Survey of Seed Oils for Use as Diesel Fuels

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ABSTRACT: Fifty-one out of 364 plant seeds being surveyed had fatty acid contents greater than 15% (dry weight), and their methyl esters had cetane indices higher than 50. Rambutan seed was an exception, with a lipid content of only 14.7%, but a high cetane index (67.1); thus, it was included in this report. Twenty seed oil methyl esters had cetane indices greater than 60. Three seed oils from the Sapindaceae family not only had high cetane indices but also contained long-chain fatty acids of 20 carbon atoms. Gross heats of combustion of the fatty acid methyl esters were slightly higher than those of neat oil, ranging from 38.2 to 40.8 J/g, whereas the heating values of the oils ranged from 37.4 to 40.5 J/g. Thus, these plant seed oils have great potential for development as diesel fuel or diesel fuel extender.
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KEY WORDS: Cetane index, diesel fuel, fatty acid composition, heat of combustion, iodine value, saponification number, seed oil.

Vegetable oils and their methyl esters have long been considered as potential alternative fuels for diesel engines (1–3). However, there have been both technological and economical problems to be solved prior to such utilization. Some technological problems, such as the high viscosity of vegetable oils, are solved by replacing the glycerol moiety with three molecules of monohydric alcohol. The molecular weight and viscosity of the esters are greatly reduced. The problems of coking and gumming in the injector line and combustion cylinder by oils of a high degree of unsaturation are partly overcome by proper selection of oils of less unsaturation or may be solved by partial hydrogenation.

The economic problem is much more difficult to tackle. At present, vegetable oils have their own economic uses, and their prices are much higher than that of petroleum. In fact, prices of vegetable oils have always been higher than petroleum prices, even in periods of petroleum crises (4). Thus, the use of vegetable oils or their methyl esters as diesel fuel is viable only in countries with large excesses of vegetable oils. Although Thailand is an agricultural country, oilseed production for food uses remains insufficient. Therefore, the use of vegetable oils or their methyl esters as diesel fuel is not possible at this time. However, efforts have been made to search for new seeds whose oils might be suitable for use in diesel engines and might overcome the economic problem.

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Seeds from many species have been analyzed for their fatty acid composition (5–11). The purpose of most of these investigations was to search for both new sources of industrial oils and unusual fatty acids of academic interest. In this paper, we report on 51 oilseeds, commonly found in Thailand, which have oil contents ≥15% (dry weight) and cetane indices of their methyl esters higher than 50.

EXPERIMENTAL PROCEDURES

Plant seeds were obtained from commercial seed suppliers, groceries, and collected from wild plants. The seeds were manually dehulled, and only their kernels were analyzed. Fatty acids were identified by their ECL (equivalent chain-length) on an SP-2330 (Supelco Inc., Bellfonte, PA) capillary column as their methyl esters. Identification was carried out automatically by a basic program written on the C-R4A microprocessor. The program can identify saturated fatty acids of 12–22 carbons and unsaturated fatty acids of 16:1 (9-*cis*); 18:1 (9-*cis*); 18:2 (9-*cis*, 12-*cis*), 18:3 (9-*cis*, 12-*cis*, 15-*cis*, and 6-*cis*, 9-*cis*, 12-*cis*), 20:1 (11-*cis*), and 22:1 (13-*cis*). Saponification numbers (SN), iodine values (IV), gross heats of combustion of the oils (HO) and fatty acid methyl esters (HF), and cetane indices of the methyl esters (CI) were calculated from their fatty acid compositions.

Transmethylation. Transmethylation of plant seed kernels was carried out *in situ* as described by Harrington and Darcy-Evans (12).

Gas chromatography. Gas chromatographic analysis was carried out on a Shimadzu Model 14A gas chromatograph, equipped with flame-ionization detectors (Shimadzu Inc., Tokyo, Japan), and a 0.25 mm × 30 m fused-silica capillary column coated with SP-2330 [Poly(80%-biscyanopropyl-20% cyanophenylsiloxane)]. The chromatographic conditions were as follows: N_2 carrier gas flow, 4 mL/min; N_2 makeup gas flow 30 mL/min; oven temperature, 180°C isothermal; detector/injector, 230°C; split ratio, about 50:1. Chromatographic signals were processed by C-R4A data processor (Shimadzu Inc.).

Calculation. IV of plant seed oils were calculated from their fatty acid methyl ester compositions as $IV = \sum(254 \times D \times A_i)/MW_i$, where D is the number of double bonds, MW_i is the molecular mass, and A_i is the percentage of each component in the chromatogram. SN were calculated from the equa-

TABLE 1
Fatty Acid Composition (FA), Saponification Numbers (SN), Iodine Values (IV), Cetane Indices (CI), Heat of Combustion of Fatty Acid Methyl Esters (HF) and Oils (HO) of Some Selected Seeds

Source	Total FA				Heat of combustion[a]		Fatty acid composition (%)						
	(%)	SN	IV	CI	HF	HO	16:0	18:0	18:1	18:2	18:3	Others (%)	Unknown
Annonaceae													
Annona squamosa (sugar apple)	35.7	189.7	85.4	55.8	40.0	39.4	13.6	8.5	50.6	24.3	1.1	20:0(0.8)	1.1
A. muricata (sour sop)	21.2	188.1	73.2	58.8	40.1	39.5	26.6	5.1	38.5	21.9	0.8	14:0(0.4), 16:1(1.8), 20:0(0.7), 20:1(0.8)	3.4
Apocynaceae													
Ervatamia coronaria (crepe jasmine)	25.0	193.2	71.0	58.6	39.9	39.3	24.4	7.2	50.5	15.8	0.6	16:1(0.2), 20:0(0.7), 20:1(0.2), 22:0(0.2)	0.2
Thevetia peruviana (trumpet flower)	39.0	192.8	76.8	57.4	39.9	39.4	30.9	6.3	29.4	29.6	0.2	14:0(0.3), 20:0(1.1), 22:0(0.5), 24:0(0.5)	1.1
Averrhoaceae													
Averrhoa bilimbi (Cucumber tree)	48.4	193.9	73.0	58.0	39.9	39.3	25.5	6.2	46.5	18.9	0.4	14:0(0.9), 20:0(0.8), 20:1(0.6)	0.2
A. carambola (carambola)	40.6	188.1	81.2	57.0	40.1	39.5	21.4	6.2	42.0	26.0	0.2	14:0(0.4), 20:0(0.5), 20:1(0.3), 22:0(0.2)	2.8
Bignoniaceae													
Tabebuia pallida	22.0	186.5	67.3	60.4	40.1	39.6	13.8	21.0	38.4	19.9	—	14:0(0.4), 20:0(4.0)	2.5
Crescentia cujete (calabash tree)	51.2	190.4	74.4	58.2	40.0	39.4	16.1	11.9	48.9	18.8	1.2	14:0(0.4), 20:0(1.3), 22:0(0.5)	0.9
Caricaceae													
Carica papaya (papaya)	48.0	185.4	68.4	60.3	40.2	39.7	14.8	4.2	71.0	4.0	0.9	20:0(1.1), 20:1(0.7)	3.3
Combretaceae													
Terminalia chebula (myrobalan wood)	34.8	189.3	83.3	56.4	40.0	39.4	16.3	5.0	53.5	21.5	0.4	20:0(0.9), 20:1(0.3), 22:0(0.7)	1.4
T. catappa (tropical almond)	39.7	193.8	74.5	57.7	39.9	39.3	35.0	5.0	30.3	27.9	—	16:1(0.3), 20:0(0.4)	1.1
T. bellerica (beleric myrobalan)	16.8	184.5	86.6	56.4	40.1	39.6	17.1	12.0	29.6	35.4	0.2	20:0(1.2), 22:0(0.4)	4.1
Compositae													
Cosmos sulphureus	26.2	191.4	82.4	56.3	40.0	39.4	32.1	8.3	13.4	40.7	0.3	14:0(0.5), 20:0(1.2), 20:1(0.7), 22:0(0.8)	2.0
Zinnia elegans	23.0	190.5	85.9	55.6	40.0	39.4	19.3	21.2	10.6	43.9	—	16:1(0.3), 20:0(2.6), 20:1(0.8), 22:0(0.3)	1.0
Cruciferae													
Brassica parachinensis (Chinese cabbage)	40.4	169.5	73.8	61.2	40.7	40.3	2.8	1.4	16.3	10.8	7.2	20:0(2.1), 20:1(8.2), 22:0(1.0), 22:1(48.1)	2.1
B. juncea	33.1	171.4	73.0	61.7	40.6	40.2	3.9	1.4	10.3	13.6	11.6	20:0(0.9), 20:1(6.9), 22:0(1.1), 22:1(48.9)	1.4
B. alboglabra (collard)	23.3	165.0	74.6	62.6	40.8	40.5	3.4	1.0	14.6	13.2	8.0	20:0(0.5), 20:1(4.3), 22:0(0.4), 22:1(49.7)	4.9
Cucurbitaceae													
Cucurbita moschata (pumpkin)	36.4	193.2	88.9	54.5	39.9	39.3	22.4	7.5	35.9	33.6	0.1	20:0(0.3)	0.2
Luffa acutangula (angled gourd)	16.3	189.7	31.7	67.9	40.1	39.6	46.1	18.6	19.0	7.6	0.6	14:0(0.4), 16:1(2.4), 20:0(0.9)	4.4
Ebenaceae													
Diospyros malabarica	45.9	190.9	82.2	56.4	40.0	39.4	10.8	22.7	35.6	29.9	—	γ18:3(0.8)	0.2
Elaeocarpaceae													
Elaeocarpus hygrophilus	30.7	192.0	68.2	59.4	40.0	39.4	31.0	5.8	38.1	19.9	0.4	14:0(1.4), 16:1(0.8), 20:0(0.2), 20:1(0.4)	2.0
Euphorbiaceae													
Baccaurea sapida	21.3	185.4	73.5	59.2	40.2	39.6	24.6	8.4	23.1	30.8	6.8	16:1(0.3), 20:0(1.0), 20:1(0.2), 22:0(0.3)	4.5
Jatropha curcus	52.8	190.3	97.7	53.0	40.0	39.4	15.2	6.1	41.8	35.8			1.1
Guttiferae													
Calophyllum inophyllum (Alexandrian laurel)	40.5	190.0	74.0	58.4	40.1	39.4	12.6	19.8	45.2	20.3	0.1	16:1(0.2), γ18:3(0.7), 20:0(0.3)	0.8
Ixonanthaceae													
Irvingia malayana	57.0	247.5	2.3	67.8	38.2	37.4	3.3	0.2	1.9	0.4	—	10:0(3.4), 12:0(53.8), 14:0(36.7)	0.3
Maliaceae													
Azadirachta indica (neem tree)	43.6	187.3	61.2	61.7	40.1	39.6	21.4	20.6	35.1	17.7	0.6	20:0(1.1), 20:1(0.6)	2.9

TABLE 1 (*continued*)

Source	Total FA (%)	SN	IV	CI	Heat of combustion[a] HF	HO	Fatty acid composition (%) 16:0	18:0	18:1	18:2	18:3	Others (%)	Unknown
Malvaceae													
Abelmoschus esculentus (okra)	28.8	194.0	89.8	54.2	39.9	39.2	32.4	3.6	19.8	41.9	0.1	14:0(0.3), 16:1(0.4), 20:0(0.4), 22:0(0.2)	0.9
Hibiscus sabdariffa	22.0	190.6	87.7	55.2	40.0	39.4	25.0	4.0	31.5	34.8	—	14:0(0.2), 16:1(0.6), 20:0(2.1)	1.8
Gossypium herbaceum (cotton)	29.9	187.2	86.9	55.9	40.1	39.5	31.8	3.1	16.7	41.4	—	14:0(1.0), 16:1(1.1), 20:0(0.2)	4.7
Mimosaceae													
Pithecellobium dulce (madras's thorn)	17.0	179.1	73.8	60.2	40.4	39.9	18.5	3.8	30.8	27.3	1.8	16:1(0.2), 20:0(2.6), 22:0(9.5)	5.5
Parkia speciosa	23.7	186.6	93.7	54.4	40.1	39.5	22.0	4.7	14.0	47.0	—	20:0(1.4), 20:1(0.6), 22:0(8.0)	2.3
Moringaceae													
Moringa oleifera (horse-radish tree)	22.3	184.2	68.8	60.4	40.2	39.7	5.8	4.2	75.6	0.7	0.2	16:1(1.1), 20:0(2.6), 20:1(2.2). 22:0(5.7)	1.9
Myristicaceae													
Myristica fragrans (nutmeg tree)	27.7	223.1	5.4	69.5	39.0	38.3	6.6	0.4	5.5	0.4		12:0(0.4), 14:0(84.9)	1.8
Myritaceae													
Myrica esculenta	44.5	182.3	87.8	56.5	40.2	39.7	15.0	5.2	41.8	28.1	0.5	16:1(3.0), 20:0(0.2), 20:1(0.7)	5.5
Ochnaceae													
Ochna kerkii	38.3	198.8	49.7	62.6	39.8	39.2	52.5	1.6	32.5	12.4	0.5	16:1(0.4)	0.1
Ranunculaceae													
Clematis subpeltata	36.4	185.4	82.5	57.2	40.2	39.6	11.0	6.5	57.8	18.7	0.2	16:1(0.3), 20:0(1.3), 20:1(0.4), 22:0(0.9)	2.9
Rhamnaceae													
Zizyphus mauritiana (Indian jujube)	29.3	186.5	78.6	57.9	40.1	39.6	10.4	5.5	62.8	12.4	—	20:0(1.8), 20:1(2.6), 22:0(1.2), 22:1(1.7)	1.6
Z. mauritiana	31.4	189.4	86.0	55.8	40.0	39.4	10.2	6.6	51.9	22.5	0.2	20:0(2.5), 20:1(3.3), 22:0(2.8)	—
Rosaceae													
Prunus persica (peach)	37.56	186.7	83.6	56.7	40.1	39.5	8.9	2.1	70.4	12.3	0.2	12:0(1.1), 16:1(1.1), 20:0(0.3), 20:1(1.1)	2.5
Rutaceae													
Murraya paniculata (orange jasmine)	65.0	192.2	64.1	60.3	40.0	39.4	18.7	11.0	42.3	12.1	6.2	16:1(7.3), 20:0(1.1), 22:0(0.4)	0.9
Citrus aurantium (orange)	29.0	190.3	58.6	61.8	40.0	39.5	39.5	6.8	23.0	21.0	1.9	14:0(0.7), 16:1(2.1), 20:0(0.7), 20:1(0.7)	3.6
C.reticulata	43.1	188.7	85.0	56.1	40.0	39.5	25.9	6.4	23.0	37.5	3.3	16:1(0.5), 20:0(0.4)	3.0
C. maxima (pummelo)	44.8	193.4	62.2	60.5	39.9	39.4	37.1	7.9	25.0	22.9	3.1	14:0(0.5), 16:1(1.3), 20:0(0.5)	1.7
Sapindaceae													
Cardiospermum halicacabum (heart pea)	42.0	171.6	61.8	64.2	40.6	40.2	4.0	2.1	19.5	7.4	6.2	γ18:3(0.4), 20:0(12.9), 20:1(36.2), 22:0(1.4), 22:1(5.4)	4.4
Nephelium lappaceum (rambutan)	14.7	179.0	42.9	67.1	40.4	40.0	6.3	7.6	38.3	2.1	—	16:1(0.8), 20:0(33.1), 20:1(7.2), 22:0(2.7)	1.9
Sapindus emaginatus	26.8	178.2	71.8	60.7	40.4	40.0	5.9	1.6	52.6	7.4	4.0	20:0(5.6), 20:1(17.2), 22:0(1.0), 22:1(0.5)	4.2
Sapotaceae													
Manilkara achras (sapodilla plum)	25.3	183.5	62.2	62.0	40.2	39.8	21.8	8.1	55.4	8.2	0.2	20:0(0.5), 20:1(0.6), 22:0(0.2)	5.0
Mimusops elengi (bullet wood)	26.9	182.0	71.6	60.2	40.3	39.8	13.4	10.8	54.5	14.0	0.3	16:1(0.2), 20:0(1.2), 20:1(0.6)	5.0
Simaroufaceae													
Brucea javanica	32.1	181.1	76.5	59.2	40.3	39.8	11.9	8.0	56.5	15.5	0.1	16:1(0.4), 20:0(1.2), 20:1(1.1)	5.3
Umbelliferae													
Coriandrum sativum (coriander)	36.7	183.6	91.2	55.5	40.2	39.7	3.5	0.9	77.6	14.1	0.1	16:1(0.3), 20:0(0.1)	3.4
Heracleum gracillius	20.7	182.8	86.6	56.7	40.2	39.7	6.0	1.2	74.2	13.0	0.6	14:0(0.2), 16:1(0.5), 22:0(0.2)	4.1

[a]Expressed in joules per gram (to convert to cal/g divide by 4.187).

tion: $SN = \Sigma(560 \times A_i)/MW_i$. CI, HO, and HF were calculated according to Krisnangkura (13,14). Total lipid was estimated from the equation: Total lipid $= \Sigma A_i \times W_{17:0} \times 100/A_{17:0} \times W_{sample}$, where $W_{17:0}$ and A_{sample} are weights of heptadecanoic acid (internal standard) and sample, respectively; $A_{17:0}$ is the percentage area of heptadecanoic acid methyl ester in the chromatogram.

RESULTS AND DISCUSSION

Pryde (15) suggested that vegetable oils used in diesel engines should have cetane numbers higher than 35–40, and IV should be between 80 and 145. He also noted that cetane numbers determined by the indirect method were usually about 10 units higher than those obtained by the direct method. Oils of higher IV are easily oxidized and polymerized. These undesirable reactions not only lower the storage life of the oils but they also increase gum formation and coking in the diesel engine. Normally, oils of higher degrees of unsaturation have good benefits for human and animal health. If such highly unsaturated oils are developed, they will undoubtedly be diverted to food and feed industries. Therefore, only seed oils whose iodine values were <100 with fatty acid contents higher than 15% are reported in Table 1. Rambutan seed oil was an exception in that it contained only 14.7% lipid, but its methyl esters had a high CI (67.1). Thus, rambutan seed oil is included in Table 1. Fatty acid compositions of some seed oils listed in Table 1 have been reported elsewhere. Pattamapongse and Showler (6) reported that rambutan seed contained only 9.7% lipid, which was considerably lower than the figure in this report. The difference is probably due to the method of extraction or the variety of rambutan. *Abelmoschus esculentus* (okra) and *Hibiscus sabdariffa* have been reported to contain 3 and 6% epoxyoleic acid (10,11), respectively. However, this oxygenated acid, if present, may have been destroyed by the acidic conditions (16) and was not detected in this study.

Of 364 seeds commonly found in Thailand, 21 seed oil methyl esters have CI >60. Some seeds, such as rambutan, Papaya, orange, okra, peach, and Indian jujube, are food industrial waste products, which can be collected in large quantities. Thus, they may have great potential for the development of oils as diesel fuels or fuel extenders. Three seeds from the family Sapindaceae had high amounts of long-chain fatty acids of 20 carbon atoms, and their methyl esters had high CI. These oils might also be developed into specialty chemicals. The methyl esters of oils whose IV were <100 usually had CI >50.

Heats of combustion of most seed oils and seed oil methyl esters varied only slightly. Heating values of the oils and the methyl esters ranged from 37.4 to 40.5 and 38.2 to 40.8 J/g, respectively.

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