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Optimization, kinetics and thermodynamic studies on oil extraction from *Daturametel Linn* oil seed for biodiesel production

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ABSTRACT

In this research, *Daturametel Linn* seed oil was investigated for the first time as a promising non-conventional feedstock for preparation of biodiesel fuel. The maximum extraction of oil was observed to be 38.57 (wt) % and the activation energy Ea (25.8 kJ mol^{-1}) was calculated. Further the thermodynamic properties for oil extraction were determined as activation enthalpy = 25.051 kJ mol^{-1}, activation entropy = −241.25 J mol^{-1}, and the Gibb's energy = 105.39 kJ mol^{-1}. This present study also reports the new single-step ultrasound production of biodiesel from high fatty acid *D.metel Linn* oil using sulfuryl chloride as catalysts in which 95.50% yield was achieved with 2 h. Different reaction parameters for oil extraction and biodiesel production were optimized. This analysis confirms that *Daturametel Linn* biodiesel is appropriate alternative to petroleum diesel with recommended fuel properties as per specified standards.

1. Introduction

The whole world has been invigorating the search for alternative sources due to the depletion of oil reserves, increase in crude oil prices, and the environmental concerns [1]. Today methyl and ethyl esters of fatty acids are used as substitute to petroleum based diesel fuel generally known as biodiesel. Since biodiesel has great molecular similarities to paraffinic diesel fuel compounds, it is considered as a direct replacement to fossil fuels used for diesel engine. However, the cost of biodiesel depends mainly on the cost of the feedstock and catalyst used [2]. Reports reveal that production of biodiesel shows greater concern, when using edible vegetable oil such as palm, soybean, sunflower, and sesame oils [3,4] as they battle with food resources [5]. In addition, devouring of edible oils is relatively more in developing countries like India, which deliberates the vegetable oil to cost more and so the usage of such oils for extraction process remains senseless. The availability of used cooking oil is very small as it is used till the end; hence focus needs to be shifted to non edible sources [6].

Nowadays, biodiesel has become the leading alternative energy source though its intensification is slowed down by the production cost. Naturally large amounts of the non-edible oil plants are available all over the world. These non edible oil crops can be grown in waste lands with minimum cultivation cost and high yield. So utilization of this kind of oily crop for biodiesel production could minimize the cost of feedstock. Non edible oil sources provide a clear opportunity as substitute for fossil fuel in view of economic as well as environmental benefits. Among many non-edibles oil trees only few such as linseed, castor, Karanja, neem, rubber, jatropha and cashew have caught the interest of researchers for biodiesel production others not in use.

In this work, for the first time *Daturametel Linn* is considered as a source for the production of biodiesel. The plant is native to Asia and Africa. This underutilized plant is grown on roadside as ornamental plant and occurs throughout India [7]. It is called as Vellai ummathai in Tamilnadu, India. And it belongs to the Solanaceae family in the Plantae Kingdom. This plant tolerates all kinds of soil types and it can grow best in rich, light sandy soil.

From the survey of literatures, it is known for its antibacterial activity [8] and antifungal activity against phyto pathogens [9] also meant to serve as an insecticide [10] but not for biodiesel production. There is a limited literature survey was existing for the oil extraction from *D. metel Linn* non edible feed stock.

Extraction is unique and significant process to recover oil from oleaginous seeds [11]. Oil seeds are extracted in two ways, by mechanical pressing and extraction with various chemical solvents. Solid liquid extraction is a common and efficient method in producing oil from seeds. Solvent extraction involves the transfer of a

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soluble fraction from a solid mass to a liquid solvent hence it imparts higher yield and less turbid oil.

For the development of large-scale solvent extraction system, the oil extraction rate considered a prominent factor. Extraction rate usually depends on the nature of the solvent which is used for the extraction, reaction time between the biomass and solvent, process temperature, particle size of the source, and solvent-solid ratio. Most biodiesel fuels are presently synthesized with alkaline catalysts because for its high conversion and low cost [12]. But this process is not suitable for high free fatty acid (FFA) content feedstock. The heterogeneous solid catalyst are non-corrosive in nature, leading to safer and more eco-friendly operations, but these heterogeneous catalyst is quiet expensive and complicate to synthesize, which limits their industrial application [13]. On the other hand acid-catalyst eradicates the process saponification reaction and has catalyzed the high FFA contents vegetable oils or animal fats [14,15]. The only demerit of the acid catalyst leads to longer time reaction and possible corrosiveness. But this can be rectified by Ultrasonic irradiation. Accordingly, for the need of the hour it is attractive to discover more efficient and cheap acid catalysts that have higher tolerance to water and FFA in oils and can simultaneously catalyze both the esterification and transesterification reactions for application of commercial production.

The ultrasonic technique is one of the non conventional techniques used for the production of biodiesel at relatively lower energy cost since this practice requires only one third of the energy required by mechanical stirrer thermostat for the transesterification reaction [16]. Ultrasonic irradiation is a useful tool for emulsification of immiscible liquids and generates cavitations bubbles and shock wave when they are collapsed by implosion and is presumed to enhance the mixing of the oil and methanol in the transesterification reaction [17]. The main goal of this present work is the extractability of *D. metelLinn oil* and its convertability to biodiesel by using sulfuryl chloride as catalyst. The extraction parameters were optimized to get higher oil yield. And the kinetics and thermodynamics studies for oil extraction were illustrated. In addition production process parameters as catalyst loading, reaction heat and methanol to oil ratio were studied.

2. Experimental sections

2.1. Materials

Anhydrous grade (99.99%) methanol, Sulfuryl chloride, anhydrous sulphate, Methanol, petroleum ether, Phenolphthalein of 1% and sodium hydroxide of 99% purity and other reagents utilized in this work were bought by Merck, India. The solvents were reused after preliminary distillation.

2.2. Collection of seeds

In favor of this research the *D. metel Linn* seeds were collected from local areas near Pondicherry, (India) in the month of July–August. The specimen was acknowledged as *D. metel Linn*, accession number CASBAH 1007, and validated at Centre for Advanced Studies in Botany, University of Madras, and Chennai, India. The collected seed was dried to remove the presence of moisture content in it. An appropriate amount of the seeds were taken and make it into powder form with high speed blender, then the powder dried in an air circulating oven at 60 °C for 1 h. And it is repeated for several times to achieve a constant weight.

2.3. Extraction set up

The total oil yield was measured using extraction method. This process was carried out in a 250 mL cylindrical flask, as a batch process. The middle neck of the flask was fitted with reflux condenser the entire setup was made to partially immerse in a thermostat shaker.

2.4. Extraction

The appropriate weight ratio of seed and solvent (petroleum ether) were taken, and the mixture stirrers' speed was kept at 400 rpm. The partition coefficient decides the distribution of the oil between the seed and solvent and the transfer rate of solute depends on extraction parameters. In this process mixing being kept idle and the mixture subsequently allowed to cool, after probable attainment of appropriate time. The solvent has been removed by distillation and the quantity of oil extracted at each time interval was determined gravimetrically.Further the oil extracted was evaluated to check the content of oil in the seed with respect to time for different temperatures. Following the collection of oil, optimization study was carried out with suitable solvent. To determine the order of the reaction, reaction rate constant, activation energy and thermodynamic properties the kinetic study for oil yield process was carried out.

The oil yielded during extraction was determined by following equation [18].

Oil yield (wt %) = Total weight of oil extracted/Total weight of seed *100.

2.5. Production set up

The biodiesel synthesis was done using apparatus consisted of 500 mL flask, whose middle neck fitted with condenser which was kept in the ultrasonic cleaning bath (40 kHz, 130 W). A thermostat was also used for the synthesis of biodiesel.

2.6. Ultrasonicated single step production process

Transesterification process is considered as an improved process due to the easiness and the usage of the by-product formed. *Metel Linn oil* has a high FFA content. In this process, preferred amount of acid catalyst is added with methanol and seed oil mixture in a conical flask and stirred for a few minutes. The mixture was transferred to the reaction chamber and then subjected to ultrasound waves. Ultrasonic waves obtained from sonicator were applied to accomplish the transesterification reaction in the presence of methanol using SO_2Cl_2 as a catalyst. A set of experiments was carried out to determine the effect of Ultrasonication on the transesterification reaction. Sulfuryl chloride (SO_2Cl_2) is a colorless an inorganic liquid compound with pungent odor at room temperature. The water which is present in Linn oil reacts vigorously with SO_2Cl_2 under intense mixing forms strong acids such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) [19].

$$\text{Sulfuryl chloride} + \text{Water} \rightarrow \text{Sulfuric acid} + \text{Hydrochloric acid}$$

The sulfuryl chloride catalyzes both esterification and transesterification reactions in a single step. After the reaction is completed, the mixture is left over night for the glycerol layer (by-product) to settle down at the bottom of the separating funnel and the top layer as methyl ester was separated. Anhydrous sodium sulphate was used to dry the product. The operating temperature, the molar ratio, and the catalyst concentration are the important parameters for the transesterification step that must be optimized to achieve maximum methyl ester yield. The optimum of each parameter was varied one at time to identify each optimum state and the reaction was investigated step by step while the rest of the