Preparation of Biodiesel of Undi seed with In-situ Transesterification

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Abstract

The biodiesel fraction from oil content of Undi (Calophyllum innophyllum L.) is found 60-70 %.The extraction of oil is a primary step in any biodiesel production system. To escape this step in-situ transesterification method is used in which the Undi seed crush is directly converted into biodiesel with in-situ transesterification which is fatty acid methyl & ethyl ester composition. The single step reaction is eco-friendly as hexane like solvents not have been used for oil extraction. These components of biodiesel were analysed by GC-MS technique.

Keywords

Biodiesel; In-situ transesterification; Undi (Calophyllum innophyllum L.); Gas chromatography–mass spectrometry (GC-MS).

Introduction

Calophyllum inophyllum Linn. [Guttifereae (Clusiaceae)], commonly known as ‘Indian laurel’ or ‘Alexandrian laurel’ is a broad leaved evergreen tree occurring as a littoral species along the beach crests, although sometimes occurring inland [1]. It is known to have cancer chemo preventive agents [2], coumarins and xanthones with antimicrobial activity [3].

The oil has various medicinal uses in rheumatism, skin diseases, joint pains and haemorrhage [4-6]. The aqueous extracts of the root bark and leaves are used as a cicatrising, and those of the fruit have analgesic properties and are used in treatment of wounds and herpes [7]. Oil is also used as illuminant, lubricant, for soap making, etc. The timber from the tree is used for beams, furniture, railway carriages and shipbuilding [8]. Calophyllum species are gaining importance as a source of anti-HIV medicines [9-13]. Calophyllum. inophyllum possesses potential threat due to decline in the population because of various biotic [14] and abiotic factors.

The fruit being a drupe has a hard endocarp with long dormancy period and low rate of germination. Calophyllum inophyllum is a littoral species, the seeds are taken away in the tidal water thereby limiting the propagation rate [15]. Conventional propagation via vegetative cuttings is not practised due to difficulty in rooting in almost all species of Calophyllum and immediate protective measures are essential for the continued existence of the genus [16]. Tissue culture technology would be a useful tool for overcoming these limitations and accelerate mass propagation of this important medicinal tree. The undecorated Undi seed picture is shown in figure 1.

Figure 1. *Undecorated Seed of Undi (Calophyllum innophyllum L.)*

The tree is 20–30 m high, and has a thick trunk covered with a rough, black and cracked bark. The numerous fruits, arranged in clusters, are spherical drupes. Kernels have very high oil content (60-75%). It is obtained by cold expression and yields refined, greenish yellow oil, similar to olive oil, with an aromatic odour and an insipid taste. Once grown, a tree produces up to 100 kg of fruits and about 18 kg of oil [17].

Seed storage behaviour is recalcitrant; the seeds are very oily, quickly losing their germinative power with lapse of time. There are up to 200 seeds/kg can be obtained. This viscous oil is known as domba oil, or pinnai oil, or dilo oil. It has a disagreeable taste or odour, as it contains some resinous material that can easily be removed by refining. The concentration of resinous substances in the oil varies from 10 to 30%; it may therefore be used as a varnish. Domba oil is of excellent quality for soap manufacture; it is also used as an illuminant and in local medicine. Due to high yield of oil from seeds Undi has a promising source of feedstock for making of biodiesel in India.

Very little information is available about the production and optimization of biodiesel from Undi oil [17]. As per literature survey, the in-situ transesterification of Undi seed crush is not reported before.

The aim of this research is to study the in-situ transesterification reaction of Undi seed crush for the preparation of biodiesel in single step. This study also aims to characterize the obtained product by GC-MS techniques to detect the presence of various components of the transesterified product which should give the conformity that the product is transesterified and various ethyls, methyl esters are formed which can be used as biodiesel.

Material and Method

The apparatus used for in-transesterification consisted of an oil bath, a 500 ml three necked round bottom flask equipped with digital controlled mechanical stirrer, a platinum resistance thermometer detector (RTD) temperature sensor with an accuracy of ±1ºC connected to a digital indicator and a condenser. A separating funnel with a valve at the bottom was used for collection of the final product. Undi oil was heated to 110ºC for 30 min to remove moisture and was allowed to cool in desiccators. Hundred grams of moisture free Undi oil was used for each trial.

The seeds of Undi were collected, cleaned and dried. The seeds are then grinded to fine powder by using heavy duty electric mixer of high rpm. Ten grams of seed powder was used as a starting material. It was mixed with mixture of Methanol and Ethanol. The in-situ transesterification with continuous stirring was carried out by adjusting 400 rpm oscillations. The heat is given by hot plate by keeping at 60ºC for about 60 minutes. The solid cake and

mother liquor were separated by vacuum filtration. A rotary evaporator was used for separation of solvent. The oil fraction separates at 80ºC. The oil content was preserved in airtight containers and used for further analysis.

The moisture content of dry seed powder and oil extracted by reactive extraction was obtained [18] by Karl Fischer Titrator, µaquacal$_{100}$, manufactured by Analab Scientific Instruments Pvt. Ltd. During in-situ transesterification various concentrations of potassium hydroxide [19-20] were used as a catalyst along with the mixture of methanol and ethanol. The reaction time was finalized for optimum yield is 60 minutes. The reaction was carried out at different temperatures [21-22]. The temperature 60ºC gives maximum yield whereas the oil was also separated at 80ºC by rotary evaporator. The water quantity also affects the rate of reaction considerably. Increase of aqueous medium reduces the yield of reactive extraction. The observed yield is found maximum without presence of water. The product is analysed with the GC-Ms techniques.

Results and Discussion

The percentage of biodiesel from Undi seeds was found to be 74.5% in oil fraction. The moisture content of oil obtained by Karl Fischer method was 0.6% and the moisture content of seed powder is around 0.44%. The optimum temperature for in-situ transesterification is 60ºC with KOH (Potassium hydroxide) is used as catalyst. The agitation was achieved by keeping 400 rpm oscillations continuously for 60 minutes optimized time.

The product is characterized by GC-MS techniques. It shows that the fatty acid content of the seed crush is completely converted into the respective fatty acid methyl/ethyl esters. There are 46 components were shown their presence in the GC-MS analysis. The qualitative peaks are shown in the figure 2. Following esters were found in the product which is given with the percentage and Retention Time (RT) in table 1.

The result shows that the transesterification of the Undi seeds can be done successfully without extraction of oil from seeds. The ethanol might be worked as solvent in this reaction. There is no need to use the solvents like hexane for oil extraction, which are not eco-friendly.

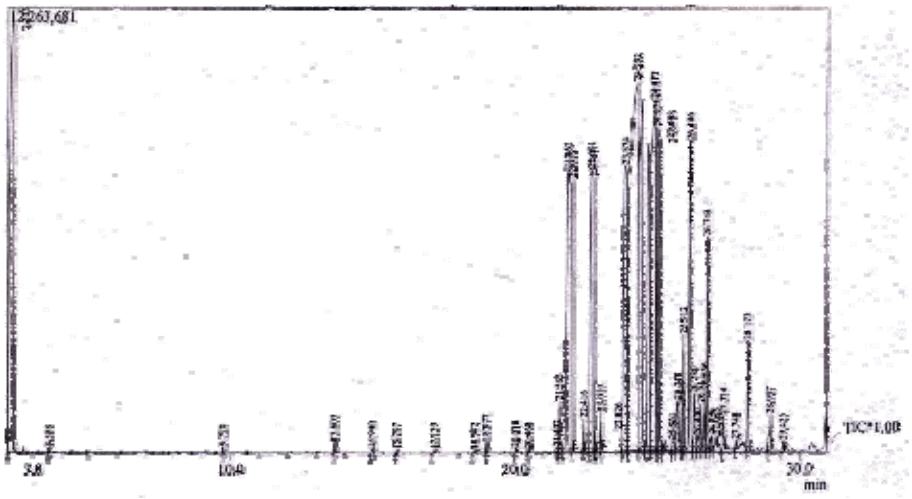

Figure 2. *The qualitative peaks of GC-MS of Undi seed in-situ transesterified product.*

Table 1. Undi Biodiesel Components with the RT, Percentage and Name of the Ester

R.T.	% Ester	Name of Ester
2.303	11.59	1) Ethyl acetate
3.558	0.02	2) Cyclohexane, metyl-
9.720	0.02	3) Octanoic acid, metyl ester
13.603	0.07	4) Nonanoic acid, 9-oxo-,methyl ester
14.940	0.03	5) Nonanoic acid, 9-oxo-,methyl ester
15.800	0.02	6) Nonanedioic acid, dimethyl ester
17.139	0.02	7) Nonanedioic acid, dimethyl ester
18.572	0.02	8) 7-Hexadecanoic acid, methyl ester (z)
18.977	0.06	9) Methyl tetradecanoate
20.018	0.03	10) Tetradecanoic acid, ethyl ester
20.468	0.02	11) Pentadecanoic acid, methyl ester
21.492	0.04	12) 7-Hexadecanoic acid, methyl ester (z)
21.563	0.43	13) 9-Hexadecanoic acid, methyl ester (z)
21.862	7.53	14) Hexadecanoic acid , methyl ester
22.016	3.25	15) Hexadecanoic acid , methyl ester
22.416	0.17	16) Ethyl 9-hexadecenoate
22.691	6.13	17) Hexadecanoic acid , methyl ester
22.767	0.63	18) Pentadecanoic acid,2,6,10,14-tetramethyl-, methyl ester
22.826	0.11	19) 9-Hexadecanoic acid, methyl ester (z)
23.019	0.22	20) Heptadecanoic acid, methyl ester
23.874	7.45	21) 9,12-Octadecadienoic acid (Z,Z)-, methyl ester
24.292	23.41	22) 2,3 – Dihydroxypropyl elaidate
24.471	6.54	23) Octadecanoic acid,methyl ester
24.678	5.50	24) 9,12 – Octadecadienoic acid, ethyl ester
24.913	10.39	25) Ethyl Oleate, ethyl ester
24.978	3.57	26) Octadecanoic acid, ethyl ester
25.058	2.95	27) Heptadecanoic acid, 15-methyl-,ethyl ester
25.225	0.04	28) Nonadecanoic acid, methyl ester
25.531	0.15	29) 7,10 – Octadecadienoic acid, methyl ester
25.718	0.67	30) Oxiraneoctanoic acid – 3 – octyl – methyl ester, cis

Table 1. Undi Biodiesel Components with the RT, Percentage and Name of the Ester

25.849	0.29	31) Oxiraneoctanoic acid – 3 – octyl – methyl ester
25.912	0.80	32) 11-Eicosenoic acid, methyl ester
26.146	3.04	33) Eicosanoic acid, methyl ester
26.280	0.51	34) 1,16-Hexadecanediol
26.400	0.21	35) 9,12-Octadecadienoic acid (Z,Z)- cis
26.511	0.35	36) Ethyl 9-hexadecenoate
26.656	0.41	37) Tricyclo [20.8.O.O (7,16)] – triacontane, 1(22),7(16)-die
26.744	1.40	38) Heptadecanoic acid, ethyl ester
26.833	0.06	39) Oxiraneoctanoic acid, 9,10-dihydroxy-,methyl ester
26.896	0.08	40) trans-9,10 Epoxyoctadecanoic acid
27.065	0.13	41) Heneicosanoic acid, methyl ester
27.314	0.31	42) Tricyclo [20.8.O.O (7,16)] – triacontane, 1(22),7(16)-die
27.748	0.07	43) Octadecanoic acid, 9,10-dihydroxy-, methyl ester
28.173	0.78	44) Docosanoic acid, methyl ester
28.957	0.39	45) Nonadecanoic acid, ethyl ester
29.425	0.08	46) Tricosanoic acid, methyl ester

The method to prepare the biodiesel is usually double or triple stage reaction but the method applied in this paper is a single stage reaction. However, the transesterified product should be checked as per national /international norms before used as a biodiesel. Such study can be performed on other non-edible oil seed feedstock to prepare the biodiesel with single step eco-friendly reaction.

Conclusions

Biodiesel can be produced directly from the seeds of Undi by in-situ transesterification reaction process with the optimum concentration of KOH, methanol & ethanol. The biodiesel fraction from oil content was found 74.5 % at 60ºC and 400 rpm oscillations for 60 minutes time and normal atmospheric pressure without addition of water in the reaction mixture. The harmful organic reagent like n-hexane was not at all used in this method. Hence this technique is environment friendly. The Biodiesel obtained has low cost. One can support the replacement of petrodiesel by biodiesel; as it is easily recovered. The catalyst used is KOH which is cheap and easily available. Fatty acid methyl ester (Biodiesel) fuel characterization is done with GC-MS techniques and results are tabulated, conclusions are drawn on the basis of standard. The esters obtained clearly indicates that the Undi plant seeds can be used directly without extraction of oil from seeds for the preparation of fatty acid methyl/ethyl esters (Biodiesel) which will be suitable for use as replacement of diesel without any change in engine.

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