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ADVANCES IN BIOACTIVE PROPERTIES OF EUPHORBIACEAE PLANTS AND OTHER FEEDSTOCKS: A REVIEW

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Abstract

The review highlights the attempts to summarize the advances in biofuel production from Euphorbiaceae species. It is known that the plant species belonging to the Euphorbiaceae family are a plentiful source of latex and the latex in turn is rich in oil and hydrocarbon. The plants discussed here present exciting possibilities for the future but the viability depends on the success which can be achieved over the next few years. The paper also updates the progress made in biofuel technologies, biomass resources, feedstock, processing techniques and fuel properties. The large dependence on biofuels is encouraging from environmental and economic point of view, as this research can significantly uplift the economic conditions of rural farmers and thus contribute to national economy. So, we put in a nutshell the efforts which are on to find and use substitute form of energy that can make a significant contribution to the world's growing energy need.

Keywords: Biofuel, Petro plants, Euphorbiaceae, Hydrocarbon, Latex, Biocrude.

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INTRODUCTION

"The use of vegetable oil as fuel might seem of no importance in our times. However, such products can gain importance in the course of time and reach an equal status compared with today's petroleum and these coal-tar products". Biofuels are fuels produced from renewable resources, especially plant biomass, vegetable oils, and treated municipal and industrial waste that possesses the potential to replace some fossil fuels. Biofuels are gaining a considerable attention because of increasing pressure on our natural resources which include deforestation, green house effect, soil erosion and other global hazards. Rising fuel prices and huge import expenditure are important issues that have augmented the demand of bio-energy as an important alternative to protect the environment. With the increase in the demand of petroleum and its limited supply, the necessity to opt for alternate technologies for production of liquid fuels has become a prerequisite. Fossil fuels are limited finite resource. This therefore, leads to the establishment of alternative renewable energy resources that can replace and prevent possible negative impacts that may result from continuous use of fossil fuels. There are various benefits of biofuels over fossil fuels which include energy security, reduced environmental impact and low emission profiles. Biofuels, because of their environmental benefits have gained significant attention [1]. To be a viable alternative for the fossil fuels, the liquid fuels not only should have environmental benefits over the fossil fuels it replaces, but should also be economically competitive with it, and be produced in sufficient quantities to make a significant impact on energy demands [2]. Green plants convert 1% of the sunshine that falls on them into carbohydrates and other by-products that are competitive with synthetic petrochemicals, such as oil, hydrocarbon etc [3].The green part of the plant(chlorophyll) absorbs sunlight and separates into positive and negative charge. The positive charges are oxygen and negative charges become active hydrogen. These positive and negative charges perform the carbon reduction cycle of photosynthesis. Carbon dioxide which enters the carbon cycle is converted to carbohydrates [4]. Carbohydrates are major end product of green plants. The carbohydrate is solid sugar which is useful for living organisms as a fuel. Melvin Calvin revived the idea that alcohol is not only a fuel for men and machines but it can also be used as a chemical raw material in place of petroleum feedstocks in various applications.

BIOFUELS, THEIR SOURCES AND PRODUCTION

Biofuel refers to solid (bio-char), liquid (bioethanol, vegetable oil and biodiesel) or gaseous(biogas, syngas and biohydrogen) fuels which are produced from biomass and have significant importance in transport sector [5-8]. Biofuels carry many advantages as they are non-toxic, biodegradable, free of sulfur and carcinogenic compounds, locally available from common biomass sources, accessible, sustainable, and reliable fuel [9-12]. Biomass is the name given to all the Earth's living matter which includes wood, woody crops, short rotation herbaceous species, sawdust, biosolids, grass, bagasse, industrial residues, agricultural wastes, waste paper, municipal solid waste, wood wastes,waste from food processing, aquatic plants and algae, animal wastes. Biomass components include cellulose, hemicelluloses, lignin, extractives, ash and other compounds (Fig.1.). Cellulose is a remarkable pure organic polymer and is a major component in plants and wood, it comes in various forms and is also a part of domestic and industrial wastes [13].

A first-generation fuel is generally one made from sugars, grains, or seeds, i.e. one that uses only a specific (often edible) portion of the above-ground biomass produced by a plant, and relatively simple processing is required to produce a finished fuel. First-generation fuels are already being produced in significant commercial quantities in a number of countries. Common first-generation biofuels include vegetable oils, biodiesel, bioalcohols, biogas, solid biofuels, syngas.Second-generation fuels are generally those made from non-edible lignocellulosic biomass,either non-edible residues of food crop production (e.g. corn stalks or rice husks) or non-edible whole plant biomass (e.g. grasses or trees grown specifically for energy).Common second-generation biofuels include vegetable oils, biodiesel, bioalcohols, biogas, solid biofuels, and syngas. Third generation biofuels are produced from algae, fungi, water melon juice, grasses etc. Third-generation biofuels are produced from extracting oil of algae – sometimes referred to as "oilgae". The juice of water melon contains 7 to 10% of sugars such as glucose, fructose, sucrose and also few quantities of amino acids. High water content in the fuel dilutes molasses in biofuels by 25% and only concentrated juice is used.

BIOETHANOL PRODUCTION

Bioethanol, which is among the most common biofuel can be produced by a well known process fermentation. The process is based on enzymatic conversion of starchy biomass into sugars. The biomass used for fermentation includes cereal crops, corn, sugarcane, sugarbeets, potatoes, sorghum, cassava [14]. The various types of feedstocks for production of bioethanol can be categorized as (1) sucrose containing feedstocks – sugarcane, sugar-beet, sweet sorghum and fruits,(2) starchy feedstock – corn, milo, wheat, rice, potatoes, cassava, barley,(3) lignocellulosic biomass – wood, straw and grasses[15].The advanced production of ethanol on which R&D

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focuses, utilizes the all available lignocellulosic materials, which include cellulosic waste, cereal straw, many fast growing plants such as poplar trees & switch grass. Table 1 shows amount of biofuel production by variouscountries. Bioethanol (20-50%) can be blended with gasoline for use in vehicles. In Brazil Bioethanol is used in pure form or with modifications like blending 24% bioethanol and 76% gasoline. This mixture of gasoline and ethanol is known as gasohol [16]. Bioethanol produced in Brazil is less expensive in comparison to that produced in Europe from sugarbeet, because ofshorter processing times, lower labor and transportation costs [6,17]. Bioethanol's global production in 2006 was 51 billion litres with Brazil and United States contributing about 18 billion litres, which is 35% of the total. Bioethanol as a biofuel has many advantages (Fig.2.) [12,18].

BIODIESEL PRODUCTION

The other most common is biofuel is Biodiesel which has different feedstock requirements & extraction procedures. It involves the extraction & esterification of vegetable oils, cooking oils using alcohols. The oil is extracted chemically or mechanically from rapeseeds, sunflower seeds, soy seeds & palm oil seeds. Hydrogenation of oils & fats is a new process that is entering the market. In this process, biodiesel can be blended with fossil diesel upto 50% without any engine modifications. New processes have been developed which involves synthetic biofuel production via biomass gasification & catalytic conversion to liquid using Fischer-Tropsch process(biomass conversion to liquids BTL). Biodiesel as a biofuel has many advantages(Fig.3.)[19].

(1) Portability
(2) Ready availability
(3) Renewability
(4) Higher combustion efficiency
(5) Lower sulfur and aromatic content
(6) Higher cetane number

Advantages come along with disadvantages

(1) Higher viscosity
(2) Lower energy content
(3) Higher cloud point
(4) Higher nitrogen oxide emissions
(5) Lower engine speed and power

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(6) Engine compatibility

(7) High price and greater engine wear

Out of the total primary energy being consumed by the world in the form of fossil fuels, 58% alone is consumed by transport sector [20]. Brazil was the first country to use bio-ethanol as a real alternative to oil based fuels. Tanzania has become a leader in biofuel because of its ideal geographic and climatic conditions for growing large variety of biofuel crops-sugarcane, palmoil, jatropha, soybean, cotton [21].

Biodiesel is an alternative fuel for fossil diesel fuel produced by transesterification of oils/fats. Transesterification is the reaction of a fat or oil(triglyceride) with an alcohol such as methanol to form fatty acid alkyl esters, methyl and ethyl esters. The reaction occurs in the presence of an inorganic catalyst. Alkali-catalysedtransesterification is much faster than acid-catalysedtransesterification. The alkalis used are sodium hydroxide, potassium hydroxide and carbonates. Any vegable oil or animal fat can be utilized as a feedstock biodiesel production. The oils/fats are triglyceride molecules(glycerin esterified with three fatty acids).Biodiesel is produced from vegetable oils using the base-catalyzed technique as it is the most economical process for treating virgin vegetable oils, requiring only low temperatures and pressures and producing over 98% conversion yield [19].

HYDROCARBON FROM PLANTS

The hydrocarbons present in the plant latex are long chains which are derived through similar chemical steps. The chain length can vary from five to fifteen to higher number of carbon atoms. Two fifteen carbon atom chains together make 30-carbom compound generally known as steroid. Hydrocarbon chains with more than 30-carbon atoms givepolyisoprenes. A major category of plants examined so far which contain hydrocarbon belong to the family Euphorbiaceae. *Heveabrasiliensis,* the rubber tree also belongs to the same family. It grows commercially on plantations in Malaysia [22]. In *Heveabrasiliensis*hydrocarbon is stored as latex which is an emulsion in water[4]. The hydrocarbon is of high molecular weight. The genus Euphorbia of Euphorbiaceae family produces a natural latex(water-oil emulsion) which is about 30% triterpenoid material. Milkweeds which belong to the family Asclepiadaceae also produces similar polyterpenes. Plants belonging to the genus Euphorbia and Asclepias are annual herbaceous plants which must be cut, dried and extracted. About 8% of their dry weight is the oil containing polyterpenoid material, 20% of the dry weight is fermentable sugar and lignin. Research has been done on two popular milkweeds *Asclepiasspeciosa* and *Asclepiascurassavica*. *A. speciosa* produces higher amount of latex than *A. curassavica* and also has a greater potential for use as fuel. Latex of *A. speciosa*consists of compounds from α-β amyrin families and a small content of ofpolyisoprene polymer. In contrast *A. curassavica*is atleast 50% cardiac muscle glycoside and contains lower amount of α and β amyrin acetate [23].

*Pittosporumresiniferum*also known as petroleum nut is a tall tree that grows in the Phillipines and Malaysia. It belongs to the family Pittosporaceae. It derives its name from the resemblance of the fruit's odor to petroleum-based fuels. The fruits are bigger than a golf ball. The fruits of the tree burn brightly when ignited, and can be used for illumination as torches or candles.Its fruit is also highly suitable for use in producing biofuel [24]. An analysis of the oil obtained from *P.resiniferum*showed small percentages of n-heptane and n-nonane. The major extractables were found to be two monoterpene hydrocarbons α-pinene(38%) and myrcene (40%) [25].

Euphorbia tirucalli, *Euphorbia lactea* and *Euphorbia lathyris*are excellent hydrocarbon producing plants. *Euphorbia lathyris*can be grown for fuel in marginal suitable land. The oil obtained from *E.lathyris*is black and tarry which resembles crude oil and consists mainly terpenes which are steroid and steroid esters. During a comparative study of three plants, *Euphorbia lathyris*proved to be a promising species for biodiesel production. The best biodiesel was produced from *Euphorbia lathyris* due to its high monounsaturation (82.66 wt.%, Cn: 1), low polyunsaturation (6.49 wt.%, Cn: 2, 3) and appropriate proportion of saturated components (8.78 wt.%, Cn: 0).*E.lathyris* came out to be a potential gasoline tree. The heptane extract of *E.lathyris*is composed entirely of triterpenoids and sterols. These compounds are major constituents of latex. The sterols obtained from *E.lathyris*could also be used in pharmaceutical industry [26,27]. An analysis of methanol extract of *E.lathyris*showed that the plant is also a storehouse of various simple sugars, glucose, sucrose, galactose and fructose which are fermentable to ethanol. These four sugars represent 20% of the plant dry weight [28].

*Jatrophacurcas*is a another potential energy crop. It is believed to have originated in South America. It belongs to the family Euphorbiaceae. the plant is traditionally used for medicinal purposes. Jatropha is not a weed, it needs to be planted. It is a bush tree that can survive on marginal lands at a height of 6-8metres.Jatropha is said to be adaptable and can grow almost

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everywhere except on waterlogged land. It grows on gravelly, sandy, and saline soils and can be found in the poorest stony soil and even in the crevices of rocks [29]. Analysis of the jatropha seeds shows the following composition – crude protein (24.60%), crude fat(47.24%), moisture(5.54%), fiber (15.50%) and ash(5.30%) [30]. The oil content from Jatropha seeds is 40-45%.Table 2 shows the fatty acid content from jatropha oil [31].The processed oil can be used after little modifications or blending with conventional diesel [32]. Jatropha oil has higher viscosity than the normal diesel, so little modifications are required to reduce its viscosity to make it more useful as engine fuel [33]. There are few chemical compounds in the seeds of Jatropha which are toxic and thus the oil is not fit for human consumption and used as an attractive energy source for biofuel production. Table 3 lists the various chemical properties of raw Jatropha oil [34]. The various other uses of Jatropha include- biodiesel production, soap production, medicinal uses, insecticide, pesticides, cooking and lighting, organic fertiliser, biogas production, fodder, combustibles, antihelminthic properties [35]. J.curcas leaves contain steroid sapogenins, alkaloids, triterpenalcohol [36]. Tanzania is considered very important for Jatrophaculivation. Jatropha plantations in Tanzania are estimated around 17,000ha which is 1.9% of global cultivation. The biodiesel obtained from Jatropha has reduced green house gas emissions and is eco-friendly than the normal diesel fuel [37]. Also, Jatropha plant served many social and economical benefits for Malaysia [38].

Algae are gaining importance to act as substitute to petroleum fuels for the future[39]. The algae which is used in the production of biofuels are the aquatic unicellular algae. This algae is having high growth rates and high population densities. Within 24 hours, the green algae can double its biomass [40,41]. About 4000 strains of algae convert sunlight and carbon dioxide into lipids and oils. It was reported that algae are the highest yielding feedstock for biodiesel [42]. Algae can produce up to 300 times the amount of oil per acre as soybeans, 24 times greater than palm oil.Algae serves various benefits. Algae do not require a particular land for cultivation. They can grow on arid land, saline soil, solid waste, fresh water, brackish/salt water. Algae cultivation do not compete with agricultural commodities for growing space[43,44]. Algae can consume higher amounts of carbon dioxide than land plants and probably help to reduce the content of greenhouse gas emissions. This conversion process converts waste carbon dioxide into oxygen and biomass through photosynthesis of microalgae[45]. After oil extraction from algae the resulting biomass acts as potential protein feed for livestock[40,46].

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SCREENING, PROCESSING AND CHARACTERIZATION OF BIOMASS FOR BIOCRUDE

In the earlier times, search was mainly focused on rubber producing plant species(latex bearing palnts) for hydrocarbon production. The first cultivation of hydrocarbon producing plant species was made by Italians in Ethiopia [47] and the French in Morocco [48].

Buchanan and his coworkers did an extensive survey in which they covered 200 plant species to check their potential source of hydrocarbon, protein, carbohydrate and rubber. The dried plant material was extracted in solvent system for the detection of oil and rubber contents. The solvent system included acetone followed by benzene. Acetone extracts being partitioned into hexane and ethanol fractions. The hexane soluble fraction was termed as oil and ethanol soluble fraction was termed as polyphenol. Out of the different plant families screened for their potential Euphorbiaceae, Asclepiadaceae and Compositae families proved to be promising candidates for biofuel production. Oil fractions were subjected to thin layer chromatography (TLC), and hydrocarbon fractions were subjected to infrared(IR) spectroscopy to determine if they were natural rubber waxes or mixtures. The samples predicted with natural rubber waxes were further examined by proton nuclear magnetic resonance(PMR) and gel permeation chromatography [22].

Using different solvent systems Adams & coworkers surveyed 80 species from southwestern U.S. and Southern Great Plains. Soxhlet extractions were preferred overother methods such as shaking and decanting. A striking result was obtained in case of *Helianthus anus*, for which methanol extract yielded 250% more material than ethanol. A considerable variation was seen in the percentage yield from extracts of various plant species. In all, five plants namely *Baccharisneglecta*, *Ilex gaba*, *Juniperusmonosperma*leaves, *Sapiumsebiferum*leaves and *Rhusglabra*showed highest bicrude yields [49,50].

Mclaughlin and Hoffmann screened over 195 species of numerous desert plants from Southwestern United States and northwestern Mexico to determine biocrude potential. The term biocrude was coined by Mclaughlin *et al.* Oven dried plant material was taken and sequential extractions was performed with cyclohexane and ethanol for 12hrs each. Energy values were estimated from elemental analysis by comparison with compounds of similar composition. Elemental analysis were performed by bomb calorimetry. Plants producing either latex or resinous exudates were emphasized. The highest cyclohexane extracts were found in resinous

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species. The resinous species in their survey belonged to the family Compositae. Infact, the cyclohexane extract proved to be a high energy component of plants for use as liquid fuels and chemical feedstocks [51].

Calotropisprocera and *Asclepiassyriaca*belonging to the family Asclepiadaceae were screened by Erdman and Erdman. Both the plants proved as potential sources of hydrocarbon like materials. Whole plants, stems, leaves and pods were used for analysis. Extractions were performed using two solvents hexane and methanol. Percentage of hexane and methanol extracts ranged between 4.4%-9.4% and 12.1%-21% respectively. Total carbon, hydrogen and oxygen determinations were performed by pyrolysis using a Perkin Elmer model 240 analyserand a model RO 17 Leco oxygen analyser connected to an IR spectrophotometer[52]. In a previous work *Calotropisprocera*was also examined byWilliam *et al.* and the plant was considered for energy use in Australia.

In the Western Ghats of India 22 taxa were screened for the production of renewable energy oil hydrocarbons and phytochemicals by Augustus and coworkers. Two plants namely *Carissa carandas* (1.7%) and *Jatrophagossypifolia* (1.7%) showed highest hydrocarbon yields. The highest polyphenol content was observed in *Dodonaea viscose* (17.1%), *Carissa carandas* (7.7%), *Swieteniamahagoni*(6.6%) and *Jatrophaglandulifera* (6.2%). NMR spectra of the hydrocarbon fractions showed the presence of cis-polyisoprene (natural rubber) and trans-polyisoprene (gutta). Both of these are potential alternative energy sources for fuel and industrial raw materials [53,54].

SOCIAL, ECONOMIC AND ENVIRONMENTAL IMPACTS OF BIOFUELS

Biofuels offer a promising alternative as they are relevant to both developing and industrialized countries. They are renewable and available throughout the world. Biofuel production costs differ according to the types of feedstocks used, conversion process, scale of production and region. Various countries such as Canada, Colombia, the European Union, India and Malaysia have adopted measures to increase contribution of biofuels to their transport fuel supplies [55]. The European Union is the world's largest producer of biodiesel. In 2004, European Union production of biofuels amounted to around 2.9 billion litres. The ethanol production amounted to 620 million litres and biodiesel amounted to remaining 2.3 billion litres. The main economic factor to be considered for input costs of biofuel production is the feedstock which is almost 75-80% the total operating cost. Also included in this are the labor costs [56]. In Brazil feedstock costs account for 58-65% of the cost of ethanol production. Because of several factors, biodiesel blends perform better than petroleum diesel, but due to high production costs the commercial production is getting limited. On the other hand, biofuels also serve some economic advantages like it decreases GHG emissions, helps to reduce a country's reliance on crude oil imports and support agriculture by providing new labor and market opportunities for domestic crops, is widely accepted by vehicle manufacturers. The production of biodiesel is done generally from soybean oil, methanol and an alkali catalyst. Methanol is less expensive than ethanol and thus preferred over ethanol [57]. Methanol produced from natural gas is readily available in chemical industry. Biodiesel has limiting factor of low performance in cold temperatures which leads to corrosion of rubber components. But this problem can also be overcome by using antifreeze and improvement in the tubing materials, but this again leads to more work [58,59].

To check the environmental impacts of biofuels various studies for comparison of diesel, natural gas and diesel/biodiesel blends have been conducted in the past [60-65]. The biodiesel impacts on exhaust emissions differ according to the type of biodiesel and on the type of conventional diesel. The use of biodiesel in a conventional diesel engine considerably reduces emissions of unburned hydrocarbons, carbon monoxide, sulfates, polycyclic aromatic hydrocarbons, nitrated polycyclic aromatic hydrocarbons and particulate matter. These reductions increases as the amount of biodiesel blended into diesel fuel increases. Emissions of NO_x increase with increasing biodiesel amount. Bioethanol has higher evaporation heat, octane number and flammability temperature, hence it has constructive influence on engine performance and reduce exhaust emissions. The outcome of Bioethanol engine test showed that ethanol addition to unleaded gasoline enhances the engine torque, power and fuel consumption and lessen the amount of carbon monoxide(CO) and hydrocarbon emissions [66].

Biofuels are essential because they substitute petroleum fuels. There are numerous benefits for the environment, nation, market and consumers in using biofuels. The major distinction linking biofuels and petroleum feedstocks is oxygen content. Biofuels oxygen levels range from 10-45% whereas petroleum has essentially none oxygen content, which makes their chemical property contradictory to each other [59].

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CONCLUSION

Biofuels have been and will continue to be an important part of our ever developing society. Oil is the chief source of energy for the whole world. It has become vital to initiate a major effort in exploring and developing substitute supplies of hydrocarbons. The plant species discussed here present interesting possibilities in the nearest future, but on the other hand their viability and production on a large scale would depend on the accomplishment achieved by R&D in this field. Great efforts are needed to enhance biocrude potential of these species through genetic manipulation. Biofuel have great potential, however the high cost and limited supply of organic oils prevent it from becoming a substitute to petroleum fuels. With the increasing petroleum fuel costs biofuels are gaining more desirability to both investors and consumers. To become an alternative fuel of preference, biofuels require a vast amount of cheap biomass. The production of biofuels on commercial scale, their production must be resolved by new and improved production technologies. In all regions, stress should be given to non-edible crops and wastelands to avoid staple food shortage and environmental dilapidation. Combined approach involving government policies, industrial and farmers involvement can lead biofuels to a bright future.

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