ALGAL BIOPLASTICS: A REVIEW

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Abstract:

The increased use of plastic is destroying the ecosystem. It causes carbon emission and is a threat to marine life and humans due to biomagnification. Recycling of plastics is a difficult process and the additives used are also toxic in nature. Hence, researchers have concluded that there is a need for an eco-friendly, biodegradable alternative to plastics. Bioplastics are a sustainable solution to this problem. One of the potential sources for bioplastic production is algae. The present review highlights algal-bioplastics, their production and applications.

Key words: bioplastics, Algal plastics, petro plastics, bioproduction, bioapplication.

Introduction:

Usage of plastics has severely affected the balance of our ecosystem. 359 million metric tons of plastic was produced in 2018 alone. Out of this, 25% was recycled, 22% was dumped in landfills or incinerated, and 42% was lost into the environment [1]. 8 million tons of plastic waste ends up in the ocean annually [2]. 15% of the total global carbon emission is due to the greenhouse gases from the plastic lifecycle [1], preventing global efforts to reduce CO_2 emissions [3,4]. Almost 90% of plastics are fossil fuel based, and though they are cost efficient and durable, they pose a huge problem to the environment as they result in 400 million tonnes of GHG emissions every year and lead to depletion of fossil resources, climate change and waste management problems [5]. Plastic decomposes slowly due to abiotic factors and the microplastic particles formed pollute our environment [6], causing biomagnification, which leads to ill effects on human health [7].

The demand for plastics keeps increasing as it is present in almost everything we use, like household packaging material, bottles, cell phones, printers etc [8]. If the present trend continues, then by 2025 there will be 1 ton of plastic for every 3 tons of fish in the ocean, and by 2050, the amount of plastic in the ocean will be greater than the number of fish [9]. This plastic debris in water bodies causes pollution, called “white pollution”, which has a serious impact on marine life [10].

Plastic recycling is a difficult process and if it is not done properly, the resulting material will be structurally weak and will have limited application. Plastic polymers contain additives to improve their properties, some of these being harmful and can cause reproductive disorders, cardiovascular diseases [11] and an increased cancer risk [12].

Instead of looking for ways to reduce the demand for plastic, we can focus on finding a more sustainable way to meet this demand. Biodegradable fossil-based polymers are not a good alternative to conventional plastic as their production from petrochemicals results in CO_2 production. Oxo-degradable plastics (contain chemicals that accelerate their degradation) contribute to microplastic pollution in the environment [13,14].

So, researchers have concluded that we need an eco-friendly, biodegradable alternative to synthetic plastics for daily use, like packaging, healthcare sector, etc., called bioplastics which can degrade to produce carbon dioxide, methane, water, biomass, humic matter, and a variety of other natural chemicals that can be easily removed [15].

Table (1): Comparing Bioplastics and Petroplastics [16]

PARAMETER	BIOPLASTICS	PETROPLASTICS
Renewable Resource	Yes or partially	No
Sustainable	Yes	No
Breakdown in the environment	Biodegradable and /or compostable	Some degradable by polymer oxidation
Polymer range	Limited but growing	Extensive
GHG emissions	Usually low	Relatively high
Fossil fuel usage	Usually low	Relatively high
Arable land usage	Currently low	None

Bioplastics:

The plastic material is defined as a bioplastic if it is either bio based, biodegradable, or biocompatible. Bioplastics are made from renewable organic sources such as sugar cane, potato starch or cellulose from trees etc., agricultural waste and microorganisms like algae. Various plant based sources like starch account for 80% of the overall market of bioplastics. Their function is similar to petroleum-based plastic [17]. With Asia (including Thailand, India and China) becoming a major producer of bioplastics, production is estimated to increase by more than 400%, according to data from the 9th European Bio plastics conference [18].

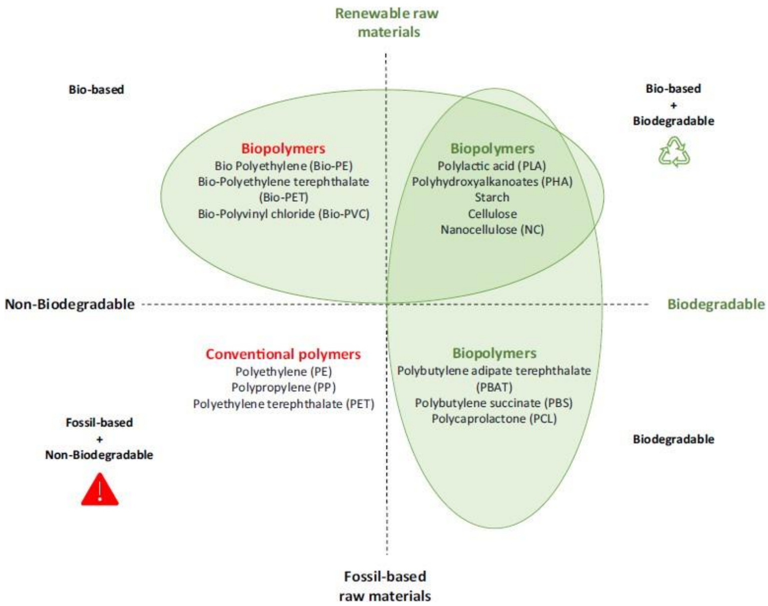

Fig (2): Types of bioplastics [19]

Types of bioplastics:

Bioplastic materials are classified into three main groups:

- Bio-based or partially bio-based plastics;
- Bio-based and biodegradable plastics;
- Fossil-based and biodegradable plastics.

Materials used in bioplastic production:

Bioplastics can be produced from lipids, proteins or carbohydrates. The main commercial ones currently being used are polyhydroxyalkanoates (PHAs), poly lactic acid (PLA), starch plastics, cellulose plastics and proteins plastic [17]. They can be synthesized from food crops like cassava, corn or sago [20,21], but using these results in resource competition [22-24]. These can't be sustainable over a long time, are not water resistant and have low mechanical properties [25].

In order to overcome this, we can use seaweed and microalgae. Microalgae are photosynthetic unicellular cells in aquatic environments that synthesize algal biomass. They have a high growth rate, high environmental tolerance [26], low maintenance and low growth requirements. They can reduce the carbon dioxide produced [27] as they grow rapidly (i.e., have a short harvesting time) and trap greenhouse gases [27-35]. They can grow on waste resources and hence don't compete with production of food. They can also grow in harsh climates and help in wastewater remediation [36]. They contain polysaccharides (> 60%) [37,38], proteins (60%) [39] and lipids (> 50%) [40,41] that can be used as raw materials for bioplastics and do not need artificial polymerization processes [42].
Macroalgae like seaweeds have a greater biomass, are rich in polysaccharides, are promising sources of bioplastics [43,44] and can be grown in a wide range of natural environments economically throughout the year. These bioplastics can have greater tensile strength and chemical resistance. The red macroalgae *Kappaphycus alvarezii* was recently investigated to produce a bioplastics for food packaging applications [45].

Hence, algal-bioplastics can be a non-toxic alternative, which reduces fossil fuels, and reduces negative impacts of petroleum-plastics on the environment [46].

Algal sources:

A few researchers investigated the synthesis of bioplastics from microalgae [46, 47].
Currently, starch, cellulose, PHA, PHB, PLA, PE, PVC and protein-based polymers are some of the examples of the compounds from algae biomass used to develop biodegradable plastics [48].
Alginate is a polysaccharide found in marine brown seaweed such as *Macrocystis pyrifera* [49], *Laminaria hyperborean* [50], etc. Alginate associated with cations like calcium has better mechanical strength and can be used to produce environment friendly packaging materials [51].

Carrageenan is a polysaccharide that is found in marine red algae (30–50%) [52] such as *Chondrus crispus* [53] and *Mastocarpus stellate* [54,26]. Poly vinyl alcohol (PVA) [55] and 5% SiO2 [56] have been used to improve its mechanical properties.

PLA is a bioplastic which is obtained from lactic acid. It is biodegradable and has low toxicity,so it is a good material for bioplastics production [54]. Microalgae such as *Chlorella sp*. [55,59] ,*Scenedesmus sp,* Synechococcus *sp.* [60] and *Nannochloropsis sp*. [61] [62,22] are rich in carbohydrates (> 60%) that can be used for PLA production. They are used for many medical applications.

Properties of PLA:

- Biodegradable, recyclable, compostable.
- Low moisture absorption and high wicking
- High tensile strength, being amorphous or crystalline as necessary, high heat resistance
- High permeability

Starch is a polysaccharide composed of amylose and amylopectin. Starch in microalgal cells like *Chlamydomonas* [63] can accumulate to more than 50% under specific conditions [38,63]. A very promising starch-producing strain is *C. reinhardtii* 11-32A with interesting plasticization properties with glycerol [63]. Thermoplastic starch (TPS) is the starch based biopolymer which is obtained by energy application (thermal/mechanical) on starch. This TPS is mostly used as the alternative to the synthetic plastic Polystyrene (PS). TPS is biodegradable, but has poor mechanical properties. It's currently used for food packaging, bottles, etc.

Plant proteins are biodegradable and have been used to produce bioplastics [17]. Many microalgae lik *Chlorella sp* and *Botryococcus braunii* [64] can accumulate ample amounts of proteins with fast growth rate [40].

Process of bioplastic production:

- *Cultivation of algae:*

There are numerous systems for cultivation of microalgae. But only some are suitable for cultivation. The open systems such as raceway ponds are the primary cultivation systems, the closed systems include photobioreactors (PBR) [65].

- *Extraction of algal sources from macroalgae:*

Extraction of polysaccharide from *Codium fragile* :

Polysaccharide from the seaweeds are the main component of bioplastics, this includes Carrageenan, agar, floridian starch and alginate. The collected seaweed is dried, mechanically grounded to eliminate impurities and later undergoes a hot extraction process to separate the polysaccharides without losing its quality and freshness. The dissolved polysaccharide mixture undergoes centrifugation to eliminate denser cellulose particles, is filtered and concentrated. Recovery of polysaccharides happens in two methods, one where the gelling temperature of polysaccharides is increased by addition of potassium chloride solution causing filtrate to gel immediately and another method where the polysaccharides are precipitated in isopropyl alcohol causing the filtrate to turn into a coagulum of polysaccharides, alcohol and water [44].

- *Method of algal bioplastic production:*

Around fifty pounds of dried *Eucheuma cottonii* was collected from the West Coastal region of India and washed and soaked in water for 24 hours. It was then chipped to a size of about 2 cm and boiled up to 120 C, by setting the water to the algae chip ratio at 7. The high temperature was slowly lowered and maintained for 1 h at 80 C. Remaining solids from gel were filtered and re-boiled and filtered again and poured over a mold to obtain handmade sheets of bioplastics after they had been sun-drying for 3 days.

The handmade sheets of bioplastics were converted into strips and soaked in water for 24 hr resulting in the setting of the water to the sheet at the ratio of 3 to develop gelation and were boiled up to 120 C. This high temperature was lowered and maintained at 80C for 15 min slowly to form gel at room temperature. The gel was then separated and mixed with latex obtained from *Artocarpus Altiris* and *Calotropis gigantea*.

- Pure red algae bioplastic was prepared without binding it with latex or glycerol.
- A mixture with glycerol (95% purity) was also prepared.

Both the mixtures were poured over frames and sheets with certain thickness were obtained finally after sun-drying continuously for about 7 days. The thickness and weight of the sheets were measured and density was calculated. A tensile test was conducted at room temperature to find tensile properties of the pure bioplastics and the latex blends.

An example of algal bioplastic usage:

- *Polyurethane:*

Polyurethane (PU) can be renewably sourced and biodegraded [66-68]. Many fungi can degrade polyester PUs with the help of esterase, urease, amidase, and protease enzymes [69].

Gunawan NR et al. [70] developed polyester polyols from algae oils and developed polyurethane (PU) foams that meet the standards for footwear that can be degraded by many bacteria and fungi that grow abundantly on PU in the natural environment.

Fig (3): Algenesis algae-based PU flip-flop prototype [76]

This PU foam had a 52% biological content by mass, as the isocyanate used was derived from petroleum sources. Degradation of the PU was examined under two conditions: through exposure to compost and soil environments, and through in vitro enzymatic hydrolysis. Samples in soil showed greater degradation.

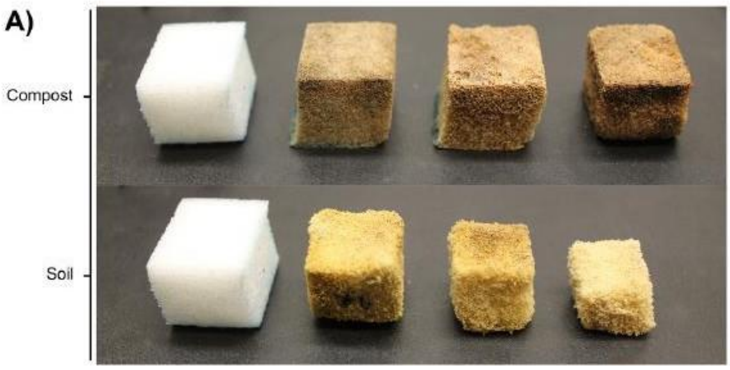

Fig (4): Biodegradation of PU cubes over 12 weeks [76]

After 12 weeks in compost and soil, several microorganisms were found on the PU. In particular, bacteria *Pigmentiphaga*, *Roseomonas*, and *Phenylobacterium*, and the fungus *Arthrographis* were found in abundance in PU from both compost and soil environments. It is likely that they produce enzymes that can cleave ester and urethane bonds in polyester PUs. *Cladosporium* sp. also caused significant surface degradation of the PU.

Four commercially available esterases were tested for their ability to depolymerize the PU foams: lipase from *Aspergillus niger*, lipase from *Candida rugosa*, esterase from *Bacillus subtilis* and cholesterol esterase from *Pseudomonas* species. Cholesterol esterase from *Pseudomonas* species performed the best and depolymerized 38% of the PU over the course of 24 h. The *Pseudomonas* genus was found in abundance in the compost sample.

This study reveals the potential to use polyester PU to create commercial products that are sustainably-sourced, biodegradable, and potentially recyclable.

Challenges of algal bioplastics:

- Identification of suitable algae.
- Selection of appropriate polymers and their extraction from algae based on conditionslike biodegradability, renewability, rate of degradation, moisture content, etc.
- Considering the impacts on the environment when bioplastics are being degraded, so thatno harmful gases are released.
- There might be an unpleasant odour in algal bioplastics.
- Waste management of bioplastics.Techniques like incineration, composting, landfilling,etc can be used [7].

Improving properties of bioplastics:

Biodegradable bioplastics generally possess poor mechanical properties and are unsuitable for many applications [71].

Glass and carbon fibers are used to reinforce bioplastics, but since they are non-biodegradable, they can be replaced by more sustainable, biodegradable materials, such as lignocellulosic fibers and lignin [72]. Other reinforcement methods are the mold temperature increase and dehydrothermal treatment [73].

Cellulose fibre has good mechanical properties and can be used as natural fillers to improve the properties of bioplastics without affecting their biodegradability [74]. Many algal taxa contain cellulose and hemicellulose such as Chlorophyta, Rhodophyta, Phaeophyceae, etc [75-77]. It is found in algae such as *Ulva fasciata*, *Lyngbya sp*. [78], and *Cladophora sp*. [79].

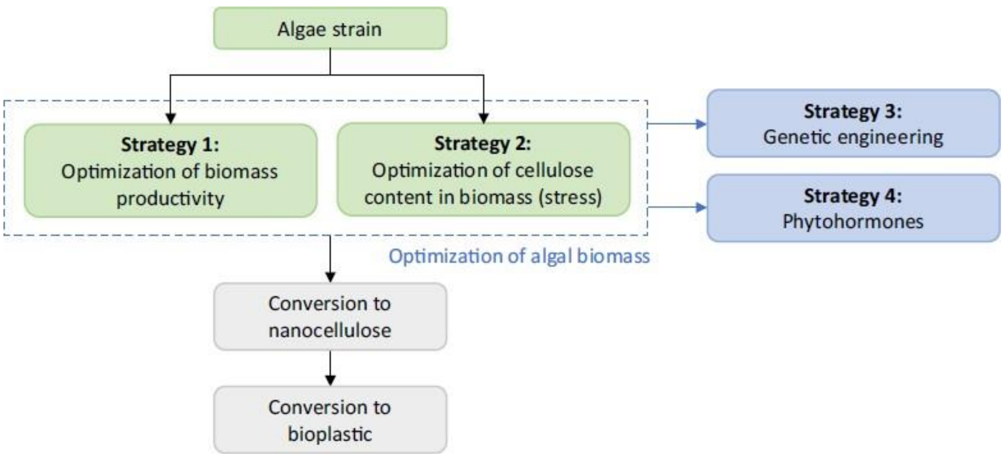

Fig (5): Optimization strategies of algal biomass for nanocellulose production [80]

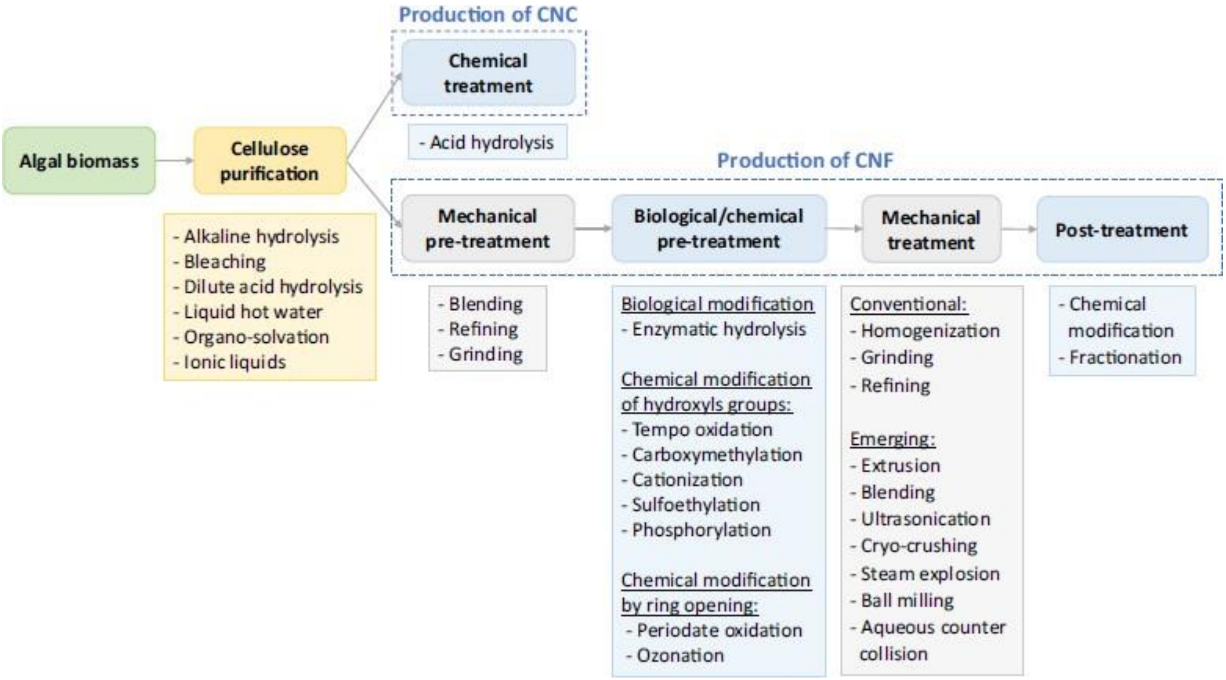

Fig (6): Possible conversion processes from algal biomass to nanocellulose materials [80]

Another way to increase bioplastic performance is by using a plasticizer. This reduces brittleness and increases toughness and flexibility [17]. Glycerol can serve as a cost effective plasticizer
[81] as it is the co-product formed during microalgal biodiesel production [82]. Various plasticizers such as urea, sucrose maltose, water etc., are added to strengthen the properties of starch as a bioplastic.

Algae is also used as fillers to improve mechanical properties in a cost-effective way (algal biocomposites). Graft copolymerization further strengthens the fillers and improves microalgal and polymer compatibility.

Blending microalgae with petroleum based plastic [65,7], natural products or polymers while producing bioplastics can help increase their lifespan, enhance their properties and mechanical performance [83]. The tensile strength and thermal plasticity of the composite made up of *Chlorella sp.* and modified Polyethylene (PE) are more satisfactory as compared to the composite made from unmodified PE. The composite also was able to be easily moulded into different shapes [30].

Studies show that particle size of algae affect the mechanical properties of the composites. Large particles show better mechanical properties. More research should be done on improving adhesion between matrix and filler, optimizing the efficiency of composite [84].

Applications of bioplastics:

- They are used in packaging materials like bottles, bags, loose-fills, cutlery etc.
- Bioplastics can be composted or used as fertilizer, which helps in maintaining moisture in the soil.
- Another application was to create a bioplastic bottle by mixing red algae powder with water. [7]
- Production of food packaging having low ecological impact. eg: cups made with PLA [85], bowls made with PLA used by McDonald's [86], bio-based trays used by Wal-Mart. [87]
- Agricultural applications include production of bioplastic nets as alternatives to polyethylene ones (used to increase the crop's quality and yield and protect it from birds, insects, and winds), biodegradable non-toxic grow bags, and mulch films [88].
- In the medical field, they can be used in implants, artificial cornea, wound dressing, diagnostic sensors, tissue and neural engineering, and pharmaceutical fields [88-90].
- Civil engineering applications include the utilization of foam composites (bio foams) [91].

Advantages of bioplastics:

- Potentially a much lower carbon footprint than oil-based equivalents.
- Lower energy costs in manufacturing.
- Reduction in litter and improved compostability.
- Less use of oil
- Novel functional properties, low GHG emissions during manufacture [92].
- Biodegradable.
- Durable
- Sustainable[93]

Limitations of bioplastics:

- Not cost efficient, mostly not water resistant.
- Preparation of starch-based polymers is challenging compared to conventional polymer production
- TPS films have less tensile strength (TS) indicating limited mechanical performances.
- PLA has a considerably slow biodegradability rate.
- PLA also has a low melting point, this makes it difficult to process and recycle alongwith other plastics.

End life scenarios for bioplastic materials:

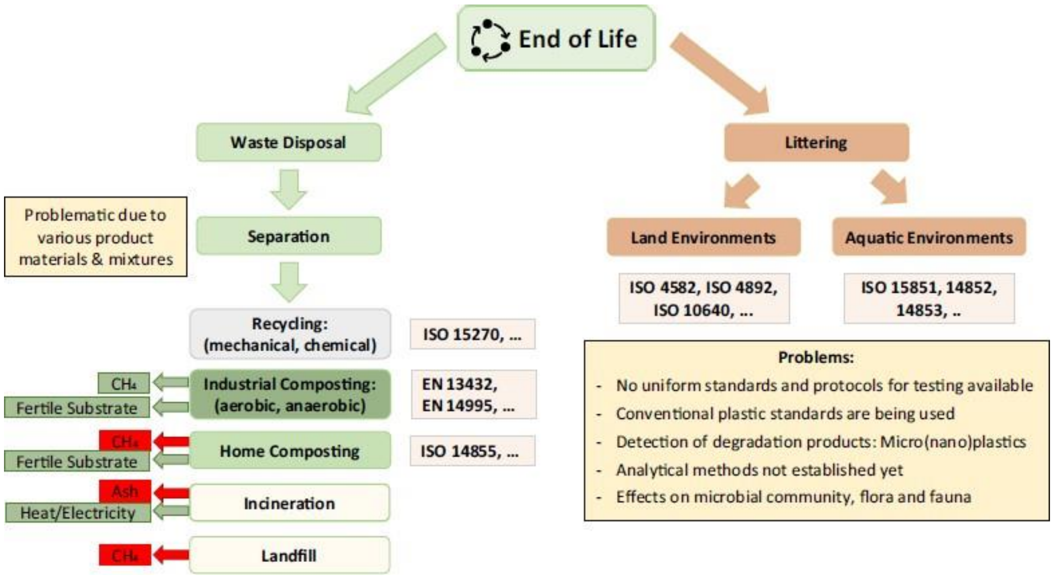

Fig (7): Possible end life scenarios for bioplastic materials [80]

The main end-of-life choices for biodegradable plastics include recycling, incineration, composting (aerobic and anaerobic), and landfill [94]. Recycling is the best solution for disposal of the bioplastics to maximize the environmental benefit and reduce the consumption of renewable resources.

Conclusion:

More research focusing on understanding the use of algae in the production of bioplastics is needed in order to attain a sustainable solution to the problems we are facing with the materials being used at present [80]. Using genetic techniques we can try to increase bioproduct production of microalgae [95]. Algal biorefineries, if established, will prove to be a good alternative to the petro-chemical industry. Further research in the field of bioplastics can lead to alow-carbon economy in medicine, packaging, automotive engineering, etc [96].

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