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HYDROCARBONS FROM PLANTS: ANALYTICAL METHODS AND OBSERVATIONS

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ABSTRACT

We have suggested that certain plants rich in hydrocarbon-like materials might be cultivated for renewable photosynthetic products. Two species were selected for experimental plantations: <u>Euphorbia lathyris</u>, an annual from seed and <u>Euphorbia tirucalli</u>, a perennial from cuttings. The yield from each species is over 10 barrels of oil/acre/year without genetic or agronomic improvement. In addition to plants, there are trees, such as species of <u>Copaifera</u> in Brazil and other tropical areas, which produce a diesel-like oil upon tapping. Each tree produces approximately 40 liters of hydrocarbon per year, and this material can be used directly by a diesel-powered car. Further efforts to develop plants as alternate energy sources are underway, as well as a continuing search for additional plant species throughout the world which have a similar capability.

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INTRODUCTION

Since the oil embargo of 1973 the realization has grown that fossil hydrocarbons--the product of ancient green plant photosynthesis--are being depleted gradually, with no foreseeable way to ever restore the "capital" to the energy bank. The time is approaching (or may have already arrived) when the world will have to live on its "annual income", the sunshine. The capital, hydrocarbon fuels and raw materials, which has been consumed during the last century was originally the product of photosynthesis taking place millions of years ago. These materials were deposited in the mud of lakes, seas and oceans and gradually converted into fossil hydrocarbons such as petroleum, natural gas or coal. Efforts should now be made to find annually renewable sources to replace the fossil hydrocarbons.^{1,2}

There is a basic problem which some people apparently do not believe exists: That is, this fossilized photosynthetic material, particularly oil, which was laid down several hundreds of millions of years ago and which we have been consuming at a rate many-fold greater than it was (and is continuing to be) laid down, will be exhausted in the not too distant future. There is a definite limitation on the amount of this material available. Rather than to discuss the price of oil (which in January 1980 was \$35/barrel) which can only continue to rise, there is another method of showing the effect of diminishing sources of raw materials. The information in Figure 1 indicates, to my mind, the fact that available fossil carbon is being exhausted. The rate of discovery as a function of the number of feet of wells drilled is a very illuminating method of showing resource exhaustion. From 1920-1950 the rate of oil discovery was constant, but the slope of the curve began to fall off around 1950 by a factor of about five. Therefore, it is necessary to drill five times as many feet of wells for the same amount of oil, or.

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for the same amount of drilling only one-fifth of the oil is obtained in the last 20 years as was obtained in the previous 30 years. The supply of fossil carbon as petroleum is being exhausted. There may be other kinds of hydrocarbons which can serve as alternate sources. It has been suggested by Professor Thomas Gold at Cornell that some methane may be the consequence of primitive carbon accumulation during the actual formation of the earth, and this is <u>not</u> a residue of photosynthesis.³ This fact has not yet been definitely established, but it is an interesting suggestion; this type of hydrocarbon would not fall within the framework of the limitation just discussed. ENVIRONMENTAL EFFECTS OF DIMINISHING HYDROCARBON SUPPLY: THE CO₂ PROBLEM

There is more coal available than oil or natural gas, and the tendency currently is to promote the usage of stored coal as a substitute for petroleum or natural gas or even oil shale (which represents another kind of stored fossil carbon). It should be possible to transform the coal or oil shale into some type of liquid, or gaseous, fuel. There are, however, environmental limitations on this source of fuel.⁴ The same reasons we were previously asked to transform our power plants from coal (dirty) to natural gas or oil (clean) still hold. If we return to "dirty" coal, the production of carcinogens from the combustion of coal in <u>any form</u> will return again; there is less hydrogen in coal than in oil (natural gas) with the consequent production of additional carcinogenic products as well as pollutants (sulfur, fly ash, etc.). <u>All</u> of these environmental problems, even the coal mining itself with the diseases and other health problems that any kind of mining entails, can be alleviated at a price.

There is <u>one</u> environmental consequence of the burning of coal (carbon which is poor in hydrogen) which cannot be avoided at any price, and that is the production of carbon dioxide.⁵ The historical record of the carbon dioxide

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in the earth's atmosphere, at five different points on the globe, can be seen in <u>Figure 2</u> and the concentration has risen during the last 15 years by about 5% and this is a global phenomenon. On an historical basis, it is possible to estimate these CO_2 levels from isotope measurements, which is where the earlier data arose, and it is apparent that in about 100 years the carbon dioxide level has risen about 15%, from 290 to 330 ppm. The projections for the future depend upon a variety of assumptions, but all of them involve the burning of coal and shale on a larger scale than at present.

The physical properties of carbon dioxide are the basis for environmental concern. CO_2 is transparent to visible light but opaque to infrared light, and therefore, it produces a greenhouse effect (Figure 3). The visible light from the sun can come through the CO_2 blanket with no difficulty. Wherever the visible light of the sun strikes the surface of the earth it must ultimately be converted into heat and re-reflected out into space. The carbon dioxide adsorbs that heat in the form of infrared and re-reflects it back to the earth's surface. It is essentially a one-way valve, allowing the energy of the sun in, but not letting it all back out, which creates the greenhouse effect.

An estimate was recently made of what this increase in CO_2 in the last 100 years really has done to the temperature of the earth, and the analysis indicates that the heating of the earth during the period 1860-1960 was 0.4° or less. The calculation was then made as to what this should have been from the CO_2 data available as shown in Figure 2. This indicated that a 10% increase in the CO_2 level would correspond to a temperature increase in the range from 0.1 to 0.4°, which is what was found by statistical analysis. The beginning of a correlation between the fact that the CO_2 has risen and its consequence on the average temperature of the earth is becoming evident.⁶ This is the

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only case of which I am aware where this type of correlation was attempted. People mostly dismiss the rise by saying that the 15% increase in the CO₂ level is within the "noise level" of weather measurement, and we really can't tell. However, the work of Hoyt is the first effort to get around the difficulty to obtain a definite answer.

The accumulation of CO_2 can be avoided only by using sunlight as it comes in, not just to produce mechanical work, but to produce the liquid fuel (renewable resource) which is needed for energy and material to run the world's economy. Any carbon dioxide resulting from the combustion of such products will have been removed from the atmosphere the previous year. My proposal is to use the best solar energy capturing machine we know, namely, the green plant, to produce the liquid fuel. We have been using the green plants' stored energy in the form of coal, oil and gas. The problem now is to develop methods of creating annually renewable energy resources using green plants.^{7,8,9} GREEN PLANTS AS SOURCES OF FUEL AND MATERIALS

The process of photosynthesis in green plants is diagrammatically expressed in <u>Figure 4</u> in a simplified fashion, and the numbers (in terms of Btu's) involved in the transformation of carbon dioxide to petroleum are indicated. The carbon dioxide is taken from the air by the sun, reduced to carbohydrate (wood, starch, sugar), with the liberation of oxygen. For many years we used the stored energy of the sun in the form of wood (a carbohydrate) with a heat value of 7000 Btu/pound. In general, wood/starch/sugar is solid fuel, and it would be better if converted into a liquid, a more convenient form, just as we eventually transferred our allegiance from solid fuels (such as coal) to liquid fuels (petroleum) or gaseous fuels (natural gas).

One possible method would be to ferment the sugars (carbohydrate) to ethanol; the sugar is converted to ethanol in a weight ratio of roughly 2:1 and the energy content of the alcohol is roughly twice the energy content of the sugar, with very little energy loss in this process. The weight is reduced by a factor of two and the solid is changed into the more convenient liquid form. The classic examples of efficient plants that produce fermentable sugar directly are sugarcane and corn, both of which belong to the same botanical family and have similar efficiencies.

So far in the United States efforts to produce a fermentation-generated fuel have not been particularly successful, primarily due to political and economic considerations. Several American states, especially Nebraska, have produced "gasohol" (10% alcohol-90% gasoline) from spoiled corn. The program in Nebraska was not only technically but also economically successful and rewarding. Calculations revealed that if 20 bushels of corn are fermented to alcohol (yielding approximately 60 gallons), the distiller's dry yeast remaining from that fermentation (about 300 lbs), when added to 80 bushels of unfermented corn and fed to cattle, increased the amount of meat obtained from those cattle by 50 lbs over what would have been the case if the cattle had been fed 100 bushels of corn.¹⁰

The gasohol discussion is still underway, both at the state and federal level.^{11,12} People who feel that the use of gasohol is positive say that oil imports would be reduced and a market created for grain surpluses. Additionally, farm prices would stabilize and it would be possible to reduce our international trade deficit. The opponents of gasohol argue that farm prices would rise and too much energy will be required to make gasohol from grain. There are other issues in the gasohol debate--automobile performance, air pollution, land

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depletion--and the issue of using food to power automobiles. Due to recent federal tax subsidies, gasohol is often cheaper than gasoline. As gasohol production expands, however, there is a major question still to be answered: Will alcohol for gasoline use more energy than it provides? There have been a number of opinions expressed in print on this matter, some clearly "yes" and some more ambiguous. Our own evaluation is shown in Table 1.

An example of a better method, using the ability of the green plant to capture and store solar energy, is Brazil's decision to substantially increase the amount of land devoted to the growing of sugarcane. Sugar from cane on these newly developed plantations is being directly converted into industrial alcohol by fermentation. This is the first petroleum equivalent from green plants on a current basis. The industrial alcohol so produced is being used as a source of ethylene and other chemical intermediates as well as fuel for automobiles.^{13,10c}, The increased sugarcane production in Brazil is the result of a government decision made in 1975 which increased sugarcane acreage through low interest loans and increased construction of fermentation plants. Brazil has a stated goal of 20% alcohol in liquid fuels by 1982-1984, and it is entirely likely that this will be successful. The Brazilians in 1974 produced 700 million liters of fermentation alcohol, 2.7 billion liters in 1978, and in 1979 the production was 4 billion liters. One of the main reasons for this success is the availability of large areas of inexpensive land that can be machinecultivated to produce cane, with the resultant creation of energy-efficient and cost effective sugar plantations. Sugarcane has become one of the major sources of chemical raw materials in Brazil.

In connection with the availability of fermentation alcohol for fuel, the Brazilian automobile industry has taken steps to modify automobile engines,

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Table l

ENERGY ANALYSIS FOR ETHANOL FROM CANE & CORN

			MCal/ha/yr	
			cane	corn
juni,	Ene	rgy used		
	Α.	Agriculture	4,138	12,008
	Β.	Alcohol plant	10,814	26,146
			14,952	38,154
II	Ene	rgy produced		
	Α.	Alcohol	20,050	23,512
	Β.	Residue	17,550	41,418
			37,550	64,930
III	Net	energy product (+)	22,598	26,776
IV	Etha	anol liters/ha/yr	3,564	4,179

by adding a heat exchanger, so that the cars are capable of using alcohol fuel alone instead of petroleum with no loss of efficiency. Because Brazil has no local primary automobile industry, the automobiles (American, German, Japanese)which are imported, are modified on assembly in Brazil for use with fermentation fuel. One of the unexpected results in the use of alcohol fuel is the reduction of air pollution; the cars run as efficiently as gasoline models and they smell better!

When you examine Figure 4 you can see that most plants are doing only one-half the job. They take the carbon dioxide, which is fully oxidized, synthesize carbohydrate, which is half reduced. We can improve that ratio by a yeast fermentation which eliminates some of the carbon as CO_2 and increases the hydrogen-carbon ratio in the alcohol product. It would be very useful to find a way to get the green plant and the sun to go all the way to hydrocarbon which has an energy content of 19,000 Btu/lb. HYDROCARBONS FROM PLANTS

Sometime in 1973, when it was necessary for me to wait in a gasoline line as a result of the oil embargo, I realized that there are plants which reduce carbon all the way to hydrocarbon. With the thirty years of basic research in photosynthesis which had been done in our laboratory in Berkeley as a background, it seemed altogether feasible to me that by using the principles we had acquired it might be possible to find plants that could make hydrocarbon directly and which could use the energy of the sun to create liquid fuel directly on an annually renewable basis.^{14,15}

One such plant in use commercially as a source of specific hydrocarbons is the Hevea rubber tree which had its original home in the Amazonian basin

of Brazil before it was transplanted to Malaysia and improved agronomically. The hydrocarbons from <u>Hevea</u>, in the form of a latex (an emulsion of oil and water), have elastomeric properties which generate a commercial crop, rubber. Before World War II, in Malaysia, the annual harvest of hydrocarbon (rubber) from <u>Hevea brasiliensis</u> was 200/lbs/acre/year, but by changing agronomic practices and improving plant breeding, commercial rubber production has been raised to 2000 lbs/acre/year since 1946. The Malaysian rubber producers now believe that because of the increased price of petroleum used in the production of synthetic rubber the availability of large supplies of natural rubber will again make that product increasingly important on world markets.

The <u>Hevea</u> is a genus of the <u>Euphorbiaeceae</u> family another genus of which is <u>Euphorbia</u> which has over one thousand species, all of which contain latex (roughly a 30% emulsion of oils in water). The latex flowing from <u>Euphorbia lactea</u>, growing in Puerto Rico, is shown in <u>Figure 5</u>. We are searching for a plant latex with a molecular weight of approximately 2,000 (the molecular weight of the latex hydrocarbon from <u>Hevea</u> is about 2 million which is too large as an oil-substitute).¹⁶

We undertook to determine if there were some of these <u>Euphorbia</u> species which could be grown on land in the United States which was not being used in food production. The various species of <u>Euphorbia</u> grow throughout the world in areas which are not very productive--southwest United States, Africa, Morocco, India, western coast of Chile. We felt that by suitable selection of plant species it might be possible to produce material (hydrocarbons) which would have direct economic use, producing the hydrocarbon in the plants which resulted from stored sunlight.

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The hydrocarbon material which can be extracted from plants resembles a crude oil. It can be treated to make all the products now produced commercially by the petrochemical industry, plus many components which may have higher value as pharmaceuticals.

It is interesting to note that over 40 years ago two efforts to cultivate hydrocarbon-producing plants were initiated in Africa, one in Ethiopia and the other in Morocco. The Italians attempted to grow <u>Euphorbia abyssinica</u> in Ethiopia in 1935-1936 to use the latex for fuel production; it is not known, however, whether or not this experiment was successful.¹⁷ Also, in Morocco in 1940 the French, using <u>E</u>. resinifera, had acreage under cultivation. They were able to obtain a yield of 3 metric tons of oil per hectare from the <u>E</u>. resinifera; we were unable to find how long these plants were grown and this number represents only one figure from one harvest.¹⁸

Our experiments at the University of California, with the plantings established in Southern California, selected two species of <u>Euphorbia</u> for the experimental plantings: <u>Euphorbia tirucalli</u> (a perennial propagated from cuttings) and <u>E. lathyris</u>, an annual (gopher plant) which grows from seeds. The <u>E. tirucalli</u> (African milkbush) grows from 3 inch cuttings and in one year is a bush about 2 feet high; this species grows throughout the world and in Brazil, for example, the trees reach 20 feet in height. This species is sensitive to frost and its range is limited to mild climates. The second species, <u>Euphorbia lathyris</u>, grows from seed to a harvestable 4 foot plant in 7 months. It is frost hardy and if it is not harvested will survive some winters and grow to seeding maturity the following year.

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Both <u>E</u>. <u>lathyris</u> and <u>E</u>. <u>tirucalli</u> can grow in semiarid regions where rainfall is about 10-20 inches/year. Neither requires good soil - and both will grow well in uncultivated rocky areas which are not suitable for food crops. Both grow upright and are adaptable to mechanized harvesting. This is important because mechanical harvesting is a crucial component in developing alternate energy sources and because the latex has an irritant property which would make manual harvesting undesirable.

After the initial selection of <u>E</u>. <u>lathyris</u> and <u>E</u>. <u>tirucalli</u>, the experimental plantings were established in Southern California in 1977.¹⁹ Growth data were kept for both species and monthly extractions were made. The <u>E</u>. <u>lathyris</u>, which produces between 8-12% of its dry weight as oil, yielded by extrapolation about 8 barrels of oil/acre, with unselected seed and no agronomic experience. The first crop of <u>E</u>.lathyris plants were preserved for seed production and were harvested in 1978. The <u>E</u>. <u>tirucalli</u> started from a 3 inch cutting was not harvested until 1978. The bush weighed roughly 2000 grams and produced the equivalent of 15 barrels of oil/acre; the <u>E</u>. <u>tirucalli</u> could either be mowed or possibly, after reaching full size, tapped.

The <u>E</u>. lathyris, shown in <u>Figure 6</u> has been growing on the Southern California plantations for three years, in Northern California at our ranch near Healdsburg and also at the University of Arizona in Tucson.²⁰ At the present time, there is more data on this species than any other.²¹ The yield data indicates a production of approximately 6-10 barrels of oil/acre with wild seed. I am confident that with selection and plant breeding it will be possible to achieve a yield of 20 barrels of oil/acre rather quickly.

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The oil from the <u>E</u>. <u>lathyris</u> is obtained in the following manner: The plants are cut, dried and then ground up into a fine powder and extracted usually with hexane or CH_2Cl_2 , followed by a separate extraction with methanol, and the residual part of the plant (lignocellulose) is then burned for the heat to recover the solvents, with the oil (and sugar) being the residue. The entire process is virtually self-contained. We have done this on a small scale in our laboratory,²² and a miniplant for solvent extraction is now under construction elsewhere.²¹ The remaining material from the hexane solvent extraction process is a black oil, which looks like crude oil and behaves like a crude oil when it is cracked.

We sent a small sample of this hydrocarbon from <u>E</u>. <u>lathyris</u> to the Mobil Corporation and they obtained a cracking pattern, using a zeolite catalyst. $(Table 2)^{23}$ The black oil produces the usual suite of products in the catalytic cracker at 500°C. Therefore, there is no question that the oil from plants such as <u>E</u>. <u>lathyris</u> can be used as the basis for materials for the petrochemical industry. The methanol residue is substantially all fermentable to ethanol.

There are other plants belonging to other families that have long been known to produce directly various kinds of oil. In California and in Australia and Spain and Portugal, the Eucalyptus is very common and grows easily, quickly and copices, that is, it can be cut and regrows again. The suggestion has been made that planting Eucalyptus, cutting and regrowing every two or three years would be a way to have the tree at maximum growth rate and also produce some useful products such as oil and wood.²⁴ The oil from the Eucalyptus can be obtained by a steam distillation of the fresh cut material and consists of a mixture of terpenes, all isoprenoids and mostly C₁₀ with some C₁₅.

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Table 2

CATALYTIC CRACKING PATTERN OF OIL FROM EUPHORBIA LATHYRIS AT 500°C

EHTYLENE	10%
PROPYLENE	10%
TOLUENE	20%
XYLENES	15%
C ₅₋₂₀ NA	21%
СОКЕ	5%
C _{l-4} ALKANES	∿ 10%
FUEL	v10%

When we were in Brazil in 1978 we learned of the existence of a tree in the Amazon Basin which produced oil directly by drilling a hole in the trunk, putting in a pipe and letting the oil run out. At that time, I was given a bottle of Copaiba oil from one of these trees. (Copaiba is the name of a group of species of the genus Copaifera which are spread throughout Brazil.) I was told that the oil came out of the tree directly without further processing or purification, but I had difficulty in believing this. In 1979 we had another opportunity to visit Brazil, and when we arrived in Manaus we found a trip had been arranged to visit the Ducke Forest to see the tree in question. We drove into the jungle and found a tree which was about 3 to 4 feet in diameter, which had a wooden bung in the trunk about 3 feet from the ground. The forester explained that he had drilled the hole about six months before, and the oil is removed from the tree approximately twice a year. A closeup of this species (C. multijuga) showing the bung in the trunk is shown in Figure 7, and it is possible to see the oil stain on the side of the tree. Catching the oil which comes from the hole is the type of "harvesting" which is done. A tree of the same genus but a different species (C. langsdorfii) in the Botanical Garden at Rio de Janeiro is shown in Figure 8.

Also in 1979 I met a sugar grower in Rio de Janeiro who has <u>Copaiba</u> trees on his plantations. I tried to learn how to get the oil from the tree, what the yield is per tapping, how often the tree is tapped and the location of the oil in the tree. He explained that the hole was drilled in the tree trunk and every six months from one hole it is possible to obtain 20 to 30 liters of the sesquiterpene diesel fuel in about 2-3 hours. The bung is replaced and six months later removed and another 20 to 30 liters of oil obtained.

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I inquired as to whether or not more than one hole, at different angles from each other, were ever drilled at one time in the <u>Copaiba</u> trunk. Apparently this was not the practice. The location of the oil in the tree, also, was not known. However, I obtained a piece of <u>Copaiba</u> wood which I had sectioned (<u>Figure 9</u>)and observed that there are small pores, or canals, about 0.2 mm in diameter uniformly distributed from the outside of the tree to the center. It is those pores which run vertically throughout the trunk of the tree which contain the oil. Because the oil is not pumped up from the roots like water, it must be made up in the canopy of the tree and run down into the pores and fill them up. When the hole is drilled in the tree, all the pores above the hole are drained of their oil. I am confident that if another horizontal hole is drilled 90° to the first one, an additional 20 to 30 liters of oil will flow at the same time from the second hole. It is not known how many holes can be drilled in the tree at the same time, but I am sure at least two would be practical.

The oil which comes from the <u>Copaiba</u> is sesquiterpene in character. The chemical composition is shown in <u>Figure 10</u> and because of the particular molecular weight and volatility the material can be used directly in diesel engines. In fact, the oil has been placed directly in diesel engines of Toyota pickup trucks, in a project that has been underway under the auspices of the Instituto Nacional du Pesquisas da Amazonia for two years. The oil goes directly from the tree into the tank of the diesel engine, with no oil companies in between!

I sent a sample of the <u>Copaiba</u> oil to the Mobil Corporation to obtain a cracking pattern.²³ It produces the same kind of mixture in general as the oil from the <u>E. lathyris</u> (mostly aromatics (50%), LPG (25%) and low molecular weight fuel gas (3 to 4%) and coke).

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The next step in our experiments was to derive an energy balance (Figure 12) for materials from a latex-producing plant which is based on 10 barrels of oil/acre/year from <u>E</u>. <u>lathyris</u>. The curved brackets represent energy input, the unbracketed numbers are material output (based on a calculation of 1000 dried tons per day). The numbers in square brackets are energy content of the material output. It is possible to calculate that if only the oil is counted, the product represents 80 tons. It appears that 3.2 energy units are being put into the agriculture with a resultant product of 2.7 energy units in the oil. However. 3.7 energy units are in the sugars, most of which could be recovered as liquid alcohol and which should be taken into account in considering the efficiency of energy production from plant material. The cellulose, some of which can be burned to recover the solvent, is in excess to the extent of about 2.8 energy units. Therefore, there is a very substantial net energy gain in this entire operation.

Comparison of three biomass candidates (corn, cane and <u>E. lathyris</u>) is given in <u>Figure 12</u> in terms of tons of material per acre. It is clear that the overall yield per unit water requirement is highest for <u>E. lathyris</u> and its value is even higher because of the high hydrocarbon content. When the production of alcohol is taken into account, there is no question that the <u>E. lathyris</u> appears to be one of the most successful candidates as a green plant for alternate fuel and material production.

In addition to the planting of <u>E</u>. <u>tirucalli</u> in Southern California, the Japanese have developed a plantation on Okinawa with great success (<u>Figure 13</u>). They have calculated a production of between 10 and 20 barrels of oil/acre/year. The oil from the <u>E</u>. tirucalli resembles that from the <u>E</u>. lathyris.

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The yield of <u>E</u>. <u>tirucalli</u> in Okinawa seems already higher than that of the <u>E</u>. <u>lathyris</u> in California, and the Japanese have expanded their acreage and are making substantial efforts to develop a suitable extraction process for the latex.

There are still other plant families which are more widespread in North America than Euphorbias and which may have similar potential. These are the plants of the family called <u>Asclepias</u> (milkweeds). The extraction of the material from the Asclepias is just now being studied in a quantitative way, and the resulting hydrocarbon material is similar to that from <u>E</u>. <u>lathyris</u> or <u>E</u>. tirucalli, but the question of amount, exact chemical composition, quantitative yields, are yet to be determined.

SUMMARY

The use of green plants to produce hydrocarbons of suitable molecular weight and structure for fuel and materials is a concept whose time has come. The choice of the particular plants for large-scale development has yet to be made for each climatic and soil condition and will depend on growth rates, hydrocarbon productivity, harvest adaptibility and process development. Initial experimental plantings in Southern California, Arizona and Okinawa have indicated the economic feasibility, under today's oil price/availability, of the production of oil and alcohol from hydrocarbon-producing plants. In addition, the existence of a species of tree in Brazil (and other areas of the tropics) which produces diesel fuel directly without additional processing, indicates that there are still many more species of plants and trees whose chemistry can be adapted to production of renewable resources. With the continued increase in the cost of petroleum from ancient fossilized photosynthetic residues and a continued decrease in availability, the development of alternate energy sources based on annual renewability is necessary and feasible. REFERENCES _16-

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FIGURE CAPTIONS

- Figure 1 Cumulative U.S. crude oil discoveries as a function of depth of exploratory drilling (King Hubbert)
- Figure 2 Carbon dioxide in the earth's atmosphere, 1860-2040 (Kellogg)
- Figure 3 Greenhouse effect

Figure 4 Simplified photosynthesis scheme

- Figure 5 <u>Euphorbia lactea</u>, Puerto Rico, showing flow of latex (photograph by G. E. Calvin)
- Figure 6 Euphorbia lathyris, Southern California (photograph by G. E. Calvin)
- Figure 7 <u>Copaifera multijuga</u>, Ducke Forest, Manaus, Brazil showing bung inserted into trunk, from which diesel oil flows (photograph by G. E. Calvin)
- Figure 8 <u>Copaifera langsdorfii</u>, Botanical Garden, Rio de Janeiro, Brazil (photograph by G. E. Calvin)
- Figure 9 Copaiba wood section, showing pores through which diesel oil flows
- Figure 10 Chromatogram of products obtained from Copaiba oil
- Figure 11 Euphorbia lathyris flow chart for energy and materials
- Figure 12 Euphorbia tirucalli, Okinawa, Japan

Figure 13 Comparative biomass yields

Productivity: Tons of material/acre.

Full bar: Total dry weight

Single slope lines: Dry weight of fermentable carbohydrate Cross hatched segment: Alcohol weight obtainable For <u>Euphorbia lathyris</u>: Additional dry weight of oil is represented by partially filled cross hatch, with alcohol equivalent of this oil shown in last separate bar on righthand side.



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Fig, 1



W.W. Kellogg Bull.Atom.Scien., Feb. 1978

XBL 783 - 3858

Fig. 2



Figure 3



XBC 7911-15944





Figure 6



Figure 7

CBB 799-11785



Figure 8

CBB 790-15767





1 cm







Fig. 10



XBL 802-4031

Fig. 11



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Figure 12



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