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Chemical Characterization of *Pongamia pinnata* L. and its Value Chain By-Product as an Economically Viable Feedstock in Biofuel Production

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Abstract *Pongamia pinnata* is one of the most appropriate non-edible oil tree species in India because of its high nitrogen fixing capability and not grazable by animals. It is observed best from sea level to an altitude of nearly 1200 m. The study was carried out in three climatic regions of Karnataka, viz., coastal, hilly and plain regions to evaluate the effect of environmental factors on physical and chemical characteristics of pongamia oil and deoiled cake. Acid value is one of the important criteria used in the trans-esterification reaction to decide whether the oil is to be treated in single stage or double stages. The coastal region has the highest acid value, followed by hilly region and the plain region showed the lowest acid value. The iodine value followed an increasing trend with increase in distance from the sea. Hilly region showed the highest, followed by plains and the lowest iodine value was present in coastal region. The density of oil varies with API gravity of oil and the temperature conditions of the surroundings. Higher unsaturated fatty acid, higher is the iodine value which increases the viscosity. The results indicated that the oil cake obtained from the *Pongamia pinnata* L. seeds consisted of good amounts of N, P and K 5.24%, 0.027% and 0.69% respectively. This showed that the deoiled cake could be used as manure in agriculture where it can act as a source of plant nutrients.

Keywords *Pongamia pinnata*, Oil, Physico-chemical, Deoiled cake.

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Introduction

Pongamia pinnata is one of the most appropriate non-edible oil tree species in India because of its high nitrogen fixing capability and not grazable by animals. It is a medium-sized glabrous tree commonly known as Karanja in Hindi language, Indian beech in English. It is suitable tree for tropics and sub-tropical zones with soil having good drainage and more sunny days. It is observed best from sea level to an altitude of nearly 1200 m (Sahni 1998).

It grows easily by seed. Historically, this crop has been used from long time in India and neighbor regions as a source of green manure, traditional medicines, timber, animal fodder, fish poison and

fuel (Savita and Nagpal 2010).

Pongamia oil has good physico-chemical properties that can be transformed to biodiesel by transesterification by methanol in the presence of potassium hydroxide (KOH) (Konthe 2006, Konthe 2002). The saturated and unsaturated fatty acid composition was 20.5% and 79.4% respectively. The main mono unsaturated fatty acid was oleic acid (46%) whiles linoleic acid (27.1%) and linolenic acid (6.3%) forms the total polyunsaturated fatty acid (Natanam et al. 1989, Nagaraj and Mukta 2004).

De-oiled seed cake, a by-product of oil seed after oil extraction has the potential of being used as fuel and feed stock for animals. However, the nutrient composition of de-oiled seed cake also suggest that it could be used in the formulation of de-oiled cake based fertilizers (Chaturvedi et al. 2009). The pongamia seed cake generated after extracting oil form pongamia seeds is a rich source of organic manure (Ramanathan 2006). Pongamia seed cake is observed to have quicker pyrolysis rate because of higher cellulose and lignin content advocates the de-oiled seed cake residues as a potential biomass feedstock for thermochemical transformation. The average nutrient composition that present in its oil cake is around 3.97% N,0.94% P_2O_5 and 1.27% K_2O (Krishnamurthy 1978).

Materials and Methods

This study was carried out in three climatic regions of Karnataka, viz., coastal, hilly and plain regions. The seeds were collected from the Dakshina Kannada, Hassan and Bengaluru districts of Karnataka.

Oil extraction

Gerhardt Soxtherm apparatus was used for estimating of oil content in seeds of pongamia. It works on the principle of solvent extraction method.

Acid value of oil

The acid number is defined as the mg of KOH needed to neutralize the free fatty acids available in 1 g of sample. 1 g of oil was dissolved in 50 ml of neutral solvent in a 250 ml conical flask. Few drops of phenolphthalein indicator was added and it was titrated against 0.1 N potassium hydroxide, till pink color which persists and stays for 15 seconds.

Iodine value of oil

Iodine number of the oil is a measure of the degree of unsaturation present in oil. It is expressed as a number of grams of iodine absorbed by 100 g of oil. The excess of iodine remaining is estimated by titrating against sodium thiosulfate ($Na_2S_2O_3$).

Determination of oil density

The density of the oil was determined by pycnometry.

Determination of oil viscosity

The resistance to flow of a fluid under gravity is known as kinematic viscosity. Kinematic viscosity of oil was determined using calibrated Cannon-Fenske viscometer.

Determination of N, P and K
content in deoiled cake

Total nitrogen

The total nitrogen of *Pongamia pinnata* L. deoiled cake sample was determined by Kjeldahl's method. A powdered sample of 0.5 g was digested using concentrated sulfuric acid with a digestion mixture (containing $CuSO_4$ 5 H_2O and K_2SO_4 in the proportion of 1:10). The digested material was distilled in alkaline medium containing 40% sodium hydroxide : The liberated ammonia was trapped in boric acid and titrated against standard sulfuric acid.

Total phosphorus

2 ml of di-acid digest was taken for total phosphorus determination by vandomolybdophosphoric yellow color method in nitric acid system as described by Jackson (1973).

Total potassium

2 ml of the di-acid digest was diluted to 25 ml with

Table 1. Acid value of oil. * Significant at 5% level of significance.

Region	Statistic	Oil acid value (mg KOH/g)
	Mean	1.32
Plain (Bengaluru)	Std Dev	0.37
	CV(%)	28.03
	Mean	2.66
Coastal (Dakshina Kannada)	Std Dev	1.38
	CV(%)	51.87
	Mean	1.69
Hilly (Hassan)	Std Dev	0.64
	CV(%)	37.86
Significant (probability) value		0.0169
Significant		*
Mean		1.87
Standard Deviation		0.89
CV(%)		47.50

Table 2. Iodine value of oil. * Significant at % level of significance.

Region	Statistic	Iodine value (g I_2/100 g)
	Mean	78.03
Plain (Bengaluru)	Std Dev	5.11
	CV(%)	6.54
	Mean	75.29
Coastal (Dakshina Kannada)	Std Dev	1.53
	CV(%)	2.03
	Mean	81.60
Hilly (Hassan)	Std Dev	3.66
	CV(%)	4.48
Significant (probability) value		0.0060
Significant		*
Mean		78.56
Standard Deviation		3.73
CV(%)		4.75

distilled water and fed to a calibrated flame photometer. By comparing the flame photometer readings of the sample with the calibration curve of potassium and percent potassium in the plant sample was calculated (Jackson 1973).

Results and Discussion

Investigations were carried out to know the physical and chemical characteristics of *Pongamia pinnata* L. oil and deoiled cake in coastal, hilly and plains of Karnataka. This part presents the results of the study in tabular and graphical form along with the discussion to interpret the outcome of the study . The results are discussed below.

Acid value of oil

Acid value is one of the important criteria used in the trans-esterification reaction to decide whether the oil is to be treated in single stage or double stage. The data in Table 1 clearly shows that there were significant differences between plains, coastal and hilly regions with respect to acid value of oil. The coastal region (Dakshina Kannada) has the highest acid value (2.66 mg KOH/g),followed by hilly region (Hassan) (1.689 mg KOH/g) and plain region (Bengaluru) showed the lowest acid value (1.32 mg KOH/g). The highest acid value might be due to the edaphic factors and environmental factors. In biochemical pathway of lipid synthesis, initially the fatty acids are formed and then the fatty acids are converted to mono, di and tri glycerides. Subsequently, environmental factors affect the synthesis process.

Iodine value of oil

The iodine value is the mass of iodine in that is consumed by 100 g of a chemical substance. The higher the iodine number, the more unsaturated fatty acid bonds are present in a fat. Iodine value is a useful parameter in studying oxidative rancidity of oils, since higher the unsaturation the greater the possibilities of the oils go rancid.

Table 2 shows that there were significant differences among the regions with respect to iodine value of pongamia oil. The results indicate that samples from hilly region have highest iodine value (81.60g I_2/100 g) followed by plains (78.03g I_2/100g). The least iodine value was recorded in coastal region (75.29 g I_2/100 g).

The iodine value followed an increasing trend with increase in distance from the sea. This could be due to the activity of de-saturated enzyme inhibited in saline water condition; hence the iodine value of

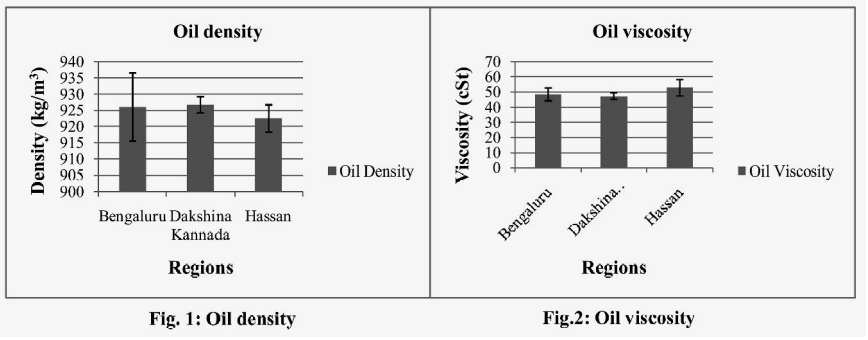

Fig. 1. Oil density.

Fig. 2. Oil viscosity.

the oil was less in the coastal area. Similar findings were also reported earlier in case of sunflower. Higher unsaturated fatty acid cause higher iodine value.

Density of oil

Oil density is the ratio of the mass of oil to its volume. The density of oil varies with API gravity of oil and the temperature conditions of the surroundings.

The oil density was not significantly different between regions, the samples collected from coastal area (Dakshina Kannada) showed the highest density (926.71 kg/m^3) followed by plain area (Bengaluru) (826.05 kg/m^3) and hilly area (Hassan) showed the lowest oil density (922.51kg/m^3) (Fig. 1). Similar findings was reported by (Bobade and Khyade 2012).

Oil viscosity

The resistance to flow of a fluid under gravity is known as kinematic viscosity. The results indicate that there were significant differences between the three climatic regions with respect to oil viscosity (Fig. 2). The samples from hilly region (Hassan) showed the highest oil viscosity (52.77 mm^2/sec) follwed by Bengaluru as plain region (48.52 mm^2/sec) and coastal region (Dakshina Kannada) had the lowest oil viscosity (47.38 mm^2/sec).

Variation between regions with respect to viscosity of oil might be due to temperature, fatty acid composition and presence of water. Fatty acid composition is responsible for viscosity and iodine value of the oil. Higher is the unsaturated fatty acids higher is the iodine value which increase the viscosity.

Pongamia deoiled cake
NPK content

Nitrogen content

The results indicate that there were significant differences among the regions with respect to nitrogen content of deoiled cake. The plains had the maximum nitrogen content (5.81%), coastal regions had less nitrogen (4.55%) and hilly regions showed moderate by high in nitrogen (5.35%).

Phosphorus content

The results shows that hilly area samples had highest phosphorus content (0.03%) followed by coastal region (0.027%) and the lowest phosphorus content was present in the samples from plain region (0.026%), but there were no significant different among regions.

Potassium content

With respect to potassium content of deoiled cake, there were no significant differences between the three regions. The results indicate that samples from hilly region had the highest amount of potassium (0.75%) followed by plains (0.72%) and the lowest potassium content was present in the samples collected from coastal region (0.58%).

The results indicated that the oil cake obtained

Table 3. Deoiled cake characters. * Significant at 5% level of significance, NS : Not significant at 5% level of significance.

Region	Statistic	Nitrogen (%)	Potassium (%)	Phosphorus (%)
	Mean	5.81	0.026	0.72
Plain (Bengaluru)	Std Dev	0.36	0.0035	0.21
	CV(%)	6.19	13.46	29.16
	Mean	4.55	0.027	0.58
Coastal (Dakshina	Std Dev	0.44	0.002	0.15
Kannada)	CV(%)	9.67	7.40	25.86
	Mean	5.35	0.03	0.75
Hilly (Hassan)	Std Dev	0.40	0.0016	0.13
	CV(%)	7.47	5.33	17.33
Significant (probability) value		<.0001	0.0739	0.1035
Significant		*	NS	NS
Mean		5.24	0.027	0.69
Standard Deviation		0.40	0.002	0.16
CV(%)		7.70	8.88	24.23

from the *Pongamia pinnata* L. seeds had of good amounts of N, P and K and were 5.24%, 0.027% and 0.69% respectively. This showed that the deoiled cake could be used as manure in agriculture as a source of plant nutrients. Similar findings was reported by Krishnamurty (1978) who reported that pongamia cake contained 3.97% N,0.94% P_2O_5 and 1.27% K_2O while Dahama (1999) reported 3.9% N,0.9% P_2O_5 and 1.2% K_2O in pongamia cake.

The deoiled cake collected from coastal region was low in nitrogen and could be due to the following reasons :

In coastal regions leaching of soil organic matter and soil nutrients is high due to heavy rainfall in monsoon season. Therefore, the organic matter and nutrients in soil will also be low. This might have resulted in low accumulation of nutrients.

In Bengaluru the trees are present in valleys and productivity, nutrient regaling, organic matter and nutrient accumulation is more, therefore then therefore the nitrogen content of the deoiled cake is high (Table 3).

Conclusion

Pongamia pinnata is one of the most appropriate non-edible oil tree species. It grows easily by seed. The major mono unsaturated fatty acid was oleic acid (46%). The oil extract exhibited good physico-chemical properties and could be used as a biodiesel feed stock for industrial application. Acid value one of the important criteria used in the trans-esterification reaction to decide whether the oil is to be treated in single stage or double stage. The coastal region showed the highest oil acid value. The iodine value followed an increasing trend with increase in distance from the sea. The fatty acid composition is responsible for viscosity and iodine value of the oil. Higher the unsaturated fatty acid, higher is the iodine value which increase the viscosity. The pongamia seed deoiled cake is a rich source of N, P and K and were 5.24%, 0.027% and 0.69% respectively.

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