LBL-7270

Presented at the II Latin-American
Botanical Congress, Brasilia, Brasil,
January 22 - 27, 1978

FERMENTATION AND HYDROCARBONS

Melvin Calvin

January 12, 1978

Prepared for the U. S. Department of Energy
under Contract W-7405-ENG-48

LBL-7270

DISCLAIMER

FERMENTATION AND HYDROCARBONS*

Melvin Calvin

Laboratory of Chemical Biodynamics
University of California, Berkeley, California 94720**

* Presented at the II Latin-American Botanical Congress, Brasilia, Brasil. January 22-27, 1978

** The work described in this paper was sponsored, in part, by the U.S. Department of Energy, Divisions of Biomedical & Environmental Research, Physical Research & Solar Energy

ABSTRACT

Photosynthesis is examined as a possible annually renewable resource for material and energy. The production of fermentation alcohol from sugar cane as a major component of materials for chemical feedstocks is examined as well as the direct photosynthetic production of hydrocarbon from known plant sources.

Experiments are underway to analyze the hydrocarbons from Euphorbias, Asclepias and other hydrocarbon-containing plants with a view toward determining their various chemical components. In addition, experimental plantings of plants of this type have begun to obtain data on which species would be the most successful. Work is also underway on the development of chemical process techniques for the extraction of plant materials after harvesting.

In addition, efforts are underway to construct synthetic systems on the basis of our knowledge of the natural photosynthetic processes. These systems could be used to produce fuel, fertilizer and power. As a result of studies of the natural quantum conversion process in green plants, we can envisage several photoelectron transfer processes, some of which have already been demonstrated in synthetic systems. Methods of constructing systems of this type and the principles of their use are described.

INTRODUCTION

I will discuss work that is the practical application of a basic research activity in which our laboratory has been engaged for over thirty years. We got into this practical application by a crossing of two quite different opportunities that gave rise to the present situation. Most of you may remember the oil embargo of the fall of 1973 when at least in California we couldn't go to the local gas station and get our tanks filled immediately. We had to wait in line, sometimes for as much as an hour or more, to get to the gas pump. During one of those periods of waiting, I had ample opportunity to think about this situation with the idea of discovering if we, as scientists, could prevent a similar situation from recurring.

During this interval I recognized that my wife's gardening activities on our ranch might actually contain at least a partial solution to the problem. The juxtaposition of the existence of the latex-containing plants growing on our ranch in Northern California and the realization that the latex was a hydrocarbon emulsion which many green plants produce led to the whole structure of the present activity.

May I introduce first the nature of the energy problem. Energy use in the United States in 1976 is shown in Figure 1. This diagram contains three messages. First, you should recognize that natural gas, coal and oil (all fossilized photosynthetic products) represent a little more than 95% of our energy supply, the rest of our resources are very small compared to those three. Secondly, about half of the total energy contained in the supply is lost in a non-useful fashion, called rejected energy, in which the heat or energy content becomes available at too low a temperature

to be useful in any practical way. The largest fraction of useful energy, on the other hand, results from the fact that the significant energy uses are industrial, and commercial and residential heating; those uses represent the relatively efficient uses of energy because energy in terms of heat is not limited by the Carnot limitation, i.e. it is not used to creat mechanical work. Most of the energy used for heating only, therefore comes out at useful temperatures. When the energy must be converted into mechanical work (as in automobiles) or when it is used to turn a turbine in an electric generator, then the efficiency is set by the Carnot limitation which is determined by the difference in the two temperatures between which the machines work; the efficiency is very much less. Large fractions of our energy are lost in non-useful forms, either through the radiator of the automobile or out the exhaust pipe; the same thing can be said of turbines of the electric generating system. The third message is that in 1976 there were 15 units of imported energy. You may remember that in 1973 or 1974 we instituted our Project Independence and the energy imports that year were 12.9 units. This difference in the imported energy units and the backwards progress we have made in the two years between 1974 and 1976 shows that the problem of imported energy cannot be solved by application of ordinary efforts. The petroleum material simply is not available for discovery, which is another reason that the energy supplies cannot be increased by an increased rate of petroleum discovery.

ENERGY: PRESENT USE, COSTS AND AVAILABILITY

Raising the price of petroleum and natural gas cannot increase production indefinitely. When you realize that oil and natural gas supplies are, for the most part, the fossilized remains of photosynthetic activity of several million years ago, there must be a limit as to how

much is available. Many people have tried to estimate what that supply limit is; I am not going to try to reproduce all the arguments to indicate that there is a limit. It stands to reason that there must be a limit, and one can make calculations, assuming that all the oxygen in the atmosphere came from the reduced carbon that is in the ground.

A more practical way to estimate availability is to find and measure the rate of discovery. The rate of discovery of oil as a function of the number of feet of well drilled, which is a very good measure of the effort it takes to find oil, is shown in Figure 2. For the period 1920-1950 the rate of oil discovery per unit well drilled was about the same. For every 100 million feet of well drilled there were about 20,000 million barrels of oil discovered, and that was constant for almost thirty years. By 1950 the slope changed very sharply and the rate of discovery per 100 million feet of well drilled was much smaller: about 7000 million, roughly a factor of three. The oil and natural gas are being used up, and it is necessary to drill more and deeper wells in order to find the same amount of oil. The discovery rate is clearly approaching zero. If I had used dollars instead of feet, the curve would have been even sharper, because the cost of drilling a million feet in 1940 was much less than in 1970. The millions of barrels per dollar spent would have been very much less in 1970 than it was in 1940. I feel, however, the drilling measure is better, since it reduces the role of the inflation and other factors. The data on Figure 2 indicate the real measure of the difficulty of new discoveries, that is, a measure of the exhaustion of the supply. An almost identical graph can be produced for natural gas in the United States. The same type of difficulty of discovery and exploration is occurring with natural gas supplies as with petroleum supplies.

Information about the world oil discoveries, excluding the USSR, Eastern Europe and China, is shown in Figure 3, which has time as an abscissa instead of feet of well drilled. Even though the number of feet of well drilled per year worldwide has increased, the actual global supplies are dropping. This information includes the extrapolation of the more recent discoveries from Alaska, the North Sea, etc., so you can see that the supplies are diminishing worldwide.

There is another method of measuring the oil reserve, or supply, which could be done through the price. Price, however, is not only a consequence of supply but also has in it some political or social decisions. The price reflects not only lack of supply but also the political factors which control the supply, in addition to the geological factors. The price history of oil, coal and natural gas is given in Figure 4. For about ten years the price stayed almost constant; it started up in 1971, with a trememdous increase occurring in 1973. The price is still rising. Prices will undoubtedly go even higher, and the extrapolations represent what the chemical companies use as projected future costs in order to construct factories based on those costs. There is hardly any question about what will happen to the price of fossil hydrocarbon in the next decade or two. There will, of course, be short-term price fluctuations, but the trend is clear.

The purpose of the last three figures is to try to convince you that our supply of fossil hydrocarbon is gradually being exhausted in spite of the comment that if we spend more money, more oil will be discovered. I think there is a limit as to how far that argument can be carried. The fossilized photosynthetic carbon is being consumed, and I doubt that there is any ambiguity about the evidence.

I want to show one more piece of evidence, from King Hubbert, who has been discussing this problem publicly for at least five years; that evidence is his famous diagram (Figure 5) of how the fuels, specifically coal and oil, come into and go out of use. If information on wood had been included, it would have shown that wood was the most important fuel about 1800; but consumption fell off as coal was discovered and then oil took over in the early twentieth century, so that by 1970 oil was the dominant source. However, by the year 200, the prediction is that oil will have peaked out. I believe King Hubbert is correct in his guesstimates: we may peak out before that time, and then the oil will be exhausted. The area under the dark region represents the total amount of oil which is available for use and, similarly, the area under the shaded region, marked coal, represents the amount of coal energy available for use.

Constraints on the Use of Coal as a Petroleum Substitute

You can easily see that there is an enormous amount of coal still available. This fact has induced the President of the United States to say last spring that we should devote our biggest effort to finding ways to use coal as an energy source in place of oil and natural gas. There are incentives now to induce industry to transform their power plants from oil and gas to coal, if it can be done. This is the reverse of the trend introduced thirty years ago, when industry converted from coal to oil and natural gas. Now that the relatively clean fuels are being exhausted the political planners of the United States are trying to reverse their use; I believe this actually will occur.

There are other constraints on coal which have only recently come to light, largely since people are beginning to think about the expansion of coal as a source of energy. It is not that these effects were unknown; it

is simply that the other constraints on the use of coal are being taken somewhat more seriously. The well-known effects are: (1) the environmental cost in terms of the land itself (strip mining) and (2) the environmental health aspect, which has been well established as a serious occupational hazard.

Some of you may recall what England looked like 50 years ago, when practically their entire energy supply came from the burning of coal. It was pretty black, particularly around Manchester, Birmingham, and the Midlands area. When I left the University at Minneapolis I went to Manchester, where I arrived on a Sunday night in 1935. It was very dark. Not only was it dark, but the buildings were all black. They were burning coal, and the ash and soot collected on the buildings; they had not yet learned to clean them up. When we returned to Manchester about ten years ago, the buildings had been cleaned; it was hard to recognize the city. The British have been going away from Coal for the last twenty years as an energy source. One of the consequences of burning coal is the production of soot. In more scientifically designed combustion chambers there is not as much soot produced, but the CO_2 problem is not eliminated. The particulates (carcinogenic hydrocarbons) that come out of the stacks can be reduced by better combustion processes or filtration. The one thing that cannot be done is to eliminate the carbon dioxide.

While I call your attention to the potential carcinogen production by extended use of coal (Figure 6), you must also recognize that it is possible to prevent that, at a cost. If coal is liquefied (for example, in a 25,000 ton of coal/day plant), the liquid will contain 200,000 pounds of polycyclic aromatic hydrocarbons and 10 lbs./day of benzopyrene, one of the most potent aromatic carcinogen-producing chemicals, whose mechanism of action we have some reason to believe we understand. This is not a completely insoluble problem, because at a cost the benzopyrene can be removed from the oil, or

it can be prevented from appearing. Natural petroleum in the ground contains 1-5 ppm of benzopyrene, while oil produced from coal contains 10-100 ppm, i.e. 10-20 times the concentration of the natural petroleum. We will need the coal plants for future energy supplies, but they need to be cleaned up.

We need all of the energy sources that can be called upon to fulfill the needs that will be forthcoming, not only nationally but globally. In the United States we will probably be "short" about 20 quads by the year 2000, it is estimated. You will recall that our total use in 1976 was about 70 quads, and it is projected that we will be short 20 quads by 2000. To give you some idea of the significance of that shortage: the shortage in 1974 as a result of the oil embargo was one quad. A shortage of 20 quads will be very large indeed. Therefore, we will need all of the sources we can call upon: coal, nuclear, solar.

Effect of Increased Carbon Dioxide Concentration in the Atmosphere

The longer-term global effects of increased coal consumption should also be recognized. When fossil carbon of any kind is burned, the carbon from the stored pool in the ground is converted to carbon dioxide which is released into the atmosphere. To close that cycle, the plants have to take the carbon dioxide from the atmosphere and reduce it again: one sink for the CO_2 which is put into the atmosphere is photosynthetic activity and the other is the ocean itself in the form of a calcium salt which dissolves in the ocean. As the carbon dioxide dissolves in the ocean, the calcium carbonate falls to the bottom. Both of these sinks, and perhaps others as yet unknown, are not keeping up with the rate at which CO_2 is entering the atmosphere. The evidence for this is contained in Figure 7, which gives the history of the carbon dioxide level at Mauna Loa Observatory in Hawaii over a sixteen-year period (1958-1974). In the winter the CO_2 level rises and every summer it falls, but only about half of the CO_2 entering in the winter comes out in

the summer. The net result is a constant and continuing rise of the carbon dioxide concentration each season. For example, there has been a rise from 315 to 330 ppm of CO_2 in the last 16 years. Similar results have been obtained from stations in the Arctic and the Antarctic. The cycles at the poles are not as sharp as at Mauna Loa (20^0 north), but they show the same percentage rise. We must extrapolate back for the previous hundred years, using carbon-14 measurement on tree rings; from that we can calculate the approximate CO_2 level for the previous hundred years. This method also indicates that the CO_2 level has risen another 15% from 1890 to 1958. In about one hundred years the level of CO_2 in the atmosphere has increased 15%; in the last 15 years it has increased 5%. It is rising much faster now than it did 100 years ago. There is no ambiguity about the fact that the rate of injection of CO_2 into the atmosphere is about twice as large as the rate of removal, and the injection rate is growing.

The consequence of the increase in carbon dioxide concentration is, as yet, theoretical, because the 5% change in level is still too small to permit unambiguous attribution of climatic consequences. Nevertheless, we know enough about carbon dioxide to be sure that the CO_2 is transparent to the visible light of the sun and opaque to the infrared light reflected from the earth. Therefore the CO_2 acts as a blanket over the earth's surface and one can expect that the heat load on the earth will increase. This so-called greenhouse effect is shown in Figure 8. When the sunlight strikes anywhere on earth (water or land), a fraction is turned into infrared light which is reabsorbed by the CO_2 and reflected downwards. One of the consequences of the rising CO_2 level is an increase in the average global temperature. We have seen the concentration of CO_2 increase over the past 15 years, but there has not been a clearly recognized corresponding change in the global climatic conditions. The meteorological models currently available are not sophisticated

enough to tell us what the climate should be, and what effect the CO_2 increase has now and will have. Also, the CO_2 increase is inside the "noise level" of the annual climatic fluctuations, so far; however, if we wait until the concentration has increased to the point where it becomes a noticeable factor in climatic change (using meteorological models), it will be too late to change the effect. The CO_2 concentration increase could change the entire worldwide agricultural production pattern on the earth's surface, and the pattern of living would be markedly different 100 years from now from what it is today.

MATERIALS AND ENERGY FROM THE SUN

The methods I prefer to use to increase our energy prospects are those which use the sunshine in some useful way, that will allow us to harvest the sunshine on an annual basis as it comes to the earth's surface, with a minimum environmental problem: no CO_2 problem, no carcinogen problem. Let us see what we can do using the sunshine which is a constant and annually renewable source. Figure 9 shows how the present-day sunshine is used on the surface of the earth, plotted in terms of green plant reducing carbon. The green plants catch the sun and reduce the carbon. This is particularly effective on the equator, where the plants are most productive. There, the green plants reduce 1 kg/m^2/year of carbon along the equatorial region, where the weather is warm and there is plenty of water. Other areas of the world which are warm, unlike the equatorial region, often have a problem with lack of water -- South Africa, Chile, the Southwest United States, and North Africa. It is not possible by ordinary methods to use the green plant as the factory in many of the semiarid areas of the world.

The distribution of sunshine in the United States is shown in Figure 10 in watts/m^2; it is obvious that the Southwest United States is the area of

choice. However, that area still does not have adequate supplies of water if we are going to use the best solar energy factory we have, namely, the green plant.

I wish to repeat that the best solar energy capturing mechanism we have is the green plant; we must learn how to use it in the most efficient way, both for itself and for the model it provides for synthetic devices. The photosynthetic carbon reduction cycle in shown in Figure 11. The plant captures the CO_2 from the atmosphere and, with the aid of sunshine, reacts with water, separates the hydrogen from the water, and reduces the CO_2. The CO_2 is first reduced to carbohydrate (sugar), where there is only one oxygen atom on each carbon atom. Eventually, some plants can take this carbohydrate and reduce it all the way to hydrocarbon, with no oxygen at all on the carbon atoms, which is essentially what petroleum is. Most plants store their sunshine as half-reduced carbon--carbohydrate: wood, cellulose of various kinds, sugar or starch. The sunshine enters the plant, is captured by the green chlorophyll, and the light-capturing step separates the charge on either side of a membrane. There is a positive charge on one side of the membrane and a negative charge on the other. The positive charge eventually shows up as molecular oxygen and the negative charge is active hydrogen which is used by the plant to reduce the CO_2 to carbohydrate. If there is no CO_2 available, some of the active hydrogen may show up as molecular hydrogen; there are plants that can do that. While most plants store the energy of the sun as carbohydrate, there are some that store their energy as hydrocarbons. It is this combination of chemical storage of the sunshine that I wish to discuss in further detail.

Sugar Cane

Let us talk first about the plants which store most of their energy as carbohydrate, which is the majority of the plants of the world. The classic

example of the efficient plant which produces fermentable sugar directly is the sugar cane of Brazil or the corn in Nebraska, both of which belong to the same family and both of which have the same kinds of efficiencies.

One of the steps in the preparation of sugar cane for harvest in Australia is shown in Figure 12, a sugar burn in Mackay, Australia. The cane is burned in approximately 10-acre plots at one time. The reason for the burn, just before harvest, is that the lower leaves are dense, dry, and very sharp; neither man nor machine can get into the cane fields while the dry leaves are still intact. The leaves are therefore burned off, leaving the stem (or stalk) of the sugar cane intact although dead. The cane is then cut and harvested within one day after the sugar burn. The sugar cane is then moved to the mill, where it is crushed with water, the water washing goes to the evaporator for extraction of sugar, and the cellulosic residue goes to the boilers where it is burned.

Therefore, in a sense, a sugar plantation is a self-contained energy farm; no new energy has to enter the system except the sunshine itself. The sugar cane captures the sun, stores a very large fraction of fermentable sugar or cellulosic residue, and the sugar mill uses both. Sugar is obtained by washing with water, steam is made by burning the cellulosic residues (bagasse), and the steam is used to run the machinery of the mill. There is excess steam from this process which is run through turbines to generate electricity. The factory collects the cane and generates sugar from the juice, alcohol from the molasses, and electricity from the excess steam. A sugar plantation really is an "energy farm" in the terms we have been discussing for some time.

As one example of a better method to utilize the ability of the plant to capture and store solar energy, the Brazilians have decided to use land which is capable of growing sugar cane in high yield as a method of "harvesting

the sun". The areas in which sugar cane is grown in Brazil are shown in Figure 13. The sugar from cane on these lands is converted into alcohol, the chemistry of which is shown in Figure 14. In converting the sugar to alcohol there is very little energy loss, so while the weight is reduced by a factor of two, very little of the energy is lost in that conversion. The Brazilians, who are the largest sugar cane growers in the world, have made the decision to try to fulfill some of their fuel and material demands through sugar cane.

The petrochemical industry in Brazil and throughout the world depends upon petroleum as its principal raw material. The route to renewable resources for the petrochemical industry in shown in Figure 15. You can see that the petroleum is refined to naptha and goes through the naptha cracker to ethylene; from ethylene, the carbon goes on to all other chemical raw materials.

Sugar cane can fulfill at least part of the need for chemicals for materials. The fermentation ethanol can be dehydrated over alumina to ethylene. Thus, it is possible to feed into the stream of petrochemicals via ethylene, which has its origin in sugar cane. Many other materials can be made from the cane juice by different types of fermentation processes. Eventually these alternative processes will become more significant as a source of chemicals than they presently are.

Sugar cane, in its unusual condition of going to seed, is shown in Figure 16. This photograph was taken in front of the sugar museum in Maceio, Brazil. This same plant is now becoming one of the major sources of chemical raw materials in Brazil. In November of 1975 the Brazilians, realizing that they had no accessible petroleum source of naptha for their ethylene or, for that mater, for their gasoline, decided that they would encourage both new plantations for sugar cane and new fermentation facilities

to make alcohol directly from the sugar cane juice. To do this, they provided government loans at low interest. They decided to manufacture ethanol from their cane juice. Approximately seven or eight tons of raw sugar were produced in 1974, which yielded 700 million liters of 95% alcohol by fermentation of the residual molasses. It is entirely possible that Brazil will achieve its stated goal by 1980, because of the remarkable rate at which they are constructing new fermentation facilities and the rate at which new sugar cane acreage is being introduced, especially in the San Francisco River region and other parts of northeastern Brazil (Figure 17). It should be noted that one of the main economic factors which has made this transformation of sugar cane from food to fuel possible in Brazil is the availability of large amounts of relatively inexpensive land which can be machine-cultivated to produce the cane. The sugar cane-alcohol-cellulose-sugar cane cycle on the large self-sufficient sugar plantations is efficient and cost-effective.

It appears that most of the industrial alcohol of Brazil is made by the fermentation of the molasses which remains after the crystalline sugar has been removed. This constitutes one of the most efficient ways to convert fermentable sugar into a liquid fuel which can be used in the internal combustion engine or as a chemical raw material.

Gasohol

In the United States we have practically no fermentation industrial alcohol at the present time. This method of making alcohol went out of style about 1950, when it became possible to obtain industrial alcohol by adding a water molecule to ethylene, having obtained the ethylene from naptha. It now appears that we might return to the earlier methods of making industrial alcohol because of our lessened petroleum reserves. In some parts of the United States this kind of development is already occurring.

You may recall that in the oil embargo days of 1973-74 there was a note in one of the U.S. newspapers that the legislature of the State of Nebraska had passed a law reducing the state tax on gasoline if is contained as little as 10% fermentation alcohol. The reason for this legislation was that the storage facilities for corn were strained, and a substantial percentage of the corn crop spoiled that year and could not be used for food. The spoiled corn was taken to make fermentation alcohol which was added to gasoline (gasohol). This program was very successful. The State of Nebraska now has a program to show that the production of "gasohol" is an economic process even today. The chemical engineer (Prof. William Scheller) in charge of this particular program at the University of Nebraska has produced a chart showing the consequences of various uses of corn in Nebraska. If 100 bushels of corn grown on one acre of land is fed to cattle, a weight gain of about 480 pounds results. If, instead, the 100 bushels is split into 80 bushels and 20 bushels, and the 20 bushels is fermented to alcohol (60 gallons, approximately) with the remains of the fermentation, the distilled dry yeast (about 300 pounds) now added to the 80 bushels of original unfermented corn and fed to the cattle (i.e. the original 80 bushels plus the 300 pounds of distiller's dry yeast) will yield in this latter process 520 pounds of meat instead of 480 pounds. Thus, 60 gallons of fermentation alcohol and 50 pounds of additional meat is created by diverting 20% of the corn to the fermenter. The process of converting the starch to alcohol also involves the creation of yeast protein. That is the single factor which makes the difference: the yeast protein can be fed to cattle in place of the 20 bushels of corn which has been diverted for fermentation, resulting in both products.

A few months ago there was a headline in a Nebraska newspaper to the effect that the Nebraska legislature was seeking to reduce the acreage for

the corn crop by 10% by using farm support mechanisms. This seemed a poor choice. If, instead, that same amount of money were invested for the construction of fermentation plants with a concomitant increase in the capacity for production of "gasohol", the price of corn would remain at a higher level, andalso a capital expenditure would have been made which would create a permanent market for the raw material, i.e. corn. I feel this process of using part of the corn production to create fermentation alcohol for fuel additive has a real possibility of success in Nebraska, Iowa and other such areas. This may be our first real breakthrough in terms of solar energy conversion in the United States -- liquid fuel production and chemical raw materials production.

Rubber

I have previously mentioned that some green plants do indeed store their energy as hydrocarbons, and the one plant that comes most immediately to mind is the Hevea rubber tree. The rubber tap from a Hevea tree is shown in Figure 18, and the latex produced is hydrocarbon. The hydrocarbon from the Hevea latex is an example of a green plant which has reduced the carbon all the way to hydrocarbon.

The idea that plants which contain hydrocarbon-like materials such as latex from Hevea which could be used as a source of hydrocarbons and materials gave rise to the work which is currently underway in our laboratory. Another more personal reason was that we had on our ranch in Northern California plants (members of the Euphorbiaceae family) which do contain latex similar to that from Hevea, although chemically it is not quite the same. This turned our minds to the whole family of plants to which the Hevea belongs, the Euphorbiaceae. Another genus, Euphorbia, has about 2000 to 3000 different species. We then began our search for some species of Euphorbia which would grow in the dry, semiarid lands of various parts of the United States.

Guayule

There are other latex-producing plants in addition to the Euphorbiaceae. There is a member of the Compositeae family known as guayule which grows in the northern deserts of Mexico and in the southern United States. This desert shrub is known to produce a high molecular weight hydrocarbon which could be used as natural rubber. During World War II, when the supply of natural rubber from Malaysia was cut off, efforts were made (especially in California and other areas of the western U.S.) to grow guayule as a source of rubber. Because of the concurrent development of synthetic rubber, however, it was not deemed feasible to continue the development of guayule for this purpose after the war; and the efforts, at least in the United States, ceased.

However, the Mexican government has recently instituted once more the development of guayule plantations, in the northern areas near Saltillo; and the production of guayule in this region has markedly increased. The interest in guayule in Mexico and elsewhere in the southwest has increased to the point where several international conferences have recently been held with a view toward bringing together the experts from various disciplines to focus on the problem of improved plants, increased production, and other aspects of a project of this type.

Guayule is a desert bush, growing in semiarid regions, a photograph of which is shown in Figure 19. It cannot be tapped, as Hevea, and for harvesting the bush is taken out of the ground (like sugar cane) to extract the rubber-like material. The rubber in guayule is not in tubules as in the bark of Hevea. The rubber droplets are captured individually in individual cells, and every single cell has to be broken to extract the rubber. The plant grows to a height of about three feet, then pulled out of the ground for harvesting. In Mexico they are currently harvesting the wild plants.

I am discussing guayule not because it is a source of hydrocarbon for us in the southwest United States but as a source of rubber. The Firestone Company has about 100,000 acres in west Texas which it intends to devote to guayule cultivation for rubber production. Guayule is already a commercial crop in Mexico and will, of course, become commercial in the United States soon in the same type of area which we are exploring for the production of oil-producing plants.

Euphorbias

While we were in Brazil two years ago looking at the Hevea and the sugar cane, we observed another plant growing around the sugar cane plantations. This plant, the Euphorbia tirucalli, is shown in Figure 20 and is popularly called the African milk bush. It is a latex-bearing plant which has also been found to grow well in southern California; it probably would also grow well in Arizona and Texas. The E. tirucalli is another candidate for a hydrocarbon-producing plant, the latex in this case being somewhat similar to that of other Euphorbias.

In the course of our travels we visited Puerto Rico in the spring of 1977, where we attended an energy conference at the University of Puerto Rico. The Puerto Ricans wanted to begin the development of solar energy using their capabilities, but they were thinking in terms of sugar cane, an important crop there, and using it to make fermentation alcohols in a way similar to what has been done in Brazil. We visited the dry side of the island in search of other species of Euphorbias which might be candidates for hydrocarbon production. We found Euphorbia lactea, which grows to a height of 10-15 feet. A knife inserted into the bark of the tree produces a flow of latex in a manner similar to that for Hevea (Figure 21). We have examined that latex chemically in the laboratory and are becomming somewhat familiar with the chemical composition of latexes from various species of

Euphorbias collected from all over the world. It is clear from these tests that there are at least two major candidate families for this purpose, the Euphorbiaceae and the Asclepiaeceae, with individual plants in the family Sapotaceae and Moraceae as well.

PETROLEUM PLANTATIONS

I would now like to discuss what we have done in terms of cultivation of oil-producing plants. Some of the plants which I have discussed as possible candidates (E. tirucalli and E. lactea) are trees which take several years to reach harvestable maturity. We finally chose the Euphorbia lathyris (gopher plant), which is an annual, for the first experiments with cultivation in Southern California. The petroleum plantation is shown in Figure 22; these plants (about four feet high) achieved their development in seven months (they were planted from unselected seed in February 1977. We are able to obtain a yield plot for the E. lathyris by cutting individual plants, weighing them, and measuring their hydrocarbon content. The yield data on the first plot is shown in Figure 23 for E. lathyris, for the growing season of February to September.

The overall view of the petroleum plantation is shown in Figure 24. Two different species of Euphorbias have been planted, the E. tirucalli and the E. lathyris. The former is a perennial and the latter is an annual. This planted area is the beginning of a horticultural experiment where wild plants are being cultivated under controlled conditions. Our intent is to grow the plants under different conditions: different seasons, different irrigation requirements, etc., to obtain yield data.

The yield rates for E. lathyris have been converted into equivalents of barrels of oil at 8% by weight. The plant is actually more like 10% by weight oil, but 8% has been used because it is unlikely that all of the

oil can be extracted from the plant material. Using a figure of 8% yield by weight converts to about 10 barrels of oil/acre/year, which is a minimum yield .

Hydrocarbon Construction in the Plant

The oil from the E. lathyris extractions is an isoprenoid similar to rubber, the difference being that when water is taken away from rubber latex a solid remains. This is because the molecular weight of that polyisoprene in the case of Hevea brasiliensis is between one-half million to two million. On the other hand, when water is removed from the E. tirucalli latex, a liquid remains, the molecular weight of the isoprene being much less than that for rubber. Figure 25 shows the molecular weight distribution of polyisoprenes isolated from Hevea brasiliensis and Euphorbia tirucalli, using the method of gel permeation chromatography. This molecular weight distribution is bimodal for a particular clone. The molecular weight for E. tirucalli latex is about 20,000. All of the Euphorbias which have been described in the literature produce an isoprene-like material. There are cyclic isoprenes as well, such as terpenes, diterpenes, sterols, etc., which represent about one-half of the hydrocarbon in the emulsion.

The chemical mechanism for the plant's conversion process of carbohydrate into isoprenoid hydrocarbons is shown in Figures 26 to 28. We think that we know all of the chemical steps involved in building these large molecules, and we will eventually want to modify the plants genetically so that they will produce molecules "to order" so to speak and not in the random natural fashion.

The carbon cycle (Figure 11) shows that carbohydrate is created by taking carbon dioxide through the cycle; the carbohydrate then produces pyruvic acid, which is essentially the first carbon-fixation product of the plant which has been modified to be sure with the same redox level as

glyceric acid. The pyruvic acid loses a carbon dioxide molecule, to give acetyl CoA (four carbons) two of which condense to create acetoacetyl CoA. A third acetyl coA goes on the carbonyl function to make a tertiary alcohol, leaving one of the acids free. This is reduced via CoA to mevalonic acid (Figure 26), which then goes through a series of steps via phosphorylation on the primary alcohol group and finally dehydration and decarboxylation (Figure 27) to isopentenyl pyrophosphate (IPP), a five-carbon containing compound, from which the polyisoprenes are constructed. The IPP is then isomerized to dimethylallyl pyrophosphate, producing an allylic pyrophosphate which can drop the pyrophosphate and become a carbonium ion which reacts with another to create a diterpene (Figure 28). This reaction can continue, to build up the chain. The reason for pointing out the mechanism of polyisoprene manufacture (Figures 26 to 28) is to indicate that every one of the enzymes involved in going from carbon dioxide to hydrocarbon is known, probably not well enough to modify their action, but we have the beginning.

The question arises as to what factors determine the length of the chain that is to be constructed and what factors make the chain elongation cease. My belief is that these events occur in an oil (rubber) droplet, which is actually an emulsion polymerization. On the end of the chain is a pyrophosphate with an allylic double bond; the terminal of the long chain being made from the rubber (oil) droplet itself. There are also detergents in the oil emulsion which stabilize the droplet. This incipient carbonium ion then reacts with the electron pair of the IPP to form a carbon-carbon bond; then the proton is removed, and the result now is a polyisoprene with a longer chain.

A chain elongation cannot occur without a catalyst of some type, and not much is yet known about the catalyst. It probably is a transition metal complex of some kind whose character has yet to be identified or determined.

The shape and activity of the catalyst is determined, I believe, by the radius of curvature of the rubber (oil) droplet. As the droplet grows with the increasing molecular weight, the radius of curvature decreases, which could change the activity of the catalyst. In other words, the catalytic action shuts down at a certain size. This may be the physical method by which the green plant determines the molecular weight. Each strain of plant differs from others by either the detergent which is used to stabilize the micelle, or in the nature of the catalyst, or both.

The frontier of this work on the rubber and the polymerization of isoprenes is now at the point where it is necessary to discover the nature of the catalyst, on the one hand, and the chemical composition of the detergent, on the other. We know that the molecular weight of the polymerization reaction is determined by the particular strain of plant, and we must now examine the catalyst and the detergents which are critical to understanding the molecular weight distribution of latexes from the plants.

We can eventually modify the hydrocarbon molecular weight to come down into the few thousand region. We also want to reduce the degree of unsaturation, i.e. put more hydrogen in, thus "engineering the cells" of the plant to have them create the desired chemical products. I suspect that our yields will not be limited to the unsaturated hydrocarbon, which is what the plants produce today in the natural state. The yield of desired products from the plants which will be cultivated could undoubtedly be raised substantially, by selecting seeds properly, even without "cell engineering".

When I showed the yield data to representatives of people experienced in plant breeding, they predicted that with proper seed selection the yield from these hydrocarbon-producing plants could be raised to 20 barrels of oil/acre/year. There is no doubt that when any selection program is started on the wild plants that the yields will immediately double. We recently

visited the petroleum plantation and observed that in some of the plots the plants are growing at a more rapid rate than in others. Therefore, the growth rate is variable, and it will be possible to select the faster growing plants and seeds for continued cultivation.

As an example of improved production through breeding, I would like to cite the Malaysian rubber story. After the end of World War II, during which time synthetic rubber had been developed in the United States and Western Europe, the Malaysians became aware that the market for natural rubber had disappeared, until its price became competitive with the synthetic products. Up until then, the yield per acre for rubber was 200 lbs/acre/year. By 1965 the commercial production of rubber had risen to 2000 lbs/acre/year, an increase by a factor of ten in 20 years. There are now plots in Malaysia which produce 4000 lbs/acre/year of rubber and individual trees which if they were grown at the same density, would achieve a production of 8000 lbs/acre/year. I mention this development to show that I have no doubt that the yield of oil from hydrocarbon-producing plants can be doubled in three generations.

Current Status of Search for Renewable Resources

The type of exploration described above gives two practical approaches to renewable resources: (1) to use the hydrocarbon as it comes from the plant itself (the 2% to 10% by weight) as a crude oil, refine it, rescue the sterols which it contains, crack the rest of the compounds to ethylene, propylene, etc. and then reconstruct the desired chemicals from those products. I feel that this particular approach can be developed immediately. (2) To learn how the molecular weight is controlled and manipulate the plant to construct materials of the desired molecular weight for whatever purpose is desired. This approach will be longer and more complex, using the plant as the collecting and constructing vehicle.

The hydrocarbon-producing plants which have been described earlier can be grown on land which is today nonproductive. There is a great deal of land of this type in the United States and other areas of the world. This cultivation of hydrocarbon-producing plants can be started almost immediately even without genetic improvement of the plants, using the plants as they are in the wild condition. We have begun our experimental planting in Southern California toward this end.

When you talk to professional horticulturists about these plants (the Euphorbias), they know nothing about the methods of large-scale cultivation because they have never before been planted as a "crop". It is as though we were back in the Stone Age learning how to domesticate wild plants, like the beginnings of the cultivation of sugar cane, wheat, corn, etc. several thousand years ago.

We are try ing to introduce an entirely new plant(s) as a commercial crop, which requires a great deal of thinking of a type which the professional agriculturalists do not usually do. Their role is to improve the crops already available (wheat, corn, rice, sugar, etc.), and it is difficult for them to assimilate the concept of an entirely new crop(s). They are bothered by such factors as the type of fertilizer to be used, yields per acre, amount of water for irrigation, type of soil, amount of sun, etc. The answers to questions of this type are generally not well known for wild plants. One of the purposes of the "gasoline tree plantation" in Southern California is to get some initial answers to some of the practical questions regarding cultivation of these species of plants.

Economics of the Petroleum Plantation

What does the production of hydrocarbons from plants mean in terms of the present energy situation? How much can the production of hydrocarbons from a new source help fulfill our needs? As you are aware, the price of

oil today is an artificial one, not less than $14/barrel, and this price will surely rise. What would be the costs of producing crude oil from plants? We are trying to use land which does not produce anything today, i.e. nonproductive in the sense that agricultural land is productive. We have selected plants which will grow in dry, semiarid areas of the United States and other parts of the world. My agricultural colleagues have informed me that one acre of this type of plant could be grown for about $100. Our extraction method, which I have described to my chemical engineering colleagues, projects a cost of about $10/barrel. If it costs $100 to grow the material for 10 barrels of oil and $10/barrel to extract and produce the oil, then the cost of this type of hydrocarbon would be $20/barrel today. If the yield of hydrocarbon could be improved by a factor of two or three and if the extraction process itself could also be improved, the price of this material is already on the edge of being practical. If the costs of petroleum rise another 10% to 20%, the use of hydrocarbon-producing plants, especially for feedstock materials, will become practical from an economic point of view. The development of the concept of the petroleum plantation and the cultivation of hydrocarbon-producing plants is only one type of development.

ARTIFICIAL PHOTOSYNTHESIS

Earlier I mentioned how the green plant uses a membrane to separate a positive charge on one side and a negative charge on the other. We are learning more about that process, which is another important consequence of our study of how the green plant captures the energy of sunlight. This concept involves eliminating the plant entirely and reproducing the capturing apparatus of the quantum, e.g. capture the quanta and store it in some useful fashion. This process could eliminate the plant and the quality

of the land, and would require merely the energy of the sun. In order to develop methods for synthetically capturing the energy of the sun (which is done in the plant by chlorophyll), we need to learn in greater detail the mechanism of the quantum conversion process. When the energy of the sun is picked up by the chlorophyll in the plant, a charge separation occurs at that point; we know some of the details about this, and we are now trying to learn the mechanism of that process as well.

The actual quantum conversion process in the plant takes place in the chloroplast. The chlorophyll-containing proteins which capture the quanta are actually in the membranes. We know that the light is acting on a membranous structure which separates the oxygen side from the hydrigen side of the energy conversion. It should be noted that the green plant itself can separate the oxygen and hydrogen, and if no CO_2 is present some plants actually have the ability to generate hydrogen.

The ideal of constructing an artificial membrane (modeled on the natural membrane in the chloroplast), putting the correct materials on it with oxygen evolution on one side of the membrane and hydrogen (or methane) evolution on the other, is what we are attempting to do in the laboratory. To do that, we need to know the materials from which the membrane is constructed. There is, of course, chlorophyll, but there are many other substances as well. Our experiments indicate that there are iron-containing compounds on the other, where oxygen is generated. It appears that there is a lipid membrane inbetween to separate the hydrogen from the oxygen.

The relationship between the natural photosynthetic electron transport membrane (top) and various forms of synthetic systems which are being organized to perform part or all of the quantum conversion process that the green plant performs is shown in Figure 29. Each of the systems noted here is under study and development in at least one laboratory throughout the

world, and most of them are being examined in many different laboratories. With these basic ideas, we can begin the design of a synthetic membrane (Figure 30). On each side of the phospholipid membrane there are sensitizers (S_I, S_{II}) which represent the chlorophyll molecules of various types. The excited molecule ejects an electron to an acceptor (X) and the acceptor then hands the electron to an iron-containing compound which reduces the proton to molecular hydrogen. The proton comes from the left side of the membrane, where the hole that is left (S_{II}^+) takes an electron away from the manganese to make high-oxidation state manganese which then oxidizes the hydroxide ion to molecular oxygen. In that process it is reduced to the original manganese redox level again. We thus have an iron catalyst on one side of the phospholipid membrane and a manganese catalyst on the other, the manganese catalyst producing the oxygen and the iron catalyst producing the hydrogen. At present we have some information about the iron catalyst but very little information on the manganese catalyst.

When it is possible to determine the type of surfactant dyestuff to insert, it will be possible to construct a synthetic membrane and mount the entire quantum conversion apparatus on a hollow fiber, creating hydrogen on the inside and oxygen on the outside of the fiber. We would then have achieved a synthetic hydrogen-producing device which will not require land, i.e. a hydrogen-generating solar machine. This development is really not so far away, and it may be possible, using the same principles, to construct a methane-generating solar machine.

With the development of a "synthetic" solar energy capturing apparatus it should be possible to make almost any materials we need, by reducing carbon dioxide (directly or indirectly); these materials would be fuel or chemical raw materials. I believe this idea is one which can be brought to fruition within five to ten years.

SUMMARY

It thus appears that the first and immediate possibility for the development of an economically useful solar energy and materials system is an outgrowth and, in a sense, a return to an older system, that is, the use of the best existing solar energy capturing source we know -- the green plant -- by selecting and modifying it to produce the materials we would like to have, namely, hydrocarbons of suitable molecular weight and structure. The choice of the particular plants with which to begin such a large-scale development has yet to be made and will depend upon growth rates and habits, hydrocarbon productivity and harvest adaptability. We are already, of course, capable of growing a carbohydrate-storing plant (sugar cane) and converting the fermentables into convenient form (alcohol).

Finally, in the longer term as we learn more about the quantum converting apparatus of the green plant, we should be able to construct such an apparatus synthetically, thus being liberated from the agricultural limitations which the growing of a natural and complete plant places upon us. A synthetic system is already visible in principle which would capture and convert solar energy into a stream of hydrogen (using only water as its raw material), which could be inserted into our present fuel and materials systems with a minimum of difficulty.

REFERENCES

General References

1. Hall, D. O. (in press, 1978). Solar Energy Conversion through Biology--Is It a Practical Energy Source? J. Inst. Fuel.
2. Stanford Research Institute (1974)."Effective Utilization of Solar Energy to Produce Clean Fuel", report June 1974.
3. The Royal Society (1974). "Energy in the 1980s". London, England
4. Wilson, C. L. (ed). (1977). "Energy: Global Prospects 1985-2000". McGraw-Hill, New York.
5. Carr, D. E. (1977). "Energy and the Earth Machine". W. W. Norton, New York.
6. Halacy, D. S., Jr. (1977). "Earth, Water, Wind and Sun: Our Energy Alternatives". Harper & Row, New York.
7. Brinkworth, J. (1976). "Solar Energy for Man". John Wiley and Sons, New York.
8. Buvet, R., et al. (eds). (1977)."Living Systems as Energy Converters" Elsevier, Amsterdam.

Specific references in a given area of discussion in the paper are given below.

Sugar Cane

1. Inojosa, E., (ed). (1976). Acucar e Alcool: Um Grande Projeto Economico do Brasil. APEC/COPERFLU, Rio de Janeiro.
2. Kelly, F.H.C. (1977). A Feasibility Study of the Production of Ethanol from Sugar Cane; private communication.

Gasohol

1. U.S. Senate, Republican Conference (1977). Alcohol: The Renewable Fuel from Our Nation's Resources.
2. Scheller, W. A. (1977). GASOHOL: Food and Fuel for the Future. University of Nebraska, Omaha.

Rubber

1. Agricultural Research Service, U.S. Department of Agriculture (1967). Plants Collected and Tested by Thomas A. Edison as Possible Sources of Domestic Rubber. Report ARS 34-74, July 1967.
2. Hall, H. M. and Long, F. L. (1921). "Rubber Content of North American Plants". Carnegie Institution of Washington, Washington, D.C.
3. Vanderbilt, B. M. (1971). Rubber from Goldenrod. In "Thomas Edison, Chemist (Chap. 9)". American Chemical Society, Washington, D.C.
4. International Rubber Conference, Kuala Lumpur, Malaysia, Oct. 1975; proceedings.

Guayule

1. National Academy of Sciences (1976). Guayule: An Alternative Source for Natural Rubber.
2. McGinnies, W. G. and Haase, E. F. (eds). (1975). International Conference on Utilization of Guayule. University of Arizona, Tucson.
3. Campos-Lopez, E. (ed) (1978). International Guayule Conference, Saltillo, Mexico, 1977; proceedings.

Petroleum Plantations

1. Calvin, M. (1977). Energy Res. 1:299.
2. Calvin, M. (1977). In "Living Systems as Energy Converters", R. Buvet et al. eds., Elsevier, Amsterdam, p. 231.
3. Nielsen, P. E., Nishimura, H., Otvos, J. W. and Calvin, M. (1977). Science, 198:942.
4. Calvin, Melvin (1977). Chem. Tech. 7:352.
5. Calvin, Melvin (in press, 1978). Pure & Applied Chemistry.

Artificial Photosynthesis

1. Porter, G. and Archer, M. D. (1976). Interdisciplin. Sci. Rev. 1:119
2. Matsuo, T. (ed) (1978). Proc. symp. on "Biomimetic Chemistry", Kyushu University, Sept. 1977.
3. Calvin, M. (1978, in press). Accts. of Chem. Res.

U.S. ENERGY FLOW – 1976

(PRIMARY RESOURCE CONSUMPTION 72.1 QUADS)

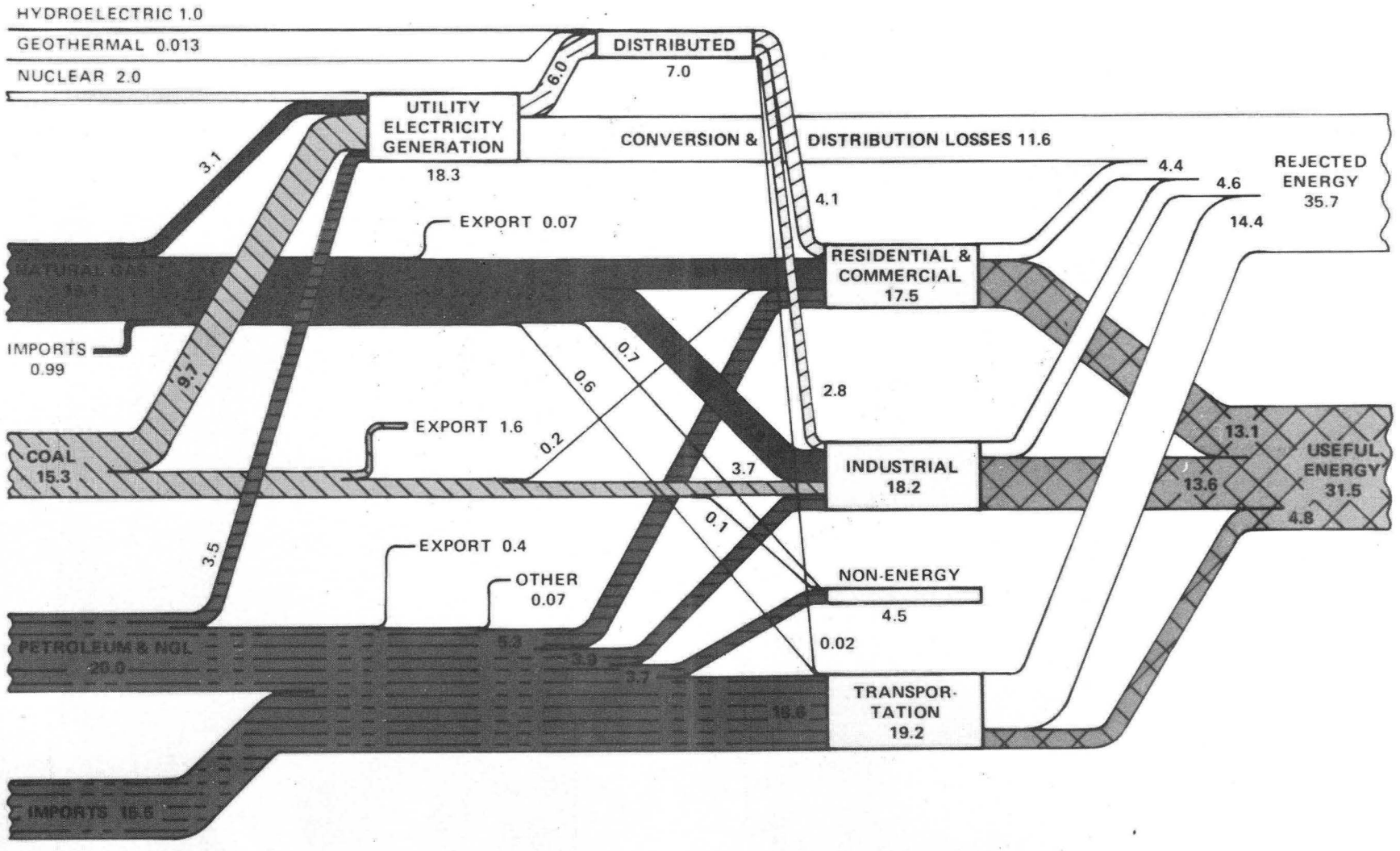
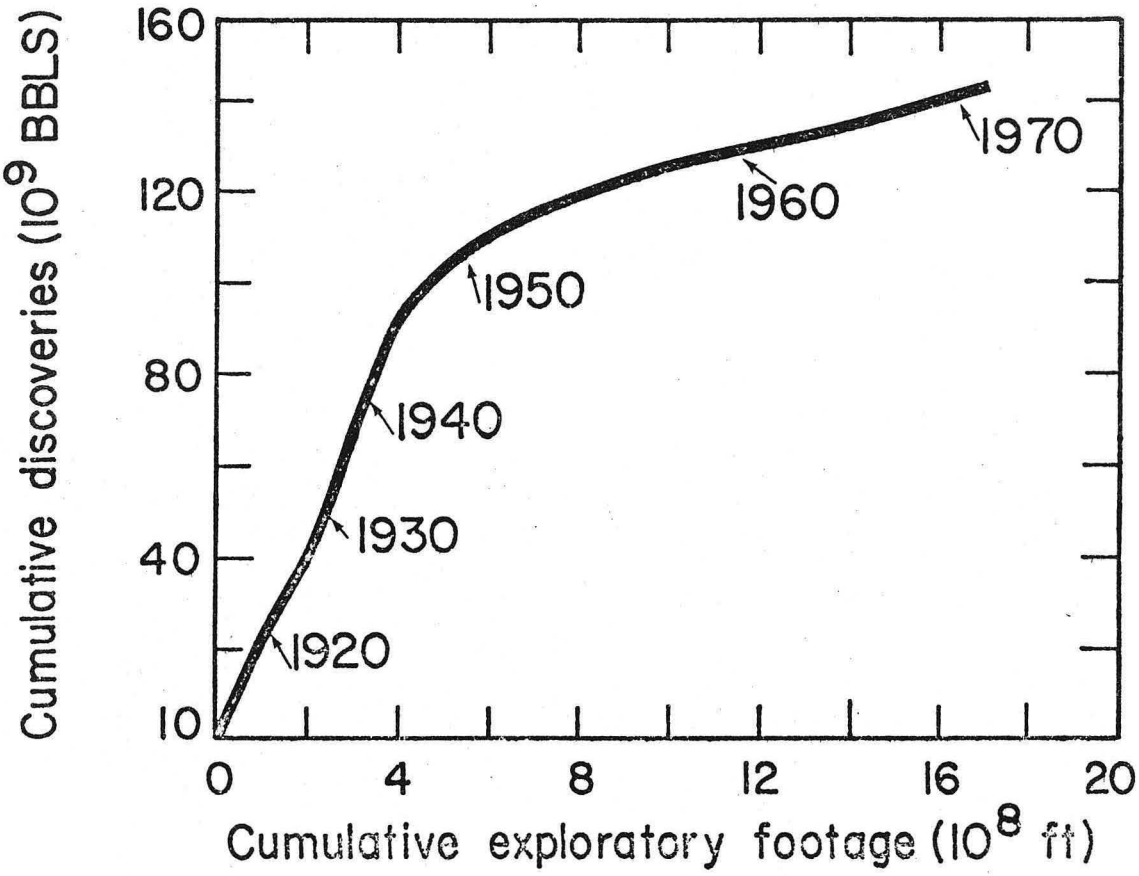


Fig. 1 U. S. Energy Flow, 1976

XBC 776-5733

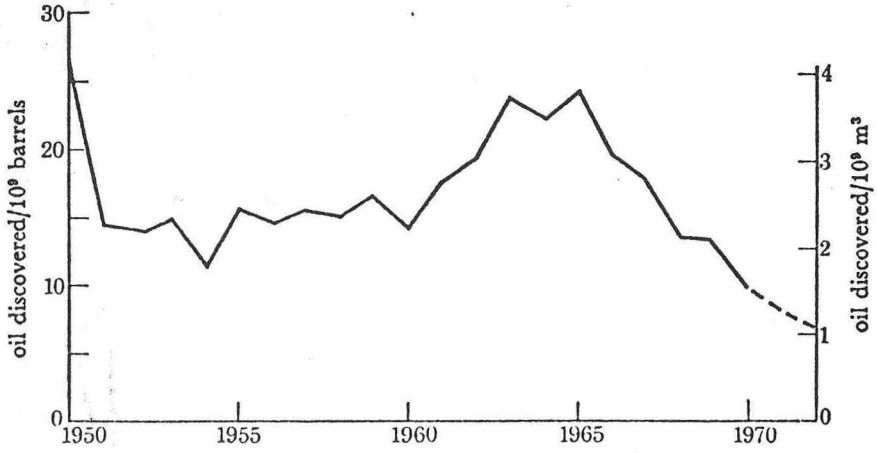


Cumulative U.S. crude-oil discoveries as a function of cumulative depth of exploratory drilling. (King Hubbert, 1974)

XBL 776-4467

Fig. 2

Cumulative U.S. Crude Oil Discoveries as Function of Depth of Drilling



World oil discoveries, excluding U.S.S.R., Eastern Europe and China – 5-year running mean.

XBL 776-4465

Fig. 3
World Oil Discoveries

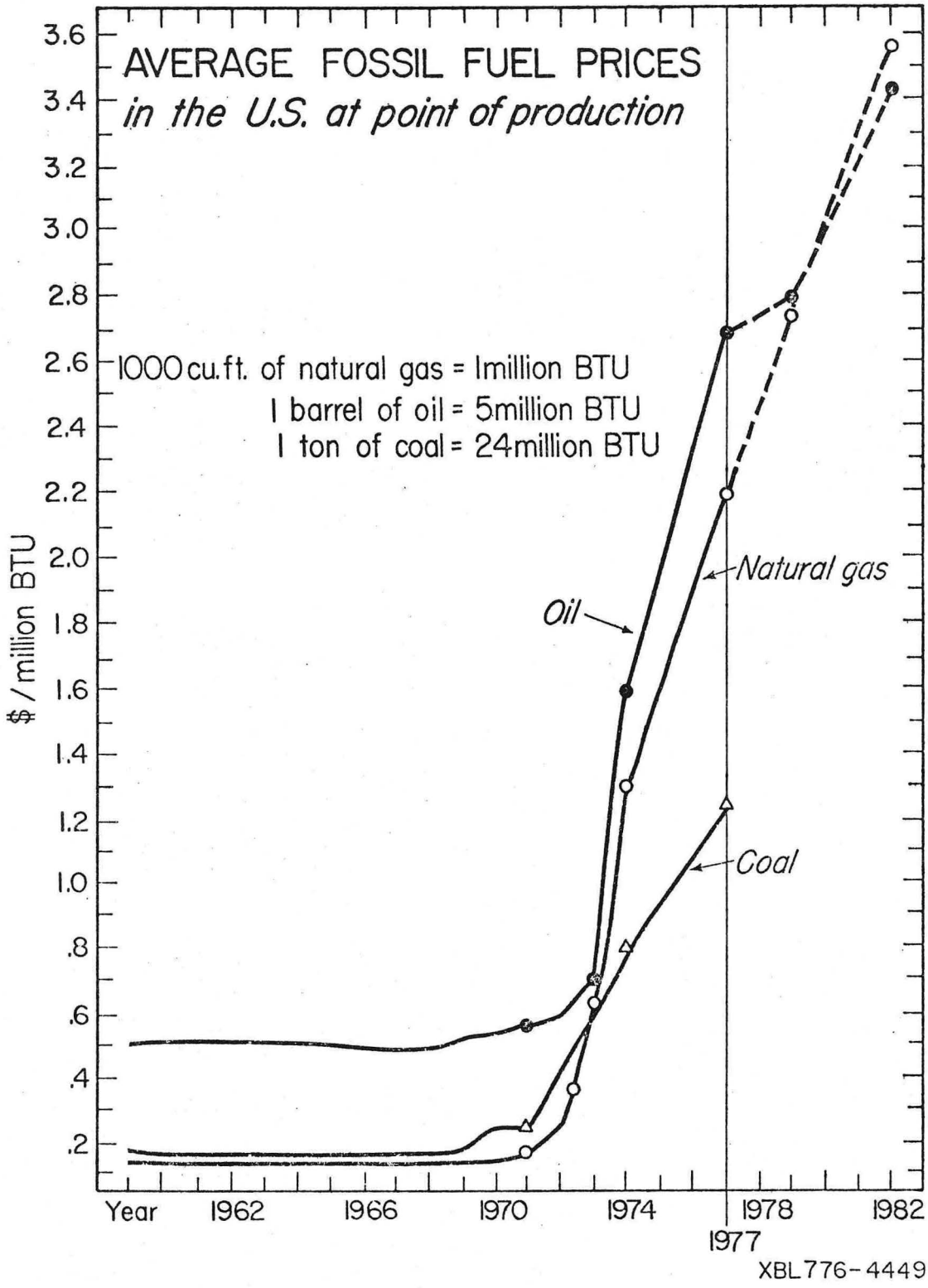
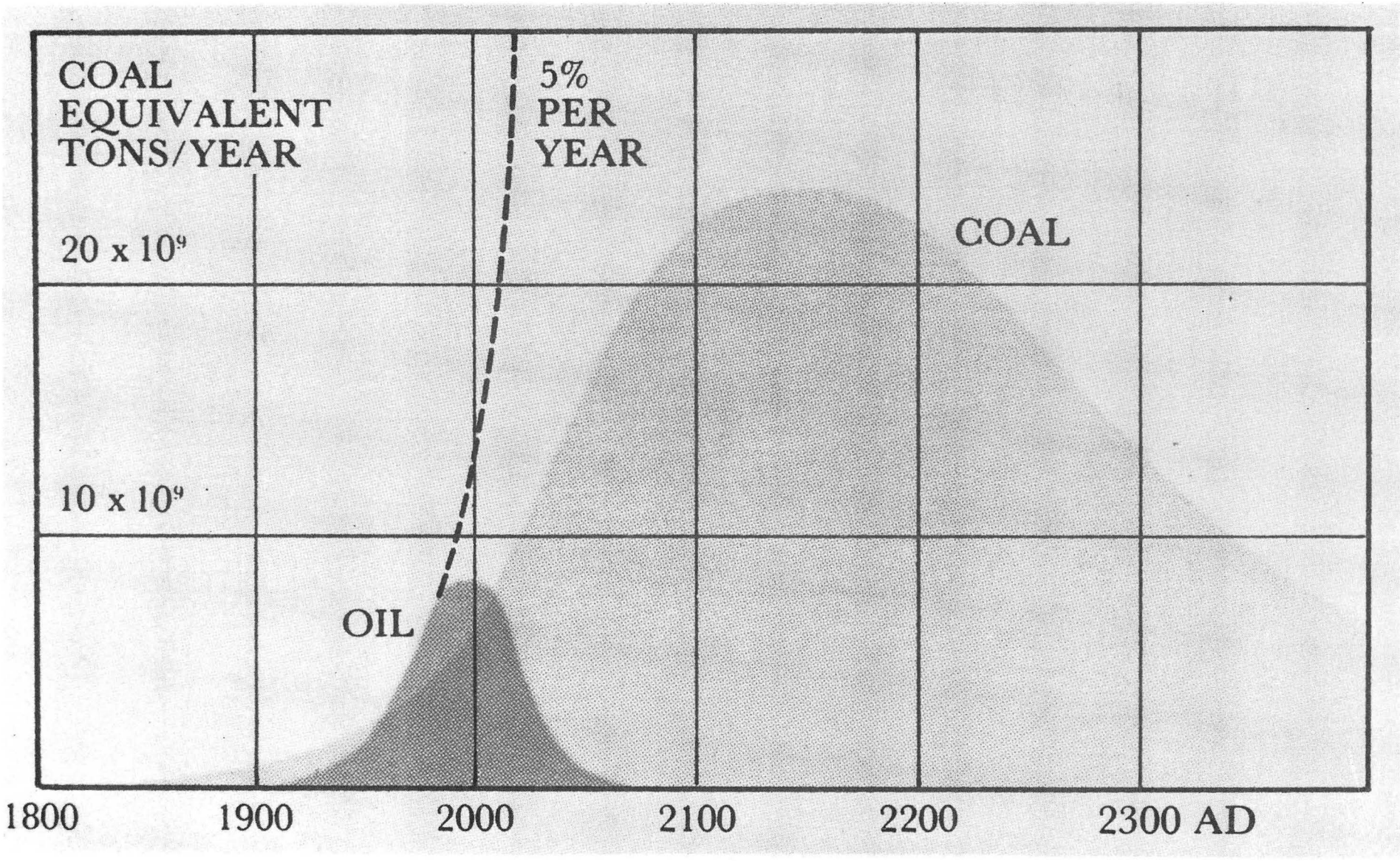


Fig. 4

Average Fossil Fuel Prices in
U.S. at Point of Production



XBB 778-7577

Fig. 5 Oil and Coal Use Cycles

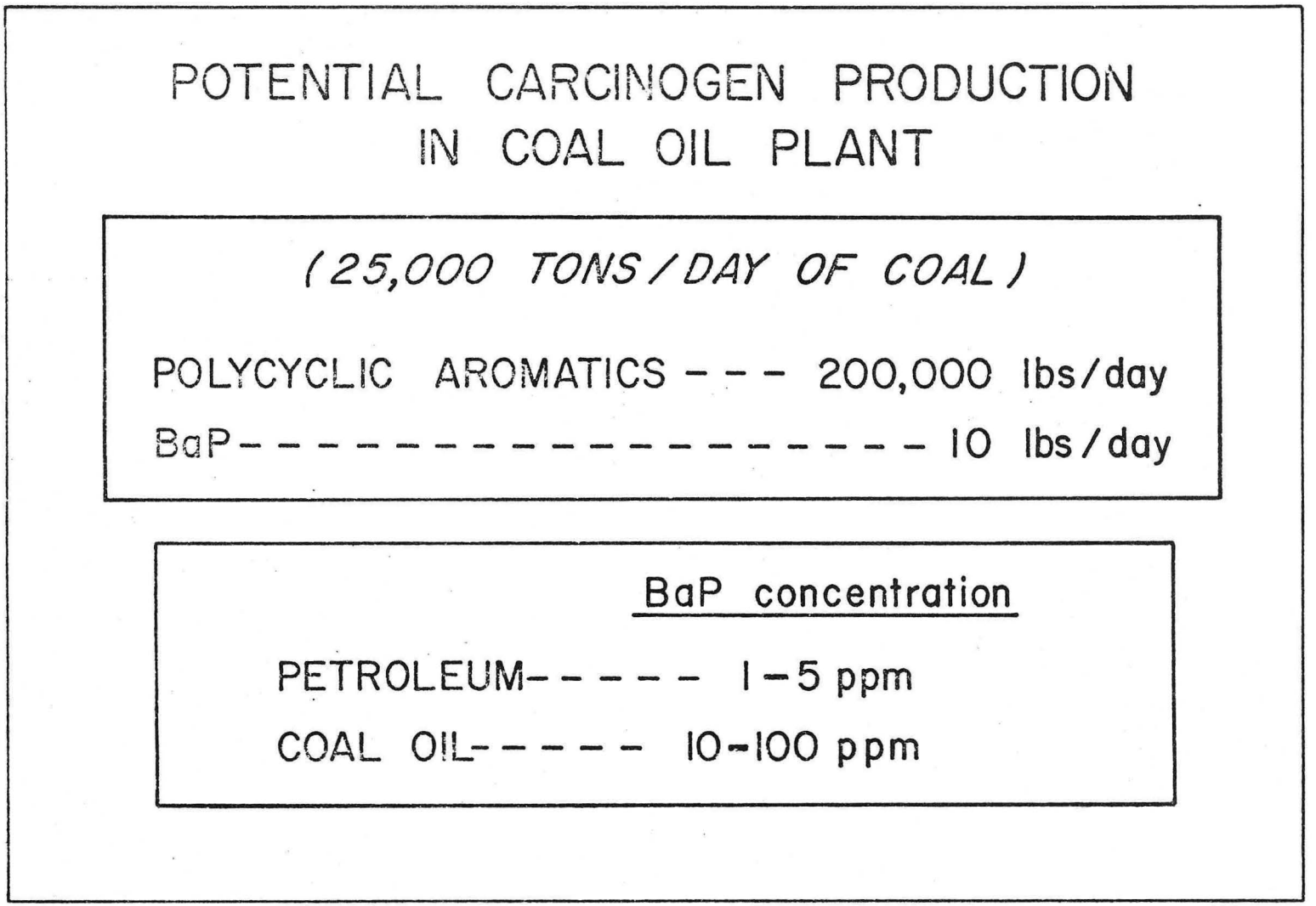
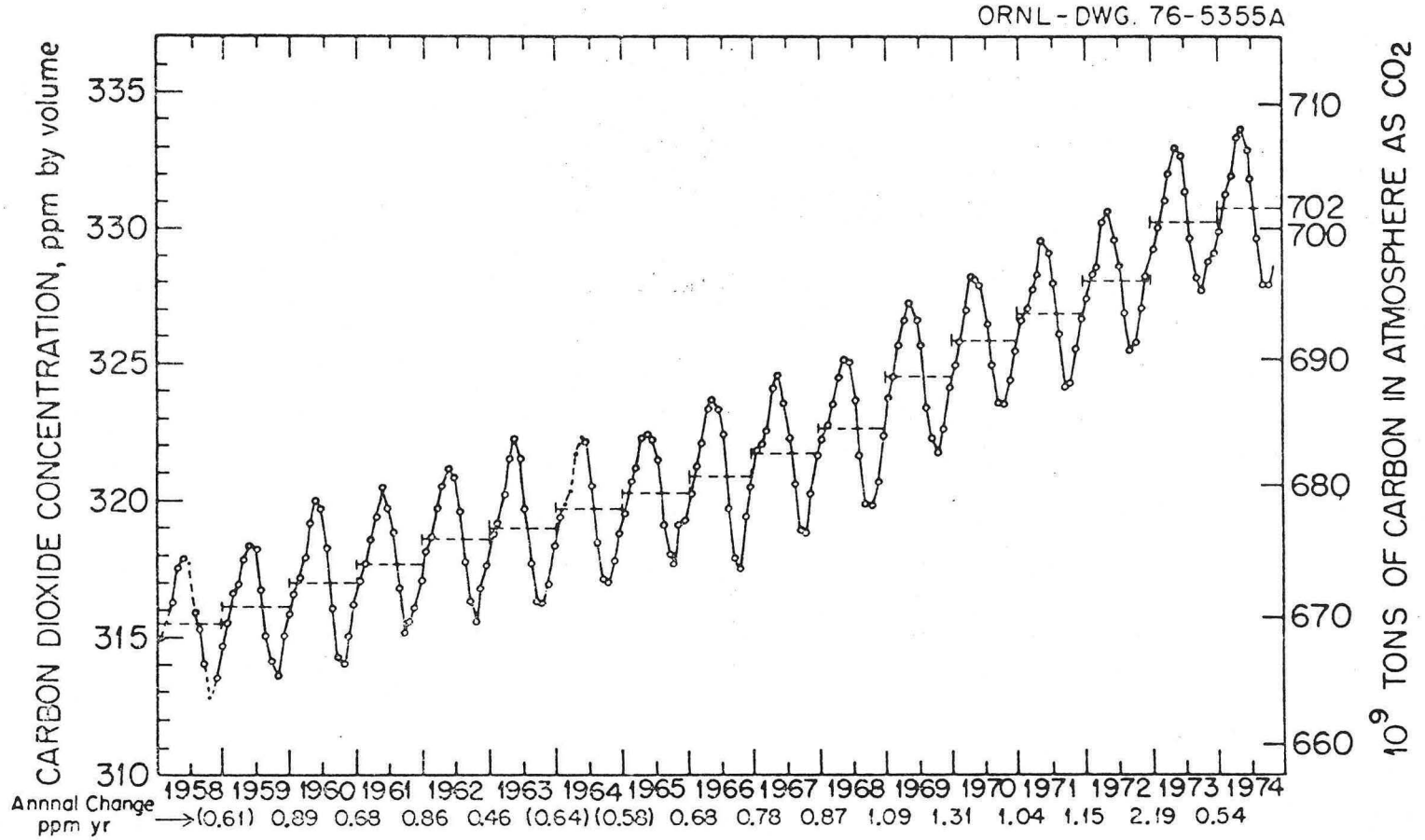


Fig. 6
Potential Carcinogen Production
in Coal Oil Plant

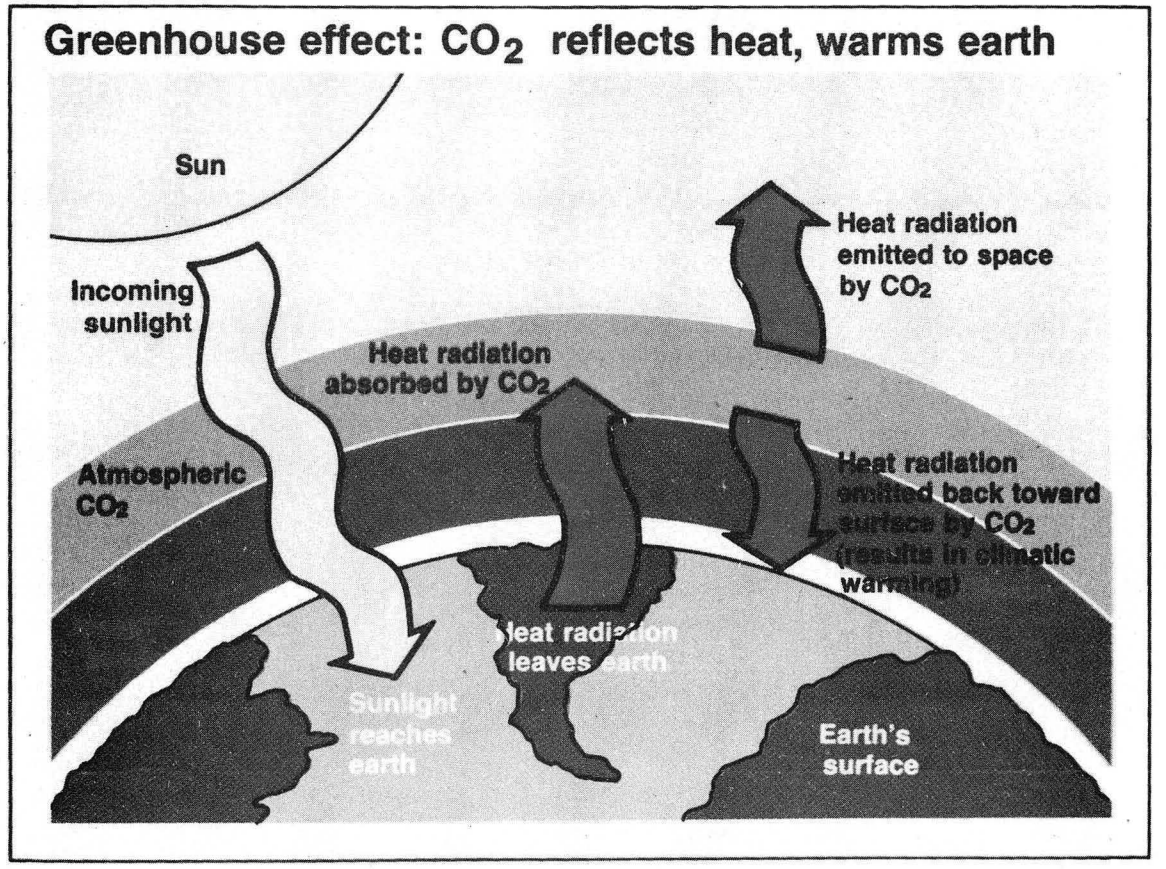


Atmospheric carbon dioxide concentration at
Mauna Loa Observatory, 2500 m (From Keeling)

XBL 772 - 4161

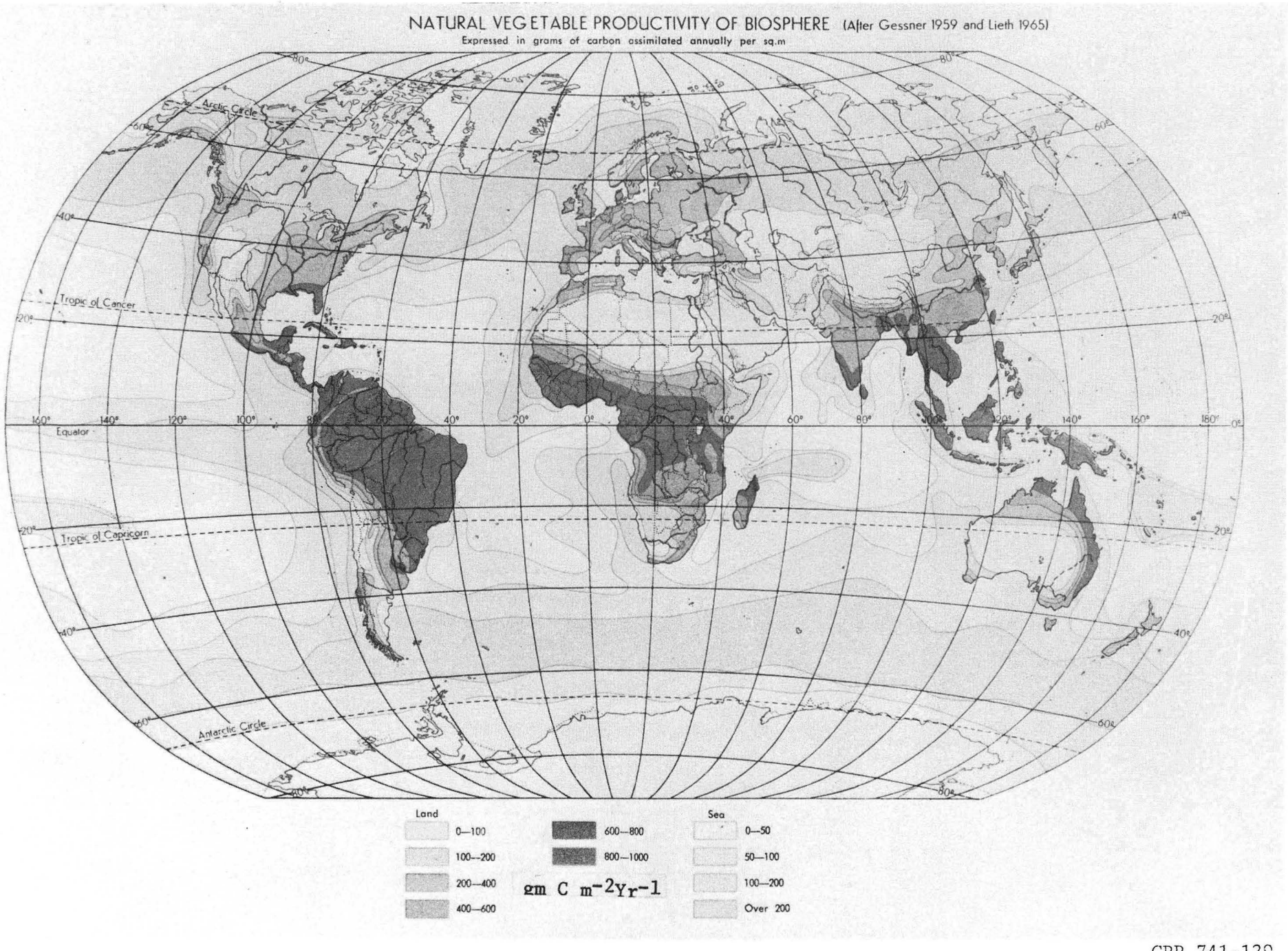
Fig. 7

Atmospheric Carbon Dioxide Concentration at Mauna Loa Observatory



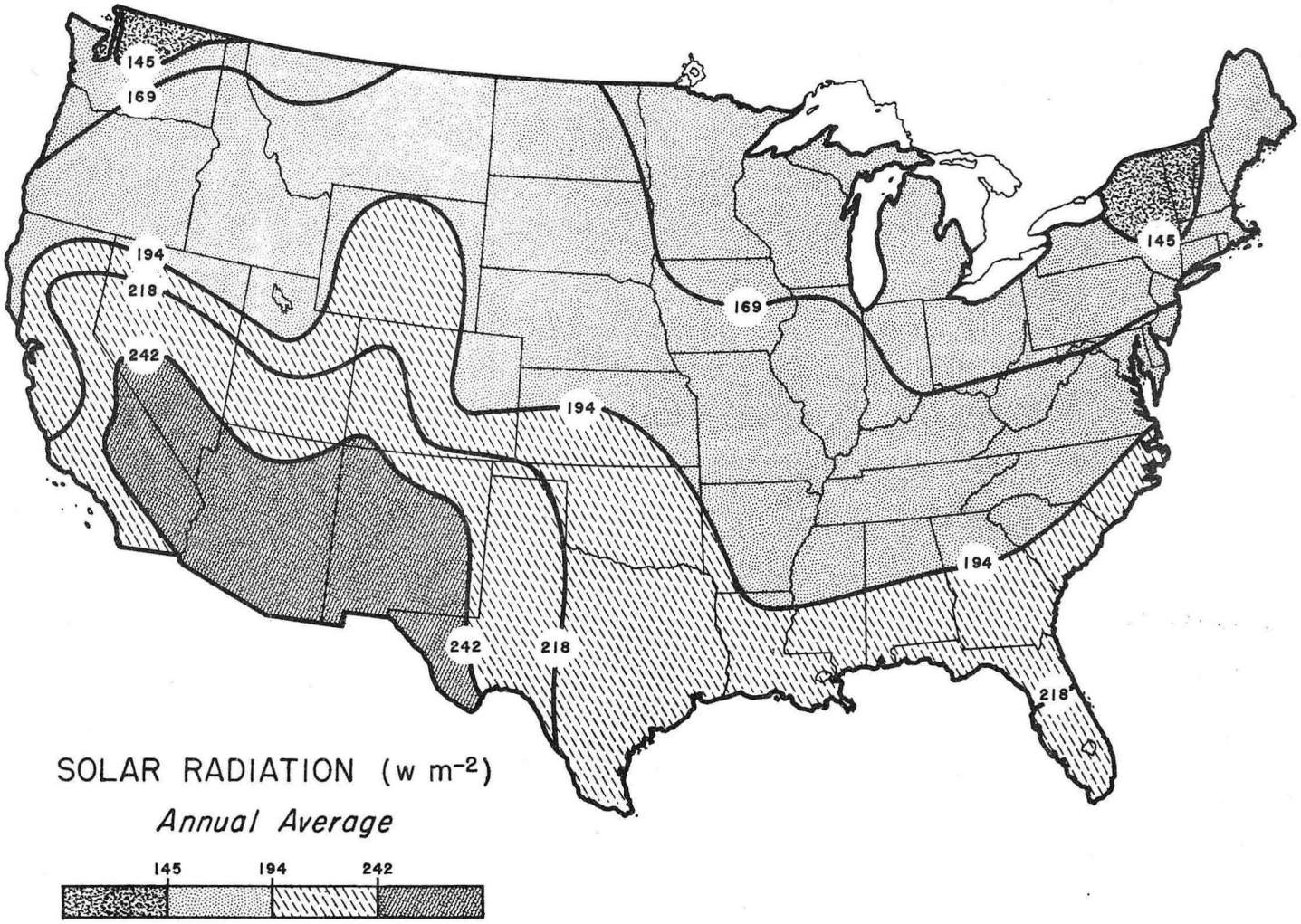
XBB 779-8871

Fig. 8 Greenhouse Effect



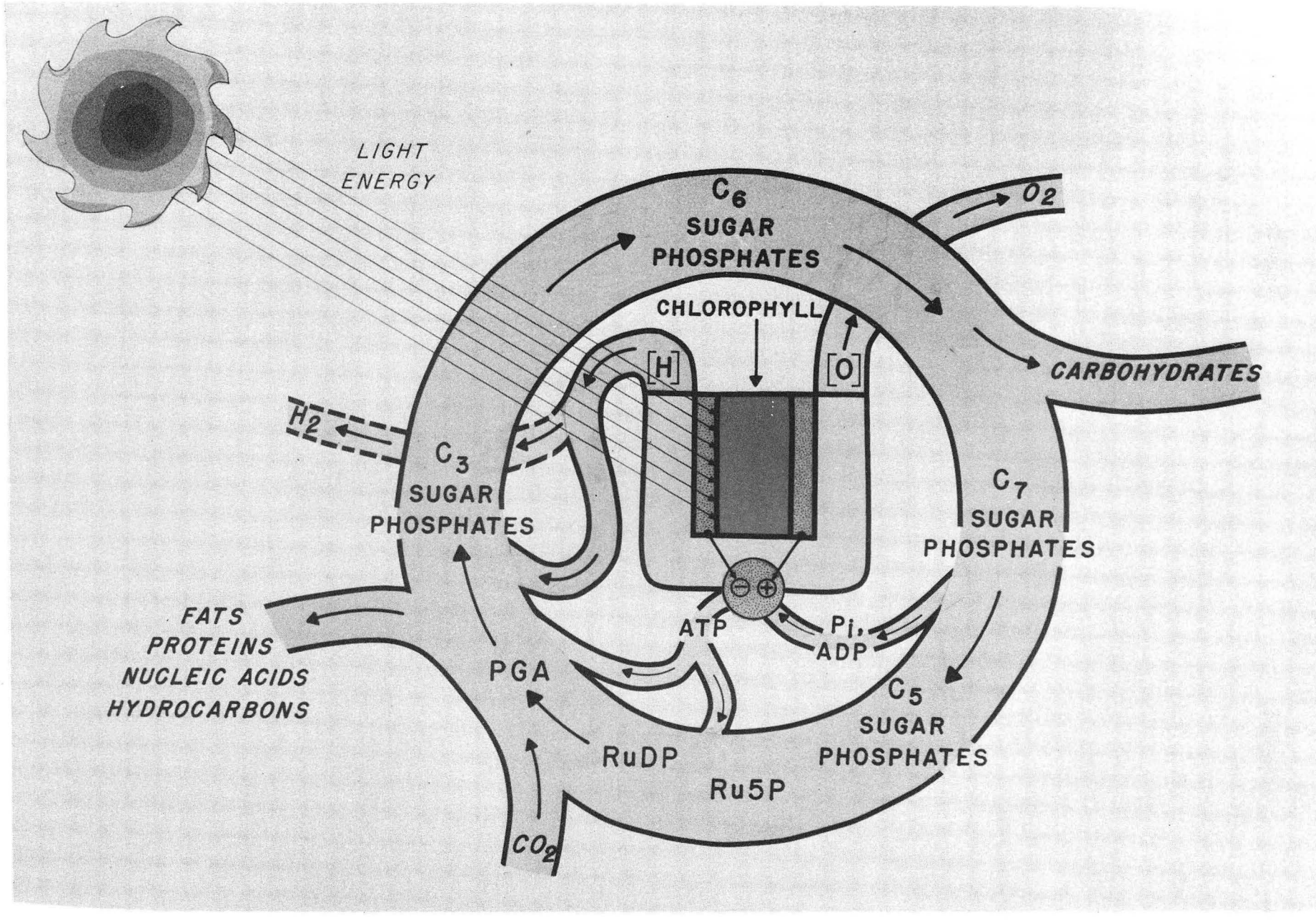
CBB 741-129

Fig. 9 Natural Vegetable Productivity of the Biosphere



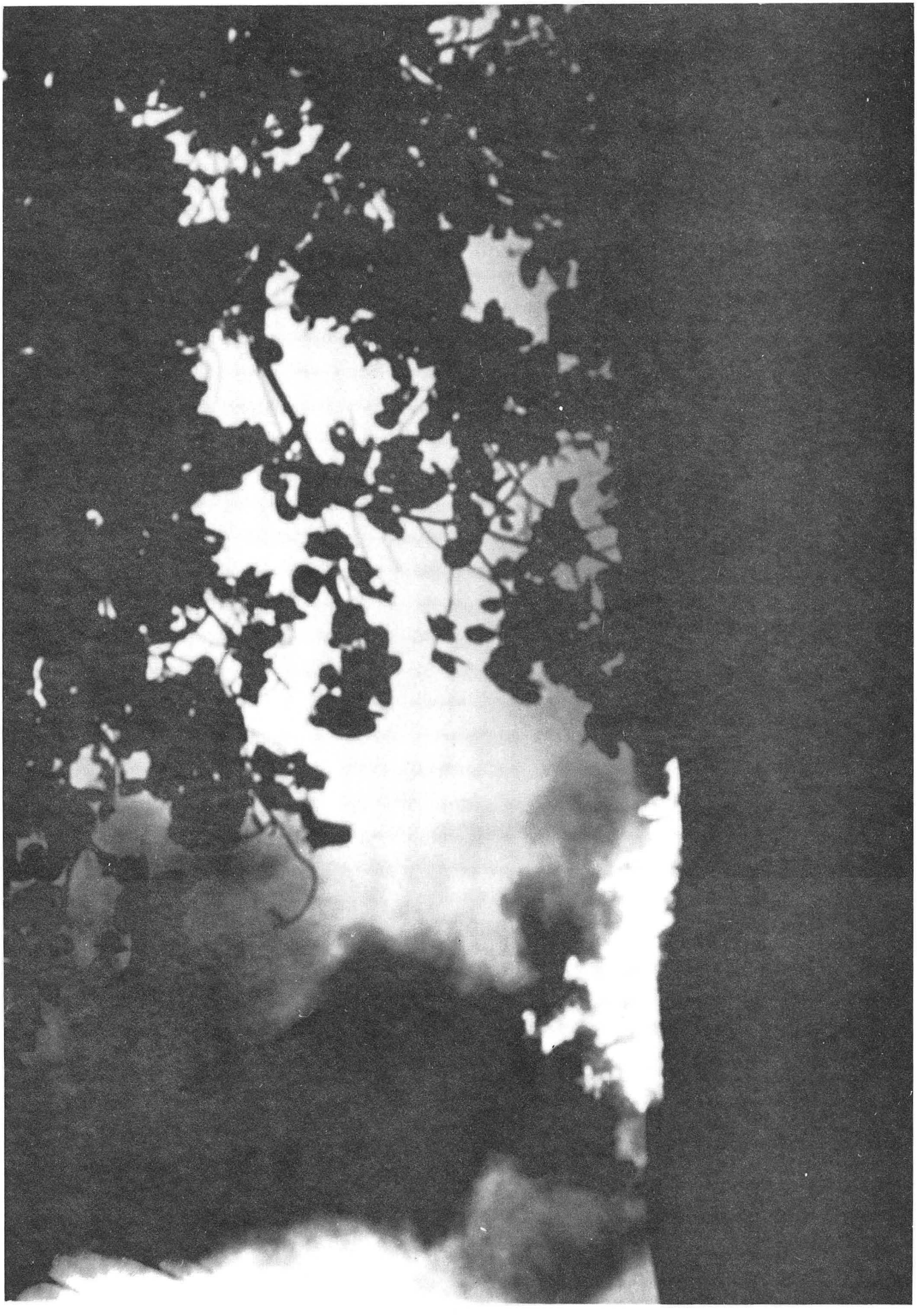
XBL731-4620

Fig. 10 U.S. Insolation



CBB 740-6756

Fig. 11 Photosynthetic Carbon Reduction Cycle



CBB 770-11766

Fig. 12 Sugar Burn, Mackay, Australia

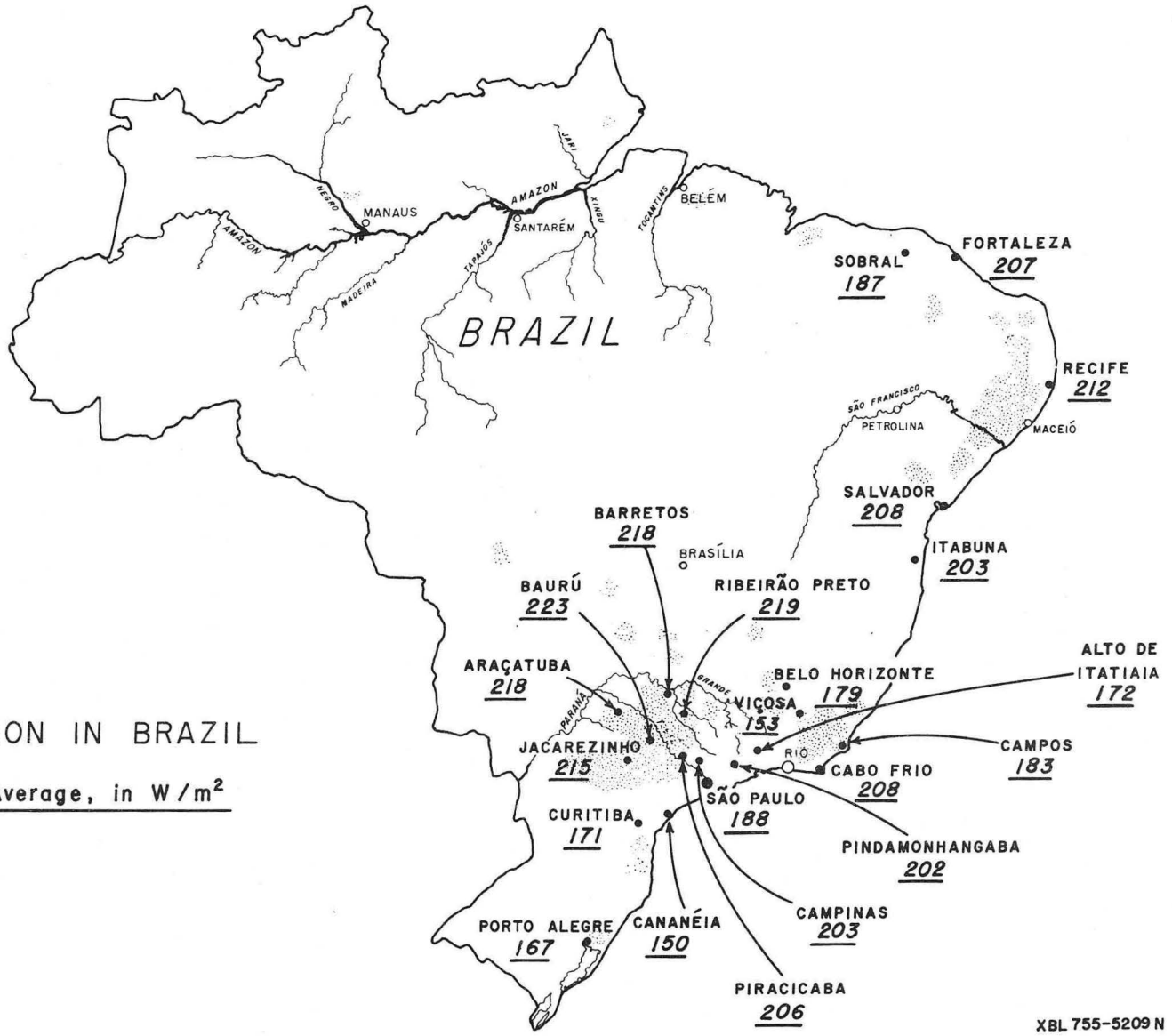


Fig. 13 Insolation in Brazil

$$C_6H_{12}O_6 \longrightarrow 2\,C_2H_5OH + 2\,CO_2$$

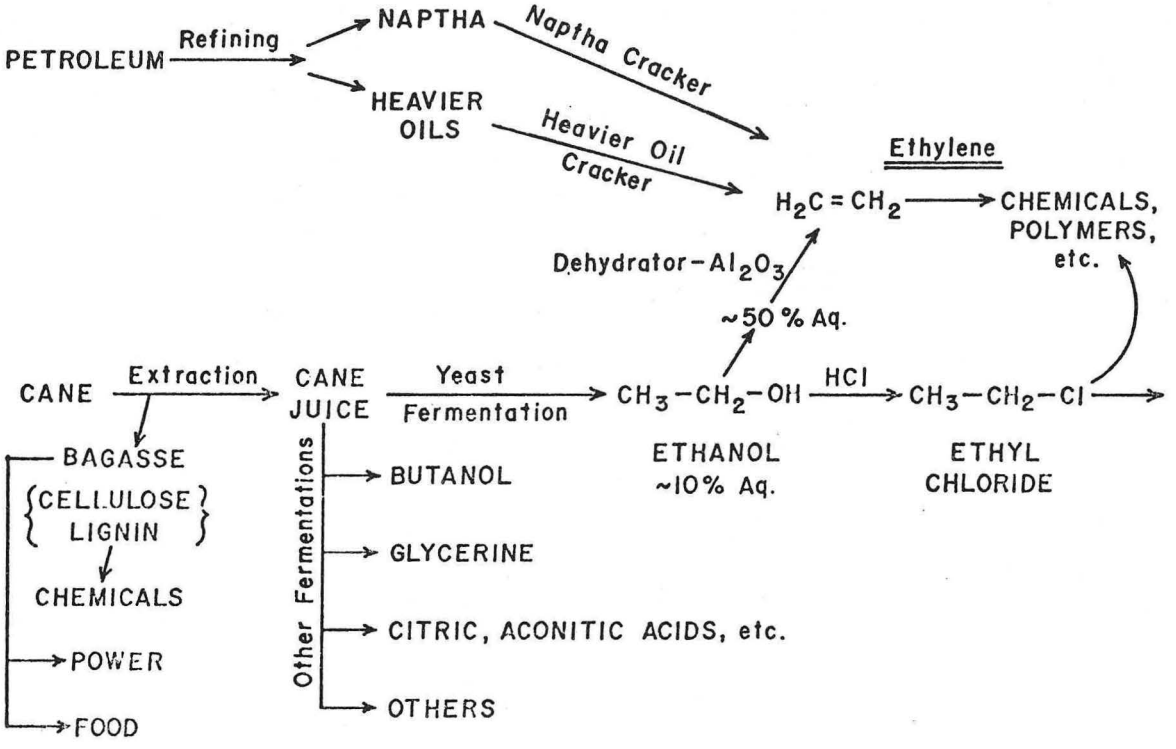
180 gm (673 Kcal) — 92 gm (655 Kcal)

12.88 lbs ⟶ 1 gal. (84,356 B.T.U.)

Cost / gal. = raw material + ~20¢ process cost

XBL7411-8086

Fig. 14
Fermentation Reactions



RENEWABLE RESOURCE FOR CHEMICALS

XBL754-5207

Fig. 15

Renewable Resources for Petrochemicals

CBB 757-5362

Fig. 16 Sugar Cane, Maceio, Brazil

CBB 772-1105A

Fig. 17 Sugar Cane, San Francisco River, Brazil

CBB 757-5366

Fig. 18 Rubber Tap, Brazil

CBB 778-7592

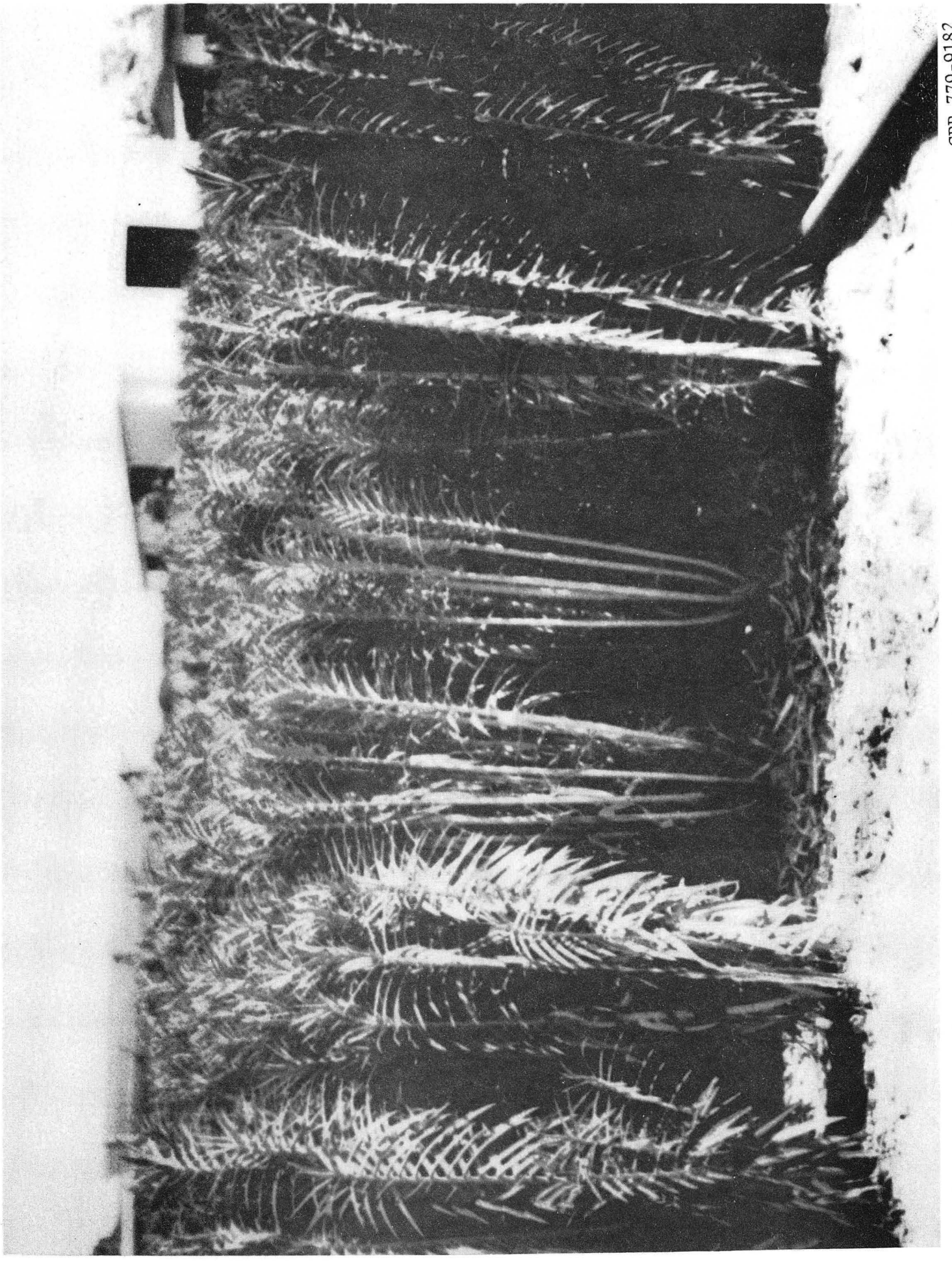
Fig. 19 Guayule, Saltillo, Mexico

CBB 768-7677

Fig. 20 Euphorbia Tirucalli, Brazil

CBB 778-7446

Fig. 21 Euphorbia Lactea, Puerto Rico, Showing Flow of Latex



CBB 779-9182

Fig. 22 Euphorbia Lathyris, South Coast Field Station, Santa Ana, California

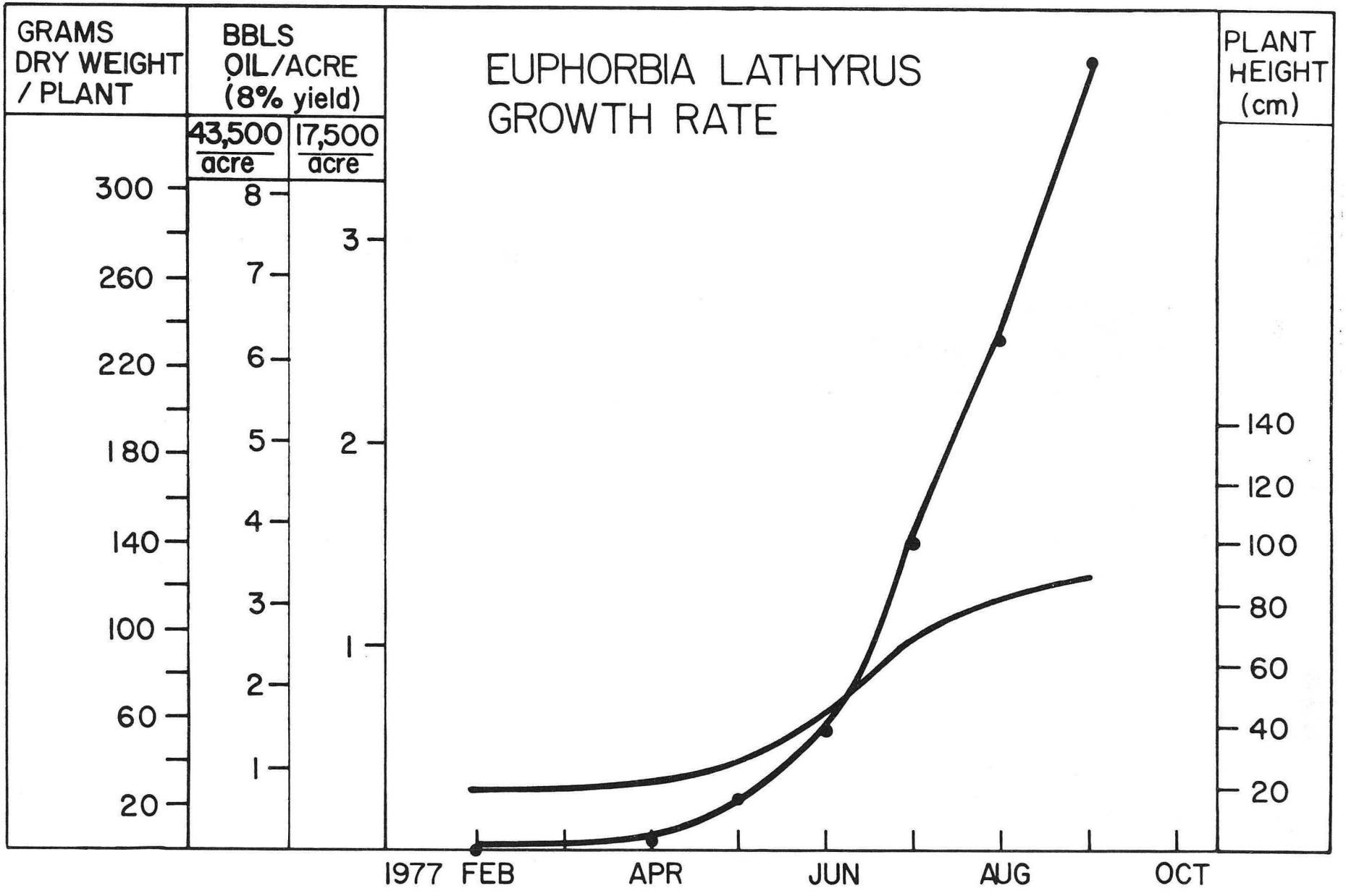


Fig. 23 Euphorbia Lathyris Growth Rate

CBB 777-6959

Fig. 24 Euphorbia Lathyris, South Coast Field Station, Santa Ana, California, Showing Entire "Petroleum Plantation" CBB 779-9180

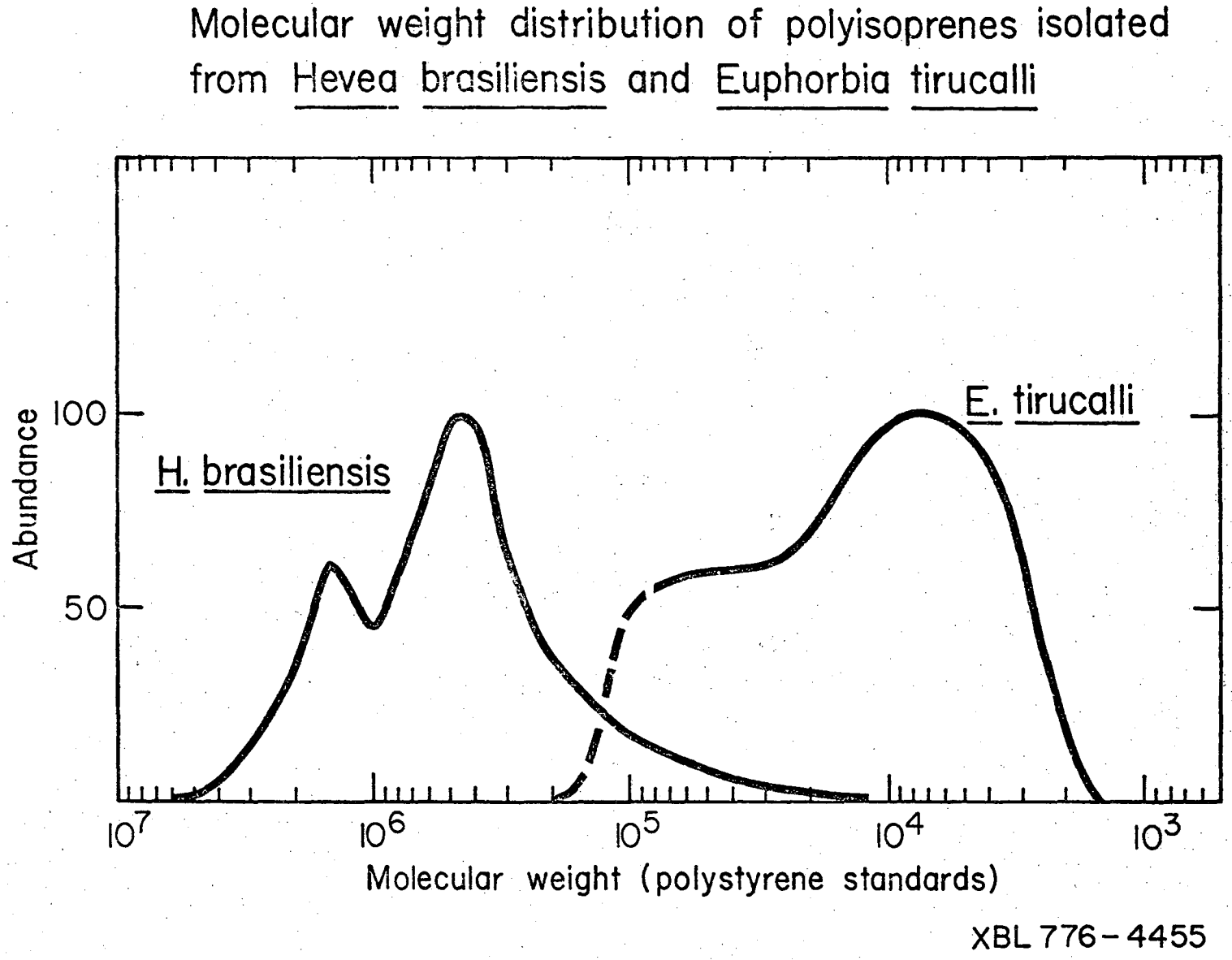
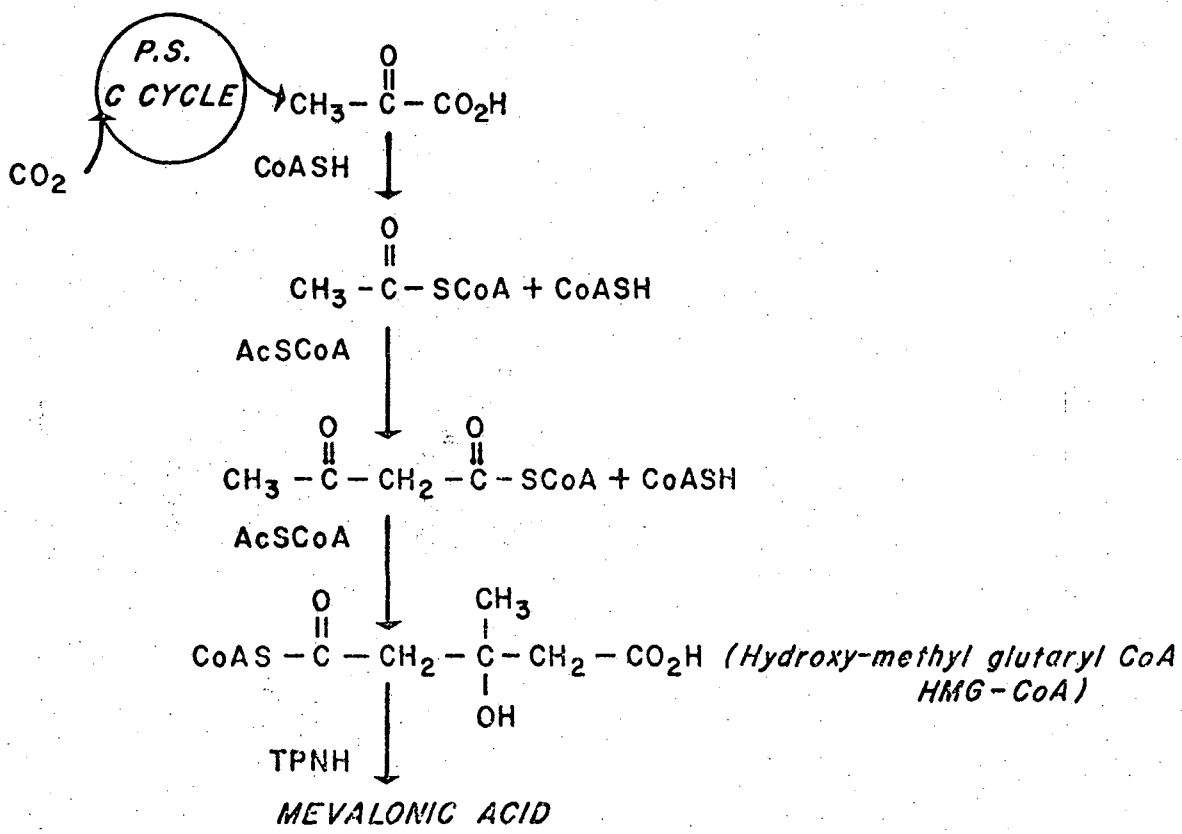


Fig. 25
Molecular Weight Distribution of Polyisoprenes from Hevea Brasiliensis and Euphorbia tirucalli

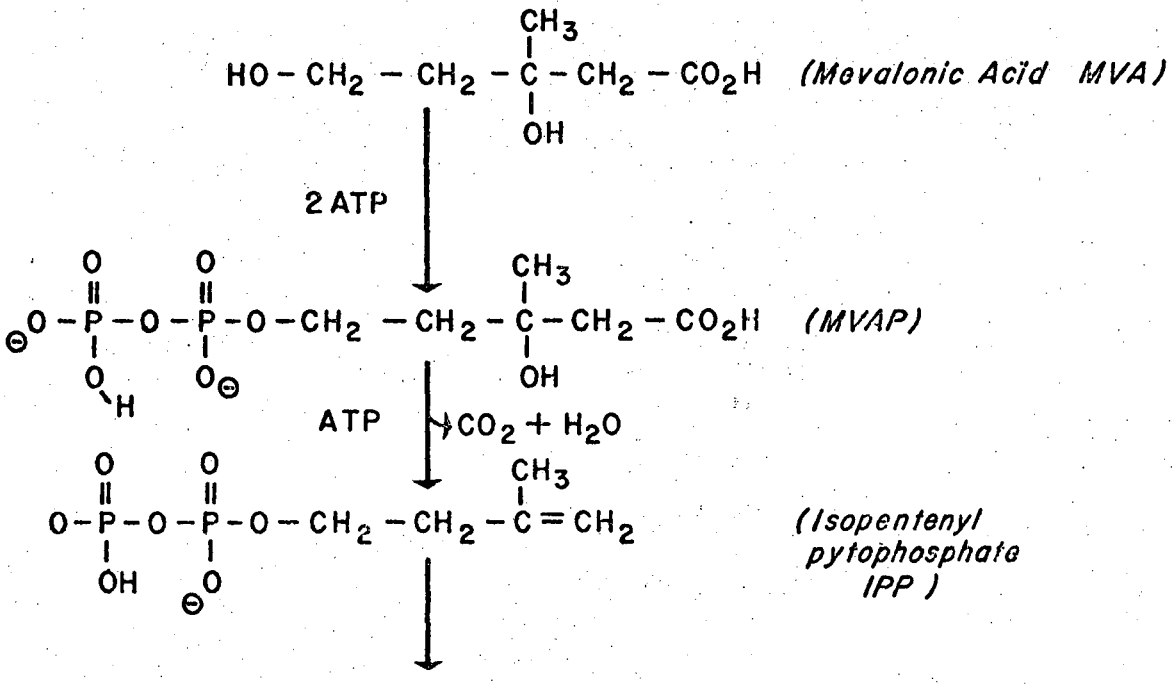
SYNTHESIS OF MEVALONIC ACID (MVA)



XBL 7711-4780

Fig. 26
Synthesis of Mevalonic Acid

SYNTHESIS OF ISOPRENE



XBL7711-4779

Fig. 27
Synthesis of Isoprene

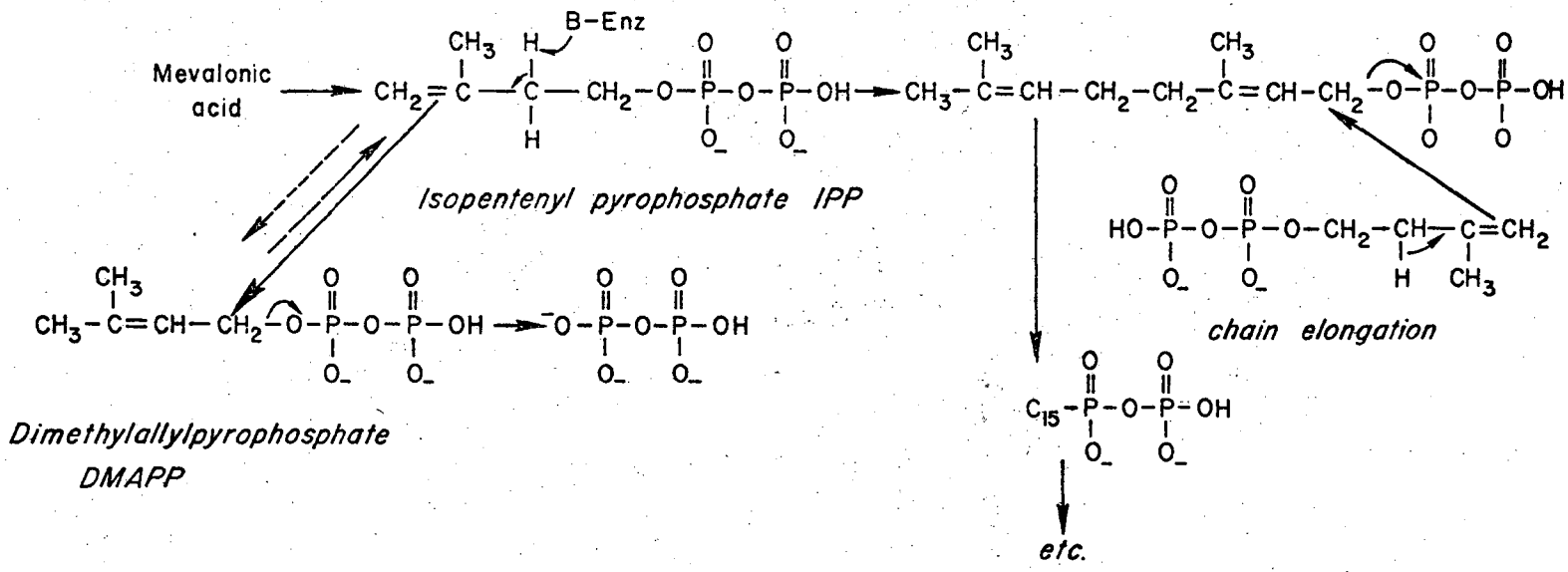
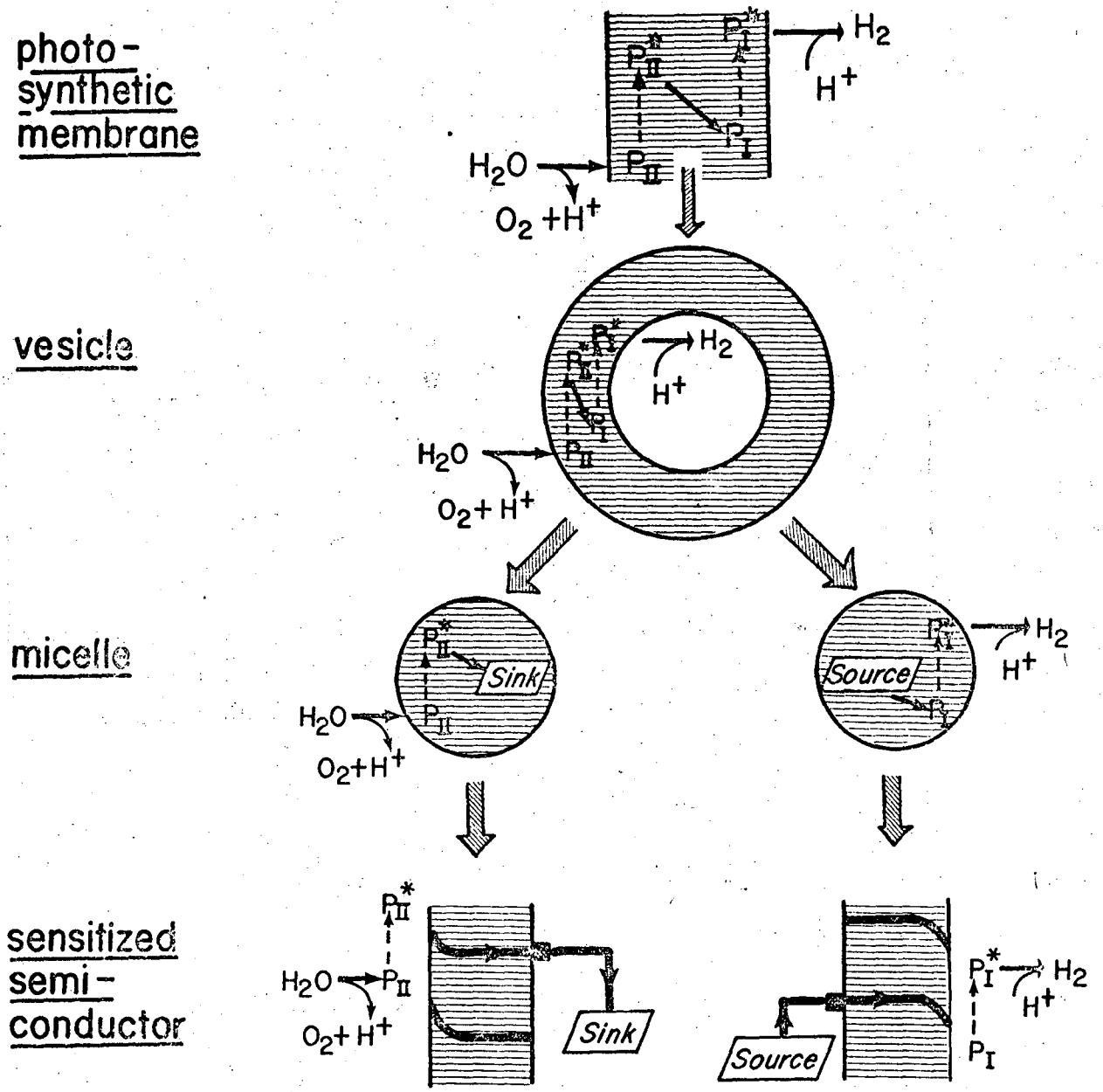


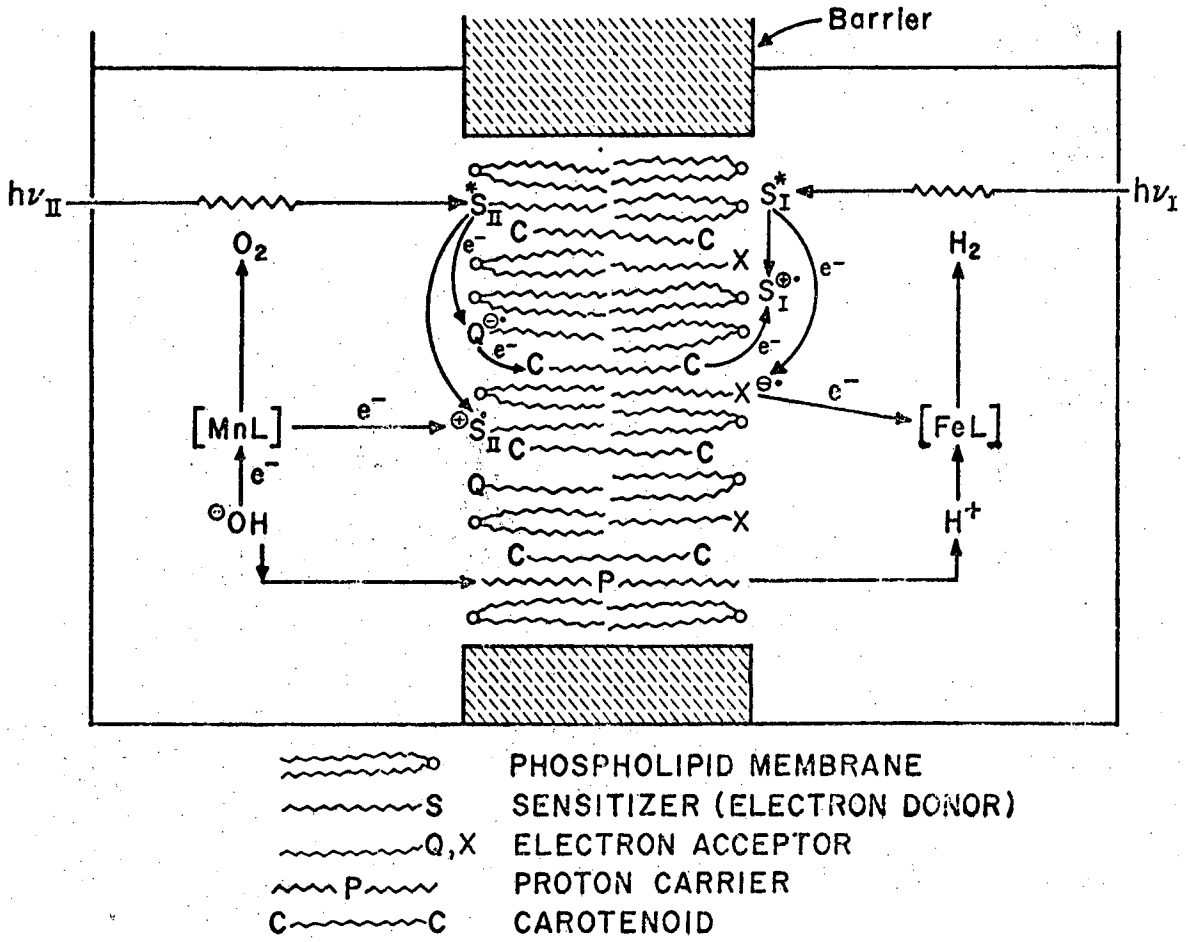
Fig. 28
Polymerization of Isoprene

PHOTOELECTRON TRANSFER SCHEME



XBL 774-4350

Fig. 29
Overall Photoelectron Transfer Scheme



PHOTOCHEMICAL CELL MODELED ON PHOTOSYNTHETIC MEMBRANE

XBL7411-7888

Fig. 30

Photochemical Cell Modeled on Photosynthetic Membrane

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720