

Bio-oil separation from potential antioxidant source

Cassia Auriculata

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Abstract

Extraction of oil from crushed *Cassia Auriculata* seeds was done by Solvent extraction using an improved soxhlet apparatus set up. Polar solvent mixtures (Methanol, Acetone and Isopropanol) and non-polar solvent mixtures (Chloroform, hexane and toluene) were used for oil extraction. The bio-oil was characterized using Fourier Transform Infrared Spectroscopy (FTIR), Gas Chromatography / Mass Spectrometry (GC/MS) and the results were discussed. The extraction parameters like choice of solvents and extraction time were examined to obtain the optimum yield of oil. Basic fuel properties such as saponification value, iodine number, specific gravity, carbon residue content, kinematic viscosity, flash point, fire point, calorific value were determined to examine the bio oil quality. The maximum oil yield of 27.25% was extracted with the Isopropanol at 82.6° C with an optimum extraction time of 2.5 hrs. Due to high energy content of *Cassia Auriculata* oil which can be used as a calorific enhancer of other bio oils and promising to partially blend with diesel as an alternative fuel.

Keywords: Bio-oil, *Cassia Auriculata*, Solvent extraction.

1. Introduction

We are in need of energy as a major source for our existence. As need of energy increases globally, it results in large consumption of oil and leads to the depletion of available resources. The depletion of natural resources becoming a major concern for established nations. When there is an increase in the demand of fossil fuels, it leads to environmental issues like huge emission of CO₂, oxides of Nitrogen and it results in global warming. It was estimated that the world fuel energy demand will rise up to 53% by 2030 (Kumar, Das, Giri,

Rene, & Verma, 2019). The petro-based fuels are exhaustible, we can use them for few decades only and they are not renewable. If the present consumption rate of fossil fuels continues, then the oil and gas sources will be abased in 40 and 60 years respectively (Iha et al., 2018). The established nations heavily depend on imports of petroleum crude and it will get paralyzed and because of this there will be price variability. Thus we have to search for some alternate fuels to meet out the energy requirement. The exploration of new alternative energy must satisfy the conditions of technical feasibility, healthy environment and abundant availability (Rakopoulos, Antonopoulos, Rakopoulos, Hountalas, & Giakoumis, 2006). Numerous replacements including wind energy, hydro power, solar energy, nuclear power and biofuel are kept under research.

Diesel engine was invented by Dr. Rudolf Diesel and run with 100% peanut oil at the World Exhibition in Paris in 1900. In 1912, Diesel said, "The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in course of time as important as petroleum and the coal tar products of the present time."

After the death of Dr. Diesel's in 1913, his engine was modified to run on the petroleum based fuel as named "diesel". Nevertheless, his idea of using agriculture as the source of fuel provided the foundation for a society fuelled with clean, renewable, locally grown fuel. Globally, countries are developing technologies to use biofuel as a renewable source, to reduce global warming and pollution (Oliveira et al., 2019). Research on biodiesel based on non-edible and edible oils is already advanced in major European countries, Japan, Malaysia, Australia etc., where regular production is at full pace (Islam, Mourshed, Masud, Sozal, & Sabur, 2019). Major automobile companies have also approved the use of 10-20% bio-diesel mixture in their automobiles (Kumar et al., 2019).

Hence it's a necessity of time to utilizing bio-oils as fuel in diesel engines. It was reported in many literature that biofuels are better than diesel fuel in terms of sulphur content, flash point, aromatic content, having lower emission of particulates like HC, CO and CO₂ (Arun, Gopinath, & Sharma, 2012; Dutta, Sarkar, & Mukherjee, 2014; Gumaling et al., 2018; John Abraham, Chindhanaiselvam, Subramanian, & Mahendradas, 2017; Puhan & Govindan, 2010). As per the fuel consumption rate of India, the nation consumes up to 40 million tons of biodiesel and ranked fifth in the world among the nations consuming fossil fuels (Govindhan, Tamilarasan, & Dharmendira Kumar, 2017; John Abraham et al., 2017). So the Indian government recently proposed a 'National Biodiesel mission' to find the ways to increase the fuel source and to find a cheap, renewable fuel. Hence a limelight is on bio oil all over the world and it states the scope of bio oil in future. One such kind of bio oil source is *Cassia auriculata* (Avarampoo).

Avaram senna has seeds containing enormous amount of bio oil in it, which also non-edible in nature. It belongs to the family of Fabaceae. It is commonly known by its local names matura tea tree, ranawara or avaram (Tamil version avarai or the English version avaram senna) (Meena, Baruah, & Parveen, 2019). It occurs in the dry regions of India and Sri Lanka. It is common along the sea coast and the dry zone in Sri Lanka. It was reported that the bio oil from *Cassia Auriculata* is being non-hazardous, decomposable and basically free of sulphur and oncogenic ring elements (Rao, Kumar, Dhandapani, Krishna, & Hayashi, 2000).

The present research work deals with extracting oil from *Cassia Auriculata* seed kernel to utilize it as a biofuel. Thus the basic fuel properties were examined, reported and discussed in a meticulous manner. The extraction of bio oil was done with the solvent extraction technique using six different solvents including 3 polar and 3 non-polar solvents to find out the best out of the six solvents. A molecule is said to be polar if it possess nonzero dipole moment (Methanol, Acetone and Isopropanol) and similarly, molecules which possess zero in dipole moment are said to be non-polar (Chloroform, hexane and toluene). To the best of our knowledge, this is the first time, *Cassia Auriculata* Seed bio oil optimization was tested with six different solvents. The solvent extraction was done with the help of Soxhlet apparatus set up.

2. Materials and methods

2.1 Raw *Cassia Auriculata* seeds

Cassia Auriculata seeds used in this research were collected in the krishnagiri (Dt) and Periyar University, Omalur, Salem (Dt). The seeds were selected by naked eye without the insect infection and separated the flora adjoined to them. Initially, the flora removed seeds were dried and preserved at ambient temperature. Well dried seeds were grinded and meshed to obtain grain sizes of less than 2.5 mm.

2.2 Extraction solvents

In this research work, best solvent were chosen from the six different solvents based on percentage of bio oil yield. Three polar solvents such as methanol, acetone and isopropanol and three non-polar solvent such as chloroform, hexane and toluene were purchased from MERCK, Mumbai. The properties of the solvents are displayed in the (Table 1.)

Table 1 Properties of six different solvents

Solvent	Density (kg/l)	Purity (%)	Cost per litre/Kg (Rs)	Boiling Point (°C)
Methane	0.793	99.8	205	64.7
Acetone	0.790	99.8	400	56
Chloroform	1.498	99.7	560	61.2
Isopropanol	0.785	99.9	215	82.6
Hexane	0.655	99.9	1243	68
Toluene	0.867	99.7	283	110.6

2.3 Extraction process

The extraction was carried out in round bottom flask Soxhlet extractor apparatus of 1 litre capacity. The extraction solvent was placed on the round bottom flask and Soxhlet extractor was placed on top of round bottom flask. Bulb condenser was fixed above the Soxhlet extractor to condense the vapour using cooling water.

The solvent was heated to its boiling point and vapor rises and passes through the connecting tube. The vapour condensed at bulb condenser and condensed solvent then fills up the thimble chamber which filled with crushed seeds. When the Soxhlet upper chamber was full, extracted solvent was passed through the return tube automatically by siphoning action and collected in lower reservoir (round bottomed flask). After series of several cycles with predefined time period, bio oil was extracted completely from the crushed seed. The bulb condenser confirmed that there was no loss of any solvent vapour from the system. The schematic representation of the Soxhlet apparatus is shown in Figure.1.

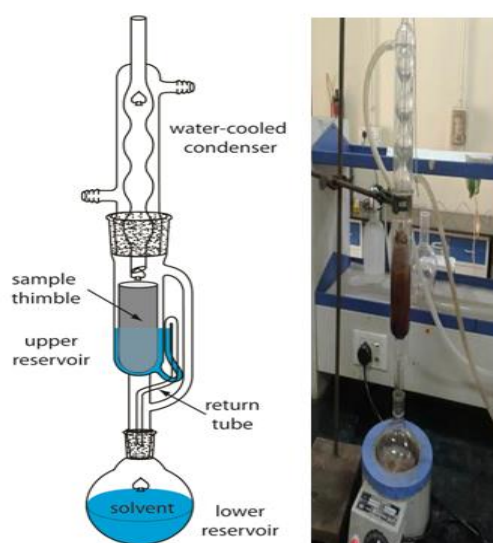


Figure 1 Schematic diagram of soxhlet extractor

The crushed seeds were arranged systematically as a tubular filled bed of cotton bag and placed inside the thimble chamber. As solvent reaches the thimble area every time, it extracted the oil and leached the seed effectively without carry any solid extract of the crushed seeds. The leached seed in tubular cloth was removed from thimble chamber and then dried and weighted at the end of the test.

2.4 Choice of solvents

The nature of the solvent characteristic and the solubility parameter of oil in different solvents define the efficiency of solvent extraction process (Demirbas, 2005). The extraction was carried out at various time durations of 1.0, 1.5, 2.5 and 3.5 hours (h) with different solvents of methanol, acetone, chloroform, isopropanol, hexane and toluene at their respective boiling point mentioned in Table.1 with a constant cursed seed weight of 75 g and constant 400 ML volume of solvent in the Soxhlet lower reservoir. Process of oil extraction starts, when the selected solvent reaches their respective boiling points and continued until a clean liquid was obtained in the thimble area. Then, bio-oil from the resultant solvent-oil mixture was recovered by simple batch distillation method.

The percentage of oil yield was calculated from the following equation (Dutta et al., 2014).

$$\% \text{ Oil yield} = (W2/W1) * 100$$

Where, W1 is the initial amount of seed taken (g); W2 was the amount of oil extracted from seed (g).

2.5 Optimization and characterization of Bio-oil

Fourier transform infrared spectroscopy (FTIR) was used to analyze the oil samples for characteristic functional groups. FTIR results were recorded and plotted as transmittance versus wave number. The functional groups of the oil samples were identified using standard IR spectra of hydrocarbons . Gas chromatography / mass spectrometry (GC/MS) analysis was used to determine the fatty acids present in the oil sample. Specific gravity was measured by ASTM D4052-91 standard method using standard pycnometer. Iodine number was determined by the AOAC CD1-25 standard method. Saponification value was measured under the AOAC CD3-25 standard method. Calorific value was determined using ASTM D3286. The fire point was calculated using ASTM D93. The flash point was determined using ASTM D93. The kinematic viscosity was measured using a Saybolt viscometer under ASTM D445 standard method. The amount of carbon residue present in the oil was calculated by evaporate the oil using the Conradson Carbon Residue test (CCR) as per ASTM D 189. The pour point of the bio-oil was determined using ASTM D 97.

3. Results and Discussion

3.1 Effect of different solvents on oil yield

Oil yield percentage of various solvents were listed in Table 2 and shown in Figure 2. When using isopropanol as solvent, the oil yield percentage of *Cassia Auriculata* was calculated as 27.25%. With Hexane as solvent, oil yield percentage was 26.75%. Yield with acetone, chloroform, toluene and methanol was 25.01%, 24.3%, 23.65%, and 20.35% respectively. Hence, the optimum yield was found to be 27.25% at 82.6°C with isopropanol as a solvent.

Table 2. Cassia Auriculata oil yield with different solvents

Time	Oil yield (%)					
	Polar Solvents			Non-polar Solvents		
hrs	Methanol	Isopropanol	Acetone	Chloroform	Hexane	Toluene
1	12.85	18.95	15.92	15.1	10.45	6.88
1.5	19.75	26.4	23.25	22.45	19.37	14.22
2.5	20.35	27.25	25.01	24.3	26.75	23.65
3.5	23.01	28.35	27.35	26.45	27.9	25.3

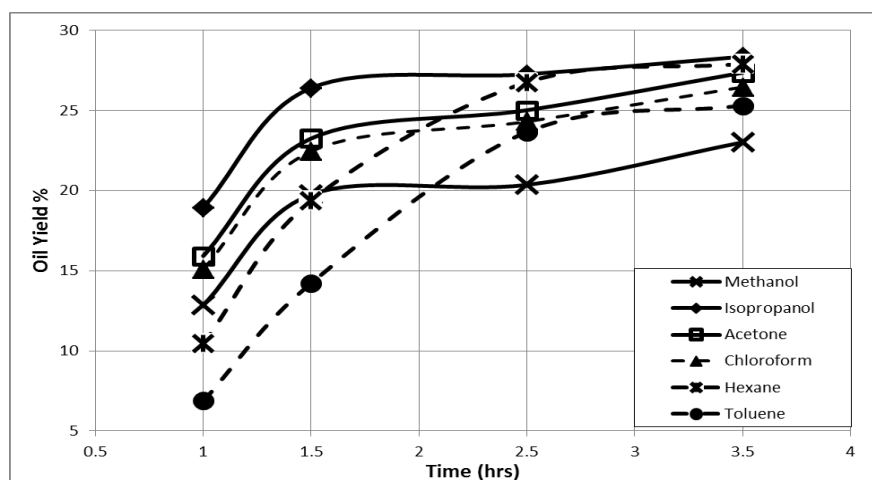


Figure 2 Cassia Auriculata oil yield with different solvents at various time interval

3.2 Effect of extraction time on oil yield

Oil yield percentage of *Cassia Auriculata* were recorded at various time intervals in Figure 2 and listed in Table.2. As shown in figure 2, after 2.5 hours of extraction process, all the solvent curves shows the saturation trends except solvent hexane. At 2.5 hrs, maximum percentage of oil yield was obtained compared with the extraction time of 1 and 1.5 hrs. When extraction time was increased to 3.5hrs, oil yield percentage attains a saturation point for all the solvents as shown in the figure.2. Notably rate of percentage of oil yield is less for 3.5hr compared to 2.5hr. Hence, 2.5 h was marked as the optimum extraction time for *Cassia*

Auriculata oil yield. In addition, figure 2 shows that in all time intervals, oil yield percentage of the solvent isopropanol was attained maximum, which justify choosing it as a best solvent for extraction of Cassia Auriculata seed.

3.3 FTIR analysis

Figure 3 shows FTIR spectra of extracted Avaram Seed oil (Cassia Auriculata) and its functional groups presented were given in Table 3.

Table 3. Functional groups present in Cassia Auriculata oil based on FTIR Analysis

S.no	Frequency (cm ⁻¹)	Group	Class of compounds
1	2922.36	Unsaturated -CH stretching	Alkanes
2	2854.64	Asymmetric stretching of CH ₃	Methyl group
3	1643.15	Carbonyl stretching C=O	Ketones, carboxylic acids, Aldehydes, Esters
4	1457.04	C=C stretching	Alkenes
5	1369.32	Bending vibration of CH ₃ and CH ₂	Aliphatic alkanes
6	720.60	CH=CH bending plane	Alkenes

3.4 GC/MS Analysis

The results of GC/MS analysis were illustrated in Figure 4 and Overall 31 free fatty acids were listed in Table.4. Among the list, proposition of Oleic acid was about 52.3% and Linoleic acid was about 17% of the total acid composition. Both Oleic and Linoleic fatty acids were unsaturated, where as Oleic acid is mono-unsaturated, has one double bond. So, extracted Cassia Auriculata oil might have lower oxidative and lower thermal stability (Govindhan, Karthikeyan, & Dharmendra Kumar, 2017; John Abraham et al., 2017).

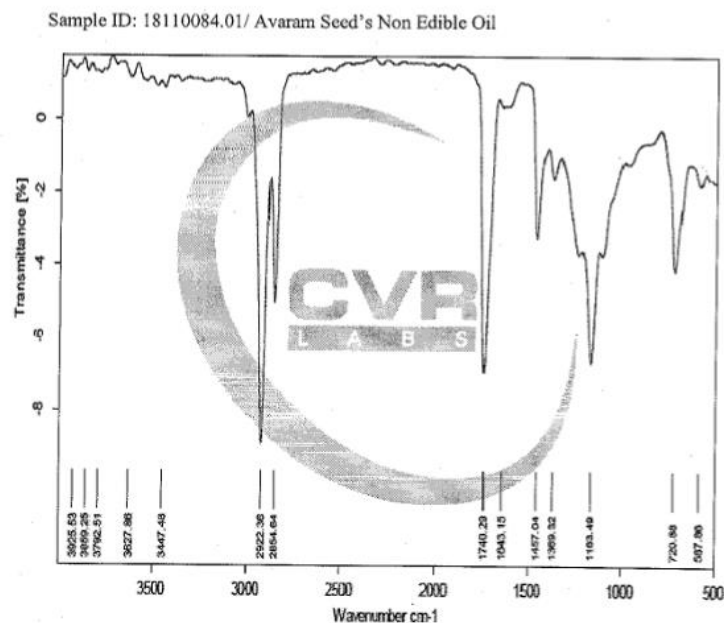


Figure 3 FTIR analysis of Cassia Auriculata oil

3.5 Optimization of reaction Parameters for Cassia Auriculata:

Cassia Auriculata bio-oil was tested for standard fuel and physicochemical properties such as fire point, flash point, acid value, iodine value, saponification value, calorific values, pour point, percentage of carbon residue, specific gravity and kinematic viscosity. All tested results were listed in Table 5.

3.6 Comparative study of Avaram Seed (Cassia Auriculata) oil with other Bio-oil:

Bio Oil Performance of Cassia Auriculata oil was comparatively studied with other bio oils on specific gravity and Calorific value as shown in Table 6.

The specific gravity of Cassia Auriculata seed oil was equal to 0.945 which is relatively high compare to other bio oils listed in Table.6. The breakup of fuels in the ignition cylinders depends upon specific gravity of the fuel.

Table 4. GC/MS analysis on fatty acid composition of Cassia Auriculata oil

Peak #	RetTime [min]	Area %	Name
1	5.725	1.42155	Butyric acid
2	8.540	1.82313	Caproic acid
3	11.115	2.07206	Caprylic acid
4	13.609	2.21957	Capric acid
5	14.981	0.00000	Undecanoic acid
6	16.467	0.00581	Lauric acid
7	17.431	0.00000	Tridecanoic acid
8	17.837	0.00000	Tridecanoic acid
9	19.067	0.03160	Myristic acid
10	19.136	0.03163	Myristic acid
11	19.370	0.03167	Myristic acid
12	19.751	0.03168	Myristic acid
13	20.487	0.00784	Myristoleic acid
14	21.364	0.01073	Penta decanoic acid
15	22.373	0.00000	Cis -10- pentadecanoic acid
16	23.447	10.28054	Palmitic acid
17	23.569	0.03594	Palmitoleic acid
18	24.087	0.08911	Hepta decanoic acid
19	25.329	0.14080	Cis- 10- heptadecanoic acid
20	26.427	7.19665	Stearic acid
21	26.675	0.00000	Elaidic acid
22	27.078	52.38846	Oleic acid
23	27.413	0.00000	Linolelaidic acid
24	28.008	17.00413	Linoleic acid
25	28.727	0.01623	Gamma- linolenic acid
26	29.144	3.73534	Alpha- linolenic acid
27	29.382	1.61758	Arachidic acid
28	29.944	1.15345	Heneicosanoic acid

29	30.804	0.03681	Eicosadienoic acid
30	30.922	0.02831	Eicosatrienoic acid
31	32.100	0.00000	Erucic acid

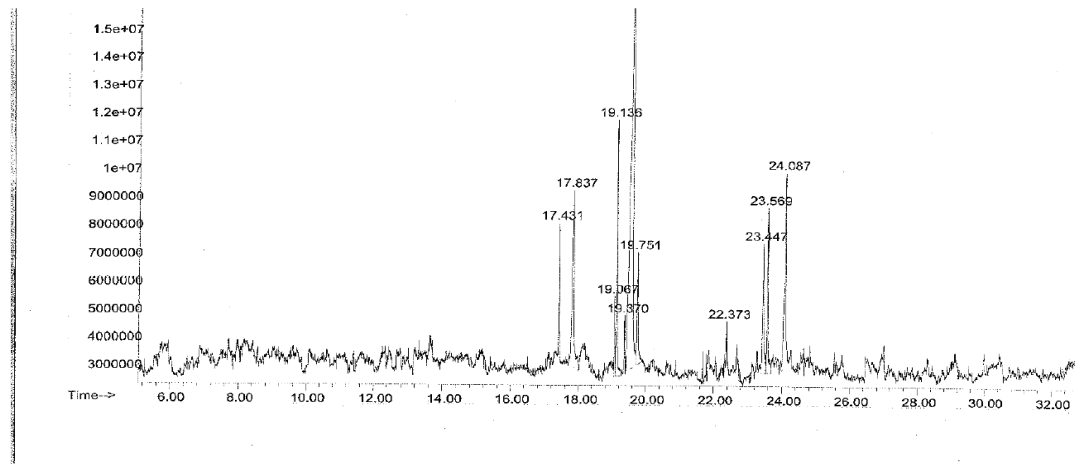


Figure 4 GC/MS analysis of Cassia Auriculata oil

When the specific gravity increases, the compression ratio gets increased and it results in the rise in fuel injection level (Canakci & Van Gerpen, 2001). Specific gravity has an impact on both the injection spray patterns and timing (Puhan & Govindan, 2010). Higher density fuels will emit more amount of particulate pollutant matters and oxides of nitrogen while comparing to lower density fuels (Rakopoulos et al., 2006).

Table 5: Parameters of fuel properties.

Constituents	Cassia Auriculata Seed oil	Testing Standard
Fire point (°C)	213	ASTM D-93
Flash Point (°C)	207	ASTM D-93
Acid Value (mg KOH/g)	10 ± 0.2	AOCS method
Iodine value (g of I ₂ /100 g of oil)	85.8 ± 1.2	ASTM - D5554-15
saponification value (mg KOH/g of oil)	168 ± 2.1	ASTM D5558
Calorific values (kcal/kg)	8745	ASTM D-4809 standard
Pour point (°C)	-4°C	ASTM D-97
Carbon residue %	0.84	ASTM D-189
Specific gravity	0.945	ASTM D1298
Kinematic viscosity (cSt at 40°C)	24.5	ASTM D-445

Table: 6 –Specific Gravity and Calorific values of various bio-oils [24]

List of Bio oils	Specific gravity @15 °C	Calorific value (kcal/kg)
Cottonseed oil	0.885	6570
Soybean oil	0.850	6250
Sunflower oil	0.940	5667
Corn oil	0.870	5875
Palm oil	0.938	5875
Sunn Hemp oil	0.989	8151
Cassia Auriculata seed oil	0.945	8745

The calorific value of Cassia Auriculata oil is 25% higher than most bio oil listed in Table.6. The Calorific value of Cassia Auriculata seed oil was found to be 8745 kcal/kg, which is higher than Sunna Hump bio oil, 8151 kcal/kg (Dutta et al., 2014), which is reported as the highest calorific value biooil. Calorific value of diesel is 10604 kcal/kg which is closer Cassia Auriculata seed oil, can be mix partially with diesel as an alternative fuel. Due to higher specific gravity, Cassia Auriculata might not the best candidate in the list of solo bio oil, but due to higher calorific value, which can be used as a calorific enhancer.

5.4 Conclusion

Isopropanol is the best among all the solvents as the bio-oil yield was found to be 27.25%. The pour point of the Cassia Auriculata seed oil was equal to -4°C, which was very low, can be very favorable in cold weather. The specific gravity of Cassia Auriculata seed oil is 0.945 which is relatively high compare to other bio oils, which makes it less favorable for choosing it as direct replacement to diesel. Significant finding of this research is the energy content (calorific value) of the Bio-oil and it found to be 8745MJ/kg. When compared with other bio oils, which is 25% higher and it can be used as a calorific enhancer and blend partner for green alternative fuels.

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