Biocrude and Biomass Yield of Some Euphorbia Species : A Comparative Study

*Shobha Johari

ABSTRACT

Biomass and biocrude both can be ecofriendly solution for fuel requirement. Biocrude is a complex mixture of organic compounds having wide range of molecular weight. It can be extracted from a plant using a non polar solvent. It includes oil, water, triglycerides, waxes, terpenes and other modified isoprenoid compounds. Oils being rich in hydrocarbons can be cracked to produce chemical feedstocks and gasoline mixtures and hence such plants are also called as petro-crops. In many researches attention had been given to plants as a source of fuel. Among many latex yielding plants *Euphorbia* latex has received increasing attention because it contains a mixture of light hydrocarbons in its latex. There are many species of *Euphorbia* available locally in the state of Rajasthan like- *E. hirta, E. tirucalli, E. lathyris , E. caducifolia, E. neriifolia , E. antisyphilitica* and *E. nivulia*. Plants contain a variety of natural products that are readily extractable their various combinations were used to estimate extractables of all these seven *Euphorbia* species and a comparative study was carried out to find best suitable non polar solvent and plant species to give maximum yield of biocrude.

Key Words: Biomass, Biocrude yield, *Euphorbia* species, non-polar solvents

INTRODUCTION

Biomass can be defined as the collection of all organic matter composing biological organisms, but the main components utilized for biofuel production are sugars and lipids (Kumar 2001; Hill et al. 2006; Roy and Kumar 2013; Dugar and Stephanopoulos 2011; Caspeta and Nielsen 2013). Presently plant biomass provides 10% of global primary energy mainly as ethanol and biodiesel production are both expected to expand to reach, respectively, almost 135 and 39 billion liters by 2024 (5OECD/FAO. Agricultural Outlook, 2015, Available online, https://doi.org/10.1787/data-00736-en) (Smith et al. 2014; Woods et al. 2015). Liquid biofuels are generally produced from food crops but hydrocarbon yielding plants are more suitable as energy crops. It is possible to produce liquid biofuel from plants growing on marginal lands and which produce latex (Kumar, 2020). Plants contain a variety of natural products that are readily extractable with non-polar organic solvents like triglycerides, oils, waxes, terpenes, phytosterols and other modified isoprenoid compounds. These extracts have been considered as a potential source of fuels and chemicals. Latex remains in special cells and/or vessels, called laticifers, and is a byproduct of photosynthetic conversion of solar energy into biochemical energy. Isoprenoids and terpenoids present in latex are rich in hydrocarbons wchich can be converted into catalytic cracking system (Kirkby and Keasling, 2009; Yau and Easterling, 2018). The latex of some plants are very rich in reduced photosynthate materials (polyisoprenes and sterols) comprising upto 80 percent of dry weight, making these species bright, prospective candidates for future petrochemical plantations (Nielsen *et al.*, 1977). The entire biocrude mixture of several oil yielding xerophytic species could be cracked to produce chemical feedstocks and gasoline mixtures (Haag *et al.,*1980; Sarkar, 2012). *Euphorbia* latex has received increasing attention because it contains a mixture of light hydrocarbons which have a molecular weight of the order of 20,000 instead of 2 million. The hydrocarbons from *Euphorbia* are primarily a blend of C_{15}, C_{20} or C_{30} compounds (Nielsen *et al.,*1979; Johnson and Hinman, 1980) that, when subjected to catalytic cracking yield various products virtually identical to those obtained by cracking naphtha (Maugh, 1979), a high quality petroleum fraction that is one of the principal raw materials used in the chemical industries. Euphorbiaceae is one of the families considered as promising petro-crop family (Bhatia et al.1984). Therefore first aim was to screen various species of *Euphorbia* for their potential to produce biomas and biocrude using different solvents and their combinations.

General Description of Selected Plants

***E. antisyphilitica* Zucc.** (Syn: *Tricherostigma antisyphilitica* Klotzsch and Garcke : *E. certifera* Alcocer).

E. antisyphilitica is native of Chihuahuan desert of Mexico. Mean atmospheric temperature of Mexican desert remains 30 to 48^{0}C in summers and 25 to 30^{0}C in winter months. Annual rainfall is less than 20 mm and sand is a dominant soil type. Common name of this plant is Candellila . Besides the rich latex contents, it possesses a thick cuticle of wax throughout the surface of This plant has been successfully introduced in arid and semi-arid conditions of Rajasthan. Although it does not grow wild in India but, it has been raised under cultivation in Central Arid Zone Research Institute, Jodhpur; National Botanical Research Institute (NBRI), Lucknow and Forest Research Institute, Dehradun. It does not grow wild in nature in India and is multiplied through vegetative cutting. *E. antisyphilitica* is unarmed, almost leafless shrub ca 1.0 m high, profusely branched from base. Stem is cylindric, pale green and leaves linear and caducous.

***E. lathyris* Linn.**

It has common name as Gopher plant, Mole plant (English) and Caper Spurge . *E. lathyris* grows wild throughout California, preferring open, relatively mesic habitats in temperate zones of the world. It has also been found to occur in arid South-West Australia. *E. lathyris* is an annual, 2-3 ft tall plant with leaves long, lance-linear, those of inflorescence- ovate-acuminate.

***E. tirucalli* Linn.**

A small tree, 12-30 ft (or unarmed shrub), trunk 6-10" in diameter, green, cylindric, densely branched, branches spreading, cylindric scattered whorled or clustered. Leaves absent or few, small, ¼-½", linear, oblong, caducous, obtuse, flaccid, pubescent at length, glabrous. Involucres shortly pedicelled, clustered in the forks of the small branches, chiefly female, small, $^1/_{12}$" long, turbinate, subsessile with two small leaves at the base of the pedicel, lobes short, hairy, glands transversely ovate, capitate. Capsule ¼" long, dark brown, seeds ovoid, smooth. The plant has several common names as - Stick plant, Kayu urip (Indonesia), African milkbush (English), Paya-rabia (Thailand), Suerda, Pobreng Kahoy (Philippines), Sehund and Konpal (India).

E. tirucalli is a native plant of Africa where it is used as live fencing around houses. It is also common in Brazil and Israel. In India it is found in wild state in South India and is naturalized in West Bengal. In Tamilnadu it is found mainly in rocky hillocks in wild form. Besides, *E. tirucalli* has also been found in Gujarat, Goa, Madhya Pradesh and Himachal Pradesh.

E. caducifolia **Haines** (Syn: *E. neriifolia* auct. plur. non L. nec Roxb).

A pale green, dense, fleshy, dendroid shrub, upto 2 m high, with numerous branches arising from the very base. Branches more or less erect 3-5 cm in diameter somewhat cylindrical with small, rather distant, slightly raised, non-confluent tubercles, the latter arranged in 5 spirals, each tubercle with a black areole, bearing a pair of 5-9 mm long, glabrous, pointed, divergent spine, reddish when young, black at length. Leaves arising singly from the areoles, very variable in shape and size and form 1.9 x 1.4 cm, ovate or ovate-oblong, straight or with various degree of conduplications, margins entire, cripsed or undulate, apex acute or cuspidate, fleshy, rigid, glabrous, pale-green, caducous. Involucre solitary or 2-3 together, on short, fleshy peduncles, when 3, the central usually male, laterals hermaphrodite, pedicels stout, 1-5 mm long, arising in the axil of triangular, ovate bracts. Involucre 4-5 mm in diameter, lobes broadly oblong, obcuneate, toothed, scarsely fimbriate glands, transversely oblong, glabrous, filament glabrous or pilose, anthers yellow, subglobose, erectopatent, non-apiculate. Female flowers pedunculate, perianth lobes 3, minute rounded at apex: style 3, connate up to half of their length. Fruit and capsule sharply 3 lobed, lobes transversely planoconvex, glabrous, 10-12 mm in diameter. Seeds 3; 3 mm in diameter, one in each locule, globose, smooth (Bhandari, 1978).

Euphorbia caducifolia **Haines (Syn: *E. neriifolia* auct. plur. non L. nec Roxb).**

Plant is commonly called as 'Danda thor' or 'thor'. This is one of the most characteristic rock plants of the area, growing or barren rocks, covering almost the whole hillside wherever it occurs. It is more common on hillocks around Jodhpur and Barmer but less so around Jaisalmer where it is found only near Amarsagar. It forms favourite support for a number of climbers. Rarely it is also found on gravel at the foot hills. *E. caducifolia* is also common on dry hillocks of Andhra Pradesh. It also occurs in Maharashtra, Satpura hills of Madhya Pradesh and in Gujarat.

E. neriifolia **Linn.** (Syn: *E. ligularia* Roxb.)

A small tree, 15-20 ft, glabrous, branches ¾" diameter and upwards. Branches jointed cylindric or obscurely 5-angled with short fleshy obovate oblong or subspathulately obovate acute. Tubercles subconfluent, in 5 irregular rows. Leaves deciduous, 6-12" long, terminal on the branches, waved, narrowed into a very short petiole, stipular thorns solitary or short petiole, stipular thorns solitary or in pairs. ⅓-½" long. Involucres in small, stout, dichotomous short peduncled cymes from the sinuses; hemispheric, smooth, yellowish, the lateral ones of the cymes shortly thickly pedicelled, central sessile, lobes large, erect, roundish, cordate, fimbriate; glands transversely oblong; bracteoles most abundant, fimbriate, stigma capitate, capsule about ½" broad, deeply 3-lobed. Styles connate high up undivided, cocci compressed, glabrous (Hooker, 1954). *E. neriifolia* is commonly distributed in rocky areas almost throughout the Deccan peninsula and often cultivated as hedge plant throughout the country. It is naturalized in Bengal, Bihar, Orissa, Gujarat and Maharashtra. Majority of hills of Rajasthan are comprised of *E. neriifolia* vegetation.

***E. nivulia* Buch. - Ham.** (Syn: *E. neriifolia* Roxb., *E. varians* Haw.)

A large shrub or tree, fleshy, glabrous, 20-25 ft branches whorled, subcylindric with pairs of sharp stipular spines arising from low tubercles. Tubercles arranged in a spiral; distant, conical and truncate. Leaves 6-12", alternate linear or obovate-oblong, fleshy, deciduous, nerveless, tip rounded, midrib stout beneath. Involucres 3-nate forming small short-peduncled cymes from above the leaf scars on the tubercles hemispheric smooth, styles connate to the middle undivided, cocci compressed glabrous. Stigma capitate, capsule about ¼" broad, deeply 3-lobed. Seeds smooth (Hooker, 1954). *E. nivulia* has common name 'Kantathohar' and is distributed throughout the India in dry and rocky regions. It is common in Punjab, dry hills of U.P., in Himachal Pradesh, Madhya Pradesh, Orissa and Bihar. It is also found in Gujarat, Karnataka and Tamilnadu.

***E. hirta* Linn.**

An erect or decumbent annual, 1-3 cm high. Stem simple or dichotomously branched, rather coarsely pilose with yellow, spreading pubescence of minute, curved, subadpressed haris. Leaves very variable in size, 1.5 x 0.5-1.8 cm, opposite, obliquely lanceolate or ovate or rhomboid, oblong acute or subobtuse cuneate at base on one side of the midrib, the other side rounded, finely serrate along the margin, thinly pubescent on the both surfaces, more minutely so or glabrous above; nerves distinct, 2-4 mm long, pubescent as the stem, stipules subulate, from a broad base, rarely pectinate, pubescent, soon falling, cymes in alternate axils of the subsequent pairs of leaves 6-12 mm in diameter, more or less globose, dichotomously dividing at the apex of a 6-12 mm in diameter, more or less globose, dichotomusly dividing at the apex of a 5-10 cm long terete penduncle, thinly puberulent with minute curved hairs. Involucres densely crowded, minute, very shortly pedicellate, obconic or cup-like with 4 glands and 5 truncate apex. Fruit a capsule, globose, trigonous, 1.0 mm long as much broad, thinly puberulent with minute, hairs. Seeds 7-8 mm long, oblong, 4-angled, slightly transversely rugose, reddish (Bhandari, 1978).

E. hirta has a common name 'Dudhi'. This is one of the commonest and most variable of the species of Indian desert plants. It grows in open grasslands throughout the India. It is abundant in Sri Lanka, Thailand, Indonesia, Malaysia, Nepal and Philippines.

METHODS AND RESULTS

Plants were screened for their organic extractables using solvent acetone benzene and hexane-methanol extractions separately. Stock plants of *E. antisyphilitica* and *E. tirucalli* were raised from the cutting obtained from National Botanical Research Institute (NBRI), Lucknow, *E. lathyris* was raised from the seeds obtained from Prof. Melvin Calvin, USA. *E. caducifolia* (Udaipur and Achrol), *E. nivulia* (Galtaji, Jaipur), *E. neriifolia* (Bharatpur) and *E. hirta* (Jaipur) were collected from different parts of Rajasthan.

Table 1: Dry biomass and biocrude yield of different *Euphorbia* species

Name of the plant	Dry Wt. (%)	Acetone Ex. (%)	Benzene Ex. (%)	Acetone + Benzene Ex. (%)	Hexane Ex. (%)	Methanol Ex. (%)	Hexane + Methanol Ex. (%)
E. antisyphilitica	10.00	11.53	1.32	12.85	7.00	11.50	18.50
E. lathyris	22.63	9.45	0.49	9.94	5.57	21.56	27.13
E. tirucalli	8.80	4.85	0.91	5.76	3.48	6.31	9.79
E. caducifolia	13.31	8.83	0.98	9.81	6.60	11.36	17.96
E. nivulia	11.30	8.61	0.55	9.16	6.40	12.00	18.40
E. neriifolia	11.59	10.82	0.65	11.47	6.31	7.13	13.44
E. hirta	20.00	4.75	0.17	4.92	2.12	4.50	6.62
Ex.=Extractables %=wt./wt.							

Stock plants of *E. antisyphilitica* and *E. tirucalli* were raised from the cutting obtained from National Botanical Research Institute (NBRI), Lucknow, *E. lathyris* was raised from the seeds obtained from Prof. Melvin Calvin, USA. *E. caducifolia* (Udaipur and Achrol), *E. nivulia* (Galtaji, Jaipur), *E. neriifolia* (Bharatpur) and *E. hirta* (Jaipur) were collected from different parts of Rajasthan. Plants were allowed to grow for six months and then harvested. After harvesting whole plants were dried in oven at 30^0 C for seven days or more till their complete dryness attainment. Only aboveground part of each species were powdered finely and 100g dried powder were taken to run in soxhlet using different solvents. Procedure was performed with ten replicates each. Dry weight of extracted material were measured.

Acetone extractables were maximum in *E. antisyphilitica,* followed by *E. neriifolia, E. lathyris, E. caducifolia, E. nivulia, E. tirucalli* and *E. hirta*. Benzene extractables were maximum in *E. antisyphilitica* followed by *E. caducifolia.* Minimum benzene extractables were recorded in *E. hirta.* Total extractives (Acetone + Benzene) were maximum in *E. antisyphilitica* followed by *E. neriifolia* and minimum in *E. hirta* (Table-1, Fig. 1).

Maximum hexane extractables were recorded in *E. antisyphilitica* followed by *E. caducifolia, E. nivulia, E. neriifolia, E. lathyris, E. tirucalli* and *E. hirta*. Methanol extractables were maximum in *E. lathyris* followed by *E. nivulia. E. hirta* was poorest among all the species in methanol extractables. Hexane + Methanol extractables were maximum in *E. lathyris* followed by *E. antisyphilitica* (Table-1, Fig.1).

Maximum dry weight production was recorded in *E. lathyris* followed by *E. hirta.*

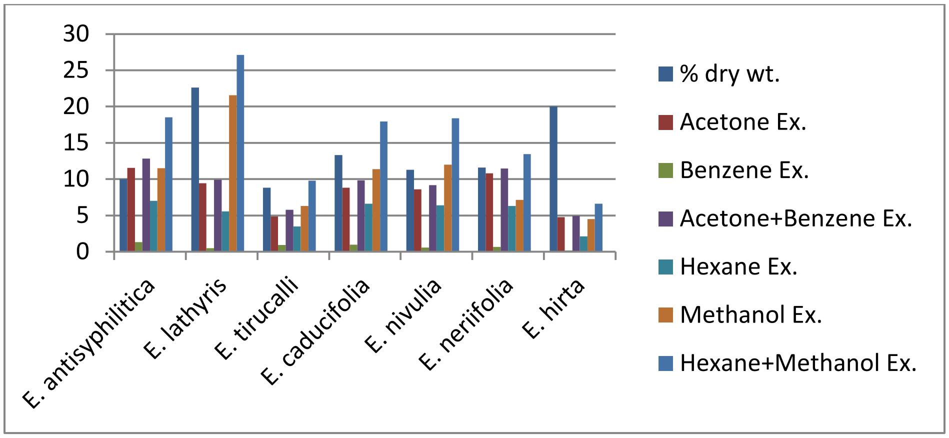

Fig.1- Biomass and biocrude yield of different *Euphorbia* species

Discussion

Many scientists studied laticiferous taxa as a source of energy and reported oil, hydrocarbons, polyphenol and proteins from plants belonging to families Asclepiadaceae, Apocyanaceae , Euphorbiaceae, Urticaceae etc. A large number of laticiferous plants have been reported to yield hydrocarbons which could be converted into petroleum like substances. Biomass is a versatile form of energy which can be used in solid, liquid and gaseous forms through direct combustion, carbonization/ pyrolysis, liquefaction and gasification. Direct combustion of low moisture biomass remains the major route of utilization at present. When the possibility of obtaining liquid fuels from plants by direct extraction was introduced, the emphasis of bioenergy research began to shift from maximization of biomass production towards an interest in the quality and quantity of certain plant constituents. The presence of whole plant oils called biocrude became an important criterion in the selection of potential energy crops .Because of greater economic value of reactive chemical intermediates which can be obtained from latex yielding plants, the production of chemical feedstocks is now considered to be an attractive short term goal in the development of bioenergy crops. Such bioenergy plants contain a variety of natural products that are readily extractable with non-polar organic solvents. They contain triglycerides, oils, waxes, terpenes, phytosterols and other modified isoprenoid compounds. These extracts have been considered as a potential source of fuels and chemicals. The entire biocrude mixture of several oil yielding xerophytic species could be cracked to produce chemical feedstocks and gasoline mixtures (Haag *et al.,* 1980). In present study different organic solvents have been applied to extract hydrocarbons present in oils, waxes, terpenoids, sterols triglycerides etc. of various species of *Euphorbia* which has been reported rich in latex contents

(Kumar et al,1995; Johari and Kumar, 2021; 2022). Although combination of hexne plus methanol extracted maximum biocrude of all the *Euphorbia* species taken, acetone plus benzene combination and non polar hexane was found to give maximum biocrude yield in *E. antisyphilitica*. *E. lathyris* and *E. neriifolia* were also promising latex yielding plants and *E. caducifolia* is next in potential in biomass and biocrude yield.

***Professor & Head**
Department of Botany
L.B.S Govt. College, Kotputli (Raj.)

References

1. Bhandari, MM (1978). Flora of the Indian Desert. Scientific Publishers, Jodhpur. pp. 339-342.
2. Bhatia, VK, Srivastava GS, Garg VK, Gupta YK, Rawat SS. (1984). Petro-crops for fuel. *Biomass.* 4: 151-154.
3. Caspeta L, Buijs NAA, Nielsen J. (2013). The role of biofuels in the future energy supply. *Energy Environ Sci.* 6:1077.
4. Dugar D, Stephanopoulos G. (2011). Relative potential of biosynthetic pathways for biofuels and bio-based products. *Nat Biotechnol.* 29(12):1074–1078. https://doi.org/10.1038/nbt.2055
5. Haag, WO, Rodewald PG, Weisz PG (1980). Catalytic Production of Aromatics and Olefins from Plant Materials. In: *2nd Chemical Congress of American Society.* Las Vagas, Nev. pp. 63-76.
6. Harborne JB (1998). Phytochemical methods : a guide to modern technique of plant analysis, Vol 3. Chapman and Hall, London, pp 60-66.
7. Hill J, Nelson E, Tilman D, Polasky S, Tiffany D (2006). Environmental, economic and energetic costs and benefits of biodiesel and ethanol biofuels. *Proc Natl Acad Sci.* U S A 103:11206–11210. https://doi.org/10.1073/pnas.0604600103
8. Hooker, JD. 1954. *Flora of British India.* L. Reeve and Co. Ltd. Kent, London. Vol. 5. pp. 255.
9. Johari S, Kumar A(2021). Growing *Euphorbia antisyphilitica* on wasteland soils of Rajasthan. *J Pl Sci Res.* 37(2):289-295.
10. Johari S, Kumar A (2022). Effect of some micronutrients on biomass, latex yield, sugar and chlorophylls of *Euphorbia antisyphilitica*. *J Pl Sci Res.* 38(1):249-256.
11. Johnson JD, Hinman CW (1980). Oils and rubber from arid land plant. *Science.* 208:460–464.
12. Kirkby, J and Keasling JD (2009). Biosynthesis of plant isoprenoids: perspectives for microbial engineering. *Annu Rev Plant Biol.* 60:335-355.
13. Kumar A, Johari S, Roy S. (1995). Production and improvement of bio-energy sources. *J. Indian Bot. Soc.* 74A: 233-244.

14. Kumar A (2001). Bioengineering of crops for biofuels and bioenergy. In: Bender L, Kumar A (eds) From soil to cell: a broad approach to plant life. Giessen + Electron. Library GEB, pp 14–29 . http://geb.uni-giessen.de/geb/volltexte/2006/3039/pdf/FestschriftNeumann-2001.pdf
15. Kumar A (2008). Bioengineering of crops for biofuels and bioenergy. In: Kumar A, Sopory S (eds) Recent advances in plant biotechnology. I.K. International, New Delhi, pp 346–360.
16. Kumar A (2018). Global warming, climate change and greenhouse gas mitigation. In: Kumar A, Ogita S, Yau YY (eds) Biofuels: greenhouse gas mitigation and global warming next generation biofuels and role of biotechnology. Springer, Heidelberg, pp 1–16.
17. Kumar A (2020). Synthetic biology and future production of biofuels and high value products. In: Kumar A, Yau YY, Ogita S, Scheibe R (eds) Climate change, photosynthesis and advanced biofuels: role of biotechnology in production of value-added plant products. Springer, Singapore.
18. Maugh TH (1979). Unlike money, diesel fuel grows on trees. *Science.* 206: 436.
19. Nielsen PE, Nishimura H, Otvos JW, Calvin M (1977). Plant crops as a source of fuel and hydrocarbon-like materials. *Science.* 198*:* 942-944.
20. Nielsen PE, Nishimura H, Liang Y, Calvin M (1979). Steroids from *Euphorbia* and other latex bearing plants. *Phytochemistry.* 18: 103-104.
21. Roy A, Kumar A (2013). Pretreatment methods of lignocellulosic materials for biofuel production: a review. *J Emerg Trends Eng Appl Sci.* 4(2):181–193.
22. Sarkar N (2012). Bioethanol production from agricultural wastes: an overview. *Renew Energy.* 37(1):19–27.
23. Smith P *et al* (2014). In: Edenhofer O et al (eds) Climate change: mitigation of climate change. Contribution of working group III to the fifth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge/New York.
24. Woods J *et al* (2015). In: Souza GM, Victoria R, Joly C, Verdade L (eds) Bioenergy and sustainability: bridging the gaps. SCOPE, Paris, pp 258–300.
25. Yau Y-Y, Easterling M (2018). Lignocellulosic feedstock improvement for biofuel production through conventional breeding and biotechnology. In: Kumar A, Ogita S, Yau Y-Y (eds) Biofuels: greenhouse gas mitigation and global warming next generation biofuels and role of biotechnology. Springer, Heidelberg, pp 1-16.