1

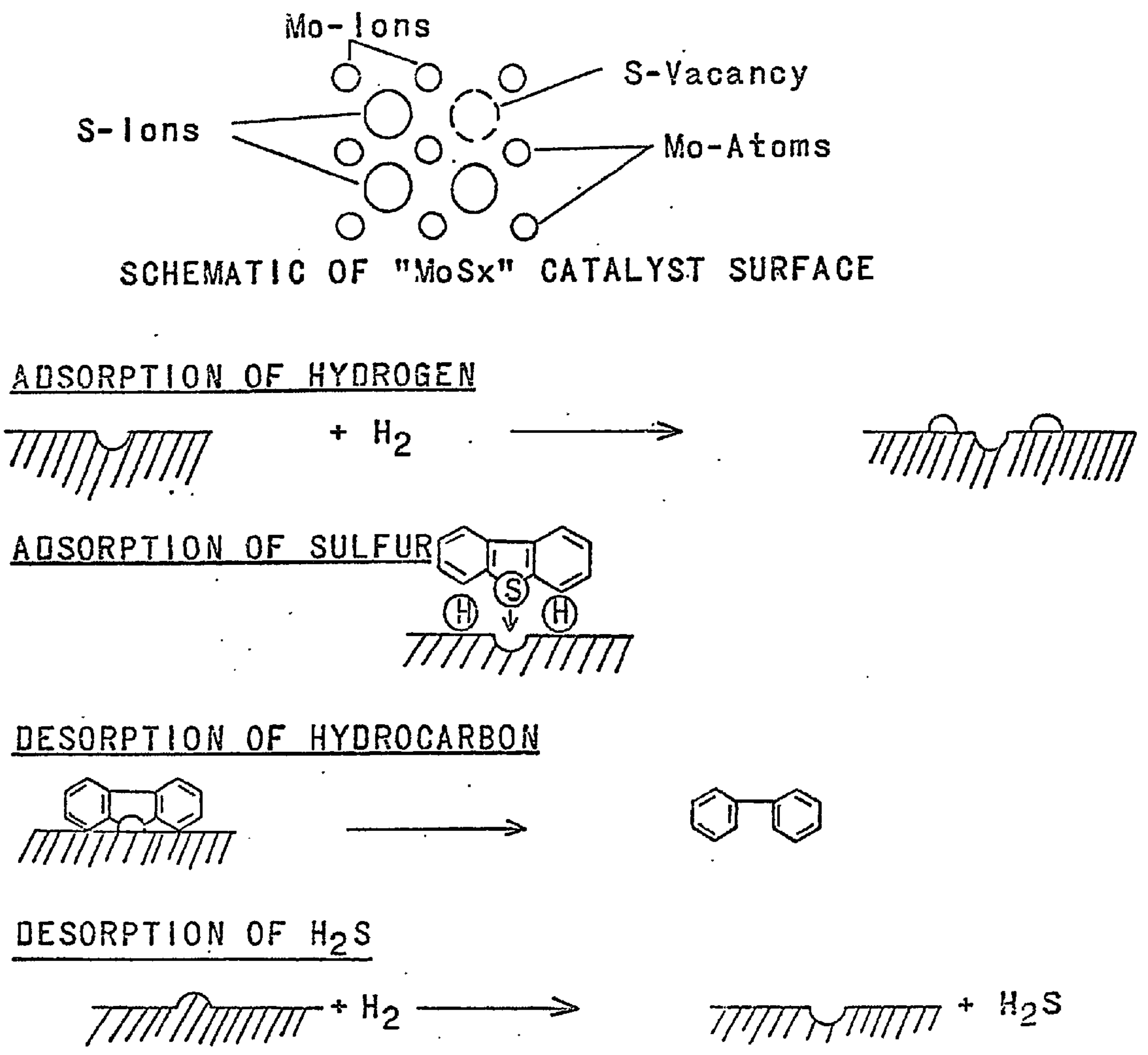

Mo-Ions
S-Vacancy
S-Ions
Mo-Atoms
SCHEMATIC OF "MoSx" CATALYST SURFACE
1. ADSORPTION OF HYDROGEN
+ H_2
2. ADSORPTION OF SULFUR
S
H
H
3. DESORPTION OF HYDROCARBON
4. DESORPTION OF H_2S
+ H_2
+ H_2S

Figure 2

DESULFURIZATION OF TYPICAL SULFUR COMPOUNDS

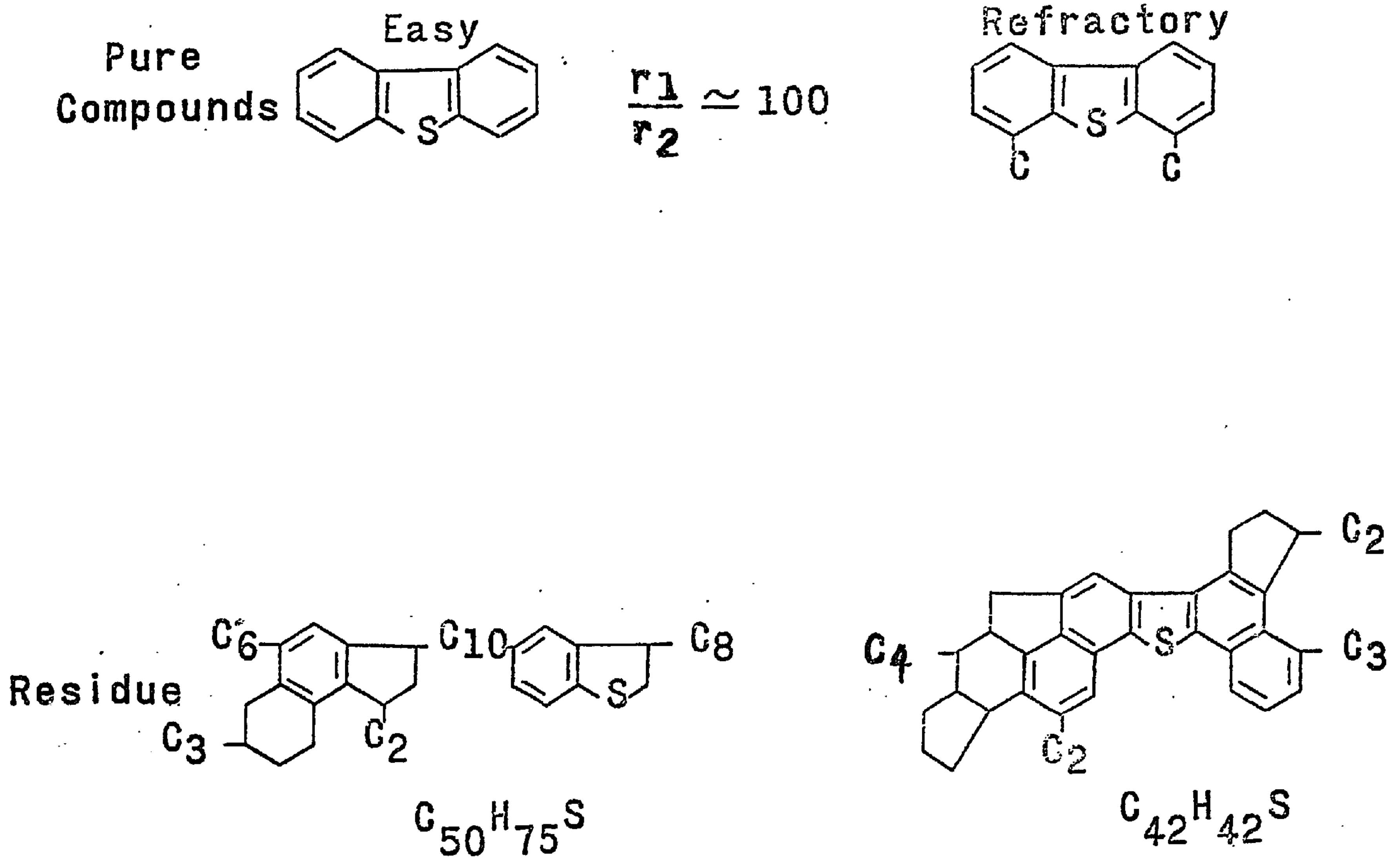


Figure 3

SCHEMATIC VIEW OF DUAL FUNCTION CATALYST
DECALIN HYDROCRACKING

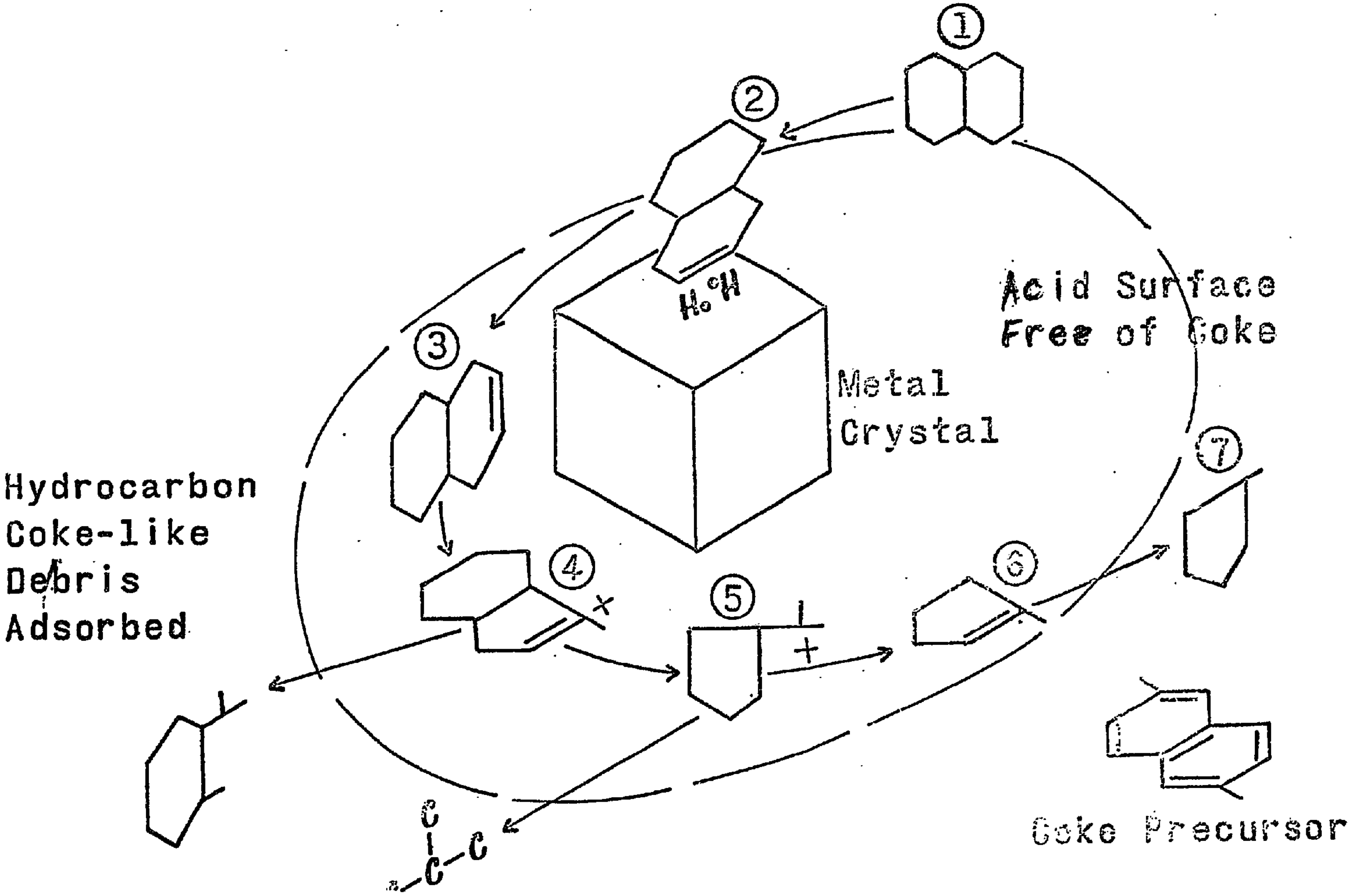


Figure 4

Models of Coke Accumulation

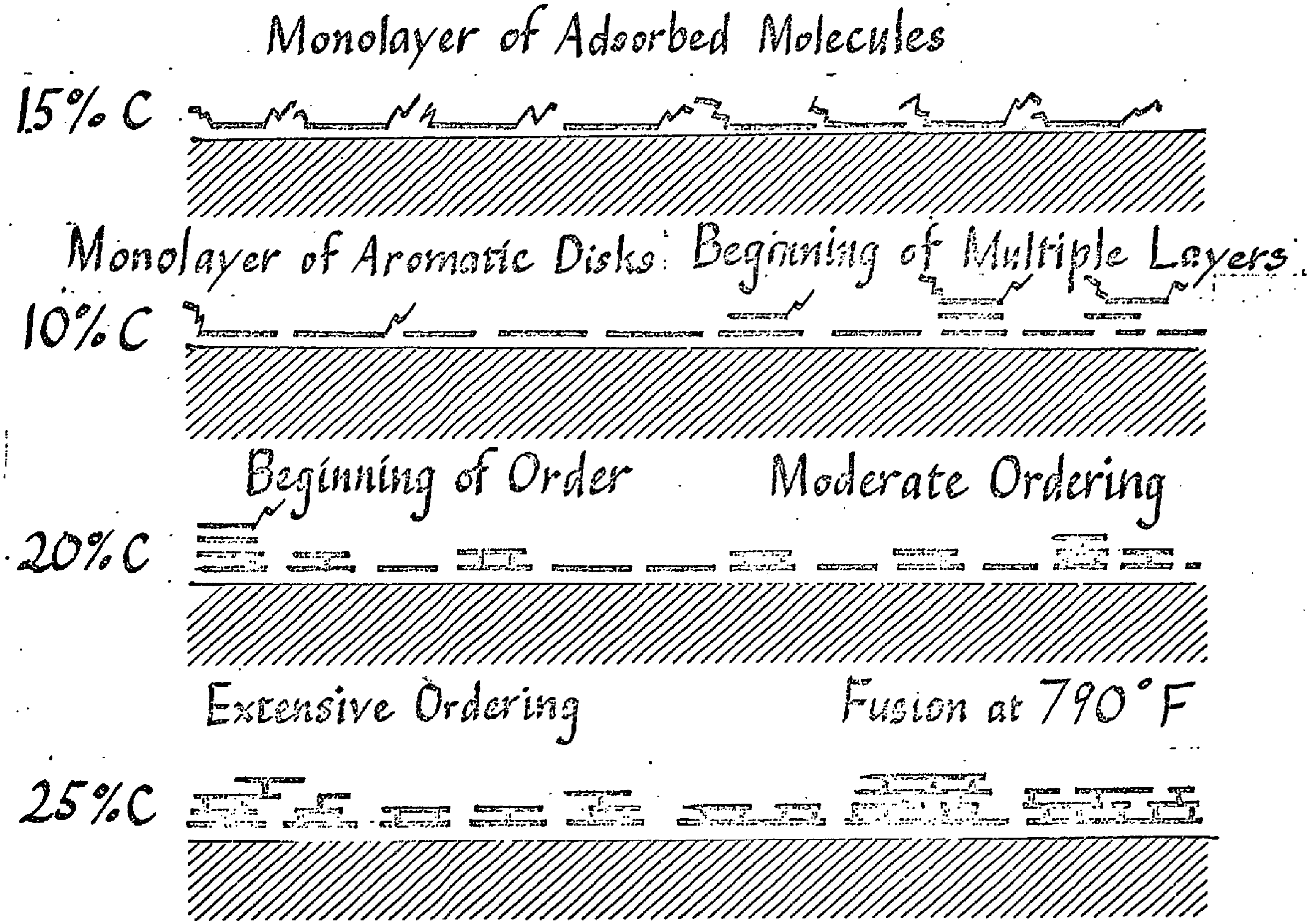


Figure 5

VANADIUM ON DESULFURIZATION CATALYSTS

Distribution of Vanadium

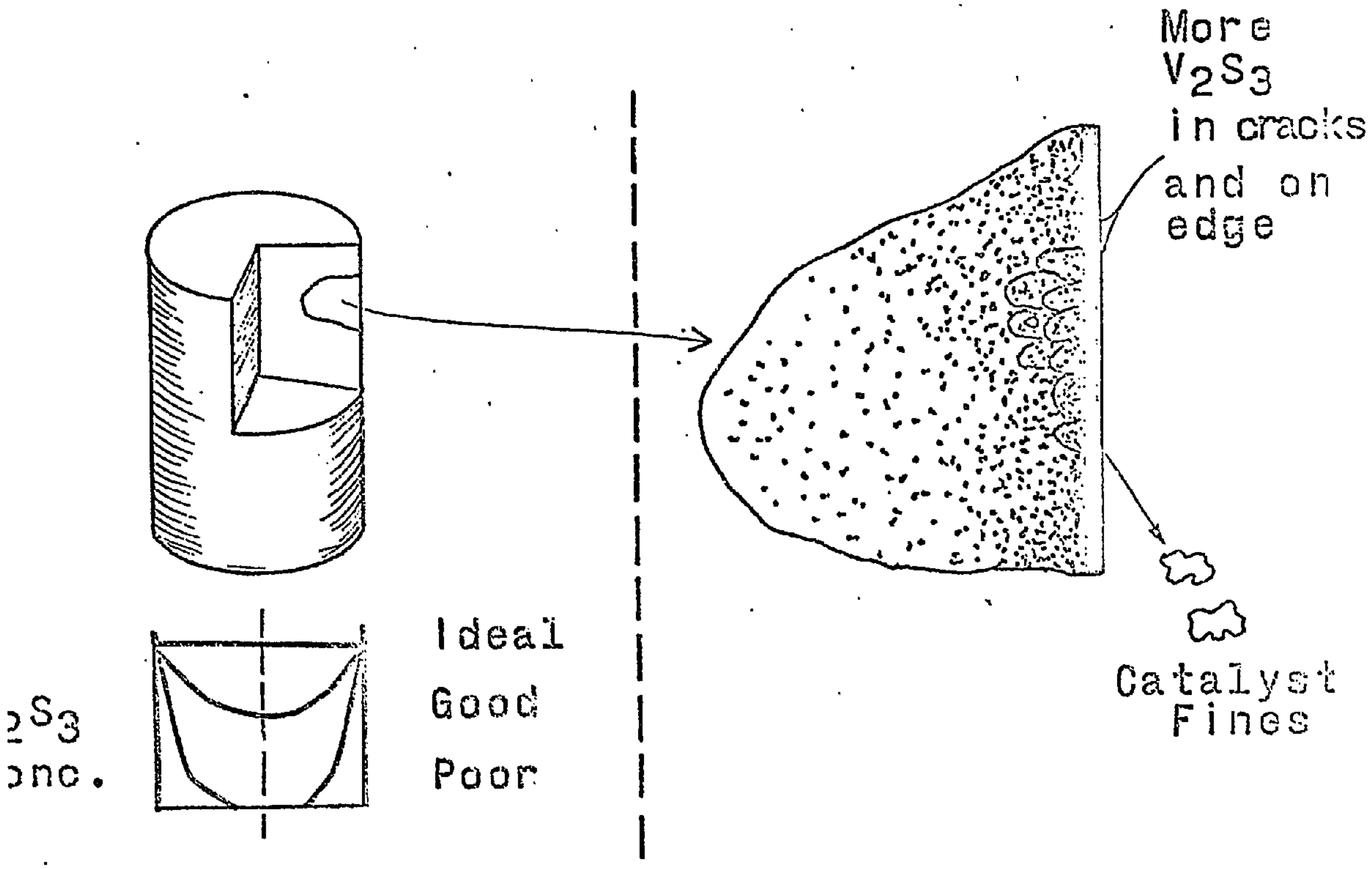
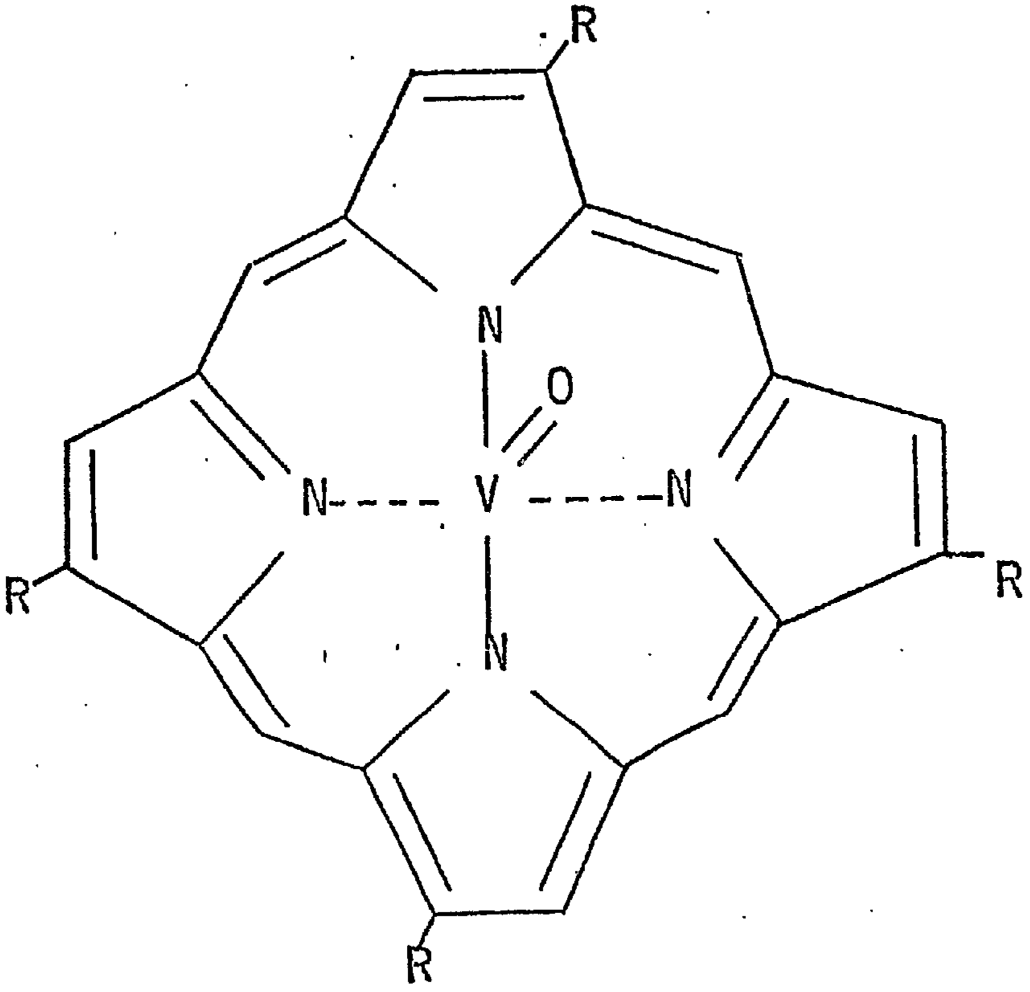
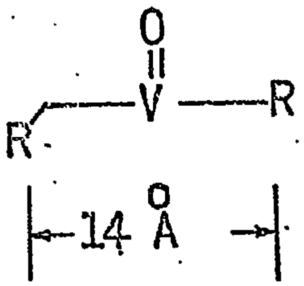


Figure 6

SIMPLEST PORPHYRINS IN HEAVY GAS OIL





BEUTHER DISCUSSIONS

L. Libby: Do you recommend desulfurization of crudes as a research for DOD support?

Beuther: Yes, I do.

Heinemann: A number of people in our laboratory, particularly Sylvester and Shane, have developed a new catalytic technique of removing heavy metals such as vanadium from petroleum prior to hydro-desulfurization. Poisoning of desulfurization catalysts with metals is bad not only because of the decreased activity but also because it's irreversible; you cannot burn the metals off like you can burn coke off in regeneration. We have found that a cheap catalyst, namely, manganese nodules, recovered from the ocean floor, is an excellent absorbent for heavy metals. We put a guard case of this material ahead of the hydro-desulfurizer, essentially under the same conditions, same pressure of hydrogen, et cetera, and we demetalize without getting appreciable desulfurization. When the catalyst is saturated and it has a long life, we throw it away, for a penny or two per pound of catalyst.

Rabo: Does that system remove the metal as a metal atom or as a molecule containing metal?

Heinemann: It removes the metal as atoms. There is no loss of hydrocarbons. There is hydrogen consumption only to the extent that the metal-containing porphyrins take up some hydrogen, but less than about one hundred cubic feet per barrel of crude.

Aside from that, the phenomena of coking problems in H.D.S. systems bears a relationship to the coking problems on boiler tubes and in turbine systems. This problem has not been satisfactorily solved. It's not on the agenda, but all Navy boilers and any other boilers using heavy fuels have a coking problem with as yet no cures. Barium and lead seem to be the elements that help most as heavy oil additives; but if the Navy is not going to go completely nuclear, it needs better solutions to the boiler and turbine problems.

Voice: Coking and sulfur poisoning need future research, not only for extension of present catalysts to the fuels we presently handle, but also for increasing the efficiency of presently used catalyst system. Not only sulfur poisoning but coke formation and sintering are phenomena that need research. Are your cokes amorphous or the dendritic-filamentary coke that is associated with metal?

Beuther: These are all amorphous cokes, and coke is just a general term applied to them. They are heavy hydrocarbons. The hydrogen content varies with the temperature of the operation and the time that they have been deposited. Coke that has been on a catalyst longer has a lower hydrogen content.

Voice: There seems to be a severe coking problem associated with formation of dendrites on the metal surfaces different than that associated with the support.

Beuther: That is a separate problem. I was talking about the coke deposited on the catalyst support. Research is needed on the relation of catalysis to acidity and what one can do to control it and understand it.

Boudart: Dr. Beuther, you stated earlier, as applied to Dr. Libby's question, that you thought that sulfur removal was an area where DOD should help. It would be very good to know why DOD should support this kind of work.

Beuther: Our petroleum supplies of the future will be, assuming we get any, the petroleum supplies of the Middle East, all of which are high in sulfur, much higher than those that we deal with now. If the Department of Defense and we in this country are to maintain clean air standards, desulfurization is needed. It has been carried out successfully in Japan and the Far East but it's still expensive. Can it be done at a lower cost?

Johnson: The Navy is turning away from use of residual oil for two reasons: one is that it can't buy residuals that are any good to burn, and secondly, it has not solved the problem of deposits from burning residuals. So even for boilers, the Navy is going to use distillate fuel.

Beuther: Highly desulfurized residual oil has very good burning qualities. In fact good enough that people have proposed catalytic cracking of these materials. When one effects desulfurization, he adds hydrogen where the sulfur was removed, and one ring of these condensed aromatic rings systems may be hydrogenated, also producing a fuel that burns well.

Johnson: It's possible that the Navy should reconsider returning to use of resids, but there are various other aspects, such as logistics, namely the fact that distillate fuel can be used both in the boilers and also in other types of prime movers and engines as well. But if what you say is true, and if it had come ten years earlier, probably it would have changed the course of history as far as Navy boilers are concerned. It will be a very interesting question for me to take back to our people in the Naval Ships Systems Command.

Wise: In what direction do you feel research should go? Dr. Boudart suggested to take the vanadium out of the crude in the interests of refining. Do you feel that is the way to do, or are there other avenues available to us, e.g., to tackle the vanadium poisoning of the hydrodesulfurization catalyst itself.

Beuther: We are working actively on the problem, and I am sure other petroleum companies are as well. The three problems I mentioned were transport property of the catalyst, namely making the catalyst so that large molecules can move in and out, improving the catalyst surface so that its tendency to make coke is far reduced and handling organometalics so that they are deposited to a minimum extent on the catalyst surface.

Cohn: Is vanadium a catalyst?

Beuther: Vanadium is a catalyst for hydro-desulfurization, but not a good one.

Beuther: I think that's an interesting development. Techniques developed previously have been very costly. A lot of work also has been aimed at establishing the kinetics of demetalization versus desulfurization, but this is not the same.

Hura: One possible use of catalysts is in combustion processes employing residual fuels. Catalysts could be employed to minimize vanadium deposits in Naval boilers. The Apollo Chemical Corporation had a note in the Environmental Science and Technology Magazine concerning the use of manganese and magnesium catalysts which prevent the deposition of vanadium oxides on boiler tubes at high temperature. Are there any research efforts being directed towards the development of catalysts that minimize the problems associated with combustion of residual fuels?

Beuther: Yes, there is work on catalysis in combustion processes, primarily catalysis in distillate fuels where one might oxidize a distillate fuel without pre-flame reaction in order to minimize NO_X formation. Any time one carries out a catalytic reaction where there is a component such as vanadium present that can deposit on the catalyst, he finds that the catalyst is short lived and replacement is necessary, so that some sort of pre-treatment of the feed stock is required to remove heavy metals. But as far as direct combustion of residual oils, I don't think that it is reasonable to use catalysts in combustion considering both the vanadium and the coke formation problems.

McCormack: In regard to the manganese nodules, it would appear they are an ideal feed stock for making steels where both these elements are needed.

Heinemann: A research of equal importance to desulfurization is understanding the mechanism of hydro-desulfurization. I have some information I cannot discuss which makes me believe that Dr. Beuther's mechanism is not the entire mechanism and that there are many things we don't understand. There are indications, for instance, that not only the metal or metal oxide or metal sulfide is important as a catalyst, but that the crystal planes of these materials play a major role in the catalysis of desulfurization. If we understood the mechanisms we could find better catalysts and better ways of desulfurization. Here is an area for academic work that is well worth the support of DOD.

Beuther: I couldn't agree with you more. Even the state of the vanadium is a factor we often overlook. There are many things that could be done on an academic scale.

McCormack: None of us do all that needs to be done in order to understand mechanisms. We focus on immediate commercial objectives: are we short of money for research; are we short on ideas? I have strong convictions that we have many more ideas than commercial funding. More complete answers would help solve the problems in a shorter period of time. In this regard, the needs of the Department of Defense match those of the national economy, and we all would benefit from more funding to implement ideas that are not being presently worked on.

Beuther: We have shown a consensus to recommend research on desulfurization. But I would like to issue a word of caution: problems of deposition of metals and formation of carbon can only be resolved by long-term, high pressure, aging work. This is costly and difficult. It's even difficult to write a detailed, operational plan on how to do it.

CATALYTIC PROBLEMS IN FUEL PRODUCTION FROM SHALE

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I'm going to talk today about some of the catalytic problems in making oil from rocks. And I'm going to give you a little review of oil shale and retorting and so on. Catalytic problems are not too severe in this area.

Back 36 to 50 million years ago, in Eocene times, sediments were laid down in these areas, Wyoming, Utah, and Colorado, sediments which were rich in organic material. The richest ones are located in Colorado.

This slide is an aerial shot showing some of the deposits along in these cliffs, layer after layer of oil shale varying in richness. Its richness is measured by a test called the Fisher assay. This involves heating the rock over a temperature range up to about 900 degrees F, and measuring the amount of oil -like material that is produced. The organic material in the oil shale breaks down to give an oil-like material.

This slide is another view of the shale cliffs, near Rifle, Colorado. Very beautiful up there. Some of this work was done in the late '50s by Union Oil Company.

This slide shows a piece of Colorado oil shale. I have some here with some of the oil produced from the shale. You are welcome to take a piece of oil shale if you want because we have gobs of it, so I'll just pass it around. I don't think you'll want any of the shale oil itself, it's pretty smelly stuff, very rich in nitrogen compounds. This shale yields about 30 gallons of oil per ton of rock. In this whole area that I showed you on the map, the shale that will yield at least 10 gallons per ton would provide at least two trillion barrels of oil. All the oil shale which will yield at least 24 gallons of oil per ton of rock contains something like 600 billion barrels of reserve.

Back in the late 50's we did conduct a mining and retorting operation in Colorado at the site that this slide shows, a rather scenic sight. This is the mine opening. Mining was done by blasting just like you would mine rock of almost any kind. The mining is a substantial part of the cost and this is being worked on now to make it more economical. This slide shows some of the oil shale from the mine being dumped into a gyratory crusher.

This slide shows the crusher jammed with some large boulders of oil shale. The men are trying to decide how to free the crusher so they can continue. Some of these large boulders get stuck in this thing and are almost like rubber; they yield without fracturing.

We had a system for conveying the shale after the crushing, sorting it out, and conveying it up to our retort. You can see it on this slide.

This slide shows the retort that we built and operated in Colorado. It was supposed to process about 700 or 800 tons a day and it got up to about 1200 tons a day. At 3/4 of a barrel of oil for every ton of rock processed, yields of about 850 or 900 barrels of oil per day were secured in this operation. The retort is a device which pumped rock upwards and the fire went downwards; the shale ash came out with no carbon on it at all. The carbon was used to provide the heat of retorting. The oil came out the bottom.

Raw shale oil of similar density to that of crude oil is a solid at room temperature. It has a pour point of about 75 to 90 degrees F , depending upon the retorting method. You can see that it's a black gunk and if you open up the bottle you can smell the odor.

Next we have a slide on shale oil from various retorts: we aren't the only people who have looked at various retorts for getting oil from shale, and we have two different varieties we are working on. We are working on a third variety right now. The sulfur content ranges from about 0.7% up to 1.0 weight %. The real tough actor is nitrogen, ranging from about 1.7 up to 2.0 weight percent. Possibly as much as 40 to 50 volume percent of the oil is non-hydrocarbon in nature; this non-hydrocarbon portion is composed of sulfur compounds, nitrogen compounds, and oxygen compounds. The nitrogen is the difficult thing to get rid of. The crude shale oil is usually contaminated with shale ash which must be gotten rid of. You can filter out some of it. A simple way of doing it is to take the crude shale oil and distill overhead as much possible using vacuum distillation. This will leave 10 to 15% of bottoms which then can be coked to give a distillate, a volatile oil which doesn't have any ash and a coke which can then be used for fuel or to generate hydrogen.

This slide shows a typical shale oil refinery, showing various steps of the process; we retort and distill to get naphtha, middle oil, heavy oil; bottoms from the heavy oil distillation gives charge stock for the delayed cokes. The heavy oil is treated in a desulfurizer similar to what Dr. Beuther described; our names for sulfur and nitrogen removal processes are hydrotreating or hydro-desulfurization or hydro-denitrogenation or Unionfining. The naphtha would be Unionfined. We make hydrogen in order to take out the sulfur as hydrogen sulfide, the nitrogen as ammonia and the oxygen as water. We also saturate the olefins contained in the crude shale oil and end up with a synthetic crude.

This slide shows a simplified way of looking at the production of commercial shale oil. Start with the oil shale, retort it, get shale oil; then coke that or a portion there of. We get a distillate which is then Unionfined or hydro-fined to remove the sulfur, nitrogen, and oxygen, and saturate the olefins. We end up with a commercial shale oil which is essentially indistinguishable from petroleum derived crude; it's quite paraffinic, more like some of the paraffinic type crudes.

This slide is a simplified diagram of a Unionfining or hydro-fining operation. Catalyst is contained in a reactor, the shale oil and the hydrogen go in here under pressure and temperature and out of the exit of the reactor comes a refined oil, plus hydrogen sulfide, ammonia, and water.

This slide shows some of the simplified reactions; the sulfur compounds which are converted to hydrocarbons, such as butanes, a mixture of iso and normal butane, plus hydrogen sulfide. This is pyridine, which reacts with hydrogen to give iso and normal pentane plus ammonia. The oxygen compounds yield water and hydrocarbons.

The next slide shows pictures of some of our catalysts that we have developed which are effective for refining shale oil. They are nickel and/or nickel-cobalt-molybdenum catalysts. All are in commercial use. They are effective for taking out nitrogen,sulfur,and oxygen and for saturating the olefins in shale oils.

The next slide shows equipment used to carry out experimental studies on catalytic processes for processing the shale oil. Once nitrogen and sulfur and oxygen are removed from the shale oil it is very similar to petroleum crude and it is a little better because it is not as high boiling. You can then process it to make gasoline, turbine fuels, jet fuels, diesel, most anything that you can get from a petroleum crude except that not much lube oil can be secured from shale oil.

The next slide shows some of the products from syn-crude refining Sulfur is down to about one part per million (ppm) in the gasoline range naphtha. There are 10 ppm sulfur in the 350 to 550 degrees F distillate which is type Jet A fuel. Nitrogen we take down to something like these levels and we can go lower. An area where we think we need some improvement is in the catalysts which are used to remove sulfur and nitrogen.

In this slide are products that can be made from shale oil. They are similar to what can be obtained from petroleum crude. Several years ago we made substantial quantities of turbine fuel and diesel fuel which were evaluated by the Navy. The Navy found them entirely satisfactory. Now, why didn't we go ahead with this back in the late 50's? Well, it wasn't economically attractive. We were close but not competitive with petroleum crude. Now we're getting closer, and with petroleum crude getting up to $6 to $8 a barrel we're going to be in business. We are at the present time running a new pilot plant, an improved version of the retorting operation we conducted back in the late 50's with some new wrinkles. It started operating about a week ago. It's a long way between making a pilot plant and operating a commercial unit, but we have high hopes for augmenting the supply of fossil fuels from resources here in the United States. And that obviously is our objective as far as the DOD is concerned.

Discussion

Rabo: What is the cost of char from the charring process? Would it be competitive with coal as a source of solid carbon raw material?

Huffman: Are you talking about the coke we get in the coking operation? Yes, it has metals in it and a lot of crude from the oil shale itself.

Rabo: It would not be particularly advantageous against coal?

Huffman: Well, we don't make much of it so we don't think it's going to be too much of a problem. Besides, we can burn it to generate power for refining facilities.

Lindquist: I've heard that for the total energy balance of the extraction process including dynamite and moving it, it takes about 10 gallons of oil per ton to extract shale oil, compared with 24-30 gallons of oil/ton extracted.

Huffman: We don't think it's that high. This is the reason we are trying to improve our retorting process and the mining process.

Lindquist: Would you say the current methods are temporary methods?

Huffman: You'll get various claims from various people who are developing retorts. We're getting close to being competitive with the present price of crude, and with where we think it is going to go we expect to be more than competitive.

Heinemann: The viscosity difference between the 26 API crude from shale oil and natural crude, is that due essentially to higher paraffin content?

Beuther: Do you believe that it's possible to handle the disposal problem of shale if one had 3, 4, or 5 plants in this area, and do you believe there is adequate water in this area to allow shale to be developed as a resource substitute for petroleum?

Huffman: The first question is a toughie and there will be some problems in disposing of the spent shale. We would supposedly stuff as much back into the mines as we could and hopefully we will not expose it to water any more than we have to. If it does get exposed to water we would try to keep it confined so it wouldn't get into the natural drainage system. The water problem is real, but our method of retorting is not too demanding for water. We think we would have enough water.

Haensel: My questions are very similar to Harold's. What is the amount of water needed for a ton of shale? Number two: What are you doing about the very fine particulate material that may be escaping in the atmosphere?

Huffman: I'll answer your second question first. There is no fine particulate material in this retorting method. The first question: I cannot quote the answer. I've got it, but I just don't remember it and I will send it to you.

Haensel: Is it substantial?

Huffman: No, it's not.

Haensel: I wish you could quantify it.

Huffman: It was quoted in the NPC study on oil from shale.

Perrine: You say that the water requirements are not large. It is particularly important to quantify it because this is a very arid area, and there is a large agriculture component which depends on that water.

Huffman: We don't argue with you one little bit; we realize it.

Somorjai: Is there any chance of hydrogenating oil underground, and if so, what is being done about it?

Huffman: We've thought about it. The Bureau of Mines people, several years ago, did some direct hydrogenation of pulverized oil shale.

Mills: It was an underground gasification, but not hydrogenation, of oil shale.

Holliday: What are the capital costs implied for the type of plant you've been working on now?

Huffman: I can't quote those. They are substantial. But I can't give you any direct figures.

Johnson: Do you recall who in the Navy tested your products?

Huffman: No, but I will find out and let you know, Mr. Johnson.

Lindquist: How serious and how widespread is the arsenic problem?

Huffman: There is arsenic along with a lot of other things in the oil shale. Some of this gets into the oil and we have to take it out. We have a way of taking it out of the shale oil.

Voice: Would there be arsenic in the waste water from the plant?

Huffman: No.

Hightower: The question was do you remove the arsenic in the waste water.

Huffman: Yes.

Boudart: The Brazilian government has given priority to the development of a shale process. Is their process good?

Huffman: I cannot tell you. I do not know. We have made proposals to the Brazilians over the years and they didn't take us up. We admitted that we needed some improvements in our retorting and mining as of 10 years ago and we are hopeful now of almost having them, and we are aided by the price of crude.

Mills: In Brazil this unit is operating and it is an indirect combustion type and my recollection is that its production is 3,000 tons a day.

Wise: There is some indication that the greater part of the fuel nitrogen ends up as oxides of nitrogen in the combustion process. Can you tell us something about the nitrogen content of the materials produced from the shale oil.

Huffman: I had those listed in my slide.

Wise: Is it large?

Huffman: No, we can get them down to a few hundred parts per million, 10 or 15 in the naphthas and 20 or 30 ppm in the turbine fuels and 100-200 in the heavier oils.

Wise: How does it compare to crude?

Huffman: Well, some crude oils will have as much as 2/10th weight percent or 2,000 ppm, some have 3000 ppm and higher. We deal in our refinery with gas oils and heavy oils, in our hydro carbon operation, that are 2,000 to 3,500 ppm. The refining processes now in use in the petroleum industry will handle this high a level of nitrogen. As you say, part of the nitrogen, when fuel is burned, goes to NOX. It depends on the conditions, but anywhere from 25 to 45% goes to NOX.

McCormack: I understand that the nitrogen in fuel contributes very little to increased NOX, at most 5% increase because the flame front is very close to equilibrium.

Wise: It simply means that even if you were to reduce the NOX produced by nitrogen fixation there still would be NOX that originates from the fuel.

McCormack: It's a very small amount; it's only 5% above the equilibrium which is a function of the flame front conditions. What are the properties of shale retort ash products with water? Can you get a cementation?

Huffman: Our present technique leaves the particles almost intact.

McCormack: So there is no cementation?

Huffman: No, our first retort in Colorado was a very high temperature retort. The temperatures in there were as high as 2000 - 2200 degrees F, and there we got considerable slagging and fusion.

McCormack: I was thinking in terms of formation reinjection where there might be a volume increase problem. You need to stabilize the strata so you don't get collapse. The ash is treated like a cement powder hydrate and stabilized as such.

Huffman: I must tell you that after the retorting by our current technique the spent material is much weaker, of course; and there may be a problem there. There are a lot of problems, but that makes it very interesting.

Lauriete: Have you looked into ways of treating this material after the crude has been extracted so that it can be used on highway construction.

Huffman: Yes, but we haven't been successful.

Lauriete: Our boss, who is an alumnus of your company, would be interested in it.

Huffman: He used to work for me by the way.

Bill Libby: Do you think catalysis could help substantially? Suppose we improve the effectiveness?

Huffman: An improvement in catalyst would lower the cost of refining the shale oil, but the retorting and the mining and the handling of the spent ash are bigger problems. We are striving to improve the catalyst now, but it won't make much of a dent on the overall economics as would the other factors.

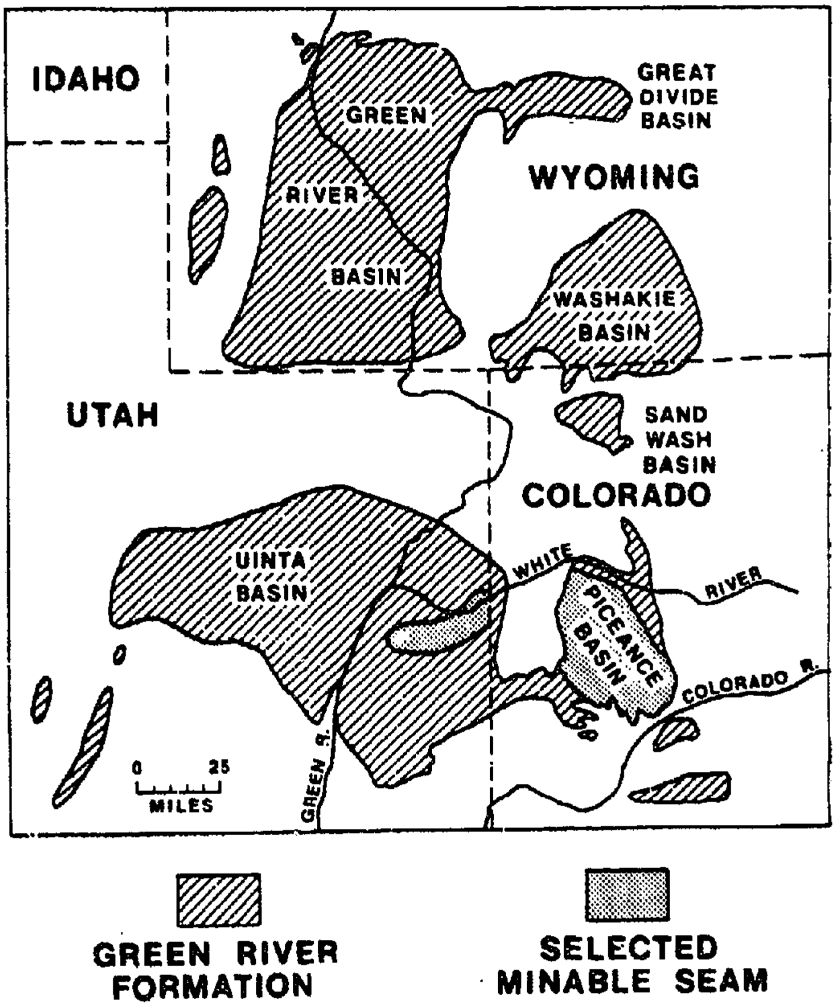
Johnson: Do your catalyst problems parallel those with crude petroleum?

Huffman: Yes.

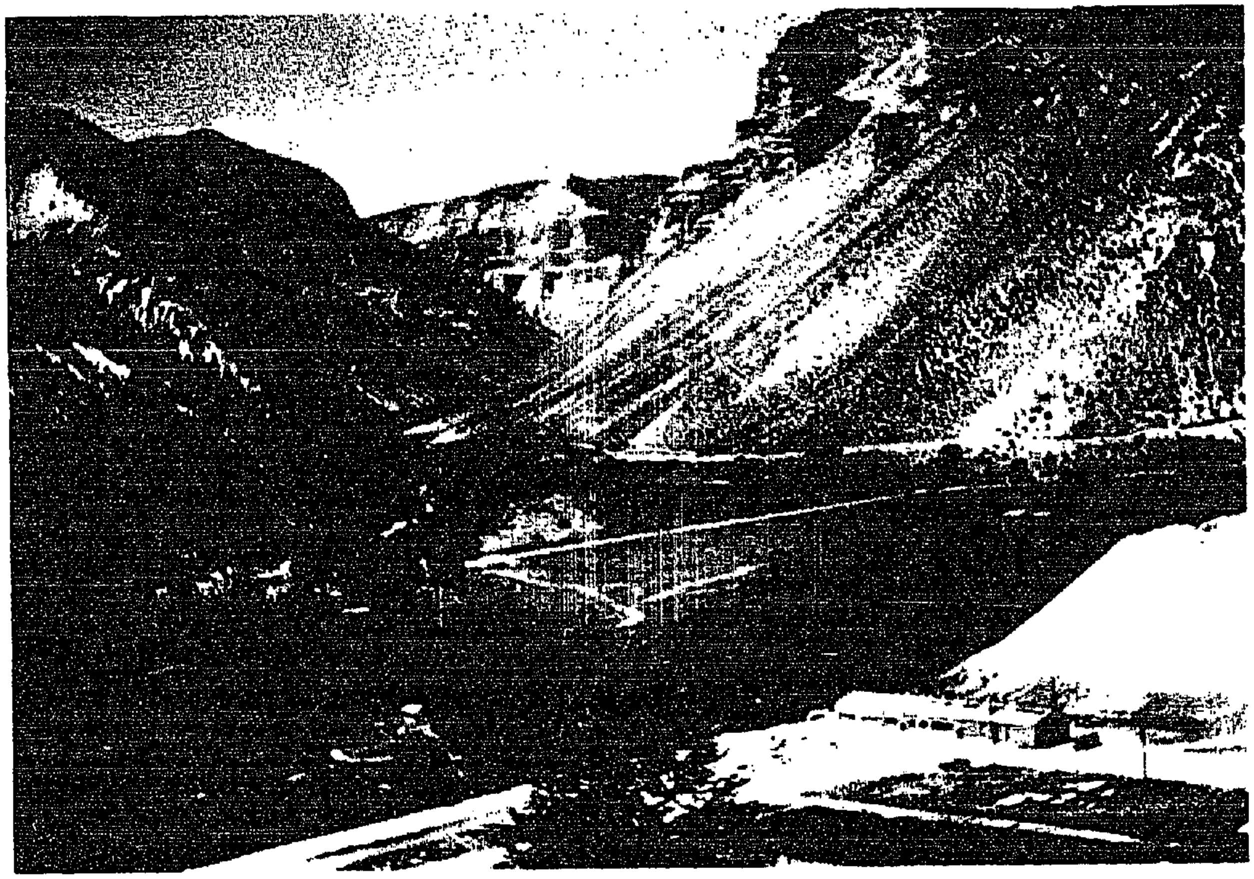
Haensel: In case your more recent retorting is successful what is the time schedule for a substantial commercial operation?

Huffman: We're now trying to estimate that, assuming that our pilot plant work is successful; perhaps 1980 or a year earlier. It takes a long time as you well know.

McCormack: Five years.


IDAHO
GREEN
RIVER
BASIN
GREAT DIVIDE BASIN
WYOMING
WASHAKIE BASIN
UTAH
SAND WASH BASIN
COLORADO
UINTA BASIN
WHITE RIVER
PICEANCE BASIN
COLORADO R.
GREEN R.
0 25
MILES
GREEN RIVER FORMATION
SELECTED MINABLE SEAM

1



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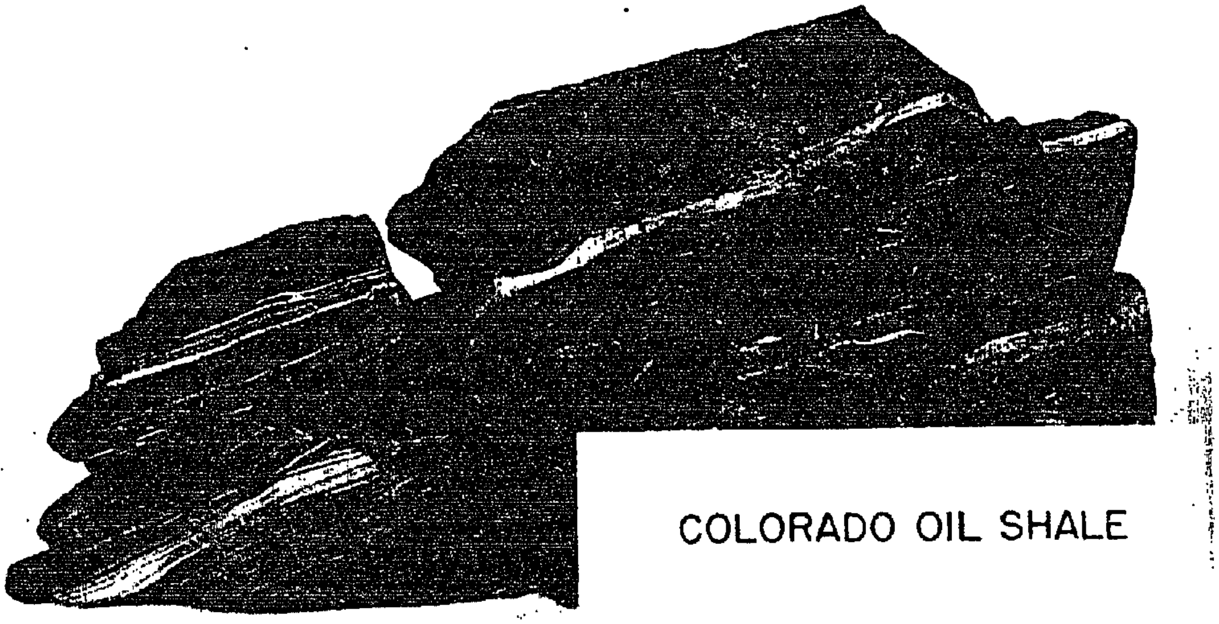

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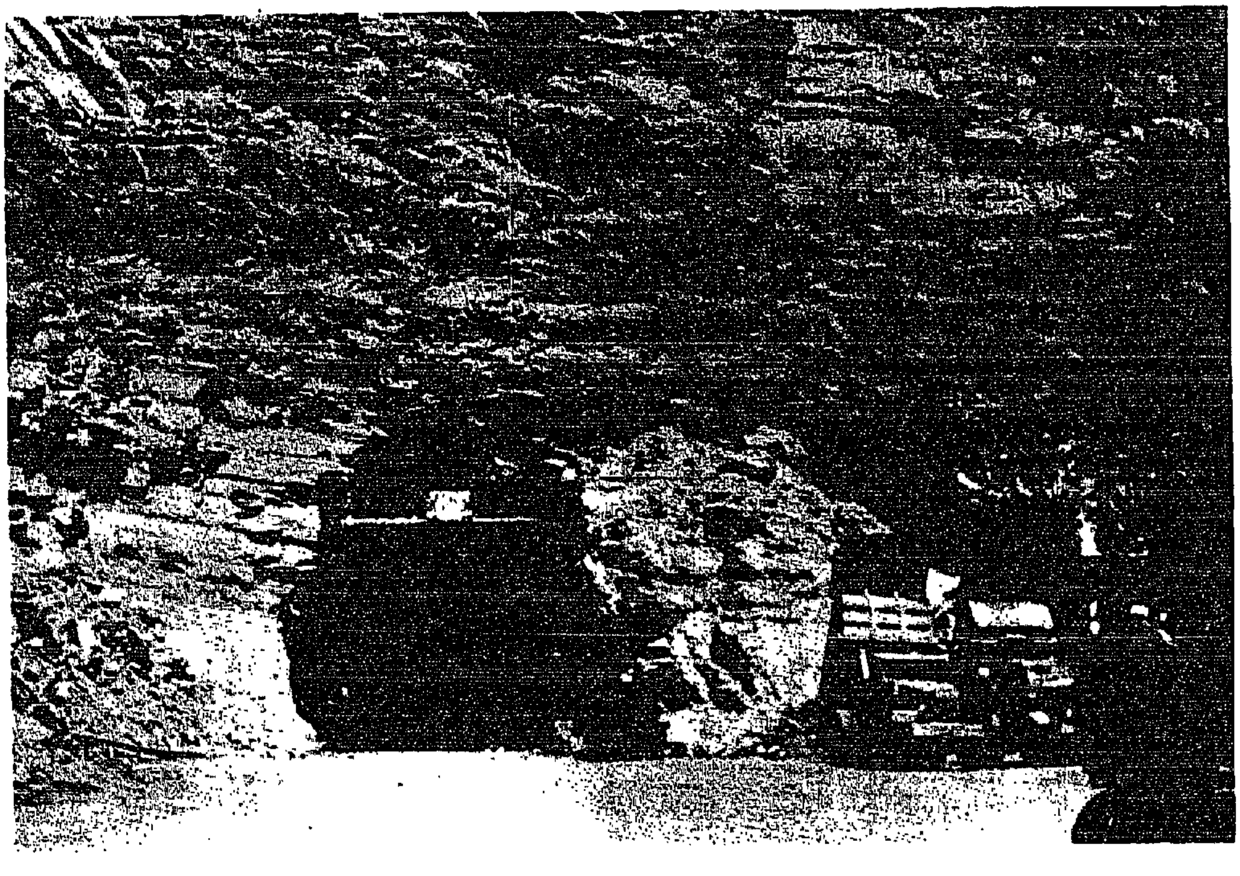

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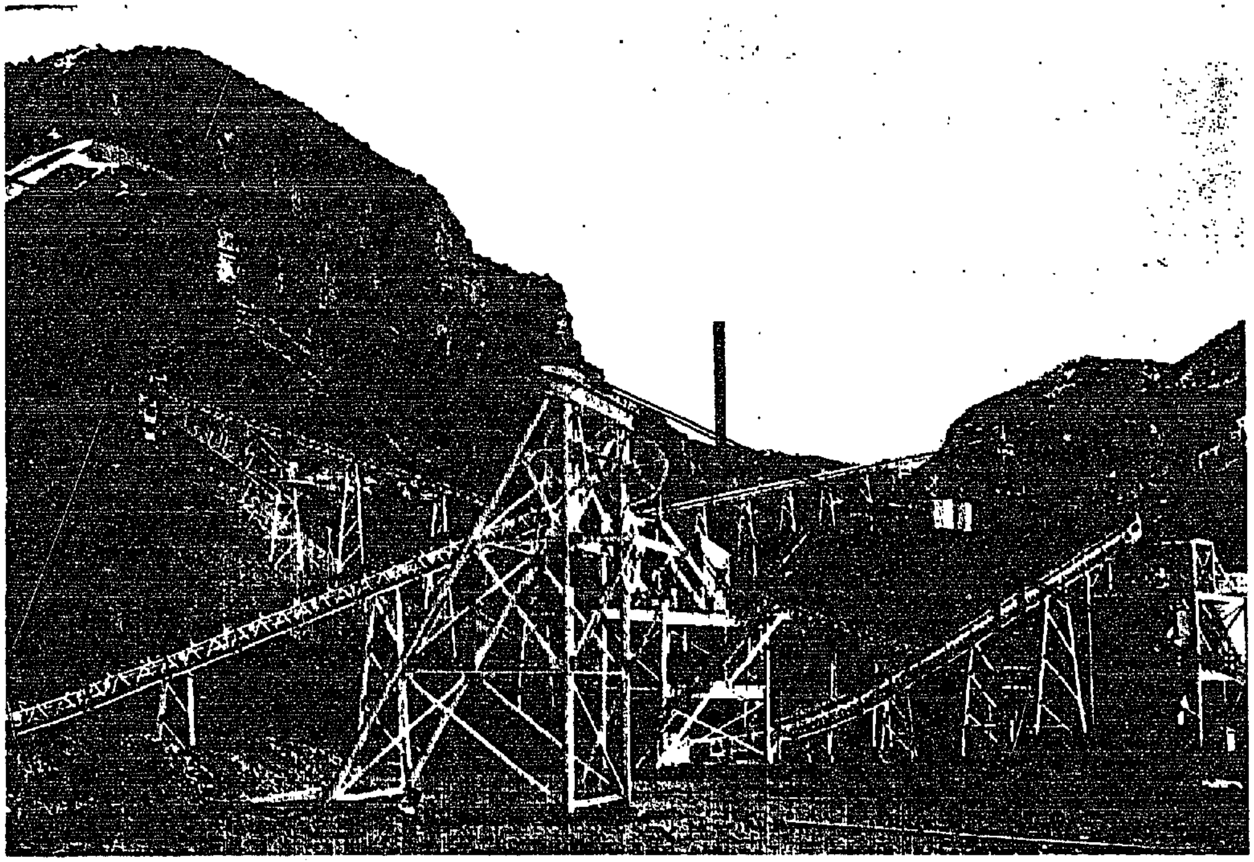

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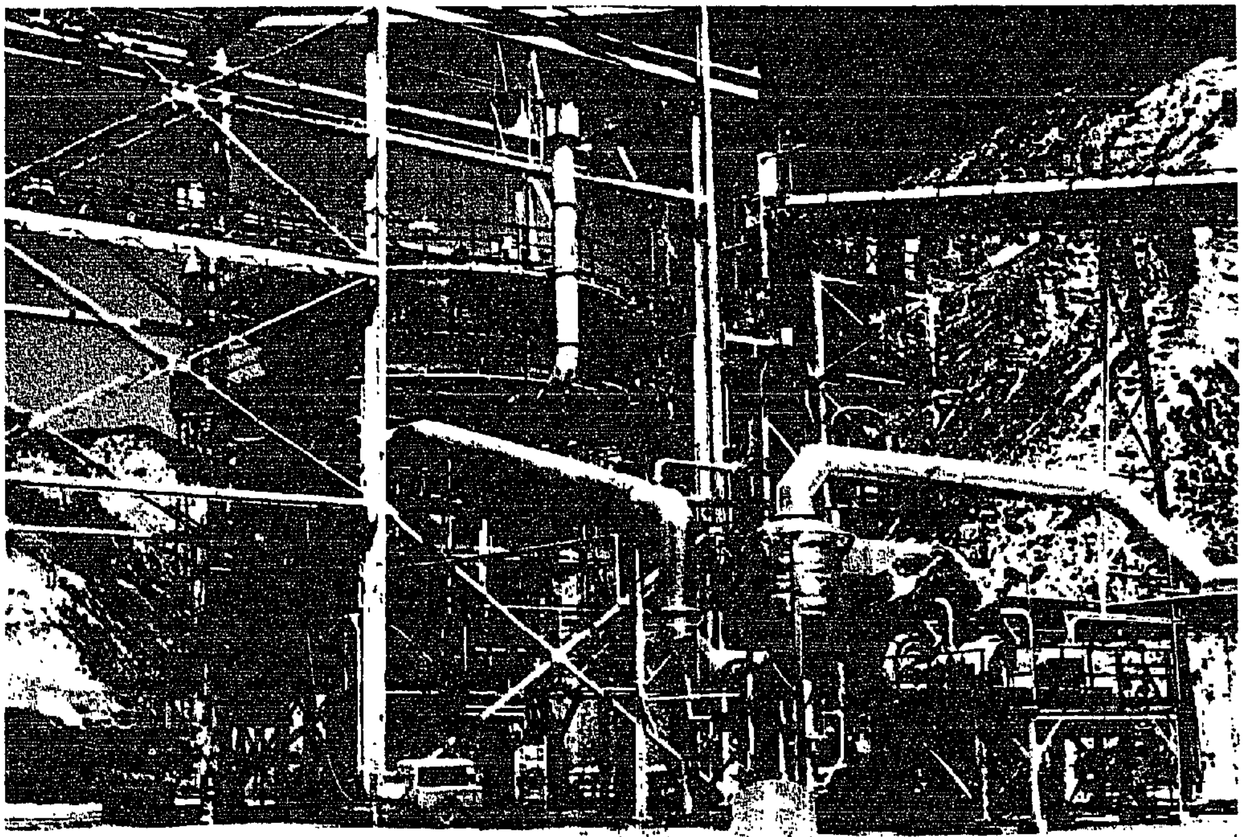

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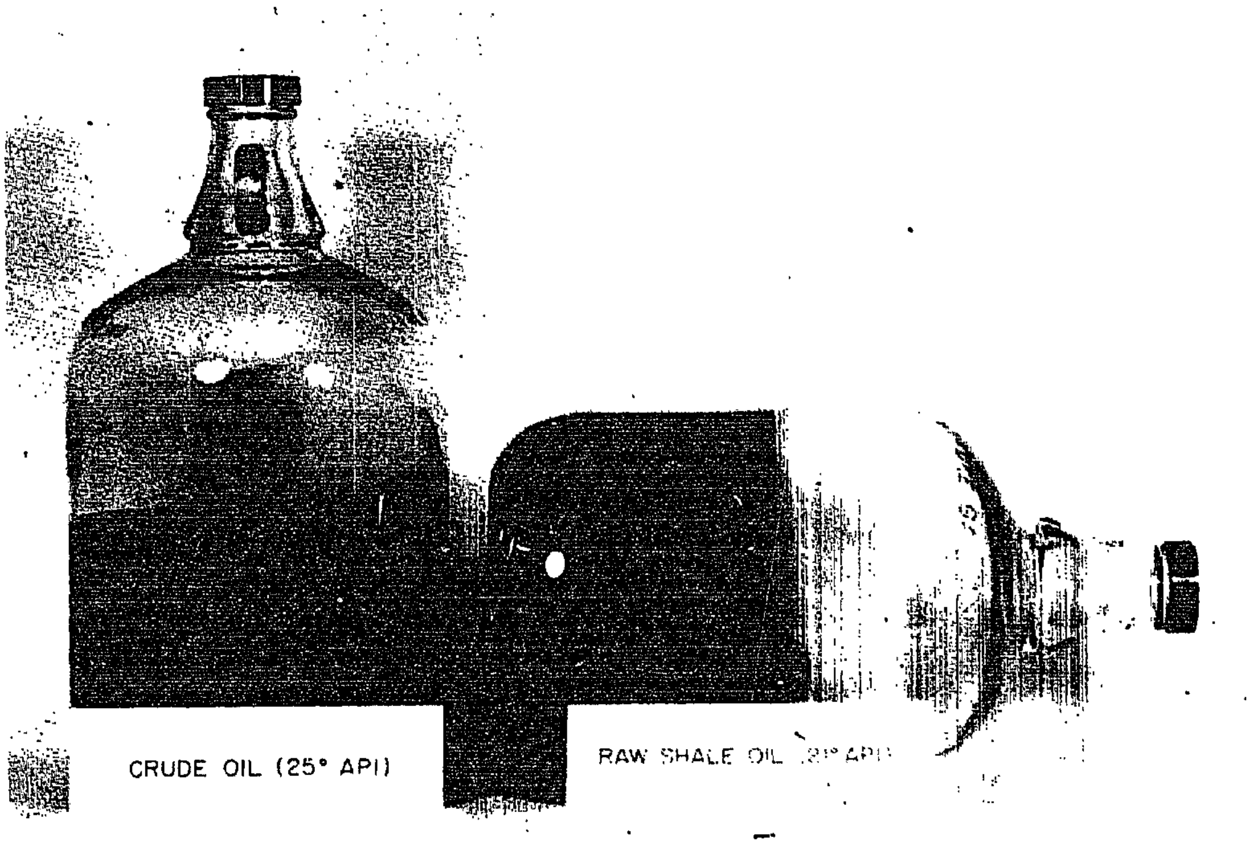

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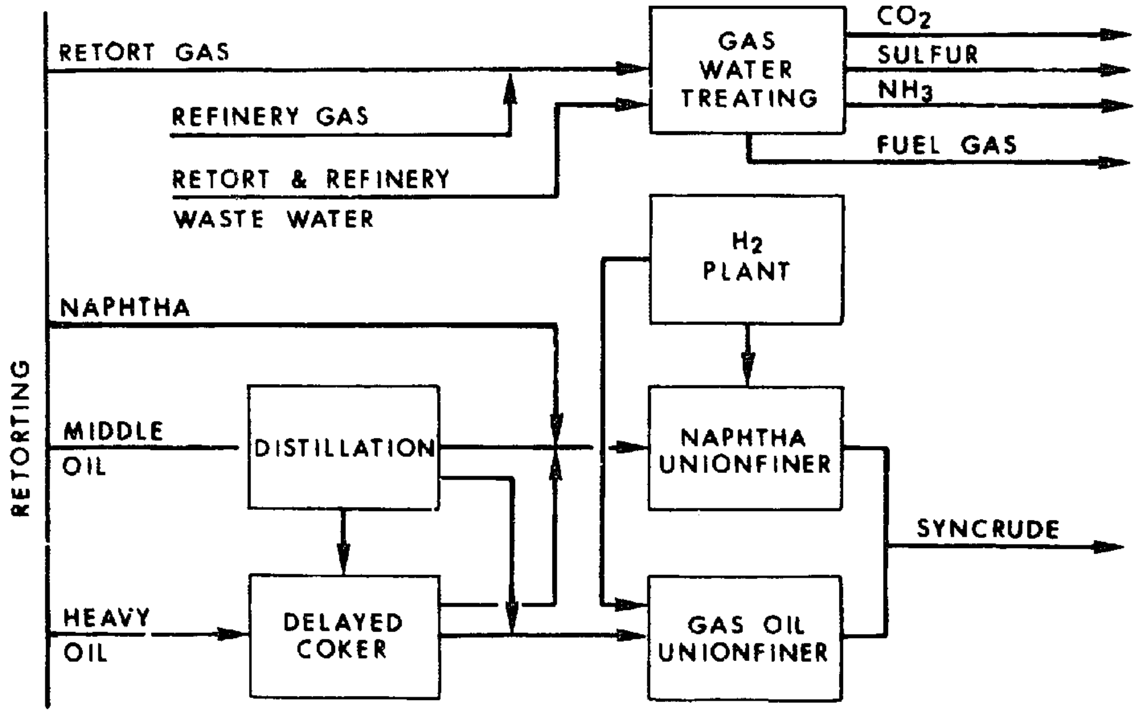
SHALE OIL REFINERY
SYNCRUDE CASE



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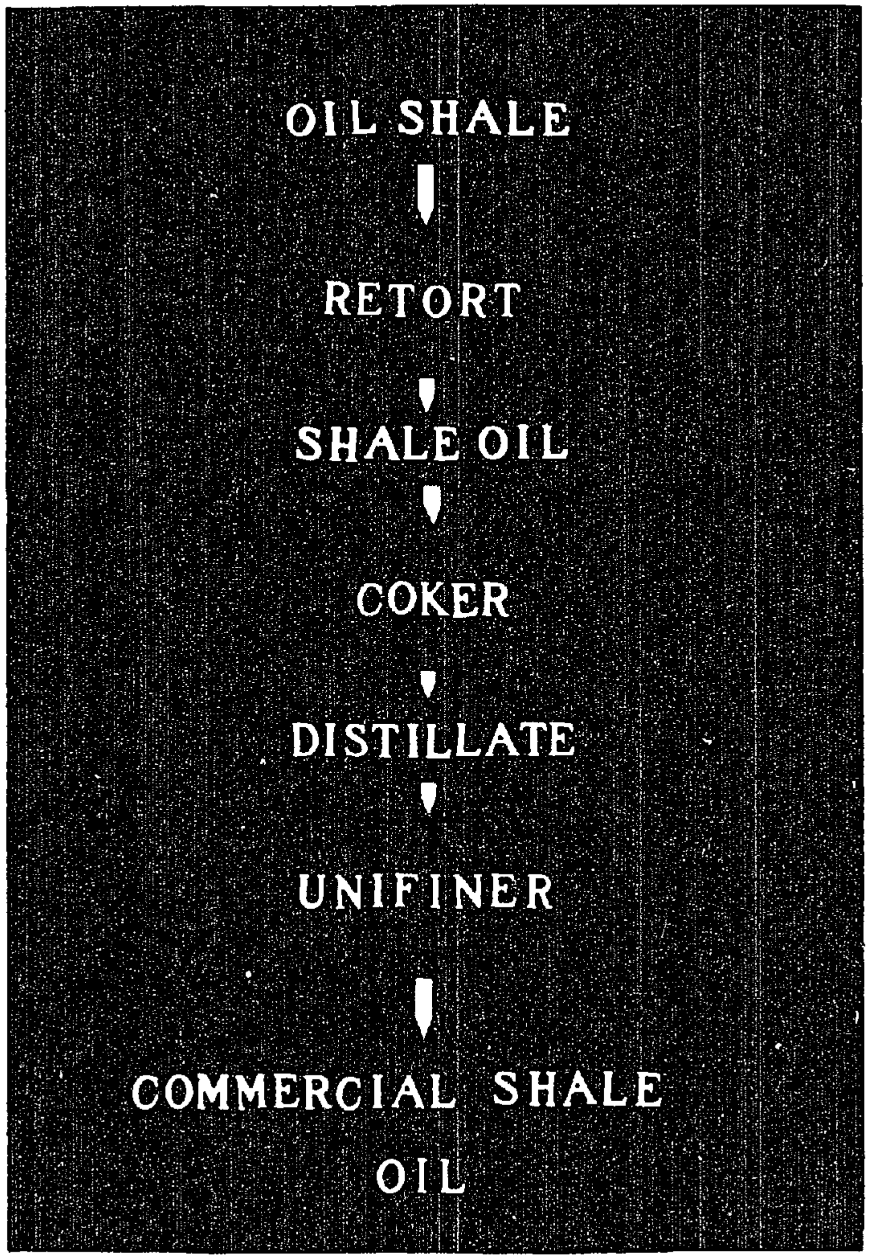


OIL SHALE

RETORT

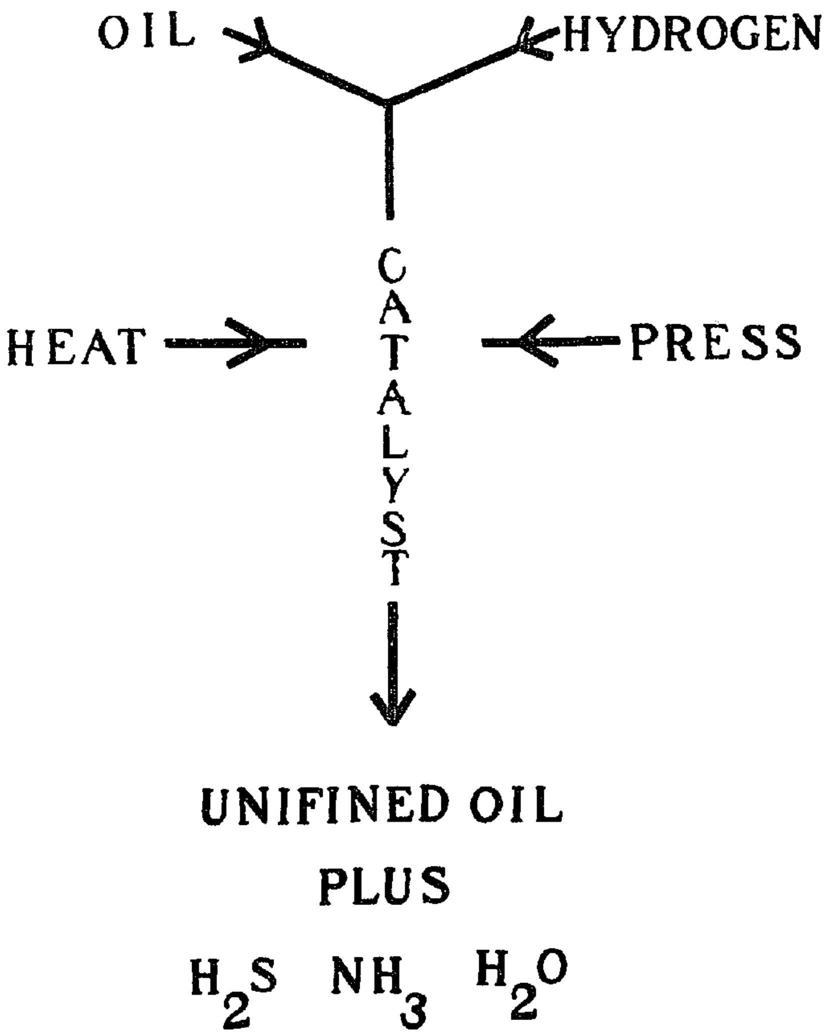
SHALE OIL

COKER

DISTILLATE

UNIFINER

COMMERCIAL SHALE OIL



OIL

HYDROGEN

HEAT

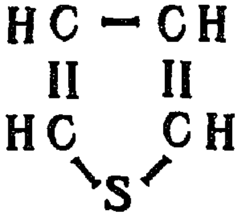
CATALYST

PRESS

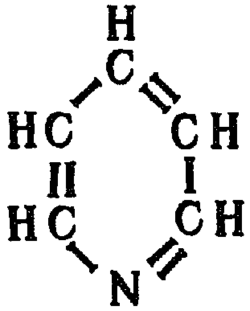
UNIFINED OIL

PLUS

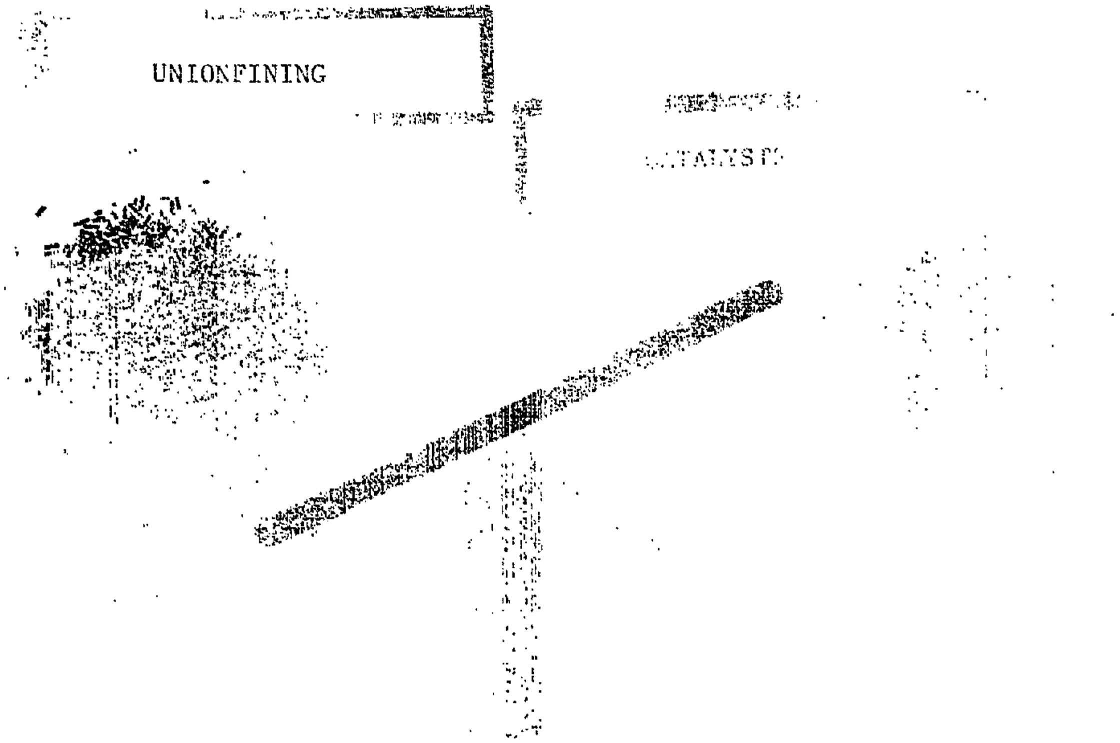
H_2S NH_3 H_2O

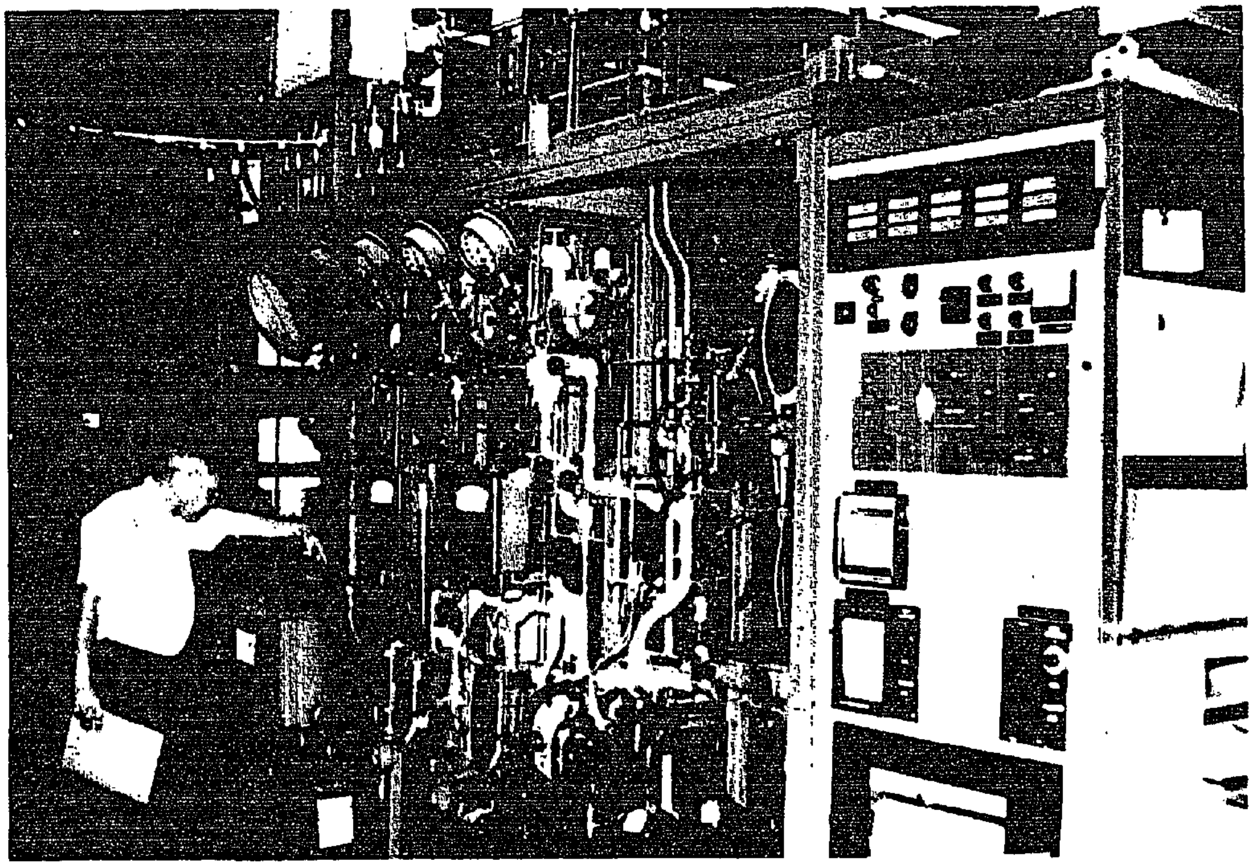


$4H_2$ C_4H_{10} H_2S



$5H_2$ C_5H_{12} NH_3





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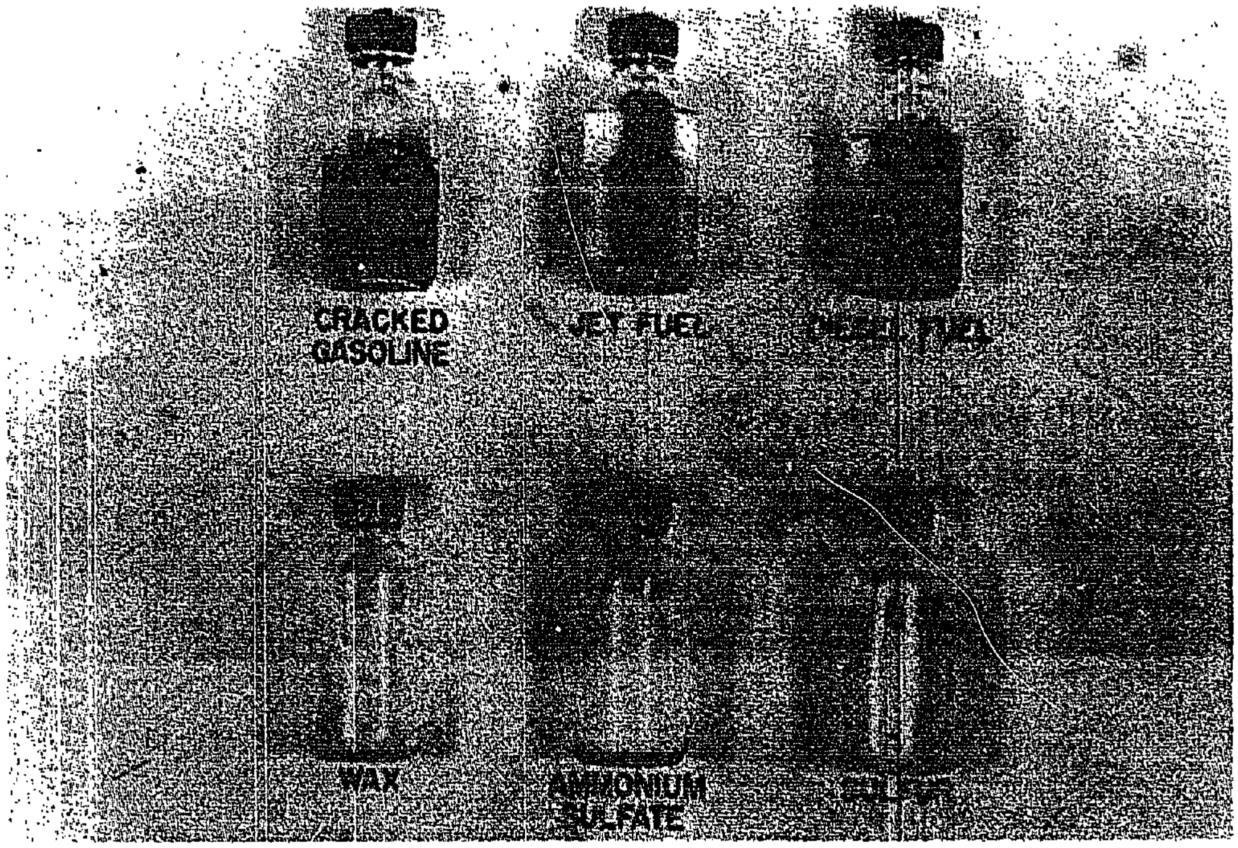
CRACKED GASOLINE
JET FUEL
DIESEL FUEL
WAX
AMMONIUM SULFATE

16

ASSAY DATA

SHALE OIL FROM VARIOUS RETORTS

TOTAL CRUDES

	UNION OIL			
RETORT	"A"	"B"	Y	Z
°API	19.7	20.3	25.8	28.0
SULFUR, wt %	1.0	0.8	0.73	0.76
NITROGEN, wt %	2.0	1.9	1.9	1.7
CON. CARBON, wt %	3.4	4.1	5.5	5.7
POUR °F	80	75	70	60

SYNCRUDE REFINERY PRODUCT QUALITY

	C_5 - 350 °F NAPHTHA	350 - 550 °F DIST.	550 - 850 °F GAS OIL
GRAVITY, °API	55	40	30
SULFUR, ppm	1	10	100
NITROGEN, ppm	10	140	1450
PARAFFINS	55		
NAPHTHENES	33		
AROMATICS	12	30 wt	
FREEZING POINT, °F		-40	
SMOKE POINT, mm		15	
POUR POINT, °F			+40

CATALYSIS IN PRODUCTION OF LIQUID FUELS FROM COAL AND HEAVY RESIDS

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Coal and resids I'm going to minimize because it was covered satisfactorily by Harold Beuther. There is, however, a limited temperature range for residue desulfurization. It must be high enough so that the metals come out, but it must be not so high that the asphaltenes drop out, because on raising temperature the asphaltenes tend to agglomerate and would kill the catalyst. Now, residue desulfurization units based on conventional trickle-flow fixed-bed technology are in operation in the Far East and also, to a more limited extent, in Europe. Currently, major attention is being turned to, and major advances being achieved, in improvement of catalysts. Desulfurization of 80 to 90 percent is possible, at least in experimental work, probably not much higher than that on a practical basis, however.

One of the best ways to apply residue desulfurization is in multiple catalyst beds. The first slide is taken from a Chevron patent, but there are many other companies beside Chevron who are active in this type of application. The idea is to have approximately three beds of catalyst, the first of such a nature that there is very little hydrodesulfurization, but which will pick up the largest part of vanadium and nickel which are the bad actors, the second one to pick up the rest of the metals, and also to do a fair amount of desulfurization, and the third to finish the desulfurization. Now in this first bed, for example, we could use Heinz Heineman's manganese nodules. And in the second slide you will see one of the schemes that has been patented, in this case by Shell, to be used particularly in the first stage, where there is a moving bed of materials of metal collectors, which have a limited capacity. This kind of bed has promise because the plugging problem has been quite severe in many of the pilot plants and semi-commercial and even commercial plants, because of rather fine particles coming through and plugging the bed.

Another area where experimental work has been done in desulfurization of residues is with bulk molten salts, particularly those with a high acidic activity. Work by Consolidation Coal Company some time ago used bulk zinc chloride. It has an advantage in that zinc chloride and hydrocarbons are highly miscible, so that coke and metals do not limit the activity in this homogeneous system, nor in coal catalysis.

Another advance that was made was in using materials that are inactive as a part of the molten salt, which then are not completely miscible with the heavy hydrocarbons, and one can have hydrocarbons passing through continuously, until the catalyst is fairly well used up, rather than having to regenerate the whole bulk of material on each pass through. Of course, there is now an alternative as far as heavy fuels are concerned, and that is the desulfurization of flue gas; however, this is applicable mainly on rather large plants. The only feasible processes long-term are those which are catalyst systems so that the material is regenerated for reuse. An example is copper oxide on alumina, in parallel beds with the flue gas not passing through the bed, but with the beds being deep enough and thin enough so that flue gas diffuses into the catalyst and out again, removing the SO_2. There is a commercial plant in operation in Japan at the present time.

Unfortunately, hydrogen is a very significant cost in processing resids and in processing other materials. Therefore, catalyst systems that are selective in the use of hydrogen are of great value. Hydrogen was at one period as cheap as 25¢ per thousand cubic feet to make. It is already double that now, in part because of the shortage of natural gas, and the price will go up as fuel prices go up.

Joe Hightower has asked that we philosophize a little bit, so I'm going to take advantage of his suggestion. In my opinion, the Arab nations have done us a favor in cutting off our supply of Middle Eastern crude so early in the U.S. fuel shortage period. Their action has certainly convinced me that the United States must become again completely self-sufficient in energy supplies as we have been until recently when energy consumption here outstripped energy supply. By 1980 it has been predicted that as much as 45% of the fossil fuels required to meet the energy demands here would have to come from imported crude. And while we may be able to cut back 10 to 20%, it is tough to cut back 45% when one is accustomed to using it. We've been spoiled, of course. We here in this room have lived in the good times in which, as we needed more energy, it became available. Those times are gone.
I'll be happy to talk with anyone about alternatives that I consider viable.

Now, if we are to become self-sufficient again in energy supplies in this country, there are several requirements. One, of course, is strict energy conservation and we've seen some of that already in the large reduction in the number of airline flights because jet fuel is particularly short. But, hopefully, this strict conservation will only be for a short term, I mean 10 years perhaps or in the order of that much, until we are able to build up our sources of materials for supplying energy. A second requirement is that there be some compromise, hopefully, only for the short term, on the proper balance between environmental conservation and the energy crunch. The third is to tap and utilize on a crisis basis our own native resources of fossil fuels other than petroleum. We have enough to last for quite a few generations. The two other fossil fuels that are available here in large quantity are oil shale and coal. We are not blessed as Canada is with enormous deposits of the third one, tar sands. And Canada is certain to take care of its own people first and limit the amount of such materials to be brought into the United States. Now, hydrogen is of more significance when utilizing oil shale or coal than is the case in utilizing petroleum.

The next slide gives the hydrogen to carbon ratio in a number of materials and the range in coals is not limited to this. In petroleum crude, on average, there is about 1.75 H atoms to one C atom, and in coal, less than half that much. Besides, additional hydrogen must be supplied to remove nitrogen and sulfur and oxygen present in the coal.

In the case of shale, the likelihood of using catalytic conversion of the oil shale is remote. There is such a tremendous ratio of inorganic materials to organic materials that it is almost out of the question. All known shale oil processes to liquify the oil from the shale are thermal coking operations. On the other hand, once the oil is extracted then the problem is an almost typical petroleum problem of refining, differing in certain directions as mentioned by Dr. Huffman.

On the other hand, the opportunity for catalytic conversion of coal offers quite distinct promise. Catalysts for the hydrogenation of coal to liquids and for gasification of coal by steam to yield synthesis gas for methanation are currently under investigation in many places. The physical disadvantage of coal compared to petroleum is largely due to its smaller hydrogen content and to the fact that it is a solid and has high ash content.

Now, of course, it is impossible for me to review all the work on the liquefaction of coal in this short time, so I will only review by example, and I shall omit the excellent Bureau of Mines work, which I'm pretty sure Alex Mills will be covering anyway in the next talk. Coal hydrocracking obviously requires a catalyst that is insensitive to the high concentration of sulfur and nitrogen and which can be readily regenerated from the compounds that are formed with sulfur and nitrogen. The cobalt molybdate used, for example, in the H-coal process meets these criteria. The bulk molten zinc chloride in the Consol process reacts to form zinc sulfide and zinc ammonia complexes, requiring regeneration back to zinc chloride, but this can be achieved. My next slide compares briefly the H-coal and zinc chloride processes under somewhat similar conditions and you note the naphtha from which many of our favorite materials are made, namely, gasoline and jet fuel, is a lot higher in this zinc chloride process. In the case of some of these molten salts, one can even make no liquid product except gasoline by choice of the salt and the conditions.

Shell has explored quite a number of molten salt catalysts, both for residue desulfurization and also for coal liquefaction. Specific examples shown in the next slide are taken from one of the patents. There is a range of materials which are suitable. If one wishes to make gasoline, antimony chloride has certain advantages. Zinc iodide with one of these inert salts in the melt allows some slippage of hydrogen sulfide and ammonia, so that they do not react quantitatively with the catalyst.

The dominant cost of coal liquefaction is the cost of hydrogen, so one prime research goal is to make a dramatic reduction in the cost of hydrogen manufacture. The partial liquefaction of coal, leaving enough coke with the ash to react with steam, and perhaps some oxygen to furnish the heat necessary, is desirable. A conventional coal gasification process being piloted in the United States and for which several companies are dickering for large-scale commercial plants is the Lurgi process shown in the next slide.

Coal, steam and oxygen come together, with ash coming out the bottom of the reactor. Waters and organic liquids that result must be cleaned up because they contain, among other things, phenols. Then there are more conventional processing steps such as in the methane synthesis side. The methane synthesis is still not worked out catalytically as well as desired because, in order to insure that the catalyst lasts a long time, one must have a catalyst which is not sulfur-sensitive, and this needs more study.

Further work on coal liquefaction catalysis as a mechanism of reducing the total energy required to produce hydrogen from water should lower the cost of production of hydrocarbon liquids from coal. Perhaps the greatest disadvantage to such urgent action is the extremely high capital costs of coal refineries. I have seen estimates which vary, for a 100,000 barrel petroleum refinery from coal, from 4 to 6 times as costly as a conventional refinery using crude petroleum, up to as much as 8 to 9 times as costly, and I am convinced the higher figures are more likely. So it is going to be extremely difficult for the petroleum companies or others to generate sufficient capital to tool up at the rapid rate needed in order for us to become self-sufficient in energy in a short time, and with that I'll stop.

Discussion:

Beuther: Our estimates were that it is no more costly to buy coal lands, to mine coal and refine the coal, than it is if one searches for oil in the United States and produces it and refines the oil. The cost of finding oil in the next decade will be very, very high, so that, overall, coal would be cheaper.

Bailey: I think you may be entirely right on that, Harold. I have not written off more oil, but the probability of finding enough to keep up with the energy requirements is small enough in my opinion that we are going to have to use coal even if it is several times as expensive. But you may be quite right, that the costs are in the same range.

Hightower: Over the last 40 years the number of wildcat holes that turned out to be producers has remained constant at about one in nine. In other words, it's remained constant even though we've found the big oil pools. Is that correct?

Bailey: I'm afraid, Joe, that the measure you are giving is not necessarily the one which is meaningfull, because it's true that the percentage of wildcats that fail has not gone up very much. The percentage of wildcats which lead to completely new, very large fields has gone down significantly. I believe that's a better measure.

Lindquist: At the First International Coal Research Conference, EXXON made an estimate that in 1980 the cost of a coal refinery would be $10,000 per barrel. The man from the British Gas Counsel said that that's not too different from the cost put into the North Sea into the production gathering facility, which right now is around $4,000 per barrel or so. I think the point is well taken. It costs a lot for coal refineries, but the off-shore oil facilities are tremendous in costs also.

Bailey: No question.

Perrine: Yes, I think it's worth considering not just how many wells you drill before you find one that produces oil, but the size of the reserve that is discovered. All the biggest reserves very likely have been discovered on the continental United States, or else we know about where they are, and they are very limited. It's off-shore overseas that you are likely to find really big ones in the future, and that's the same problem with the Arabs. It is not under our control.

Hightower: The average depth of wells is increasing all the time, too.

Bailey: Not only that, but the next place to explore in a major way is in extremely deep water, off-shore, because that has not been explored very much, whereas the lands have been explored to a very large extent. The deeper you go drilling for oil, the more expensive it becomes. Oil production is likely to become far more expensive than coal liquefaction. There's some oil well depth at which there is a balance.

Boudart: When you mention the need for improved catalysts for hydrogen manufacture you think also of electro catalysts, namely electrodes for electrolysis?

Bailey: Well, electrolysis thus far has not been economic compared with using coke or a liquid hydrocarbon to make hydrogen from, by reaction with water. On the other hand, there have been studies, one that was sponsored by NASA on which a report is about to be forthcoming and is open, which have looked at the possibility of a large nuclear reactor, far out in the waters, producing hydrogen by electrolysis and piping the hydrogen to shore. That is perhaps the approach which will lead to making electrolysis a good economic process.

Heineman: I'd like to go back to making hydrogen from coal and steam with the Kellogg process which still needs a lot of work to make it successful. This is a molten salt process, reacting coal and steam, with sodium carbonate as a catalyst in which the molten sodium carbonate is also an excellent heat transfer agent. Now, the problem with this process is that sodium carbonate is a fairly universal solvent and is very hard to contain.

Bailey: I omitted mention of this process to conserve time. A good reference is *Oil and Gas Journal* for 9/27/71.

W.F.Libby: Do you think that catalytic research would help cut the cost of coal catalysis?

Bailey: I certainly think that it might, both for producing the necessary hydrogen and for the actual coal liquifaction itself.

SLIDE 1.

MULTIPLE CATALYST BEDS FOR RESIDUE DESULFURIZATION

(BRITISH PATENT 1,298,905)

1. -------FIXED BED OF MACROPOROUS CATALYST PARTICLES HAVING HIGH METAL CAPACITY AND LOW DESULFURIZATION ACTIVITY.

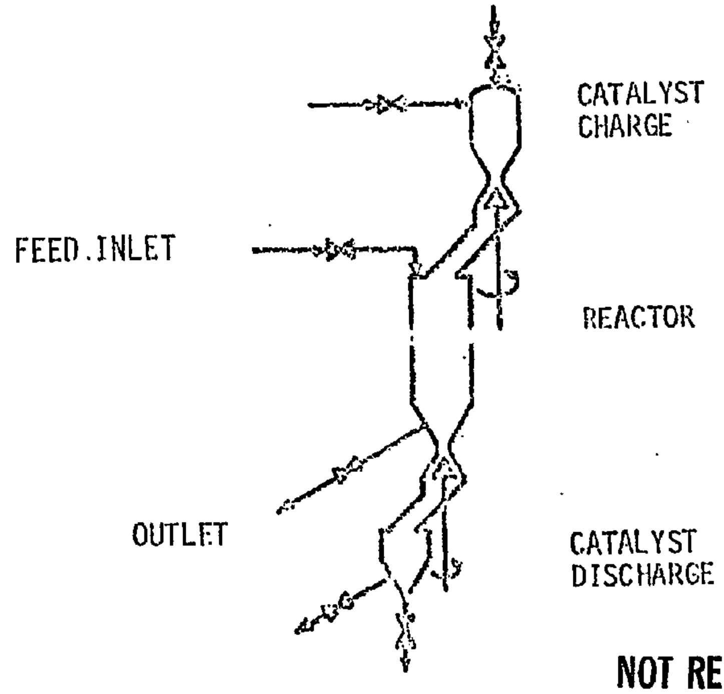
2. -------FIXED BED OF MODERATELY ACTIVE DESULFURIZATION CATALYST PARTICLES.

3. ------FIXED BED OF HIGHLY ACTIVE DESULFURIZATION CATALYST PARTICLES.

SLIDE 2

FIXED BED WITH CATALYST ADDITION-WITHDRAWAL

(US PATENT 3,730,880)



NOT REPRODUCIBLE

SLIDE 3

HYDROGEN/CARBON ATOM RATIO

COAL------------------------------------0.6 - 0.8

LIGNITE---------------------------------0.65 - 0.9

SHALE OIL-------------------------------1.1 - 1.25

PETROLEUM VAC. PITCH--------------------1.46

PETROLEUM ATMOS. RESIDUE----------------1.63

PETROLEUM CRUDE-------------------------1.76

GASOLINE--------------------------------1.94

SLIDE 4

COMPARISON OF MOLTEN HALIDE CATALYST

	$ZnCl_2$	ZnI_2	$GaBr_3$	TiI_4	$SbCl_3$
CATALYST, GM.	100	100	93	100	100
COAL (ILL #6) M.F. GM	20	20	10	20	20
TEMP., °C	350	350	250	350	350
H_2 PRESS, PSIG	1800	1750	1600	1800	1800
TIME, MINS.	60	30	30	60	60
PRODUCTS, GM/100 GM					
C_1 - C_3	8.9	6.7	2.5	9.4	4.0
C_1 - 250°C	47.7	45.4	38.5	42.3	47.5
iC_4/nC_4	15	16	5	1	12
H_2 CONSUMP. GM/100 GM	4.8	4.3	8.2	4.7	6.3

SLIDE 5

LURGI COAL GASIFICATION