

(24) - Funding -

Proposal to
Utah Energy Consortium

"Feasibility Study - Improved
Methods for Extraction and Processing of Energy -
Rich Hydrocarbons from Plants"

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Appendix - Literature Review
Background: ~~with particular reference to Guayule.~~

There is considerable interest in the possibility of using plants as sources of hydrocarbons for direct energy conversion and for the production of chemicals which until now have been produced from petroleum sources. This area has been popularized recently by Melvin Calvin in his lectures on hydrocarbons from plants [8]. A large number of plants are rich in low molecular weight hydrocarbons which are suitable as direct sources of oil. Other plants produce fairly high molecular weight polyisoprene and related hydrocarbons which are excellent sources of rubber.

Natural rubber is still considered a premium source of rubber and of great importance in the production of high quality tires. Most of the natural rubber produced in the world comes from rubber tree plantations in Malaysia and related areas. There is considerable interest in developing a natural rubber industry in the United States, largely based on a desert plant called guayule [18]. Although guayule was studied extensively during World War II as part of the Emergency Rubber Project [3,18], very little work was done on the improvement of the plant characteristics by selective breeding and genetic selection and on the improvement of processing and extraction of rubber from the plant.

It is possible to extend the growing range of guayule and related plants to less temperate regions, possibly even southern Utah, by the appropriate use of plant selection, plant breeding and genetics.

It is further possible to greatly increase the efficiency and the yield of rubber extraction from guayule and related plants by utilizing more modern technology than was utilized during World War II. The basic process for obtaining natural rubber from guayule is given in Figure A-1 in the Appendix. The rubber in guayule is present inside individual cells as micro particles. There are thus a number of key steps required. One is the coagulation of the rubber within the individual cells and the agglomeration of the rubber within the cells into a single particle. The cell walls must then be fractured to release the internal rubber content and rubber is then agglomerated into larger particles. This is more or less the present process (Figure A-1).

Another process which has been suggested is to not coagulate nor agglomerate the rubber, but to disrupt the cell walls to allow the intracellular latex to be released and separated. The latex can then be treated by conventional processes [22]. There was actually a patent issued on this process in 1938 although it has never been utilized in any sort of scale-up operation [23]. The use of very high pressure can directly squeeze the latex out of the cells and also produce a rubber-rich latex. A patent was issued on this process in 1942 [24], but the process has

not been utilized. The big problem with such processes, of course, is the prevention of coagulation of the rubber in the plant in order to be able to produce a latex which can then be further processed.

One can also utilize direct solvent extraction [25] rather than the complicated maceration process normally utilized [18, 22]. This is being examined by the Firestone Tire and Rubber Company as a process for the extraction of rubber from guayule [25]. The entire process is by selective solvent extraction.

Other related processes are under development [6,7]. Another process which is of some interest but not extensively utilized is one called "retting," which involves utilizing natural bacteria and other micro-organisms on the plant to partially attack and degrade it [1, 18, 17]. This was originally proposed for removing the resin materials which contaminate the rubber obtained by older processes, but it probably also attacks and weakens the cell walls considerably and should make the cells more susceptible to other treatments. Really, the key to extraction of rubber from guayule is understanding the location of rubber in the plant, which is reasonably understood [16], and understanding the distribution of rubber within individual cells, which is poorly understood and has not been extensively studied. Work on this subject is reviewed by Lloyd [15] and in reports by Art Schwager [2], although the actual question of the microanatomy of rubber in cells is not fully discussed even in these references. The only transmission electron microscopy study on rubber in guayule is a recent thesis by Bauer [4] which utilizes seedlings and mainly looks at mechanisms of rubber production.

It is well known that high intensity ultrasonic radiation [5, 13] can disrupt and otherwise affect cells, including plant cells. This method is widely used for the disruption of cells to release their intracellular contents. There have been a number of studies on the effects of ultrasound on plant cells [11, 14]. The potential use of ultrasonic treatment for the extraction of rubber from guayule and other plants has apparently not been considered. Ultrasonic effects on cells involves a number of mechanisms: 1) Thermal mechanisms which, depending on the loss mechanisms in the material, can lead to heating. 2) Cavitation, the formation of bubbles and/or the resonance of bubbles in the ultrasonic field, which produces severe agitation and mixing, even on a submicron level [9, 12, 20, 21]. This is one of the major mechanisms for cell disruption and for agitation and stirring in ultrasonic systems. 3) Nonthermal, noncavitation effects [20, 11]. Such effects are poorly characterized and somewhat speculative in the present literature. Acoustic streaming, local agitation within individual cells, has been studied and is reasonably well understood [9, 12, 20, 21]. Clearly the

application of ultrasonic energy to plant cells can result in significant agitation of the intracellular contents, which may be useful in terms of rubber processing. Ultrasonic radiation can also be used to emulsify and to produce highly stable dispersions and is commercially used for such purposes [11]. Other effects of ultrasonic energy may well be the actual destruction of cell membranes and cell walls, particularly if the energy is intense enough and if cavitation processes can be optimized [12]. This may be of even more suitability if cell walls have been preweakened by micro-organism attack, such as possibly in the retting process [1, 17]. Finally, ultrasonic processes produce efficient agitation and may speed up solvent extraction processes.

Rationale:

west
B
A modification of the present processing methods (~~Figure A-1~~) for the extraction of rubber and other hydrocarbons from guayule and other related plants may be possible through the use of local intense ultrasonic treatment (~~Figure A-3~~). It is possible to cause significant intracellular agitation and aggregation or agglomeration of particles by the application of ultrasound. It is possible to physically disrupt cell walls by the application of intense ultrasound, particularly if assisted by extensive cavitation. This process may be greatly facilitated by preweakened cell walls, either due to micro-organism attack or perhaps due to osmotic gradients [19]. The extraction of rubber and other hydrocarbons from partially fractured cell walls and highly agitated intracellular cytoplasm by selective solvent processes would also be facilitated by ultrasonic treatment.

A
It may, therefore, be possible to develop [a very simplified process for extracting rubber and ^{other} hydrocarbons from guayule and other related plants by the synergistic use of intense ultrasound, partially water immiscible solvents, and selective pH and temperature conditions, perhaps coupled with ~~preweakening~~ ^{enzyme} of the cell wall by either micro-organism attack, and/or osmotic gradient methods. Such a process might well eliminate much of the heavy machinery presently necessary]. *Insect*
A
for the micron maceration of guayule in the present process. The only heavy machinery required would be that for leaf removal and for the initial shredding of the plant both of which are parts of the present process (Figure A-1).

Proposed Work:

C
1. The Microanatomy of ^{Hydrocarbons plants} Rubber in Guayule

In order to understand and optimize the processing conditions, it is necessary to examine the effects of the different processing methods on individual plant cells on a submicroscopic level. This can be done effectively by optical microscopy, as demonstrated by Lloyd [15], as well as by transmission electron

should provide us with a good detail of information and enable us to make a judgment as to whether or not the destruction or at least the deterioration of ~~guayule~~ cell walls is feasible. If we find that there are on-going research programs on the retting of ~~guayule~~, we will endeavor to obtain preretted samples to study for the effect of ultrasonic treatment on such samples.

b. Osmotic Disruption - Again considerable literature work is necessary to determine the effects of osmotic gradient and solvent gradients on guayule cell wall properties. ^{and on the cell walls of certain Euphorbia.} Such studies can be done in real time in the optical microscope by examining the cells during the course of application of osmotic gradients, temperature, and solvent treatments. pH will also be used as a variable. The objective here will be to see if there is an optimum set of solution conditions which can lead to either the disruption or the deterioration of the ~~guayule~~ cell which will make it more susceptible to ultrasonic treatment. It may even be possible to develop a set of conditions to disrupt the cells which would not require ultrasonic treatment.

c. Final Processing - Assuming the above two general objectives are met, i.e., we find a suitable set of conditions which will allow the disruption of cells of ~~guayule~~ by relatively simple physical and chemical means to produce a suspension or dispersion of rubber particles in an aqueous or semiaqueous medium, then we will examine means to separate the rubber and other hydrocarbons from that medium. It is difficult a priori to predict what ultrasonic treatment might do to such a suspension. In view of the fact that ultrasonics is commonly used to emulsify and stabilize dispersions, it may well be that such a dispersion may be intrinsically stable and may need the addition of agglomerating agents and anti-dispersing agents to produce rubber flocculation; it may also be that continued ultrasonic treatment may inherently lead to agglomeration of the rubber. If the dispersion is a relatively stable one, then it would in essence be a latex or latex-like solution and the rubber can be separated by conventional latex handling technology. The final processing will probably involve antidispersing, flotation, and some selective solvent extraction processes.

Summary and Significance:

In ~~summary~~ we propose to study (Figure A-2) the effect of ultrasonic energy and osmotic and solvent gradients, and the possible synergism between these two processes, on the processing and extraction of rubber ^{and hydrocarbons} from ~~guayule~~. ^{Plant} This is a feasibility study. The main objective is to suggest whether or not a more detailed study on these potential processes is merited. Assuming that the study concludes that there are potential advantages to ultrasonic and/or osmotic treatment in guayule processing, we will conduct a very preliminary economic analysis

~~of the feasibility of the process.~~

The significance of this work is best evidenced by looking at Figure A-1 (appendix) which is the present process for the extraction of rubber from guayule. Note that this process is an extremely machinery- and energy-dependent process and is thus suitable only for fairly large plants and large installations. Figure A-2 ~~A-2~~ outlines a very speculative scheme for an ultrasimplified process for removing rubber and other hydrocarbons from guayule, which assumes that most of the assumptions made in this proposal are correct. It is clear ^{from} Figure A-2 that such a process could be done on a relatively small scale, would not require extensive capital investment, and would probably be amenable to small business development, development on Indian reservations, and utilization in developing countries.

~~The proposed work and task chronology for this project is given in Figure A-2.~~

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Budget:

1.	<u>Personnel</u> - Technician Assistant, part time including benefits	\$3,700
2.	<u>Supplies</u> - Seeds, Seedlings, Glassware, Solvents, Transducers, Electronic and Mechanical parts	1,500
3.	<u>Equipment</u> - Ultrasonic driver and crystals	1,500
4.	<u>Travel</u> - For visits to collaborators and processing sites and to information sources	800
5.	<u>Instrument Time</u> - TEM/SEM/DSC/Electronic equipment rental	1,900
6.	<u>Other</u> - Photocopying; reference materials; secretarial	<u>400</u>
	Total	\$9,800