VOL. 6, NO. 7, JULY 2011 ISSN 1990-6145
ARPN Journal of Agricultural and Biological Science


www.arpnjournals.com

EFFECT OF PROCESSING ON SEED OIL OF *Simarouba glauca* (DC): AN UNDERUTILIZED PLANT

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ABSTRACT

Refining of oil (including a series of processes like degumming, alkali refining and bleaching) are aimed to remove the impurities like free fatty acids, phosphatides, metal ions, waxes, oxidation products, colour bodies etc. so as to make oil suitable for edible and storage purposes. The above processes were applied on the *Simarouba glauca* and rapeseed oil to observe the effect of refining on different physico-chemical properties like free fatty acids, iodine value, peroxide value, saponification value, unsaponifiable matter and fatty acid composition. It was observed that the refining of oil result in the improvement of oil quality and making the oil suitable for human consumption, storage and bio-fuel production.

Keywords: *Simarouba glauca*, seed oil, degumming, alkali refining, bleaching.

INTRODUCTION

Simarouba glauca belongs to family simarubaceae, commonly known as "The Paradise Tree" or "King Oil Seed Tree", is a versatile multipurpose evergreen tree having a height of 7-15 m with tap root system. It is mainly found in coastal hammocks throughout South Florida. In India, it is mainly observed in Andhra Pradesh, Karnataka and Tamil Nadu etc. It can adapt a wide range of temperature, has the potentiality to produce 2000-2500 kg seed/ha/year (Joshi and Hiremath, 2000); can grow well in marginal lands/wastelands with degraded soils and therefore considered as a major forest tree. All parts of Simarouba are useful in some way or the other. The plant is also known for its medicinal properties. The leaf and bark of *S. glauca* contain glaucarubin, a chemical useful in curing amoebiasis, diarrhea and resistance against malaria. However, in the present context the seeds are economically very important as they contain 60-75% oil, which can be used in the manufacture of vegetable fat and/or margarine. From 1950 onwards, in El Salvador and other Central American countries the oil is marketed for edible purposes under the trade name of Manteca Vegetal "Nieve" and the oil is well accepted. As industrial oil it is well suited for the manufacturing of quality soaps, lubricants, paints, polishes, pharmaceuticals etc. Dry seeds of *S. glauca* contain 32-40% protein, with 59-62% unsaturated fatty acids which improves its nutritional profile.

Fatty oils, when extracted from vegetable and animals tissues, contain a number of impurities like free fatty acids, phosphatides, metal ions, waxes, oxidation products, colour bodies etc., which should be removed from the oil to make it suitable for commercial produce. Removal of such kinds of impurities is done in a series of processes, which includes water degumming, alkali refining and bleaching of oil, which result in production of high quality oil having a good colour, no taste or smell and remains fit for consumption, storage and transportation for long time (Wiedermann, 1981; Haraldsson, 1983). These pretreatment processes also solved the problem of oil deterioration and incomplete combustion as fuel. Further, it also increased the susceptibility of vegetable oils for trans-esterification during their conversion to biodiesel.

Rapeseed oil is considered as one of the major edible oil from long time all over the world due to its good nutritional profile. Keeping in view, six different physico-chemicals properties like free fatty acids, iodine value, peroxide value, saponification value, unsaponifiable matter and fatty acid composition of *S. glauca* and rapeseed oil were studied before and after the refining process and the results were compared together in order to see the effect of refining on *S. glauca* (an underutilized plant) oil, so as to provide useful information on the possible aspects of this under exploited food items for human consumption, food industry, bio-fuel production and other technological uses.

MATERIALS AND METHODS

The proposed study was conducted at Department of Chemistry, Chaudhary Devilal University, Sirsa, India.

Seed material

The seeds of *S. glauca* were procured from Forest College and Research Institute, Mettupalayam, Coimbatore. The rapeseeds were procured from local market, Sirsa.

Oil extraction

The *S. glauca* and rapeseeds were sun dried. The dried seeds were blended and mixed thoroughly in a Kenwood food mixer. The powdered sample was stored in an air-tight jar and kept in the refrigerator prior to the analysis. Oil was extracted by solvent extraction method AOAC (1984). Defatted oil cake of *S. glauca* and rapeseed were studied for crude protein estimation. For that, nitrogen was estimated by the micro-kjeldahl method and

the percentage nitrogen was converted to crude protein by multiplying with 6.25 as reported by Pearson, 1976. Percent oil yield and lecithin were also estimated.

Physico-chemical parameters

Saponification value of the oil was obtained by refluxing the alcoholic potassium hydroxide solution of the oil and titrated with 0.5 M HCL using phenolphthalein indicator as explained by Vogel (1980). The iodine value was determined by titrating the chloroform and potassium iodide solution of *S. glauca* and rapeseed oil with sodium thiosulphate solution using starch indicator (AOAC, 1984). The peroxide value of *S. glauca* and rapeseed oil were obtained by dissolving the oil in a solvent mixture of acetic acid and carbon tetrachloride, warmed with potassium iodide, and titrated with sodium thiosulphate solution using starch as indicator (AOAC, 1984). The unsaponifiable matter content of the oil was estimated by dissolving the oil in alcoholic potassium hydroxide and refluxed. The homogeneous soda was extracted with diethyl ether, the extract was filtered, oven dried to a constant weight (AOAC, 1984). Fatty acid spectrum was estimated by method of Luddy *et al*., (1968). The oils were converted into methyl esters using a KOH/MeOH method. The extracted fatty acid methyl esters (FAME) were dissolved in n-hexane for GC analysis.

Fractionation of methyl esters by GC

GC analysis was performed on a Chemito 8610 HT Gas chromatograph equipped with FID and a BPX70, 0.25mμ fused silica column (SGE Pvt. Ltd., Ringwood, Victoria, Australia). The carrier gas was hydrogen and injection was operated in the split mode, the split ratio being approximately 50:1. Injector and detector temperatures were 270 and 280ºC, respectively. The oven temperature was held at 70ºC for 1 min. and than programmed at 30ºC/min. to 170ºC followed by further programming at 30ºC/min. to 200ºC and held at this temperature for 6 min. Data was captured and analyzed with, Chemito 5000 integrator (Tashniwal Instruments, India Ltd.).

Degumming

It was done by the method of Sartoretto (1976) and Erickson *et al*., (1987). Crude oil was mixed with 2-3% water, and it was agitated gently for 30-60 minutes at a temperature of 70ºC. Precautions were taken in order to prevent the introduction of air and subsequent oxidation of oil. Due to this phosphatides and other impurities were settled down and were centrifuged (7000 rpm for 15 minutes) out from the degummed oil. This process thus resulted in recovery of lecithin and other materials that can settle out during shipment or storage of pure oil.

Alkali refining

It was done by the method of Erickson *et al*. (1987). For alkali refining, caustic soda (around 0.1%) was added and thoroughly mixed to ensure saponification of free fatty acids, hydration of phosphatides, albuminous and mucilaginous matter and reactions with colourd pigments. The mixture was heated to 80ºC and centrifuged (7000 rpm for 15 minutes) to separate out the caustic from refined oil. The refined oil was heated to 88ºC mixed with 10-20% soft water and was again centrifuged to separate into heavy and light phases.

Bleaching

It was done by the method of Erickson *et al*. (1987). To the oil obtained after centrifugation was added 1% activated charcoal. It was stirred for half an hour and heated to 100ºC. The slurry was filtered, cooled and subjected to GLC analysis. The identification of the peaks was achieved by retention times and by comparing them with authentic standards analyzed under the same conditions.

Statistical analysis

The data were analyzed using analysis of variance for the complete randomized design (CRD) where each observation was replicated thrice. To compare the treatments, critical difference (P = 0.05) was calculated.

RESULTS AND DISCUSSIONS

Oil yield

Oil yield (Table-1) in *S. glauca* and rapeseed were observed as 57.22 and 40.33%, respectively.

Table-1. Oil yield, protein in defatted cake and lecithin in oil of *S. glauca* and rapeseed.

	Oil (%)	Lecithin (%) in oil	Protein (%) in defatted cake
S. glauca	57.22	2.17	38.62
Rapeseed	40.33	2.57	22.18

Percent oil yield in *S. glauca* was found comparable with the percent oil yield of rapeseed oil, so *S. glauca* can be used as a potential oil yielding crop. Comparable oil yield in *S. glauca* and rapeseed were also observed by (Earle *et al*., 1960; Downy and Harvey, 1963 and Anonymous, 1959). Crude protein in defatted cake of *S. glauca* was found to be 38.62% and in rapeseed was 22.18%. Therefore, it can be said that *S. glauca* contained high protein as compared to those of some conventional defatted seed cakes like rapeseed. There are reports that *S. glauca* seed cake can be used for feeding purposes and

being good in NPK contents it can be used as good manure (Armour, 1959).

Seed oil contained phosphatides in the form of lecithin. Most of the phosphatides in the crude oils are hydratable and can be removed by water degumming (Hvolby, 1971; Dijkstra and Martin, 1989). Variations in lecithin yield were found as 2.17 and 2.57% in *S. glauca* and rapeseed oil, respectively. It was observed that once the degumming is done thereafter, no gums or waxes appeared in the oil, which result in the production of oil having good colour, no taste or smell and remain fit for storage and transportation for long time (McDonnell *et al*., 1995). The phosphatides did not combust completely, resulting in carbon deposits and lubricating oil thickening (Fangrui and Milford, 1999). Degumming of crude oil solved the above problem. Commercially obtained lecithin has wide industrial applications in food and beverages, medicines, cosmetics, tobacco, lubricants, gasket and cork products, urethan polymer, soap production etc. (Silva, 1990 and Sinram, 1991).

Physico-chemical parameters

Free fatty acid is an indicator of quality, the freshness of the fat, the efficiency of the refining process, but not a flavour predictor. Free fatty acid value (Tables 2 and 3) of *S. glauca* and rapeseed before refining were found to be 1.35 and 3.27 mg KOH/gm oil, respectively. These values compared favorably with the results obtained by (Armour, 1959; Hougen and Bodo, 1973; Ali and McKay, 1982). There were marked decrease in free fatty acid content after refining in the *S. glauca* and rapeseed oil, which were observed as 0.65 and 1.20 mg KOH/gm oil, respectively. Release of short chain fatty acids (free fatty acids) such as butyric, caproic and capric acid; cause particularly disagreeable odours and flavour whereas the long chain fatty acids (C_{12} and above) produce candle like or, at alkaline pH, soapy flavour (Sessa and Rakis, 1977). These short chain fatty acids got removed during refining. Further crude vegetable oils have abnormally high free fatty acid levels as enzyme lipase are activated by moisture in such cases which results in hydrolysis initiation and increase in the free fatty acid content, whereas in processed oils lipase activity are minimal which result in decrease of free fatty acid content in such oils (Weiss, 1983).

Table-2. Effect of refining process on different physico-chemical properties of *S. glauca* seed oil.

	Free fatty acid (mg KOH/g oil)	**Iodine value** (g/100g oil)	**Peroxide value** (meq/kg oil)	**Saponification value** (mg KOH/g oil)	**Unsaponifiable matter** (%)
Before refining	1.35	53.90	2.60	191.45	0.40
After refining	0.65	42.90	1.01	174.55	0.21
SEm ±	0.03	1.01	0.15	2.96	0.04
CD at (P = 0.05)	0.19	6.63	0.99	NS	NS

SEm = Standard error of mean; CD = Critical difference

Table-3. Effect of refining process on different physico-chemical properties of rapeseed oil.

	Free fatty acid (mg KOH/g oil)	**Iodine value** (g/100g oil)	**Peroxide value** (meq/kg oil)	**Saponification value** (mg KOH/g oil)	**Unsaponifiable matter** (%)
Before refining	3.27	112.00	7.45	184.15	1.55
After refining	1.20	96.75	2.53	172.90	0.42
SEm ±	0.07	2.63	0.13	1.43	0.12
CD at (P = 0.05)	0.43	NS	0.86	9.37	0.80

SEm = Standard error of mean; CD = Critical difference

Iodine value is the number of grams of iodine required to saturate 100 gm oil. Its value (Tables 2 and 3) in *S. glauca* and rapeseed before refining were observed as 53.9 and 112.00 gm/100gm oil, respectively. These values compared favorably with the results obtained by (Armour, 1959; Downy and Harvey, 1963). Iodine value got reduced after refining in *S. glauca* and rapeseed oil to 42.90 and 96.67 gm/100gm oil, respectively. Decrease in iodine value after refining of oil show decrease in unsaturation of oil which is beneficial in the sense that lower the unsaturation of oils and fats, greater will its oxidative stability. Therefore in present finding *S. glauca* oil having

iodine value lower than rapeseed oil can be considered good in this regard. Further, lower iodine value in oil produce biodiesel with high cloud and pour point that have poor cold performance. So *S. glauca* oil having low iodine value after refining can be assumed as a poor alternate for biodiesel production as compared with rapeseed oil. Peroxide value is measured in terms of milliequivalents of peroxide per 1000 grams of the oil that oxidize potassium iodide to iodine. The peroxide value before refining (Tables 2 and 3) for *S. glauca* and rapeseed oil were observed as 2.60 and 7.45 meq/kg oil, respectively which got reduced to 1.01 and 2.53 meq/kg oil, respectively. The results are comparable with the results obtained by Hill (1994). Low peroxide value of *S. glauca* (after refining) make it superior over rapeseed oil as it can increase its suitability for the long time storage because of having low level of oxidative and lipolytic activities. Saponification value is a measure of the alkali reactive groups in oil and found useful in predicting the type of glycerides in a sample. Glycerides containing short chain fatty acids have higher saponification value. *S. glauca* and rapeseed oil have comparable saponification value before refining i.e., 191.45 and 184.15 mg KOH/gm oil, respectively. Nearly similar reduction trend of saponification value in *S. glauca* and rapeseed oil were observed after refining having saponification velues 174.55 and 172.90 mg KOH/gm oil, respectively. It strengthens the practical utility of *S. glauca* and rapeseed oils for increased susceptibility toward trans-esterification process and bio-fuel production. Lower the value of unsaponifiable matter in oil, higher will be its purity because low unsaponifiables in the oil indicate low amount of secondary metabolites like compesterol, stigmasterol, β-sitosterol, δ-7 stigmasterol, natural fibers, gums, metal complexes, phosphatides like phosphotidyl choline, phosphotidyl inosetol, phosphotidic acid, phosphotidyl ethanolamine and other components. *S. glauca* and rapeseed oils have very low unsaponification matter i.e., 0.40 and 1.55% respectively before refining, which further reduced to 0.21 and 0.42% (after refining) respectively. *S. glauca* oil having low unsaponification matter, thus found superior than rapeseed because biodiesel derived from oil with high unsaponifiable matter cause exhaust emissions during burning in the engine (Rosenblum, 2000).

Palmitic acid, (Table-4) which has been considered as major saturated fatty acid were found before refining as 10.90 and 5.40% which got reduced to 8.76 and 4.80% in *S. glauca* and rapeseed oil, respectively. From above results it was concluded that refining can cause reduction of palmitic acid value. Nearly similar trend of reduction in stearic acid (another major saturated fatty acid) value was also observed, after refining process in *S. glauca* and rapeseed oil. *S. glauca* oil was found to contain relatively high stearic acid value (25.66 and 24.21%), both before and after refining respectively, which has been considered harmful because high value of stearic acid can cause anthrosclerotic plaque (Smith and Circle, 1972). Rapeseed oil has low saturated fatty acid count, which indicates its practical utility for edible purpose over other oils. Total unsaturated fatty acid got increased after refining process. Oleic acid, which has been considered as major unsaturated fatty acid got increased from 58.18 to 60.08% in *S. glauca* and 59.62 to 60.66% in rapeseed oil. Since the oleic acid value in *S. glauca* was found very much comparable with rapeseed oil. This indicates its edible utility. Higher levels of oleic acid are desirable to impart stability to oil during storage and deep fat frying. A potential anti-nutritional compound- linolenic acid was found low (0.35%) before refining in *S. glauca* oil as compared with rapeseed oil (9.77%). Linolenic acid concentration further reduced (after refining) to 0.21% in *S. glauca* oil but remained high (10.17%) in rapeseed oil. In this respect *S. glauca* oil was found superior than rapeseed oil. Small variation in fatty acid composition of both crude and refined oil has been noticed due to slight oxidation of Linolenic acid during process of refining (Gahavmi *et al*., 2003). Further total unsaturated fatty acid in *S. glauca* and rapeseed oil were found increased after refining. It makes oil favorable for edible purposes as it can reduce plasma tri-glycrides and was found anti-thrombogenic too.

Table-4. Fatty acid composition before and after oil refining in *S. glauca* and rapeseed oil.

	Composition (%) before refining						
	Palmitic (16:0)	**Stearic** (18:0)	**Oleic** (18:1)	**Linoleic** (18:2)	**Linolenic (18:3)**	**Total saturated fatty acids** (%)	**Total unsaturated fatty acids** (%)
S. glauca	10.90	25.66	58.18	3.30	0.35	36.56	61.83
Rapeseed	5.40	1.91	59.62	20.72	9.77	7.31	91.10
Composition (%) after refining							
S. glauca	8.76	24.21	60.08	4.21	0.21	32.97	64.50
Rapeseed	4.80	1.21	60.66	20.17	10.17	6.01	91.00

CONCLUSIONS

It can be concluded from the above study that *S. glauca* seed oil have good nutritional profile and other physico-chemical properties which got improved after the process of refining, therefore it can be used as a potential oil seed resource for edible puepose and bio-fuel production.

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