

Characterization of bio-Oil produced by Microwave Pyrolysis of Karanja Seed.



A. Mathiarasu, M. Pugazhivadivu

Abstract: Pyrolysis is one technique that produces three products in a short span of time in which both conventional and non-conventional method of heating (microwave irradiation) can be done. Karanja seed powder is taken as the feedstock in this microwave pyrolysis experiment. Proximate and Elemental analysis of karanja seed powder resulting volatile content of about 84.89% and moisture content of 10.11% whereas the Carbon of 52.08%, Hydrogen of 8.26%, Sulphur of 0.21%, Nitrogen of 4.02% and oxygen of 35.04%. Microwave pyrolysis for karanja seed was conducted for two power inputs of 700W and 800W in which bio-oil yield is high of 47% at 700W and non-condensable gases of 39% at 800W. The FT-IR results resembles the presence of aliphatic compounds. The TGA analysis was also taken for the produced bio-oil. The rheological study was made to determine the dynamic viscosity of the produced bio-oil at 50 rpm in room temperature which is averaged to 52 cP. The flash point of 90°C and fire point of 94°C was also determined for the produced bio-oil.

Keywords: Dynamic viscosity, FT-IR, Karanja seed, Microwave pyrolysis.

I. INTRODUCTION

Majority of our energy and chemical source are mostly based on fossil materials. Our dependence on fossil energy is at its extinct condition right now. Reducing usage of such energy resources reflects in reduction in greenhouse gas emissions. On substituting fossil resources, biomass which is a renewable energy resources can be used in production of bio fuels and other chemical that are said to be an efficient energy source. Biomass satisfies about 14% of world's total energy needs and the conversion of the biomass to fuel and petrochemicals is one of the effective alternate to replace other sources like the fossil fuel, oil and coal with less damage to environment[1].

Pyrolysis is one among some of the techniques that is used in energy recovering process. In absence of oxygen, thermal decomposition of biomass resulting in production of liquid product, gaseous products and char residue is called pyrolysis[2], [3]. Various works done by thermal pyrolysis using some biomass like Rice Straw[4], Barley biomass [5], corn cobs and Stover[6]etc.

Microwave pyrolysis is a technique in heat is generated through the interaction of molecules or atoms using a microwave irradiation powered by electricity using a magnetron [7]. By interaction of molecules energy transfer occurs within the material thus pyrolysis done using microwave irradiation obtains more uniform distribution of heat on comparing to conventionally heated pyrolysis. This uniform distribution of heat enables the feedstock to get completely decomposed resulting in higher yield of end products[8].

Karanja seeds originates as Indian species which possess vast application for all branches of the tree, the seeds are 10 to 20 mm long, fig oblong and light brown color. It is a tree adaptable to various climatic conditions and soil type. This has good application as biofuel[9], [10]. Usage of karanja seed for production of an effective source of bio-fuel production interests' researchers to work on it. Nayan et al[9]analyzed the effect of pyrolysis temperature on the slow pyrolysis of karanja seed and reported that the yield of bio-oil was maximum (33% of the weight of karanja seed) at 550°C. Karanja seed is also used in production of biodiesel[11]. On using catalyst, thermal pyrolysis of karanja seed results in higher production of liquid fraction [12].

II. MATERIALS

The karanja seeds were procured in Salem, India. The seeds were extracted manually from the shell, milled and sieved to the size of 2 mm. Fig 1 shows the karanja seed with shell and the seed powder.



Figure 1: a) Karanja seed, b) seed powder

The proximate analysis is determined using a muffle furnace. The moisture content, volatile matter, fixed carbon and ash contents of the karanja seed. Elementar CHNS analyser is used for elemental analysis i.e. to determine Carbon, Hydrogen, Nitrogen, Sulphur and Oxygen contents. The high heating value of the karanja seed powder is calculated using [13],

$$\text{HHV} = 0.3491(\text{Carbon}\%) + 1.1783(\text{Hydrogen}\%) + 0.1005(\text{Sulphur}\%) + 0.1034(\text{Oxygen}\%) + 0.0151(\text{Nitrogen}\%) + 0.021(\text{Ash content}\%)$$

Revised Manuscript Received on December 30, 2019.

* Correspondence Author

A. Mathiarasu*, Department of Mechanical Engineering, Pondicherry Engineering College, Pondicherry, India. Email: mathianbu77@gmail.com

Dr. M. Pugazhivadivu, Department of Mechanical Engineering, Pondicherry Engineering College, Pondicherry, India. Email: pv_pec@pec.edu

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>)

The hydrogen carbon ratio and nitrogen carbon ratio of the karanja seed powder is calculated by Eq.1 & 2 respectively as follows[14].

$$H/C \text{ ratio} = \left\{ \frac{\frac{Wt.\% \text{ of Hydrogen}}{\text{Atomic wt. of Hydrogen}}}{\frac{Wt.\% \text{ of Carbon}}{\text{Atomic wt. of Carbon}}} \right\} \text{----- (1)}$$

$$N/C \text{ ratio} = \left\{ \frac{\frac{Wt.\% \text{ of Nitrogen}}{\text{Atomic wt. of Nitrogen}}}{\frac{Wt.\% \text{ of Carbon}}{\text{Atomic wt. of Carbon}}} \right\} \text{----- (2)}$$

III. METHODODOLOGY

A. Microwave pyrolysis experimental setup

A domestic microwave oven is used for microwave pyrolysis of karanja seed which maximum input power of 800W. A triple- neck round bottom Quartz flask with a volume capacity of 250 ml is used to hold the feedstock because of its microwave resistivity nature. Left neck of the round bottom flask with N₂ cylinder. Middle neck of the flask is connected to two allihn condensers. The ends of the condensers are connected to two conical flask of 100 ml capacity for collection of condensed liquid products. A K-type thermocouple with temperature with indicator is connected to the remaining neck of the flask. Essential holes are made using drilling process on the top surface of the

oven for connecting the condenser, k-thermocouple and nitrogen inlet as shown in figure 2 [15].

The quartz round bottom flask is filled with 100 gm of karanja seed powder and placed inside the microwave cavity. For about 7 minutes N₂ gas is purged to the quartz flask before the pyrolysis experiment gets started to make it zero-oxygen zone. The nitrogen flow is nonstop until microwave pyrolysis process gets completed. At a constant rate water is circulated as coolant to the two allihn condensers which are connected to the middle neck of the flask where the volatiles passes through. The reaction temperature is monitored using the k-type thermocouple and the indicator. The produced pyrolytic bio-oil by microwave pyrolysis is collected and weighed for every experiment conducted. Once the quartz flask comes to room temperature the bio- char is calculated by a weighing machine. The uncondensed gas is left into atmosphere. The percentage distribution for bio-oil product yields, char product yields and gaseous product yields are calculated as shown in Eqn (1), (2) and (3) respectively.

$$\% \text{ Liquid yield} = \left(\frac{\text{Liquid yield}}{\text{weight of karanja seed powder}} \right) \times 100 \text{ ----- (1)}$$

$$\% \text{ Char residue} = \left(\frac{\text{Char residue}}{\text{weight of karanja seed powder}} \right) \times 100 \text{ ----- (2)}$$

$$\% \text{ Gas yield} = 100 - (\% \text{ Liquid yield} + \% \text{ Char residue}) \text{--- (3)}$$

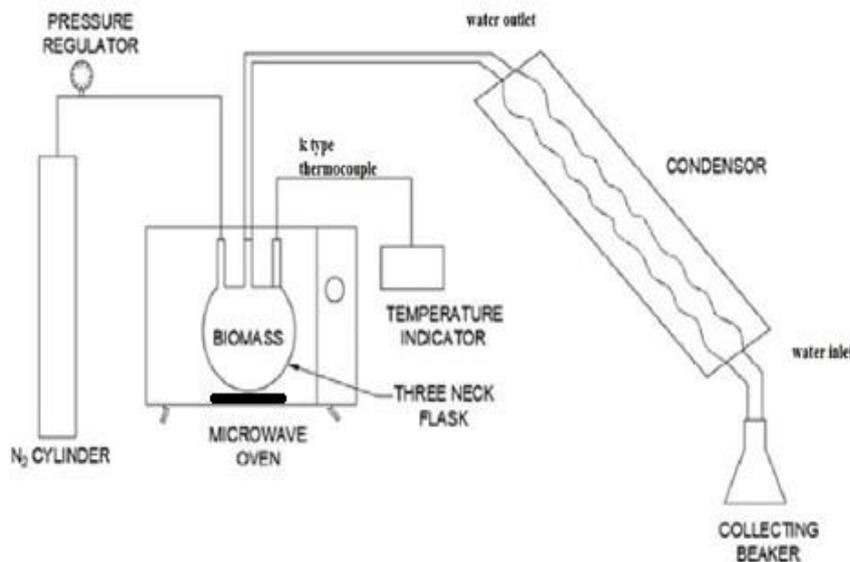


Figure 2 Microwave Pyrolysis experimental setup

B. Thermogravimetric Analysis (TGA).

To determine its thermal decomposing behavior of the karanja seed, Thermogravimetric Analysis (TGA) is carried in N₂ atmosphere. Simultaneous Thermal Analyzer (STA) (Make: Netzsch - STA 449 F3 Jupiter) is used for TGA analysis which is facilitated at Pondicherry university. Temperature is regulated from 25° C ± to 300°C at heating rate of 20°C/min in nitrogen gas atmosphere using 50 mg of sample in Al₂O₃ crucible holder.

C. Fourier transform infrared spectroscopy (FT-IR).

Fourier transform infra-red (FT-IR) spectrometry is used in determination of Functional group composition of karanja seed powder. The infra-red spectrum of karanja seed powder

was found between 5000 to 700 cm⁻¹ and 700 to 50 cm⁻¹ (Covering IR & FAR IR) with resolution of 0.1 cm⁻¹.

D. Characterization of physical properties of the bio-oil

A rheometer (BROOKFIELD R/S-CPS+ RHEOMETER) using measuring systems for Cone (Meas. Cup (C50-1/30)) and Plate (P50) is used for rheology study to determine the dynamic viscosity of the produced bio-oil. The rheological data are documented at 25±0.05°C operated at 50 rpm and the temperature was controlled accurately by Peltier temperature control system. A series of rheological data was collected and the average is taken as the viscosity of the oil. Flash and fire point of the fuel was determined by using Cleveland open-cup apparatus.

IV. RESULT AND DISCUSSION

A. Characterization of the seed powder

Table 1 shows the Proximate analysis, Ultimate analysis, H/C ratio, N/C ratio and HHV of karanja seed powder. The proximate analysis of the seeds shows prominent results of moisture content 10.11% which is likely to be a suitable feedstock for microwave pyrolysis by helping in increased polarisation during microwave heating[16]. The volatiles content of the karanja seed powder is 84.89% which seems to be likely an efficient feedstock of for energy conversion technique. The ash content of karanja seed powder is 25 and fixed carbons of 3%. On comparing to statements of the thermal pyrolysis of karanja seed[9], [12], the undried i.e. as received karanja seed powder has appreciable moisture content, which seems to be an essential character of the feedstock during microwave heating. The ultimate analysis results in presence of 53.04% of carbon,35.527% of oxygen, 7.32% of hydrogen,3.94% of nitrogen and 0.173% of Sulphur in Karanja seed. For pyrolysis, the sulphur content is to be minimum and karanja seed appear like to be an efficient feedstock for pyrolysis based on presence of sulphur content in it[17].The HHV of the karanja seed powder is determined to be 31.85 whereas H/C ratio is 1.89 and N/C ratio is 0.06.

Table 1 Properties of the karanja seed powder

Contents	Wt. (%)
Proximate analysis	
Moisture content	10.11
Volatile matter	84.89
Ash content	2
Fixed carbon	3
Ultimate analysis	
Carbon (C)	52.08
Hydrogen (H)	8.26
Nitrogen (N)	4.02
Oxygen (O)	35.043
Sulfur (S)	0.21
H/C ratio	1.89
N/C ratio	0.06
HHV (Gross calorific value) (MJ/kg)	31.85

B. Product yield of microwave pyrolysis of Karanja seed.

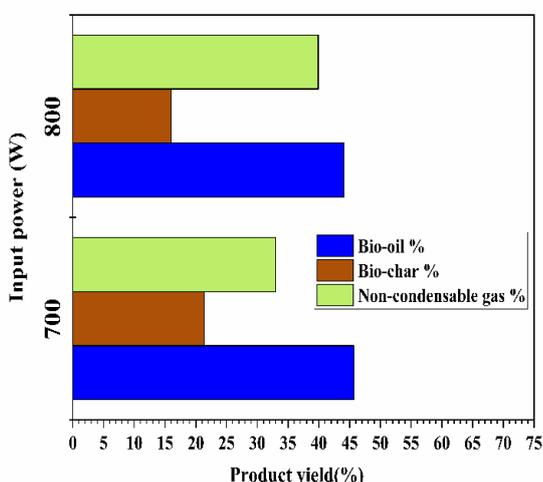


Fig 2 Product yield at two power inputs 700W and 800W

C. Analysis of the produced bio-oil

Thermogravimetric analysis of pyrolytic karanja bio-oil from room temperature to 300°C. There is a reduction in mass loss curve between initial temperature and 100°C which reveals the presence of 4% of moisture content in the produced bio-oil and also presence of volatiles (74.5%) at temperature between 50°C- 237°C and rest are fixed carbons and ash present in the bio-oil. The TGA analysis thus reveals that the produced pyrolytic karanja oil by microwave pyrolysis possess higher volatile content in it and also to be a potential alternate fuel for an engine in volumetric basis.

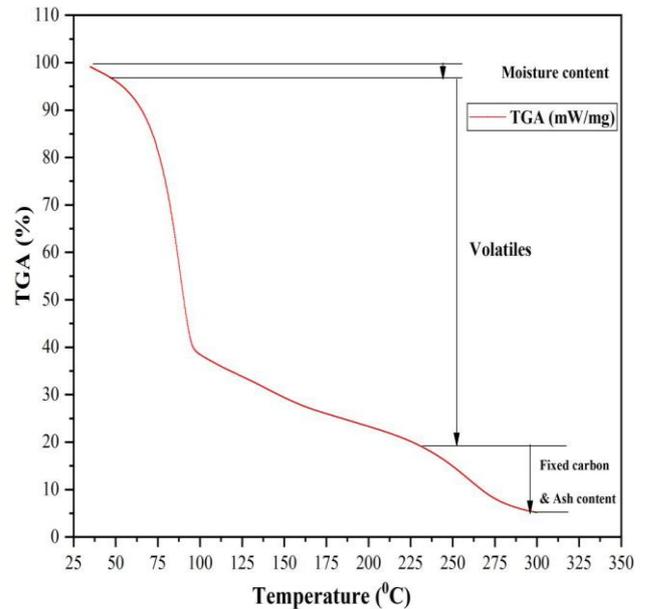


Fig 3 TGA analysis of produced karanja pyrolytic bio-oil

To study the functional groups, FTIR analysis is applied. From figure, it can be inferred that the microwave pyrolysed karanja seed bio-oil has functional groups like O–H or N–H (3340.1, 3181.6 and 3006.8 cm⁻¹) which is attributed to the stretching vibrations of aliphatic primary amine and alcohol compounds, N–H (2923.8 and 2853.4 cm⁻¹) attributed to the stretching vibrations of amine salts compounds. The C=O, C=O and C=C (1719.0, 1672.3 and 1566 cm⁻¹) which attributes to the stretching vibration of carboxylic acid, conjugated acid and cyclic alkene compounds respectively. The C–H and S=O (1461.9 and 1407.7 cm⁻¹) attributes to the bending and stretching vibrations of alkane whereas the sulfonyl chloride and CO–O–CO (1047.7 cm⁻¹) attributed to the stretching vibration of anhydride. Corresponded to lignin the maximum infrared absorbance of OH stretching (phenols) is found in karanja seed. Also, C=C stretching (aromatic skeletal mode) is found in karanja seed. The spectra of the microwave pyrolytic bio-oil produced from karanja seed indicates the typical vibration of the lignin unit at (1281.4 cm⁻¹) (C–O stretching) and (723.4 cm⁻¹) attributed to the bending vibration of alkene (C–C bending). Therefore the functional groups in karanja seed microwave pyrolytic bio-oil seems to be similar to those of other liquid products produced using pyrolysis technique [9].

Table 2 FT-IR Spectrum Table

Wavenumbers (cm ⁻¹)	Appearance	Group	Compound
3340.1	Medium	N-H stretching	Aliphatic primary amine
3181.6	Weak, broad	O-H stretching	Alcohol
3006.8	Weak, broad	O-H stretching	Alcohol
2923.8	Strong, broad	N-H stretching	Amine salt
2853.4	Strong, broad	N-H stretching	Amine salt
1719.0	Strong	C=O stretching	Carboxylic acid
1672.3	Strong	C=O stretching	Conjugated acid
1566	Medium	C=C stretching	Cyclic alkene
1461.9	Medium	C-H bending	Alkane
1407.7	Strong	S=O stretching	Sulfonyl chloride
1047.7	Strong, broad	CO-O-CO stretching	Anhydride
1281.4	Strong	C-O stretching	Aromatic ester
723.4	Strong	C-C bending	Alkene

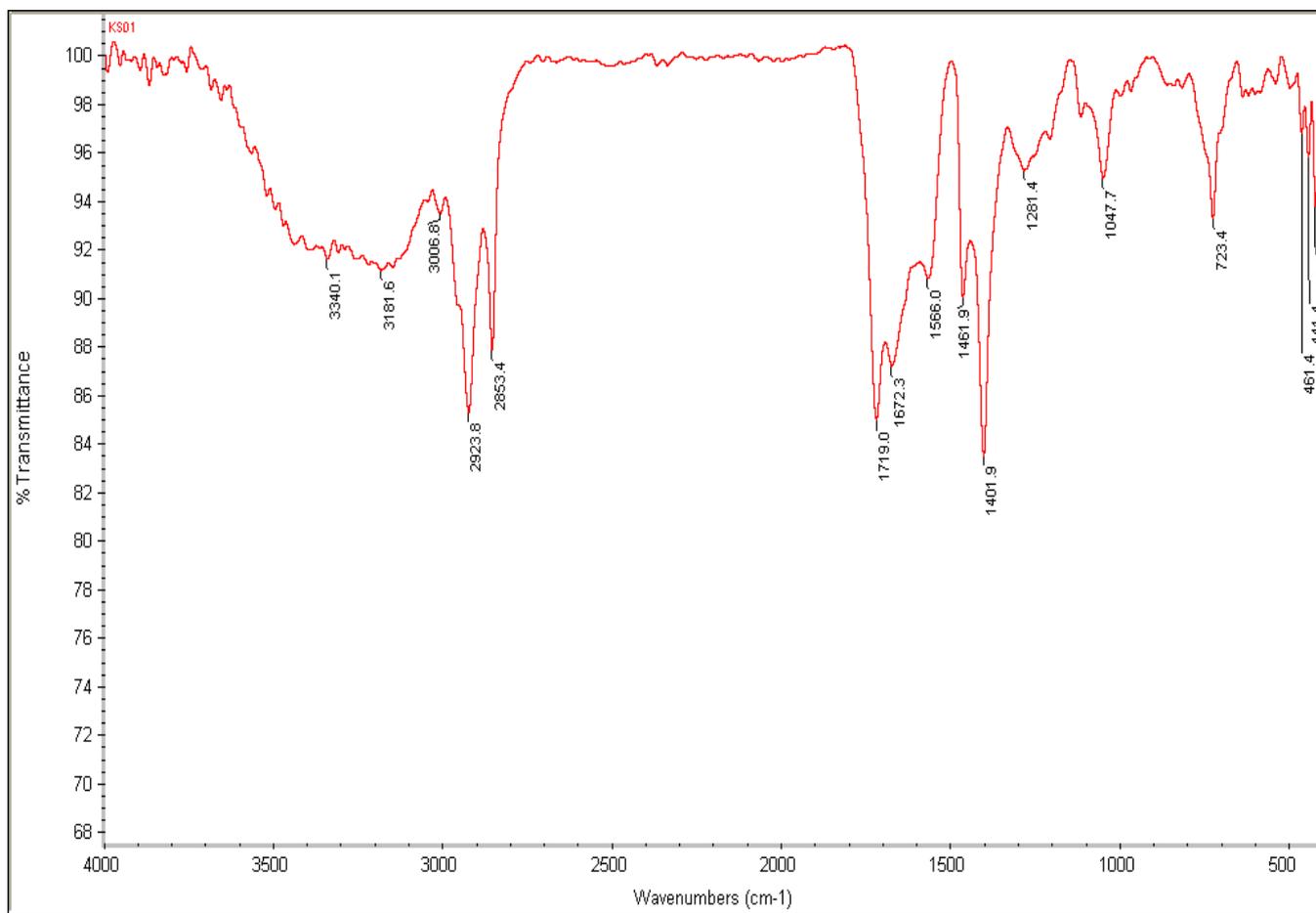


Fig4 FT-IR analysis of produced bio-oil

The measured value of its internal friction, which tends to resist the flow of the bio-oil is viscosity. Viscosity of produced bio-oil is determined to be 52 cP whereas thermally pyrolysed karanja seed produces bio-oil of viscosity 51.67cP[12]. The estimated flash point is 90 °C and fire point is 94 °C. Based on these fuel properties the microwave pyrolytic bio-oil of karanja seems to be efficient alternate by making certain improvements in the quality of the bio-oil.

V. CONCLUSION

The proximate analysis and ultimate analysis of the karanja seed powder shows volatiles of 84.89 %, moisture content of

10.11 %, carbon (53.04%) and hydrogen (7.32%) enables the it be an essential feedstock for microwave pyrolysis. The highest yield of bio-oil is noted at 700W with an end temperature of 447.8 °C. The FT-IR results resembles chain of Hydrogen and carbons in the bio-oil. The viscosity of the produced oil is 52 cP and flash point is 90°C. Further improvement on production of bio-oil by means of utilizing any catalyst can also be done.

REFERENCE

1. S. Yaman, "Pyrolysis of biomass to produce fuels and chemical feedstocks," *Energy Convers. Manag.*, vol. 45, no. 5, pp. 651–671, 2004.
2. A. V. Bridgwater and G. V. C. Peacocke, "Fast pyrolysis processes for biomass," *Renew. Sustain. energy Rev.*, vol. 4, no. 1, pp. 1–73, 2000.
3. A. V. Bridgwater, "Production of high grade fuels and chemicals from catalytic pyrolysis of biomass," *Catal. Today*, vol. 29, no. 1–4, pp. 285–295, 1996.
4. R. Ahmad, N. Hamidin, and U. F. Ali, "Bio-oil Product from Non-catalytic and Catalytic Pyrolysis of Rice Straw," *Aust. J. Basic Appl. Sci.*, vol. 7, no. 5, pp. 61–65, 2013.
5. C. A. Mullen, A. A. Boateng, K. B. Hicks, N. M. Goldberg, and R. A. Moreau, "Analysis and comparison of bio-oil produced by fast pyrolysis from three barley biomass/byproduct streams," *Energy and Fuels*, vol. 24, no. 1, pp. 699–706, 2010.
6. C. A. Mullen, A. A. Boateng, N. M. Goldberg, I. M. Lima, D. A. Laird, and K. B. Hicks, "Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis," *Biomass and Bioenergy*, vol. 34, no. 1, pp. 67–74, 2010.
7. S. Ren et al., "Biofuel production and kinetics analysis for microwave pyrolysis of Douglas fir sawdust pellet," *J. Anal. Appl. Pyrolysis*, vol. 94, pp. 163–169, 2012.
8. P. Shuttleworth, V. Budarin, M. Gronnow, J. H. Clark, and R. Luque, "Low temperature microwave-assisted vs conventional pyrolysis of various biomass feedstocks," *J. Nat. Gas Chem.*, vol. 21, no. 3, pp. 270–274, 2012.
9. N. K. Nayan, S. Kumar, and R. K. Singh, "Characterization of the liquid product obtained by pyrolysis of karanja seed," *Bioresour. Technol.*, vol. 124, pp. 186–189, 2012.
10. K. Prasad Shadangi and K. Mohanty, "Characterization of nonconventional oil containing seeds towards the production of bio-fuel," *J. Renew. Sustain. Energy*, vol. 5, no. 3, 2013.
11. M. N. Nabi, S. M. N. Hoque, and M. S. Akhter, "Karanja (Pongamia Pinnata) biodiesel production in Bangladesh, characterization of karanja biodiesel and its effect on diesel emissions," *Fuel Process. Technol.*, vol. 90, no. 9, pp. 1080–1086, 2009.
12. K. P. Shadangi and K. Mohanty, "Thermal and catalytic pyrolysis of Karanja seed to produce liquid fuel," *Fuel*, vol. 115, no. July, pp. 434–442, 2014.
13. S. A. Channiwala and P. P. Parikh, "A unified correlation for estimating HHV of solid, liquid and gaseous fuels," *Fuel*, vol. 81, no. 8, pp. 1051–1063, 2002.
14. R. F. Culmo, K. J. Swanson, and W. P. Brennan, "Calculation of Molar Element Ratios," 2013.
15. A. Mathiarasu and M. Pugazhivadivu, "Production of Bio-Oil from Soapnut seed by Microwave Pyrolysis," *IOP Conf. Ser. Earth Environ. Sci.*, vol. 312, p. 012022, 2019.
16. R. Meredith, "Engineers' Handbook of Industrial Microwave Heating," *Engineers' Handbook of Industrial Microwave Heating*. 1998.
17. M. Coulson and A. V. Bridgwater, "Fast Pyrolysis of annually harvested crops for bioenergy applications," *Proc. 2nd World Conf. Biomass Vol. I*, p. 1098, 2004.
18. F. Motasemi, A. A. Salema, and M. T. Afzal, "Microwave dielectric properties of agricultural biomass at high temperature in an inert environment," *Trans. ASABE*, vol. 58, no. 3, pp. 869–877, 2015.
19. H. Li, X. Li, L. Liu, K. Li, X. Wang, and H. Li, "Experimental study of microwave-assisted pyrolysis of rice straw for hydrogen production," *Int. J. Hydrogen Energy*, vol. 41, no. 4, pp. 2263–2267, 2016.

AUTHORS PROFILE



A. Mathiarasu, is currently pursuing Ph.D. Full Time in the Department of Mechanical Engineering, Pondicherry Engineering College, Puducherry, India.
Research Interests: Alternate fuels for IC engines
Email id: mathianbu77@gmail.com



Dr. M. Pugazhivadivu, is currently working as a Professor in the Department of Mechanical Engineering, Pondicherry Engineering College, Pondicherry, India. He has completed his Ph.D. from Anna University, Chennai, India. She has more than 20 years of teaching experience. Research Interests:

Alternate fuels for IC engines

Email id: pv_pec@pec.edu