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HYDROCARBONS VIA PHOTOSYNTHESIS

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HYDROCARBONS VIA PHOTOSYNTHESIS

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 want to take this opportunity to talk to you about a problem with which I have been increasingly concerned over the last decade from two not unrelated points of view. One aspect of that concern has been the constant realization that chemical companies are very dependent upon fossil hydrocarbon for their existence. The realization has grown that fossil hydrocarbon is gradually being used up in various ways, I have become sensitive to finding other ways to feed the chemical raw materials into the various manufacturing plants. Also, as a private citizen I had the educational experience three or four years ago of sitting in my car waiting for a line to pass through the gasoline station; this was in 1973. While I was waiting--and it took some time--I thought that I should try to do something about this situation. It seemed to me that there was no reason why I shouldn't try to find some way of applying the basic knowledge of chemistry and biology that I had acquired over a period of 35 years to the problem of hydrocarbon depletion. This is really the origin of today's discussion.

It is very clear that we have been burning our "capital account" of fossil hydrocarbon at a very substantial rate, and the time has come when this account is almost exhausted and the world will have to live on its "annual income". That annual income is the sunshine. The capital which we have been burning--the hydrocarbon fuel and raw materials--for the last 100 years or thereabouts was originally the product of photosynthesis in some living plant millions of years ago and which was laid down in the mud of the lakes, seas and oceans and gradually converted into fossil carbon. Our dependency upon that capital source is shown in Figure 1

U.S. ENERGY FLOW – 1974 (10^{15} BTU)

(Primary source Bureau of Mines Preliminary Data 4/3/75 – Total energy consumption 71.5)

Figure 1

U.S. energy flow (1974)

which is a representation of the energy flow in the United States showing that 98% of the energy and materials sources are fossil carbon of one sort or another. These fossil carbon sources are petroleum and natural gas liquids, coal and natural gas itself; the geothermal, nuclear and hydroelectric sources are relatively small compared to the total. There are three important aspects to be considered: (1) 98% of the total energy used in the United States is fossil; (2) of the total energy flow, only about one-half ends up in some useful form, the other being lost because it usually appears as low temperature heat (waste heat) which cannot be readily used; (3) about 10% of the total fossil carbon that enters the system is for non-energy uses--for chemical raw materials, i.e., feedstocks. This is a very important factor to the chemical industry, not only in the United States but throughout the world.

I would like to comment briefly about the energy loss by conversion into mechanical work by internal combustion engines in transportation, automobiles, airplanes, trucks, which represents a large fraction of the energy rejected as waste heat. A similar situation exists with the use of energy in the generation of electricity where a heat engine is involved to convert the energy into mechanical work with the result of a certain energy loss. This is due to the fact that the heat engine operates by having the heat flow from a high temperature to a low temperature and then out into the air. The two big losses involved in the conversion of energy from heat into mechanical work are the result of the Carnot (or thermodynamic) limitation which is the consequence of the temperature differences between which the engine works with efficiencies of usually less than 35%. The internal combustion engine (and the electric turbine) actually operate at an even less efficient level with overall efficiencies of only about 4%.

Two places in the energy flow diagram where energy is used directly as heat, that is, in running chemical plants (industrial heat) and the energy used for residential and commercial heating, show only a small fraction being lost because it reaches too low a temperature to be useful.

One of the objectives which I had when I began this effort was the attempt to find renewable sources for the 10% of total energy which is used for non-energy purposes, the other major thrust being to find renewable resources for any other component of the system, i.e., the energy itself. Thus, there are actually two different aspects to the problem--the materials part and the energy part.

RESULTS OF SUBSTITUTION OF COAL FOR PETROLEUM

The concern is to find renewable sources for this fossil carbon which is being diminished at such a great rate. One of the reasons for this concern is the fact that we are already exhausting our supplies of previously deposited photosynthetic carbon. We are using up the "capital" and the evidence for this is seen in increased prices for fuel and difficulties in obtaining the basic raw materials which we need.

There are, however, two other factors with which we must be concerned with regard to the continued use of fossil carbon. The general consensus currently amongst our social (politicians) and engineering colleagues is that we do have an alternative fossil resource, other than petroleum and natural gas, and that is the expansion of the enormous coal and oil shale reserves which are today a very small component of our energy picture. In spite of the fact that they represent

a large untapped resource, I am not sure that that kind of use can indeed be contemplated on the scale that is being suggested at the present time.

Part of the reason for the distrust of this relatively simple solution is the fact that the injection of all this fossil carbon, which has been stored in the ground for hundreds of millions of years, into the atmosphere will change the atmospheric composition. This is actually occurring and the change in the global atmospheric carbon dioxide concentration over the past fifteen years is shown in Figure 2. This data shows very clearly not only the gradual rise of CO_2 concentration in the atmosphere over the last 15 years but also the annual cycling-- in winter the CO_2 concentration rises and in the summer it falls. However, the CO_2 concentration never falls as much as it rises, so each year there is always a net increase in the total atmospheric CO_2 concentration. You can observe from the data that the increase is more rapid in the last 10 years than it was earlier. The actual record can be extended back about 100 years by measurement of isotope ratios in tree rings, and the evidence appears to be that the CO_2 concentration has actually been increasing for the last 100 years. It has risen about 15% in the last 100 years and about 5% in the last 15 years.

What are the consequences of the rise in CO_2 concentration? You have undoubtedly heard of the "greenhouse effect" arising because carbon dioxide is transparent to visible light but is opaque to degraded infrared radiation. The infrared is unable to get back out into space through the CO_2 , with the result being that the CO_2 acts as a valve for solar energy. Solar energy can get in, be degraded to heat, but then it cannot return to space again. This phenomenon gives rise to a gradual increase in the average temperature of the whole earth. In

ORNL - DWG. 76-5355A

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

XBL 772 - 4161

Figure 2

Atmospheric CO₂ concentration,
Mauna Loa observatory

fact, there is reason to believe that this global temperature increase has already begun, but the details of its consequences in terms of changing weather patterns, changing food supply, etc., are not yet visible. We cannot yet make a real estimate of that ultimate consequence except to be confident that if the rise in CO₂ concentration continues at a rate which would be represented by the increased combustion of all the coal and oil shale which we have available, it would be a substantial change. That change would, in turn, result in a substantial change in global climate. We should keep this concern in mind as we attempt to find alternative sources (to petroleum and natural gas) for energy and raw materials.

There is still another concern which has not yet been discussed very much and which I encountered only a few months ago. The subject of a meeting I attended was "chemical carcinogenesis". One of the bits of information which came out of that meeting was discussion of the possible source of atmospheric carcinogens from the expanded use of coal, and the summary is shown in Figure 3. You can see there the potential carcinogen production in the factories which will make oil from coal. The important numbers to notice are these: Benzo(a)pyrene (BaP) is the chemical which is present in tobacco smoke and which helps to produce lung cancer in smokers and also excess lung cancer in coke oven workers. The coke oven workers in Los Angeles, for example, have a risk factor for lung cancer about 10 times that of other distillery workers. Also, workers in the roofing industry, if they are not wearing masks, inhale the vapors from the tar which are very rich in BaP, a carcinogen, and they also have a risk factor of lung cancer of about 8 times the average.

In natural petroleum, the concentration of BaP is only 1 to 5 ppm, but in oil made from coal, the concentration of BaP is 10 to 100 ppm,

POTENTIAL CARCINOGEN PRODUCTION IN COAL OIL PLANT

(25,000 TONS / DAY OF COAL)

POLYCYCLIC AROMATICS - - - 200,000 lbs/day

BaP - - - - - 10 lbs/day

BaP concentration

PETROLEUM - - - - - 1-5 ppm

COAL OIL - - - - - 10-100 ppm

XBL 773-4287

Figure 3.

Potential carcinogen in
coal oil plant

roughly 10 to 20 times the level that is in petroleum today. Therefore, if we start to produce oil from the coal which is available in many parts of the country, there will be increased concentration of atmospheric carcinogens. For example, a single plant which converts 25,000 tons of coal per day into oil would produce a total amount of polycyclic aromatic hydrocarbon of 200,000 pounds per day which will contain ~ 4000 grams per day of benzo(a)pyrene. When you recall that it requires only a few micrograms of BaP to produce a lung cancer, you can have some idea of the magnitude of this problem.

If it is decided as a national energy policy to convert coal into oil as a reasonable method of creating more petroleum-like products, two additional problems will be created, aside from the environmental considerations of strip mining, etc. One of these is the addition of large amounts of CO_2 into the atmosphere, whose consequences we don't actually know. In addition, substitution of coal-oil for petroleum-oil will produce many tons of carcinogenic chemicals in the atmosphere whose consequences we do know. This kind of an action, i.e., the substitution of coal as our primary fossil energy source for petroleum, could not fail to increase the rate at which carcinogens are released into the atmosphere with a concomitant increase in the risk of cancer.

These two considerations, in addition to the fact that the petroleum resources are being exhausted, make it imperative that we must find a renewable resource, that is, one that is renewed every year, and, furthermore, a resource that removes the CO_2 from the atmosphere before returning an equal amount to the atmosphere. That means finding a photosynthetic organism which takes the carbon dioxide out of the atmosphere, makes a useful fuel and then returns the CO_2 to the atmosphere with no net increase of CO_2 in the atmosphere or no excess production of polycyclic aromatic hydrocarbons (carcinogen-like materials).

Some years ago the energy resources of the United States were different than they are today (Figure 4). One hundred years ago most of our fuel and materials came from renewable resources, 95% from wood, for example. But in the course of about 60 years wood disappeared as an energy and materials source, being replaced by coal; by 1920 coal was the principal source. Early in the century, petroleum and natural gas began to increase in importance, and, of course, today they are predominant. What will happen after 1980? The only thing that is certain is that consumption of petroleum and natural gas must be reduced, but it is not known what will take their place. Oil and natural gas production in the United States, at least, has already passed its peak. In Texas, California and probably in Louisiana both oil and gas production have been dropping since at least 1974. The only question that remains is what will replace the petroleum and natural gas as sources of energy and materials. The implication given in Figure 4 is that the use of coal will remain high, or rise. In estimates of the spring of 1977, coal usage would rise more steeply than it appears to do in Figure 4. However, the biggest rise is expected for solar energy, that is, the use of the "annual income" from the sun in the form of visible light, and the principal agent for collecting that visible light from the sun which is available to us now is the green plant.

One last piece of evidence for the fact that our supply of the convenient fuels (petroleum and natural gas) is indeed being exhausted is the price history of these two materials (Figure 5). The price history of coal shows a rise also, but only by virtue of the primary rise in petroleum and natural gas. The price from 1960 to 1970 was pretty nearly flat, but beginning even before the oil embargo (fall of

DRAWN BY ELIE SABBAN
COMPILED BY PAMELA JUETT
NATIONAL GEOGRAPHIC ART DIVISION

Figure 4.

U.S. energy sources

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XBL 7411-8089

Figure 5.

Average fossil fuel prices in
U.S. at point of production

-13-

1973) the price of oil and gas began to rise precipitously. The last figure I have for the price of natural gas along the Gulf Coast is about \$2.30/million Btu. This evidence, in the form of spiralling prices, causes me to be really concerned about renewable resources for energy and materials and is a direct consequence of the exhaustion of our readily available "capital" energy sources, operating through both political and economic mechanisms.

GREEN PLANT FACTORIES FOR SOLAR ENERGY

CONVERSION

If the sun is going to be our renewable resource, we must know where it is available; this is shown on the following maps. The insolation in the United States, for example, is shown in Figure 6. Here the solar radiation available for use in terms of watts/m^2 , annualized average, is given. It is apparent that the greatest concentration of the sun's available energy is in the Southwest of the United States, roughly 250 watts/m^2 , and it falls off as you go toward the northeast.

Our principal "machine" for capturing the sunshine is the green plant and the natural vegetable productivity, with its differences, in the various parts of the world is shown in Figure 7. The regions of highest productivity occur in the equatorial regions of the earth, such as the Amazon River basin, the Congo in Africa, Southeast Asia, Malaysia, Indonesia and New Guinea, where the productivity is roughly $1 \text{ kg/m}^2/\text{year}$ of carbon. These regions, however, are not the regions of largest solar activity (desert areas of Australia, South Africa, North Africa, Southwest United States, Chile). The lack of water in the desert areas of high insolation prevents the natural vegetation from achieving the

SOLAR RADIATION (w m^{-2})
Annual Average

Figure 6.

Solar radiation (insolation)
in the United States

Figure 7. Natural vegetable productivity of the biosphere

CBB 741-129

highest productivity in the regions of the highest isolation. This fact should be kept in mind, and compromises must be made between the regions of high sunshine and the regions of high productivity where the green plant is used as a natural collecting device.

The green plant is the principal solar energy collecting device which is available, and the present state of scientific knowledge is such that it is possible to understand very thoroughly how the plant captures CO_2 from the atmosphere and turns it into organic carbon. The process is shown diagrammatically in Figure 8. The sunshine is captured by the green part (chlorophyll) of the plant and generates a reducing agent and an oxidizing agent. In this diagram the reducing agent is a negative charge and the oxidizing agent is a positive charge. The oxidizing agent is eventually liberated from the plant as molecular oxygen and the reducing agent is used to reduce the CO_2 which enters the plant through a series of sugars in a cyclic system. From that cyclic system most of the green plants store the energy as carbohydrates (as cellulose or sugars), but some plants are able to store the sun's energy as fat, proteins, or hydrocarbons. Both carbohydrate and hydrocarbon are taken off from the sugar cycle that is operated by the sunshine in the plant. We know a great deal about the photosynthetic carbon reduction cycle and we know something about how the sunshine is captured by the chlorophyll and how the charge separation occurs. We need to know a great deal more about the quantum capturing system so that we can construct synthetic models based upon the natural energy capturing process of the green plants.

Figure 8.

Photosynthetic carbon
reduction cycle

MATERIALS AND ENERGY FROM THE SUN

Can we use the green plant's capturing and storage capability, mostly in the form of carbohydrates? It is possible to do this in many different ways, as for example, the burning of wood for energy which was done in such a widespread manner through the middle of the last century. This is, however, a relatively clumsy and inefficient method of using the solar energy.

Sugar Cane

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". This is done by converting the sugar (from the cane) into alcohol, the chemistry of which is shown below:

180 gm

92 gm

(673 Kcal)

(655 Kcal)

12.88 lbs

1 gal. (84,356 Btu)

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

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 and 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, and the route to renewable resources for the petrochemical industry is shown in Figure 9. You can see that the petroleum is refined to naphtha and goes through the naphtha 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. Via an extraction, the cane juice is made which is essentially a sugar solution and upon fermentation it is transformed to ethanol. The resulting 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 than they are presently as a source of chemicals.

The ethanol is what the Brazilians have decided to manufacture from their sugar cane juice. Approximately 7 or 8 million tons of raw sugar were produced in 1974 in Brazil which yielded 700 million liters of 95% alcohol by fermentation of the residual molasses. In the United States we have practically no fermentation industrial alcohol at the present time. That method of making alcohol went out of style about 1950 when it became possible to obtain industrial alcohol from ethylene by adding a water molecule to ethylene, having obtained the ethylene from naphtha. It now appears that we might return to the earlier methods of making industrial alcohol because of our lessened petroleum reserves.

RENEWABLE RESOURCE FOR CHEMICALS

XBL754-5207

CALVIN. Figure 9

Renewable resources for
petrochemicals

In November of 1975 the Brazilians, realizing that they had no accessible petroleum source of naphtha for their ethylene, or, for that matter, an accessible petroleum source for their gasoline, decided that they would encourage both new plantations for sugar cane and new fermentation facilities to make alcohol from the cane juice directly. Their policy was to provide government loans at low interest for the new fermentation facilities and new sugar cane plantations in order to increase production of sugar cane in Brazil.

Sugar cane, in its unusual condition of going to seed, is shown in Figure 10; this photograph was taken in front of the sugar museum in Maceio. This same plant has now become one of the major sources of chemical raw materials in Brazil. The Brazilian government set a goal in November of 1975 that 20% of the total fuel consumption in Brazil by 1980 should be in the form of alcohol. This represents 20 billion liters of fermentation alcohol per year. Remember that in 1974 the Brazilians produced approximately 1 billion liters of fermentation alcohol, and they have established a goal of 20 billion liters per year by 1980. They have made some progress between 1974 and 1977; there was about 1 billion liters of fermentation alcohol in 1975 and about 2 billion liters in 1976. It is entirely possible that the will achieve their 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 areas of northeastern Brazil. 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 sugar cane. This is

Figure 10. Sugar cane, Maceio, Brazil

CBB 757-5362

fermented to alcohol, and the waste products are burned to make steam/electricity which, in turn, is used in the fermentation processes. The sugar cane-alcohol-cellulose-sugar cane cycle on the large self-sufficient Brazilian sugar plantations is very efficient and cost effective.

In connection with the availability of the fermentation alcohol for fuel, the Brazilian automobile industry has taken steps to modify the internal combustion engine, with the addition of a heat exchanger, so it is capable of using the alcohol fuel instead of petroleum, with no loss of efficiencies. These alcohol-fueled automobiles are in evidence now (1977) in Brazil, and as the Brazilians approach their goal of 2 billion liters of fermentation alcohol from sugar cane per year by 1980, the number of cars of this type will increase. Because Brazil has no local automobile industry, the automobiles (American, German or Japanese) are modified on assembly in Brazil for use with this fermentation fuel. One of the unexpected results of the use of alcohol fuel is reduction in air pollution in addition to using a renewable resource as a substitution for gasoline.

In contrast, in the United States the costs of producing food, fiber and feed in terms of energy costs are given in Figure 11, and you can see that the cost of fertilizer is one of the principal ingredients in energy costs. The fertilizer in question is largely ammonia, which is made from methane. The cost of the land rental in terms of dollars is not shown in this chart, and in the United States, in terms of dollar costs, the biggest single fraction of the cost of producing food, feed and fiber is land rental; this is an even larger fraction than the costs represented by the fertilizer. The high land rental costs are one of the limitations which we in the United States will have to contend with,

Calif. Farmer, April 3, 1976

XBL764-5540

Figure 13.

Energy for food, feed and
fiber production, U.S.

in terms of using this kind of approach to renewable resources. Because of the high land costs in general here, I am not sure just how far we can go with the idea of using high priced land for renewable resources for fuel and materials; this will be discussed in more detail later.

The annual productivity of various renewable resources (rubber, cane, kelp) is compared in Table 1. It is easy to see that cane has a productivity of about 1.2% of the total captured sunlight and this is the highest for any commercial crop. Most commercial crops have an efficiency of less than 1%. Kelp is included in this table on a theoretical basis only. It is believed that kelp can be converted directly to methane, but no yield of this type has yet been obtained. There is, however, no ambiguity about the capability of getting a 1.2% yield of incident sunlight for the sugar cane in Brazil.

Therefore, alcohol from sugar cane is a viable alternative at least for one country, but I do not see it as being that kind of a resource for the United States today, largely because of the land use and availability. The only way that the United States could move in this direction would be either to grow kelp off the coast of California or hydrolyze the waste cellulose of forestry operations to glucose (a fermentable) which could then be converted into sugar.

Rubber

As I mentioned earlier, there are some plants that store the sun's energy directly as hydrocarbons. The most important commercial plant today is the rubber tree (Hevea) which has a low efficiency and produces hydrocarbons directly. These hydrocarbons are not practically useful for fuel production because of their high molecular weight, and also the material from Hevea has more useful properties, namely, the elastomeric

Table 1

ANNUAL PRODUCTIVITY OF RUBBER, CANE AND KELP

	Present Productivity (metric tons/hectare)	% of Incident Sunlight Captured	Potential Productivity (tons/hectare)
Rubber (Malaysia)	2.2 (Rubber)	0.2	4.5 to 9
Cane (Hawaii)	25 (Sugar)	1.2	> 30 (Fermentables)
	10 (Ethanol)		
	9 (Ethylene)		
Kelp	9 (Dry Weight Carbohydrate)	~ 2.0	90

properties which generate rubber. Rubber is, however, a commercial crop of hydrocarbon, harvested annually, and, in addition, the yield of that annual harvest has been improved by a factor of 30 over the last 15 years. Before World War II, the annual harvest of hydrocarbon (rubber) from Hevea brasiliensis in the Malaysian Peninsula was 200 lbs/acre/year, and with the advent of synthetic rubber from petroleum, the rubber growers in Malaysia realized that they must improve the productivity to remain commercially competitive.

By changing agronomic practices and with improved plant breeding, the rubber growers raised productivity to 2000 lbs/acre/year, which is now the commercial productivity of the Malaysian rubber plantations. There are small experimental plots of Hevea which produce 4000 lbs/acre/year, and individual trees can produce (when extrapolated to plantation size) 8000 lbs/acre/year. This is equivalent to four tons of hydrocarbon. Since one ton of hydrocarbon is the equivalent of about 7 barrels of oil, this means that 25 barrels equivalent of oil/acre/year can be obtained from hydrocarbon-producing trees. The Malaysian rubber producers began with an equivalent of only about 3 barrels of oil/acre/year and they could eventually produce the equivalent of about 30 barrels of oil/acre/year, with a current value of ^{about} 10 barrels of oil/acre/year. This is an example of what can be done with biological material when you begin with wild plants, breed and cultivate the plants under the best possible conditions.

Rubber is usually harvested by tapping, and the latex in a rubber tap is shown in Figure 12. The method is to strip the bark, not all the way to the cambium, allowing the latex to rise to the cut in the vertical laticifers. The latex then flows down the sloping surface into the cup. The latex which is produced by the Hevea is one-third hydrocarbon.

CBB 757-5366

Figure 12. Rubber tap, Brazil

Latex-Producing Plants (Euphorbias and Asclepias)

It seemed to me that a systematic effort to examine the latex from various plants and analyze it for the hydrocarbon content might be one way to establish whether or not these plants could be used on any large scale as a source of renewable materials. Therefore, we began our search for latex from plant species other than Hevea, although initially we used the latex from the rubber tree as a standard material in our analytical work to devise the methods of extraction, analysis, chromatography, etc.

The hydrocarbon in most latex-producing plants represents about one-third of the total latex. Therefore, if we could find a family of plants, the species of which contained latex, it might be a fruitful avenue for chemical research. Hevea, which grows only in tropical climates, is a member of the family Euphorbiaceae. In the genus Euphorbia, a member of that family, almost every species is a latex-producing plant, which, in turn, could be interpreted that the energy of the sunlight is stored in these plants as hydrocarbon.

If the plants produce hydrocarbon-like materials and if the yields can be improved materially (such as with Hevea), perhaps other latex-producing plants can be found which can be grown under less humid and tropical conditions, perhaps on land which would actually be arid or semiarid such as in the Southwest of the United States, the African deserts, and the deserts of Chile. There are many regions in the world which contain land which is not very productive today. In addition to making the land itself productive, by suitable selection of plant species it might be possible to produce on that land a material which would have direct economic use, such as hydrocarbons.

This idea led to a trip to Brazil where I found many species of Euphorbia. (I really was looking at sugar cane as a renewable resource, but in traveling around Brazil it was possible to see many other plants as well. There were many hundreds of species of Euphorbia there which were latex producers and some of them grew in very arid regions. It turns out that some of the species of Euphorbia which grow in the arid regions of Brazil can also grow in the arid regions of the United States such as Southern California, West Texas, New Mexico, Arizona, Nevada. One of these species, Euphorbia tirucalli (the milk bush) is shown in Figure 13. This yields a latex which can be harvested by tapping, although it can also be harvested by cutting in the same way that sugar cane is cut. To produce "oil" from the E. tirucalli the fleshy stems could be crushed, the latex extracted by suitable chemical processing, with the recovery of the solvent. Because of the characteristics of latex production in the leaves and its ability to grow in dry areas, the Euphorbia tirucalli appeared to be an excellent candidate for a "gasoline tree plantation".

In this same connection, it is interesting to note that about 40 years ago a species of Euphorbia, E. resinifera, was grown in Morocco. Approximately 125,000 hectares of land were harvested, with a production of 10,000 liters of latex per hectare, which resulted in 1700 kg of rubber (benzene extractables) and 2750 kg of gum resin (acetone extractables). It is not known whether this effort was ever repeated or whether it was done once only. It does, however, reinforce the feasibility of growing Euphorbia for the latex which they produce.

In Northern California, on our own ranch, we found another species of Euphorbia, E. lathyris, which grows in the less arid but

Figure 13. Euphorbia tirucalli (Riverside, California)

CBB 772-1251

somewhat more severe climate. This is known as "gopher plant" or "mole plant" and grows to a height of about one meter. An annual, it can be harvested by cutting, like sugar cane, with the leaves being extracted for their hydrocarbon-like material (Figure 14).

The essential feature of our effort to find renewable energy resources is that we have sought those plants which would grow in arid or semiarid regions, on land which is presently relatively nonproductive. We do not feel that it would be wise, or even politic, to explore plants which would be competitive for food-producing land. There are many other plants, of course, which perhaps might be better choices, but they might require a kind of cultivation condition which would compete with the food producing regions; we sought to avoid that.

Another genus of plant which might be useful for renewable resource production is the *Asclepias* (milkweed). This will grow in the Midwest, as well as areas of the west, and there are many different milkweeds. I have many times picked the fluffy seeds of these plants in Michigan and Minnesota, but never have analyzed the leaves for their latex content which we hope to do soon. In Brazil, the milkweeds (Figure 15) grow to a height of 8 to 10 feet, and the leaves could be crushed, extracted for their hydrocarbon content, in a manner similar to the leaves of the *E. tirucalli* and *E. lathyrus*.

On a recent (spring of 1977) trip to Puerto Rico I discovered that *Asclepias* will grow there profusely in the dry regions of the South Coast. There were a number of cases in which the thick stems of the *Asclepias* had been cut near the ground and new shoots arose just as a ratoon does from sugar cane. This species obviously would be an excellent candidate for hydrocarbon production via plants.

CBB 772-1106A

Figure 14. *Euphorbia lathyrus* (Northern California)

CBB 768-7679

Figure 15. Asclepias (Brazil)

The most outstanding plant species in Puerto Rico, however, as a candidate for our "gasoline plantation" would appear to be Euphorbia trigona. (I had seen some plants of this type in Brazil as well). These also grow along the dry South Coast, and grow not only as shrubs but even in the form of trees. One example had a tree with a trunk about 10 inches in diameter, topped with a very large spherical crown of green bush, and upon plunging a penknife into the bark of that particular Euphorbia trigona it exuded a very substantial flow of latex. This is the first of the varieties of Euphorbia that I have seen which apparently can be grown as a tree and tapped for its latex, possibly in the same way (or a similar way) as is done for Hevea.

ANALYSIS OF HYDROCARBONS IN LATEX-PRODUCING PLANTS

As we progressed in the analysis of the leaves of the latex-producing plants, I discovered several interesting historical facts. For example, Thomas A. Edison spent the last four years of his life (1928-1932) looking for domestic rubber. Edison, Ford and Firestone began this search after the rubber blockade during World War I as they felt it was necessary to find a rubber-producing plant which would grow in the United States. Edison examined about 2000 plants, and found many hydrocarbon-containing plants, but only one or two in which the molecular weight of the hydrocarbon was large enough to be considered as a possible candidate for substitution for natural (Hevea) rubber. Edison did not pursue his studies beyond that point. After his death his notebooks were published. The 2000 plants that he examined were described, and the composition of the plants, insofar as chemistry is concerned, was given. The only chemical "operations" that Edison performed on the various plants were benzene and acetone extraction of the plant parts. The acetone

took out mostly the alcohols and the oxygen-containing reduced carbon compounds (sterols, terpenols, etc.). The benzene extract removed the hydrocarbon itself. Edison reported his results as "rubber" (benzene extractables) and "resins" (acetone extractables). The resins are mostly sterols and the rubber was mostly polyisoprene. I was unaware of the work of Edison until we had begun to make our own chemical analyses, which were done in a little more sophisticated fashion than Edison could have done.

A desert shrub of the Southwest is known to produce a high molecular weight hydrocarbon that might be used as natural rubber. This plant is guayule. 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 United States, to grow guayule as a source of rubber. Because of the development of synthetic rubber, however, it was not deemed feasible to continue the development of guayule after the end of 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 Northern Mexico, specifically near Saltillo, and the production of guayule in this region has increased during the last several years. The interest in guayule in Mexico and elsewhere in the Southwest has increased to the point where several international conferences have been held with a view toward bringing together experts from various disciplines to focus on the problem of improved plants, increased production and other parameters involved in the project.

Our first efforts at the analysis of hydrocarbon-producing plants were associated with the latex from Hevea brasiliensis. We obtained

samples of latex from the Rubber Research Institute of Malaysia upon which to perform our initial experiments. Using gel permeation chromatography, it was possible to determine the molecular weight distribution of the hydrocarbons in Hevea as shown in Figure 16. This data represents rubber from a single clone obtained from the Rubber Research Institute of Malaysia. The calibration was done with polystyrene polymer from the Dow Chemical Company. The calibration is almost logarithmic, using an established molecular weight polystyrene, but it does not go below a molecular weight of 10,000. It is not possible to extrapolate this data, because the material does not behave in a very simple way on the gel. The gel we used for our analyses (Bio-Glass 1500) was excellent for rubber, which has a molecular weight distribution of around 500,000 to 2,000,000.

The molecular weight of the Hevea is determined by the clones and differs with different clones. The genetic means to determine the molecular weight in a particular clone is something which has yet to be deciphered. The curves in Figure 16 are characteristic of a particular strain of Hevea and are an identification of the strain (No. 701) from the Rubber Research Institute of Malaysia. Different strains of rubber trees produce materials of different molecular weights, but we do not yet know how and why this is achieved. Some of the distributions are single, that is, spread out over about 1,000,000, but Figure 16 represents a special clone which has a bimodal distribution.

The curve on the right hand side of Figure 16 is from one of the Euphorbias. Most of the Euphorbias we have examined have had molecular weight distributions which were much lower than real rubber, down around 20,000. Obviously, there are several different

MOLECULAR WEIGHT DISTRIBUTION FOR Hevea brasiliensis (RRIM 701)

XBL 769-9636

Figure 16.

Molecular weight distribution
for Hevea brasiliensis

molecular weight components in the latex from the Euphorbias, and we have not yet resolved them. It will have to be done with a different type of gel.

We have examined about a dozen species of Euphorbias, and most of them contain hydrocarbons of a much lower molecular weight than rubber. That is why Edison was not successful in his search for rubber. He found "oil", but did not find rubber. Perhaps I should put it the other way: He didn't find much rubber, but he did find oil. However, Edison was not interested in the oil. Today, due to changing circumstances, we have a different view. It's oil which is important. Therefore, we are re-examining many of the plants that Edison examined for their rubber-like materials (guayule is an example) as well as their hydrocarbon-like materials, to see what the "oil" in the plants really contains.

As mentioned before, the acetone extract of the leaves of the hydrocarbon-containing plants contains mostly sterols. These can be separated by gas-liquid chromatography coupled to mass spectroscopy to identify the individual sterols (Figure 17). Sterols of five different plants (four Euphorbias and one Asclepias) are shown and the numbers on the various peaks identify the sterols (C_{30} compounds) with molecular weights of the order of one thousand. In addition to the species shown in Figure 17, we have analyzed about another dozen species and the data are presented in Table 2.

The oil from the latex-producing plants is extracted essentially by a mixture of benzene and acetone, and most of the plants we have studied containing between 2% and 10% of the total fresh weight of the plant as hydrocarbon. Therefore, if you can get a yield of 50 tons/acre/year, this would result in 1 ton/hydrocarbon/acre/year at 2% yield (or 5 tons/

GLC of Euphorbiaceae Steroids

Figure 17.

Euphorbiaceae steroids as
determined by gas-liquid
chromatography

Table 2

Percent of Total Plant Dry Weight

Plant	Benzene Extract			Acetone Extract			
	Rubber	Wax	Total	Total	Glycerides	Isoprenoids	Other (Terpenoids)
<i>Asclepias cursavica</i>	0.6	<0.1	0.7	5.9	3.	<0.5	2.
<i>Cryptostegia grandiflora</i>	0.2	0.05	0.35	13.3	7.	<0.5	6.
<i>Eucalyptus globulus</i>	<0.01	0.05	0.1	12.	3.5	<0.5	7.
<i>Euphorbia lathyris</i> (leaves)	0.1	0.2	0.3	25.	13.7	2.2	8.3
<i>E. lathyris</i> (seeds)	-	-	-	40.	40.	<0.5	<2.
<i>E. lathyris</i> (stem)	-	-	-	4.5	1.9	<0.5	2.
<i>E. marlothii</i>	0.2	0.4	0.6	9.5	5.1	<0.5	3.3
<i>E. tinuicalli</i> (UCB)*	0.07	0.13	0.2	5.	2.4	<0.5	2.0
<i>E. tinuicalli</i> (UCLA)*	0.1	0.3	0.4	8.5	4.4	<0.5	3.4
<i>Hevea brasiliensis</i>	1.3	0.2	1.5	9.6	5.1	<0.5	2.6
<i>Jatropha curcas</i>	<0.1	0.6	0.7	4.2	1.5	0.8	1.4
<i>Monadenium rhizophorum</i>	1.2	0.2	1.4	16.5	9.	<0.5	6.
<i>Pedilanthys</i> sp.	<0.1	<0.1	0.5	8.7	4.7	<0.5	2.3
<i>Sarcostemma vaminale</i>	<0.1	0.8	0.8	12.3	6.6	<0.5	4.8
<i>Synadenium grantii</i>	0.4	0.4	0.8	15.	6.6	<1.5	5.7

Table 2. Acetone and benzene extractables from various plants. The compound distributions are estimated on the basis of NMR-spectra (60MHz, CDCl₃) of the extracts

* UCB = University of California, Berkeley. UCLA = University of California, Los Angeles.

hydrocarbon/acre/year at 10% yield). This yield represents not less than 2 barrels of oil/acre/year, minimum for the wild uncultivated plant. It could easily be as high as 10 barrels of oil/acre/year (equivalent to 0.5 watts/square meter) and the yield would increase still further upon cultivation, plant genetic breeding, etc.

Mechanisms of Hydrocarbon Construction in the Plant

Hydrocarbons are constructed in the plant by the pathways shown in Figure 18. The cycle (Figure 8) shows the CO_2 , light and water entering, making carbohydrates and ejecting the oxygen. Out of that comes phosphoglyceric acid which goes on to carbohydrate. The carbohydrate can come back, or go directly to pyruvic acid which, in turn, loses CO_2 and goes on to acetyl coenzyme A which then condenses with itself to make acetoacetyl CoA, containing a sulfur-carbon bond, and elongating the chain to four carbon atoms. This now condenses with another acetyl CoA, but it does not condense in the original fashion. This second acetyl CoA adds to the carbonyl function to form a hydroxymethyl compound. The methyl group of acetyl CoA adds onto the carbonyl of the acetoacetyl group to give the β -hydroxy- β -methyl CoA compound, a six-carbon compound. By reducing the sulfur ester to an alcohol, we produce mevalonic acid, which loses CO_2 and goes to isopentenyl pyrophosphate (IPP), shown in Figure 18. The IPP undergoes polymerization (Figure 19), with the double bond in the IPP first isomerized by an enzymatic isomerization to dimethylallylpyrophosphate (DMAPP), and the two react with each other. The double bond of IPP reacts with the potential incipient carbonium ion of DMAPP, releasing pyrophosphate and resulting in another allylic structure. The chain has now been elongated to make an allylic pyrophosphate of ten carbon atoms with an incipient carbonium ion which can

XBL765-5509

Figure 18.

Mevalonic acid synthesis

00004801876

-43-

XBL 771-4113

Figure 19. Isoprenoid condensation reactions

then react with another IPP to build up the chain. The chain can grow from five, to ten, to fifteen carbon atoms, and when two fifteen-carbon atom chains come together head to head to make a 30-carbon atom compound, we have the beginning of the steroids. Alternatively, the chain can keep going by allylic condensation and eventually create a polyisoprene; if it is cis, the product is rubber and if it is trans the product is chewing gum. This appears to be the mechanism for the construction of the long chain high molecular weight compounds.

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 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 is now 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 as the molecular weight increases, 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.

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 in 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 an experimental planting in Southern California toward this end, of Euphorbia tirucalli (the perennial which will take several years to mature) and Euphorbia lathyrus (an annual). By the fall of this year we will have some real data on how much of the material can be grown under these conditions. By extrapolating from the small acreage, we will be able to determine how much tonnage of hydrocarbons per acre will be available. The actual data on the yield/acre will not be available until the end of the year and then only for the Euphorbia lathyrus.

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 beginning of the cultivation of sugar cane, wheat, corn, etc. several thousand years ago.

We are trying 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 (such as wheat, corn, rice, sugar, etc.), but it is difficult 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, and these primitive questions have yet to be answered. 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/of plants.

I hope by the end of this year to have sufficient information concerning soil conditions, yield, fertilizer types, etc. so that next year it will be possible to plant another experimental "plantation" for further refinement. From that it would be possible to expand the effort to 200 to 300 acres, and the year after that perhaps to 2000 to 3000 acres. In the meantime, process development would determine the best method of extracting the oil from the leaves. One method would be to extract the residues with benzene, burn the cellulose that is left to make steam and recycle the benzene. There are three distinct stages in this process development, and three different types of organizations will probably be involved. One would be an agricultural-type company, such as a lumber company or a paper company. The second, to get the material out of the plants, would obviously be a chemical company. The third effort might be an oil company for refining and cracking the crude oil which is produced, and that material (the crude oil from the plants) would be returned to chemical companies as feedstocks.

This effort can all be put together, but I don't see any single talent for doing the entire job. Growing is one type of problem, extraction another, refining a third. This entire effort depends upon a cooperative solution for a worldwide economic and social problem.

SYNTHETIC PHOTOSYNTHETIC SYSTEMS

Before I leave the discussion of natural photosynthesis, I want to call your attention to another important consequence of our study of how the green plant captures the energy of sunlight. This concept in-

volves 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 sunshine (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, about which we know some details, 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 (Figure 20). 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 hydrogen 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 idea of constructing an artificial membrane (modeled on the natural membrane in the chloroplast), putting correct materials on it, with oxygen evolution on one side of the membrane and hydrogen 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 one side of the membrane to generate hydrogen and manganese-containing compounds on the other, where oxygen is generated. It appears that there is a lipid membrane in between to separate the hydrogen from the oxygen.

XBB 7411-7523

Figure 20. Electron micrograph of chloroplast

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 21. 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. Each of the systems and the relationships between them are shown in more detail in Figures 22a, 22b and 22c.

With these basic ideas, we can begin the design of a synthetic membrane (Figure 23). 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

PHOTOELECTRON TRANSFER SCHEME

XBL774-4350

Figure 21.

Photoelectron transfer
scheme (overall)

PHOTOELECTRON TRANSFER SCHEME

XBL 774-4347

Figure 22a.

Photoelectron transfer
scheme (detail)

PHOTOELECTRON TRANSFER SCHEME

XBL 774-4348

Figure 22b.

Photoelectron transfer
scheme (detail).

PHOTOELECTRON TRANSFER SCHEME

XBL 774-4349

Figure 22c.

Photoelectron transfer
scheme (detail)

PHOTOCHEMICAL CELL MODELED ON PHOTOSYNTHETIC MEMBRANE

XBL7411-7888

Figure 23.

Photochemical cell modeled
on photosynthetic membrane

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. This idea is one which can be brought to fruition within five to ten years. Last year, I was more optimistic about this prediction, because there had been a report in the literature that someone had actually generated hydrogen on such a synthetic membrane. However, it turns out that while the work is going in the right direction, the system only worked one time, and it has not been possible to reproduce the results. Those of you who work in the laboratory understand this kind of a situation. I felt last year I could predict that we might have a bench-top synthetic photochemical cell in five years and a factory in ten, but I feel I must delay that prediction now, but only until the original observation is again made and confirmed.

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. There are at least two major candidate families for this purpose, the Euphorbiaceae and Asclepiaceae, and there are individual plants in the family Sapotaceae and Moraceae. There may be others as yet unexplored. 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. This hydrogen could be inserted into our present fuel and materials systems with a minimum of difficulty.

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