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Potential use of *Pedilanthus tithymaloides* Poit. as a renewable resource of plant hydrocarbons

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Abstract. *Pedilanthus tithymaloides* was evaluated as an incessantly renewable and potential source of hydrocarbons. Extracts were obtained from successive extraction of whole plant material with solvents like petroleum ether (b.p. 60–80°C), benzene (b.p. 80°C) and ethyl acetate (76–78°C). A white amorphous mixture of hydrocarbons was obtained by elution of the column by petroleum ether (b.p. 60–80°C) which was found to be comparable with gasoline.

Keywords: Hydrocarbons; *Pedilanthus tithymaloides* Poit.; Renewable resource.

Abbreviations: PEE, petroleum ether extract; **BENE,** benzene extract; **EAE,** ethyl acetate extract; **PER**, plant residue left after petroleum ether extraction; **BENR,** plant residue left after benzene extraction; **EAR,** plant residue left after ethyl acetate extraction.

Introduction

Modern society depends very much upon fossil fuel. Total oil resources are being depleted, and their share of total energy supply is predicted to fall to 10% by the year 2020. To meet this acute shortage, the technology aimed at the utilization of renewable energy that can serve to replace fossil hydrocarbons, needs to be expanded. Calvin (1977) reported that latex-bearing plants are the most obvious alternative renewable source of fuel and chemical feedstock. It was seen that some higher plants can convert the initially produced carbohydrate into terpenes instead of into fatty acids and glycerides (such as seed oil). Calvin (1982) has considered *Euphorbia lathyris* L. to be a kind of "energy farm" capable of producing a mixture of reduced terpenoids which can be converted to a gasoline-like substance. The most interesting and attractive species is *Copaifera multijuga,* which produces the light yellow oil (copaiba oil) that is obtained from its heartwood by tapping (Alencar, 1982). A single hole through the stem may yield about 25 liters of oil in 24 hours—a readymade engine oil (Calvin, 1982).

It is true that the economic development of plant hydrocarbons will ultimately depend upon agronomy and conversion cost (Weisz and Marshall, 1979). *Pedilanthus tithymaloides* Poit. which grows profusely in marginal waste land in northern and eastern India without any agricultural management, was undertaken to evaluate the hydrocarbon content and its potential use as a petrocrop.

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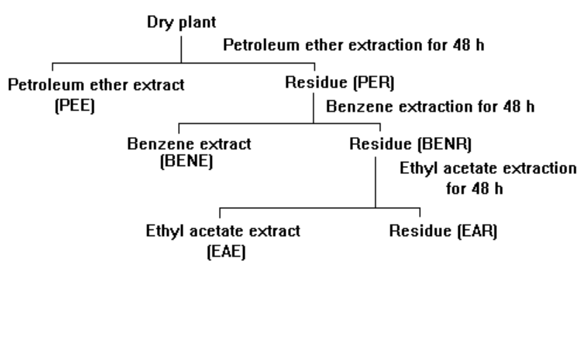
Materials and Methods

Preparation of Plant Material

About 300±5 mature plants (about 1 meter long) with shrubby growth were collected from North 24-Parganas, West Bengal (22°40' N, 88°25' E) between June and July 1988. Both stem and leaves were allowed to air dry in a sheltered area at a temperature of 35–40°C and were ground in a Wiley mill equipped with 2 mm sieve. Thoroughly mixed samples were then stored at ambient temperature in polythene bags.

Extraction Technique

About 500 g of milled sample was extracted in a Soxhlet apparatus first with petroleum ether [E. Merck (India) Ltd; b.p. 60–80°C], then benzene [E. Merck (India) Ltd; b.p. 80°C] and finally with ethyl acetate [95% S.d. fine chemicals (India) Ltd; b.p. 76–78°C] (48 hours with each solvent). All the extracts were concentrated through distillation at a temperature 5°C above the boiling point. The extracts were dried at 60°C for 24 h, then weighed for yield per g of dry sample. The plant residue after each solvent extraction was completely air dried before the next solvent extraction.



Characterization of Extracts and Residues (in Relation to Fuel Characters)

The unextracted milled whole plant sample, different solvent extracts, and their residues after each extraction were analysed for total ash content by the AOAC method (1975). Gross heat values were determined by bomb calorimetry (Anonymous, 1966), and specific gravities were measured by conventional methods.

The PEE was column chromatographed over neutral alumina. Elution of the column with petroleum ether (b.p. 60–80°C) afforded a solid, waxy, amorphous compound from the first two fractions. Melting point, gross heat value, and total carbon and hydrogen of this compound were determined through pyrolysis (Ma and Rittner, 1979). Infra-red (IR) spectroscopy was used to detect the nature of the compound.

Results and Discussion

About 175 g dry plant material was obtained from one kg fresh material. Total ash contents of PEE, BENE, and EAE were 0.11, 0.23, and 0.50%, respectively, which showed an increase with the increase in polarity of solvents used (Table 1). The respective residues after each solvent extraction also followed the same trend in having the ash contents 13.75, 15.50, 20.00, and 30.00% for dried whole plant, PER, BENR, and EAR (Table 2). Out of these three extracts yield of PEE was 26 g per kg dry plant material. The corresponding yields of the other two extracts (i.e. BENE and EAE) were 10 g and 25 g per kg dry plant material, respectively. The gross heat values were calculated as 6233, 4795, 4692, and 3903 cal/g for unextracted dry plant material, PER, BENR, and EAR, respectively. A major amount of energy-rich biocrude was obtained from different solvent extracts as evidenced by their high calorific values like 15460, 11286, 10708 cal/g for PEE, BENE, and EAE, respectively.

The experimental plant possesses an appreciably superior fuel quality as compared to *Calotropis gigantea* and also to *C. procera,* which has been recognized as a potential plant (Erdman and Erdman, 1981). The PER and BENR can also compete with conventional energy sources like wheat straw, rice straw, and wood (Table 2).

Table 1. Ash content, specific gravity and gross heat value of different solvent extracts of *Pedilanthus tithymaloides* compared to *Calotropis gigantea* and fossil fuels.

Fuel	Ash (%)	Specific gravity (g/cc)	Gross heat value (cal/g)
Pedilanthus tithymaloides			
PEE	0.110±0.02	0.470±0.07	15,460±183
BENE	0.230±0.05	0.518±0.06	11,286±176
EAE	0.500±0.05	0.996±0.09	10,708±143
Calotropis gigantea[a]			
PEE	0.42±0.03	0.570±0.02	13,734±123
BENE	0.13±0.04	0.680±0.03	9,593±95
EAE	2.90±0.05	0.984±0.07	7,414±105
Anthracite coal[b]	9.60	–	7,155
Lignite coal[b]	5.90	–	3,888
Crude oil[c]	–	0.70–0.80	11,700–11,100
		0.85–0.95	10,875–10,500
Fuel oil[c]	–	–	10,764
Gasoline[c]	–	–	11,527

[a]From De, 1991.
[b]From Bolz and Tuve, 1970.
[c]From Baumeister, 1966.

Table 2. Characteristics of the dry plant and solvent extracted residues of *Pedilanthus tithymaloides* and other fossil fuels.

Material	Ash (%)	Heat value (cal/g)
Whole plant *P. tithymaloides* (stems and leaves)	13.75±1.52	7,233±0.77
Petroleum ether extract residue	15.00±1.69	4,795±0.61
Benzene extract residue	20.00±2.30	4,692±0.74
Ethyl acetate extract residue	30.00±2.86	3,903±0.54
Whole plant *Calotropis procera*[d]	11.05	4,165
Plants (general)[e] (stems and leaves)	–	4,267
Wheat straw[c]	4.00	4,722
Wood[c]	1.00	5,000

[c]From Baumeister, 1966.
[d]From Erdman and Erdman, 1981.
[e]From Golley, 1961.

Table 3. Comparative carbon, hydrogen, nitrogen, and oxygen contents and heat values of the waxy hydrocarbon and fossil fuels.

Material	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)	Heat value (cal/g)
Waxy hydrocarbon from PER	85.5±4.5	13.9±0.8	–	–	18,990±196
Anthracite coal[b]	79.7	2.9	–	6.1	7,156
Lignite coal[b]	40.6	6.9	–	45.1	3,889
Fuel oil[c]	85.62	11.98	–	0.6	10,764
Gasoline[c]	84.90	14.76	–	–	11,527

[b]From Bolz and Tuve, 1970.
[c]From Baumeister, 1966.

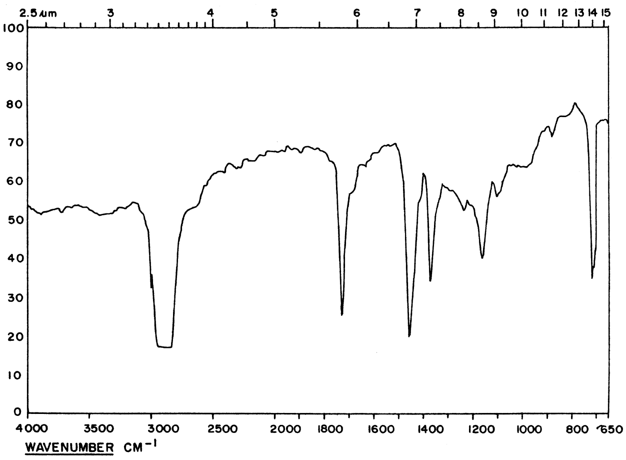


Figure 1. Infra-red bands of waxy hydrocarbons obtained from PEE of *Pedilanthus tithymaloides*.

A linear relationship exists between the heat of combustion and the carbon content of natural fuel (Sejdak et al., 1981). A high H:C ratio accounts for the high combustion value of aliphatic hydrocarbons. The absence of nitrogen and oxygen characterizes a good fuel (Wang et al., 1982). The recrystalized waxy hydrocarbons obtained from PEE possessed a melting point of 60°C and a gross heat value of 18,990 cal/g with 85.5 and 13.0% carbon and hydrogen (Table 3). Infra-red spectra of nujol pellets gave C-H stretching 3.3–3.5 μ (3030–2860 cm^{-1}) and C-H bending 6.85 μ (1460 cm^{-1}) and 7.28 μ (1374 cm^{-1}). The weak absorptions at 5.78, 13.9, and 14.3 μ suggest slight contamination of the wax. The IR spectral data indicate absence of nitrogen and oxygen and the substance is either one or a mixture of a group of alkanes as in wax (Figure 1).

From the above discussion it appears that the biocrudes extracted from petroleum ether and benzene distillation (PEE and BENE) possess much lower specific gravities and higher heat values than crude oil, and the EAE seems to be very similar to it in this respect. The recrystalized substance obtained from PEE contains a fuel quality superior to gasoline. Thus PEE can be used as a substitute for petroleum or petrochemical feedstocks.

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