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ACACIA SPECIES.: A PROBABLE FEEDSTOCK FOR BIODIESEL PRODUCTION

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Abstract

Due to competition in plantation and disturbance in ecosystem services, it is necessary to screen oil containing seed species which have capacity to grow in undomesticated and non-fertile lands. Therefore, in present studies, four acacia species (*Acacia auriculiformis, Acacia leucopholea, Acacia mangium and Acacia Cyclops*) which have ability to grow in different types of ecosystems and wide range of soils were selected. Oil content measured from the seeds of these four species suggested that *Acacia mangium, Acacia cyclops* and *Acacia auriculiformis* are high triglycerides containing seeds than that of *Acacia leucophloea*. Hence, biodiesel production was standardized from these three acacia species using transesterification process. GC-MS analysis of biodiesel samples suggested presence of essential fatty acid methyl esters which contributes in biodiesel formation. Results obtained from analysis of physicochemical parameters using ASTM standard methods suggested that biodiesel samples produced using acacia auriculiformis, acacia mangium and acacia cyclops had iodine value within the range of standard biodiesel. Even the other parameters such as kinematic viscosity, density, sulphated ash deposition, carbon residue deposition remained low in all the three samples. Hence, these oils are suitable source for biodiesel production.

Key words: Acacia cyclops, Acacia mangium, Acacia auriculiformis, Acacia leucophloea, Biodiesel. transesterification

Introduction

Recently, growing populations and climate change has increased local and global competition for land use (Messina *et al.,* 2014). There is competition between production of food plants and non-food plants in fertile lands (Ladanai and Vinterback, 2010). Also, there is an adverse impact of biofuel feedstock production on ecosystem services such as loss of native species, dominance of invasive species and loss in diversity of species (Webb and Coates, 2012). To patch up with these situations one has to go for screening of plant species which have capability to grow and adapt in less fertile waste lands with biodiesel production capacity. Acacia species can be one of them which are dispersed from tropical to temperate areas of the world (Maslin, 1989). In India, forests of acacia species are commonly found in Maharashtra, Gujarat, Andhra Pradesh, Rajesthan, Haryana and Karnataka. The genus occurs across a wide range of ecosystems such as arid, semi-arid, tropical, temperate and deserts. They are present in all terrestrial habitats such as coastal, mountains, alpine, rainforests, woodlands, grasslands, and deserts. They possess all the characteristics required to adapt harsh climatic conditions. They grow in a wide range of soil types such as limestone, laterite, granite, clay and sand. They can resist against high temperatures, heavy rains, and strong winds. After establishment acacia trees live for many years (Orchard *et al.,* 2001). Xerophytic morphological characteristics help them to cope up with harsh environmental conditions (Aref, *et al.,* 2003).

Previous studies by Khan *et al.,* 2012 reported that twelve different Acacia species of Indian origin had varied oil content from 40 to 102 g kg^{-1}. he studied fatty acid composition of nine acacia species and suggested that there was a remarkable change in the fatty acid composition in different acacia species. Palmitic (C-16 : 0) stearic (C-18 : 0) and linoleic acids (C-18 : 2) ranged from 66.0 to 192.5 g kg^{-1}, from 327.7 to 685.08 g kg^{-1} and

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from 16.7 to 275.6 g kg^{-1} respectively. These variations could be attributed to differences in ecological conditions. However, For biodiesel production from any plant source, oil content and its composition is the most crucial factor to be analysed. Acacia seeds fulfill these characteristic and can be a potential source for biodiesel production. Therefore, present studies were designed for standardization of biodiesel production from four acacia species (*A. leucopholea, A. mangium, A. cyclops and A. auriculiformis)*. The selected acacia species have capability to survive in low fertile and waste lands. Oil content in seeds of these species was measured and its potential to form biodiesel was evaluated. The physicochemical parameters and GC-MS analysis was performed to estimate the quality of biodiesel produced from each species.

Materials and methods

Seed oil extraction and transesterification

In present studies, oil from seed powder of four Acacia species (*A.leucopholia, A.auriculiphormis, A. mangium and A. cyclops*) was extracted using soxhlet extraction method. Solvent used for extraction was petroleum ether. Seed oils of all four samples were subjected to transesterification process. The process was carried out in air tight amber colored reagent bottle. It was placed on a magnetic stirrer having hot plate. Mixtures of oil and methanol were prepared in a ratio of 1:25 respectively. Then, 1% KOH as catalyst was added to each mixture. The transesterification reaction was allowed to proceed at temperature of 80°C. Time taken for each reaction to complete was recorded. After the reaction, the contents were allowed to cool at room temperature.

Physicochemical analysis of Biodiesel

The physicochemical parameters were analysed by using American Society for Testing and Materials (ASTM) and Indian standard (IS) methods in a following manner:

No.	Property	Method
1.	Kinematic viscosity at 40 °C	ASTM D445 2017
2.	Elements by ICP in MiddleDistillate Fuels	ASTM D7111-2016
	a. Calcium	
	b. Magnisium	
	c. Sodium	
	d. Potassium	
3.	Iodine Value	En 14111
4.	Sulfated Ash	ASTM D874-2013
5.	Carbon Residue- Micro Method	ASTM D4530 (MethodA)-2015
6.	Cloud Point	ASTM D2500-2016
7.	Density at 15° C	ISO 3675:2007
8.	Sulfur Content	ASTM D5453-2016
9.	Flash Point- Pensky-Martens Closed cup	ISO 2719
10.	Water Content by Coulometric KF	ISO 12937
11.	Copper strip corrosion (3h/50 ^{0}C)	IP 154/ EN ISO 2160:1998
12.	Acid Number (Inflection end-point	ASTM D664 (Method A)-2011

Characterization of methyl esters

Methyl esters of each biodiesel sample were characterized using GC-MS analysis at Column: TR5-MS, 30mm × 0.25mm, ID × 0.25 µm film, Temperature program: 290°C for 2 min, 65°C/min to 290°C and hold for 10 min, Carrier gas: helium(He) with flow rate 1 ml/min. Injection temperature: 280°C and Injection mode: split flow 10 ml/min. Mass spectral library was used to identify the compounds.

Results

In this presence studies, seed powder of four acacia species (*Acacia leucophloea, Acacia auriculiformis, Acacia mangium, Acacia cyclops*) were taken for oil extraction using soxhlet extractor. Oil content in each species was determined after extraction. Among four species, *Acacia cyclops* and *Acacia mangium* had high amount of oil content. *Acacia auriculiformis* had moderate amount of oil and *Acacia leucophloea* had very low amount of oil. It was considered from the above analysis that seeds of *Acacia mangium, Acacia Cyclops* and *Acacia auriculiformis* can be utilized for biodiesel production. Hence, transesterification process was carried out using oil of three acacia species *(Acacia mangium, Acacia Cyclops* and *Acacia auriculiformis*. The optimum mixture used in transesterification process was the oil to methanol ratio of 1:25 and 1% KOH as catalyst. The whole transesterification process was carried out in dark at 80°C temperature in air tight condition. The time period required for completion of whole process in each oil sample was approximately two and half hours. After transesterification, oil samples were allowed to cool and then physicochemical parameters were tested.

Physical and chemical properties of each biodiesel samples was analyzed using methods as described by American Society for Testing and materials (ASTM). Tests such as Kinetic viscosity, Element analysis (Calcium, magnesium, Sodium and Potassium content), iodine value, sulphated ash, carbon residues, cloud point, Density, Sulfur content, Flash point, water content, copper strip corrosion and acid number were carried out from all the three samples. Kinetic viscosity was measure at temperature of 40°C from all the three samples. It was observed from the analysis that kinematic viscosity of *Acacia auriculiformis* (0.6280 mm^2/S) was lower than that of *Acacia mangium* (0.7930 mm^2/S) and *Acacia cyclops* (0.7850 mm^2/S). *Acacia mangium* and *Acacia cyclops* were almost equivalent with each other in kinematic viscosity. From element analysis, it was observed that the calcium and magnesium content (less than 1mg) were equivalent in all the three species. The sodium content was lower in *Acacia auriculiformis* (20 mg/Kg) as compared to *Acacia mangium* (144 mg/Kg) and *Acacia cyclops* (148 mg/kg). The potassium content in *Acacia auriculiformis* (767 mg/Kg) was lower than that of *Acacia mangium* (11580 mg/ Kg) and *Acacia cyclops* (11020 mg/ Kg). Iodine value of *Acacia auriculiformis* (2.1 g/) was lower than that of *Acacia mangium* (3 g/) and *Acacia cyclops* (3.4 g/). Sulphated ash deposition in *Acacia auriculiformis* was extremely low (0.08%) as compared to *Acacia mangium* (3.40%) and *Acacia cyclops* (3.18 %). Carbon residues deposition was very low in *Acacia auriculiformis* (1.70 %) as compared to *Acacia mangium* (6.49%) and *Acacia cyclops* (9.32%). Cloud point of all three samples was equal that is -12°C. Density measured at 15°C was also equal in all the three samples [*Acacia auriculiformis* (803.8 Kg/m^3), *Acacia mangium* (820 Kg/m^3), *Acacia cyclops* (820 Kg/m^3)]. Sulfur content was high in *Acacia auriculiformis* (45mg/Kg) than that of *Acacia mangium* (less than 1mg/Kg) and *Acacia cyclops* (less than 1mg/Kg). Flash point of all the three samples was less than 40°C. Water content in all the three samples (*Acacia auriculiformis* (1.172 %), *Acacia mangium* (1.083%) and *Acacia cyclops* (1.369%) was almost equivalent. Acid number of *Acacia auriculiformis* (0.1 mg KOH/g was higher as compared to *Acacia mangium* (> 0.01 mg KOH/ g and *Acacia*

Fig. 1: Biodiesel from *A. cyclops*, *A. mangium* and *A. auriculiformis*

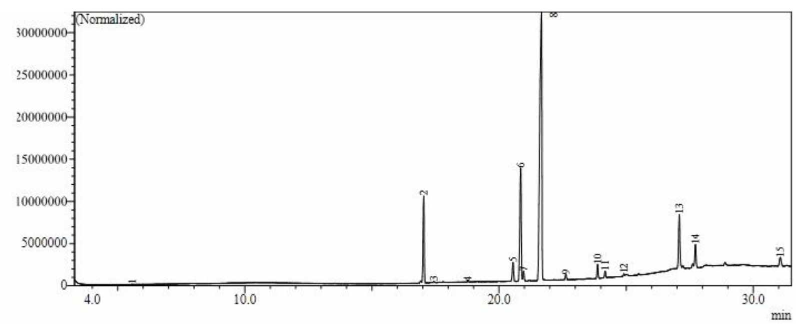

Fig. 2: GC chromatogram of *Acacia auriculiformis* biodiesel

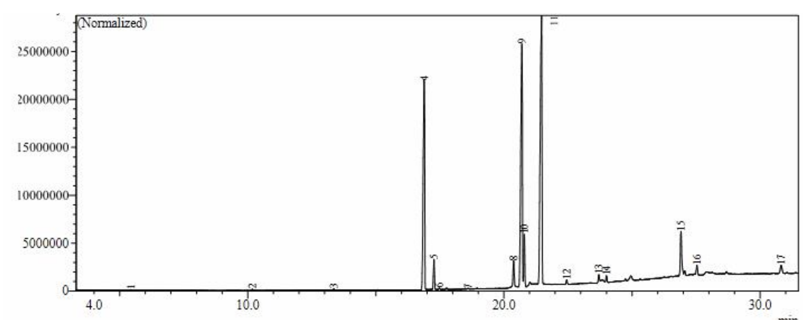

Fig. 3: GC chromatogram of *Acacia mangium* biodiesel

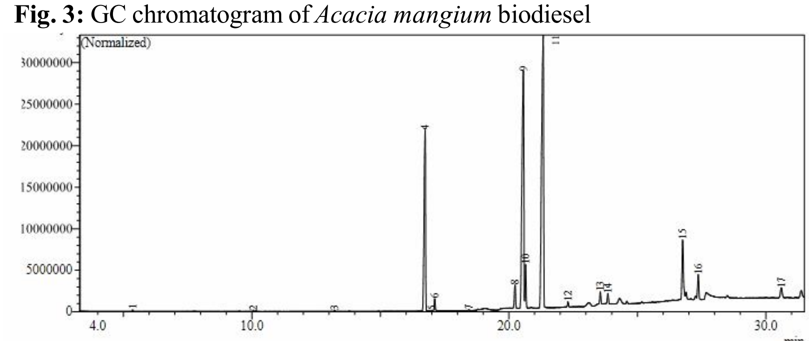

Fig. 4: GC chromatogram of *Acacia cyclops* biodiesel

Table 1: Physicochemical parameters of biodiesel samples

No.	Property	Method	Acacia Mangium	Acacia auriculiformis	Acacia cyclops	Standard Biodiesel
1.	Kinematic viscosity at 40 °C	ASTM D445 2017	0.7930 mm^2/s	0.6280 mm^2/s	0.7850 mm^2/s	As per report
2.	Elements analysis by ICP in Middle Distillate Fuels					
	a. Calcium	ASTM D7111-2016	>1 mg/kg	>1 mg/kg	>1 mg/kg	As per report
	b. Magnesium	ASTM D7111-2016	>1 mg/kg	>1 mg/kg	>1 mg/kg	As per report
	c. Sodium	ASTM D7111-2016	144 mg/kg	20 mg/kg	148 mg/kg	As per report
	d. Potassium	ASTM D7111-2016	11580 mg/kg	767 mg/kg	11020 mg/kg	As per report
3.	Iodine Value	En 14111	3.0 g 1/100g	2.1 g 1/100g	3.4 g I/100g	120 g I/100 g
4.	Sulfated Ash	ASTM D874-2013	3.40 % (m/m)	0.08 % (m/m)	3.18 % (m/m)	0.02 % (m/m)
5.	Carbon Residue-Micro Method	ASTM D4530 (Method A)-2015	6.49 % (m/m)	1.70 % (m/m)	9.32 % (m/m)	0.05 % (m/m)
6.	Cloud Point	ASTM D2500-2016	-12 °C	-12 °C	-12 °C	report °C
7.	Density at 15° C	ISO 3675:2007	820.0 kg/m^3	808.8 kg/m^3	820.1 kg/m^3	860-900 Kg/m^3
8.	Sulfur Content	ASTM D5453-2016	>1 mg/kg	45 mg/kg	>1 mg/kg	0.05 mg/kg
9.	Flash Point- Pensky-Martens Closed cup	ISO 2719	< 40 °C	< 40 °C	< 40 °C	120°C
10.	Water Content by Coulometric KF	ISO 12937	1.083 % (m/m)	1.172 % (m/m)	1.369 % (m/m)	0.05% (m/m)
11.	Copper strip corrosion (3h/50 ^{0}C)	IP 154/ EN ISO 2160:1998	1a Rating	1a Rating	1a Rating	No. 1 Rating
12.	Acid Number (Inflection end-point)	ASTM D664 (Method A)-2011	>0.01 mg KOH/g	0.1 mg KOH/g	>0.01 mg KOH/g	0.80 mg KOH/g

Table 2: Methyl esters identified from *Acacia auriculiformis*

No.	Name of compound	Retention Time	Area %
1	Hexadecanoic acid, methyl ester	17.04	9.40
2	9-Hexadecanoic acid, methyl ester,(Z)-	17.44	0.14
3	Octadecanoic acid, methyl ester	20.55	2.42
4	9-Octadecenoic acid, methyl ester,(E)-	20.85	15.71
5	9-Octadecenoic acid(Z), methyl ester	20.96	1.20
6	9,12-Octadecadienoic acid, (Z,Z)-,methyl ester	21.96	56.02
7	9,12,15-Octadecadienoic acid methyl ester	22.63	0.64
8	Eicosanoic acid, methyl ester	23.87	1.54
9	11,13-Eicosanoic acid, methyl ester	24.91	0.21
10	Docosanoic acid, methyl ester	27.09	7.36
11	Hexadecadienoic acid, methyl ester	27.72	2.99
12	Tetracosanoic acid, methyl ester	31.06	1.55

cyclops (>0.01 g KOH/g). Copper corrosion was negligible in all biodiesel samples. Further, Biodiesel sample of *Acacia auriculiformis, Acacia mangium* and *Acacia cyclops* were subjected to GC-MS analysis to confirm the formation of methylesters and to characterize the type of methyl esters formed after transesterification process. GC-MS analysis confirmed formation of methyl esters in all biodiesel samples (Table 2, 3, 4)

Discussion

Biodiesel production from these acacia species was commenced by considering certain criteria faced during previous years for large scale biodiesel production. These criteria involves food used for human consumption should not be used as feed stock for biodiesel production (Tenenbaum 2008). The land used for food crops production should not be used for growth of feed stock for biodiesel production as it creates food crisis (Andrei 2016). The feed stock used for biodiesel production should have ability to grow and adapt in non-fertile waste lands (Kumar and Sharma 2011). It should have capacity to grow in wide range of ecosystems and should not disturb the ecosystem services. If seeds are the feed stock for biodiesel production, then they should be rich in oil content. The seeds production should be high in the plant species.

Therefore, in present studies four acacia species (*A. leucopholia, A. auriculiphormis, A. mangium*, and *A. cyclops*) were selected

Table 3: Methyl esters identified from *Acacia mangium*

No.	Name of compound	Retention Time	Area %
1	Hexadecenoic acid, methyl ester	16.89	21.88
2	7-Hexadecenoic acid, methyl ester	17.27	2.26
3	Octadecanoic acid, methyl ester	20.38	2.35
4	9-Octadecenoic acid, methyl ester,(E)	20.70	28.24
5	9-Octadecenoic acid,(Z)-,methyl ester	20.79	3.72
6	9,12-Octadecadienoic acid(Z,Z)-, methyl ester	21.46	32.99
7	Eicosanoic acid, methyl ester	23.70	0.79
8	Docosanoic acid,methyl ester	26.91	4.55
9	Hexadecadienoic acid, methyl ester	27.53	0.89
10	Tetracosanoic acid, methyl ester	30.82	1.03

Table 4: Methyl esters identified from *Acacia cyclops*

No.	Name of compound	Retention Time	Area %
1	Hexadecenoic acid, methyl ester	16.74	18.09
2	9-Hexadecenoic acid, methyl ester,(Z)-	17.11	0.84
3	Octadecanoic acid, methyl ester	20.24	1.90
4	9-Octadecenoic acid, methyl ester,(E)	20.56	29.34
5	9-Octadecenoic acid,(Z)-,methyl ester	20.65	2.85
6	9,12-Octadecadienoic acid(Z,Z)-, methyl ester	21.33	35.56
7	Eicosanoic acid,methyl ester	23.55	0.94
8	11-Eicosanoic acid, methyl ester	23.85	0.80
9	Docosanoic acid,methyl ester	26.76	5.72
10	Hexadecadienoic acid, methyl ester	27.37	2.02

because they have capability to develop in low fertile and waste lands. They have ability to survive in arid, semi-arid, drought and dessert conditions. They can grow well in arid zone soils with pH range of 3 to 9.5. Also, Oil content remains high and water content remains low in seeds of acacia species. Among four species, Oil content remained high in *A.auriculiphormis, A.mangium* and *A. cyclops* therefore, oil from these species was utilized further for standardization of biodiesel production. Previous studies by Adhikesavan *et al.,* 2015 on Acacia nilotica suggested that acacia seeds can be the potential source for biodiesel production, However, pretreatments, proper purification and transesterification is required. Research studies on fatty acid profile of Acacia tumida, Acacia torulosa and Acacia elacantha seeds by Otemuyiwa *et al.,* 2016 suggested that these oils have high iodine value which is not be suitable for the production of biodiesel. However, results obtained from present studies suggested that biodiesel samples produced using *acacia auriculiformis, acacia mangium* and *acacia cyclops* had iodine value within the range of standard biodiesel (Table 1). Even the other parameters such as kinematic viscosity, density, sodium content, sulphated ash deposition, carbon residue deposition remained low in all the three samples. Hence, these oils are suitable for standard biodiesel production.

Conclusion

From the present research analysis, it was concluded that among the four species used for analysis, it was observed that seeds of *Acacia mangium, Acacia cyclops* and *Acacia auriculiformis* are high oil containing seeds than that of Acacia leucopholea. Physicochemical and GC-MS analysis from seeds of *Acacia auriculiformis, Acacia mangium* and *Acacia cyclops* suggested that they are reliable and potent source for biodiesel production as per ASTM standard.

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Conflict of interest

Authors declare that there is no conflict of interest regarding publication of present research work in journal.

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