New Utilization of Vegetable Oils

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ABSTRACT: Energy crisis and growing fuel shortage is a global concern. This phenomenon is more conspicuous in the populous, developing countries. In order to look for alternatives and extenders to the conventional fuels, studies were performed on the seed oil of some relatively unknown *Putranjiva roxburghii*, a plant that is abundantly available in the Indian tropical subcontinent. In a prototype experiment, the physicochemical properties of the *P. roxburghii* seed oil were found to be suitable for blending with diesel up to 50% without any sacrifice in performance of an internal combustion engine. Another industrially useful material, factice (vulcanized oil), was also prepared from the same oil. It was found to be suitable for blending with rubber, improving its strength, hardness, viscosity, and scorch time, and also increased its degradation temperature. This oil is not commercially traded in the market and has not yet been recommended as edible; hence industrial exploitation will not affect consumer market directly. A few more preliminary experiments indicated that the by-product oilcake is a good plant nutrient and the oil exerts profound antifungal activity. These properties need to be investigated more extensively. This plant and its oilseed deserve further attention and investigation, particularly in the tropical, coastal developing countries. *JAOCS 72*, 1591–1593 (1995).

KEY WORDS: Diesel fuel, factice, Indian amulate, *Putranjiva roxburghii*, vulcanized oil.

Shrinking natural resources, imminent energy crisis, and unabated population growth in the developing third world countries demand an extensive search for regional and national renewable resources (1) for fuels, chemicals, and pharmaceuticals. During this investigation, we paid close attention to a long list of unexplored potentialities of some vegetable oils. One such case study is presented here.

Putranjiva roxburghii (Euphorbiacae), also known as Indian Amulate plant, grows abundantly in the eastern regions of India and is found scattered all over the tropical Indian subcontinent. No products of this plant in any form have found wide or popular use. The oil of *P. roxburghii* seed is not commercially available, nor is it present in traders' lists, and the edibility has yet to be established.

The plant grows up to 15 m in height with a conical hemispherical canopy, similar to polyanthus longifolia, but the leaves are shorter and more scattered than the longifolia. The plant flowers in March and April and the fruits (average 5 mm, biconical, and very hard) usually ripen during June. Small, bead-like fruits (average 4 g dry basis) contain a single seed inside a strong, but thin, cellulosic cover. A single kernel can be found on breaking open the fruits.

Observing the chemical properties of the oil, it was envisaged that the oil is likely to be a good blend for diesel and the iodine value suggested that if it was semi-drying, but not declared edible, it could be vulcanized effectively. Thus, a raw material which is not in great demand in the market may deliver products of high industrial significance. We made successful prototype experiments and described in this report an investigation on the properties of *P. roxburghii* seed oil as fuel extenders and its factice as rubber plasticizer.

EXPERIMENTAL PROCEDURES

The seed oil was obtained by the Soxhlet extraction method from seed kernel powder by *n*-hexane or petroleum ether (b.p. 60–80°C). The dynamic viscosity was measured in a Redwood Viscometer (Adir Dutt & Co., Ltd., Calcutta, India), fitted to a standard mathematical relation by comparing the relative flow time with water at a particular temperature. The quantity of carbon deposited is determined (different from theoretical carbon content) in a Conradson apparatus [Petroleum Instruments (India) Pvt. Ltd., Calcutta, India]. A 10-g sample of the oil is heated to 570–580°C for 30 min, and the carbon deposited is weighed (expressed as percentage).

Caloric value is found by igniting one gram of the sample in a bomb calorimeter and calculating the rise of temperature and heat balance of the mass of water and the calorimeter. The flash point of the oil is determined by Pensky Martens Apparatus [Petroleum Instruments (India) Pvt. Ltd.], where the oil is heated in a closed cup under specific conditions and a pilot flame is introduced in the vapor space by opening a shutter in the lid. The temperature at which the vapor bursts with a sound is the flash point. The boiling point is determined by Capillary Boiling Point Apparatus (Remmy Company, Calcutta, India) that was electrically heated and regulated.

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The cetane number (c.n.) of the vegetable oil is determined by applying the equation:

$$\text{c.n.} = 46.3 + 548/x - 0.225y \quad [1]$$

where x is the saponification value and y is the iodine number.

A four-stroke single cylinder, diesel version, direct injection-type Petter engine (Petter, United Kingdom) (2.6 Kw at 3600 rpm) was used for comparing mechanical performance.

Thermal analysis was done in a thermogravimetric instrument (Stanton Red Croft 625; London, United Kingdom), using 15 mg of oil blends heated at 10°C/min with static or dynamic (50 mL/min) air flow.

Brown factice was prepared from *P. roxburghii* seed oil in the following way: 10 g oil was mixed thoroughly with 2 g finely powdered sulfur and heated at 150°C for 2.5 h in an inert atmosphere (N_2 or CO_2) with occasional mixing. Natural rubber has been mixed with ten parts per hundred rubber (phr) of factice in a two-roll mixing mill (10 × 12 in.) as per the following recipe: natural rubber, 100 phr; zinc oxide 5 phr; stearic acid 2.5 phr; factice 10 phr; cyclohexyl-2-benzothizyl sulfenamide (CBS), 0.8 phr, sulfur 2.0 phr. After the maturation, rheometric studies were made by a Monsanto Rheometer model R1005 (Akron, OH). Tensile strength and elongation at break of the sample was carried out at room temperature on Zwick UTM-1445 (Ulm, Germany) at a testing speed of 500 mm/min, according to an ASTM method (2) using dumbbell-shaped specimens.

RESULTS

Average 43% (overall 12%) oil is available. Chemical analysis showed an iodine value of 85, a saponification value of 183.2; gas–liquid chromatography (of the methyl esters of the fatty acids): $C_{16:0}$ (6%), $C_{18:0}$ (5.6%), $C_{18:1}$ (57.6%), $C_{18:2}$ (29.8%), $C_{20:0}$ (1%), as well as minor traces of C_{17}. The total yield of oil, iodine value, saponification value, and free fatty acid composition varied within small ranges, depending on the maturity of the seeds, harvesting seasons, and geographical location of collection sites, as well as variation in the process of extraction of the oil from seed.

Blends of 50 and 75% of *P. roxburghii* seed oil with diesel gave satisfactory, knock-free performance without observable carbon deposits at the functional parts of internal combustion unit. However, a blend of 80% and above exhibited vibration and noise. When compared to a sample of fluidized coal (moisture, 10%; volatiles, 35%; and ash, 21%) and a 10:1 blend with *P. roxburghii* seed oil showed higher flammability at 20°C, increased heat release, higher crossing point temperature, and reduced ash content. The details of the experimental comparison of diesel and the *P. roxburghii* seed oil are presented in Table 1, and the mechanical performance is presented in Figure 1.

In the case of the factice, it was observed that a 10% blend of this factice showed reduction in strength, hardness, viscosity, and scorch time, but an increase in the degradation temperature as compared to its unblended natural rubber sample.

TABLE 1
Physical Properties of Diesel Oil and *Putranjiva roxburghii* Oil

	Diesel oil	*P. roxburghii* seed oil
Density g/mL	0.882	0.917
Viscosity (centipoise) at 32°C	4.0	6.2
Boiling point (°C)	148–152	255–261
Carbon deposition index (g/100 g oil)	84–87	67–70
Calorific value (Kj/kg)	42707	36604
Flash point (°C)	39–42	52–55
Cetane number	40–50	53–55
Brake power, Kw (at 1400 rpm)	0.659	0.733
Brake thermal efficiency (%)	18.82	14.63

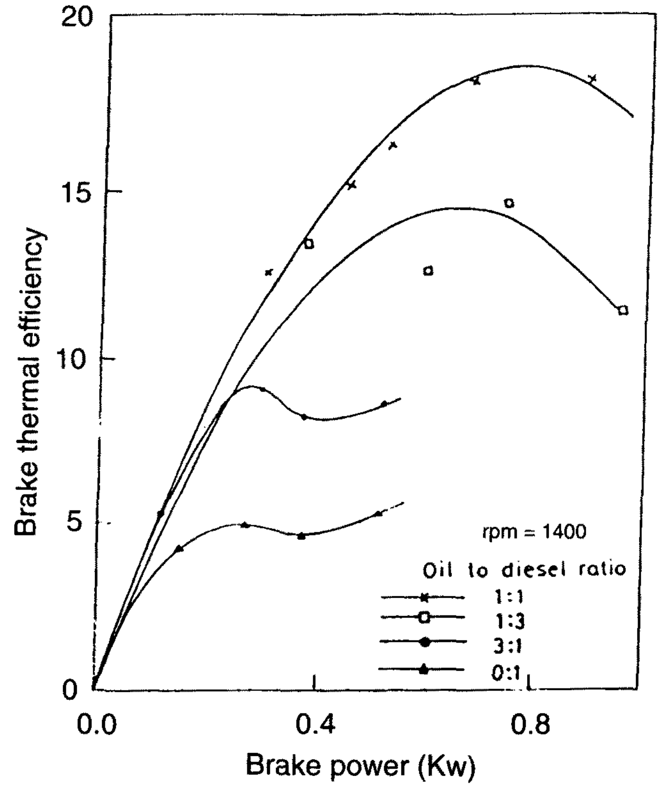

FIG. 1. Variation of thermal efficiency with brake power for different oil blends.

Figure 2 shows rheographs of natural rubber-based compounds both with and without factice. Technical details about this factice were published previously (3).

DISCUSSION

The results of the prototype experiments with the seed oil of *P. roxburghii* were sufficient to establish the usefulness of the less expensive and easily available raw material into important industrial uses, namely safely blending with diesel up to 50%. Factice made out of this oil and blended 10% with natural rubber improved the quality. A higher percentage blending also can be useful for specific purposes, i.e., cable coverings, erasers, etc.

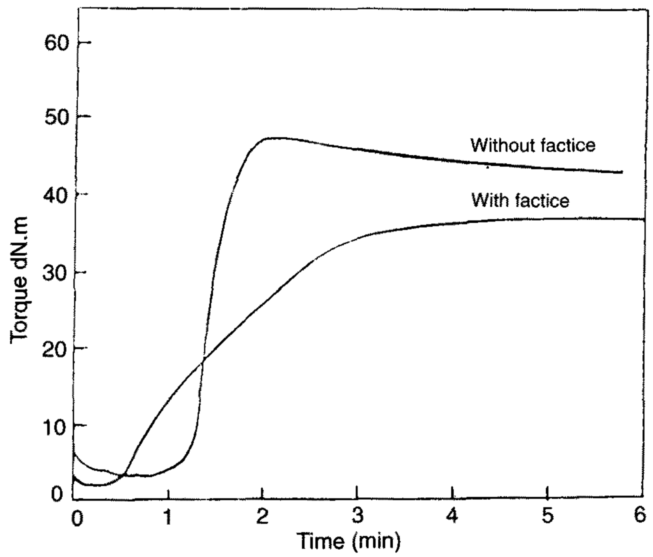

FIG. 2. Rheographs of natural rubber-based compounds with and without factice.

The presence of the trace amount of C_{17} fatty acid was not investigated in detail, and, hence, further comments or speculation on this has been avoided. Preliminary microbiological tests in petri dish culture exhibited significant antifungal properties. It also exhibited insect and termite repellent properties, but no toxic effects were observed. The oilcake showed excellent plant nutrient properties. Investigations in this direction are underway.

Putranjiva roxburghii seed, a renewable plant product, deserves attention and detailed investigation on its pharmaceutical and agrochemical usefulness.

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