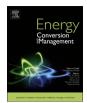
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## Biodiesel production process optimization from *Pithecellobium dulce* seed oil: Performance, combustion, and emission analysis on compression ignition engine fuelled with diesel/biodiesel blends



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#### ABSTRACT

Production of methyl esters from *Pithecellobium dulce* seed oil (PDSO) is carried out through transesterification process. As free fatty acid (FFA) content in PDSO. The effect of four process variables, such as molar ratio (oil: methanol), reaction temperature, catalyst loading and reaction time on the maximum yield of *Pithecellobium dulce* seed oil methyl ester (PDSOME) is studied and process optimization has been executed using response surface methodology (RSM) based Box-Behnken design (BBD). An optimized PDSOME yield of 93.24% is achieved at 1:6 molar ratio, 60 °C reaction temperature, 0.8 wt.% catalyst and reaction time of 90 min. The estimated fuel properties of PDSOME met with the ASTM D6751 standards. Engine tests were conducted for PDSOME, its blends (20, 40, 60 and 80 vol.%) and compared with diesel. The drop in cylinder pressure, heat release rate (HRR) and exhaust gas temperature (EGT) were observed for the PDSOME and its blends. Brake specific fuel consumption (BSFC) is increased and consequent reduction in brake thermal efficiency (BTE) is found for PDSOME and its blends. The exhaust emissions of CO, HC and NOx were decreased while CO<sub>2</sub> and smoke intensity were increased with increase in PDSOME blending percentage in comparison with diesel fuel.

#### 1. Introduction

Biodiesel is becoming an alluring substitute fuel for diesel engines due to its sustainable, non-hazardous and eco friendly nature. It can be originated from different varieties of vegetable oils. Vegetable oils of non-edible nature as a feedstock for biodiesel receives more attention for the last few decades. The biodiesel is successfully produced from non edible sources such as *Jatropha curcas*, *Callophyllum inophyllum*, *Pongamia pinnata*, *Madhuca indica* and *Hevea brasiliensis* subsequently it is used in diesel engine without any modifications in engine design [1–5]. However, biodiesel production and characterization from various oil bearing plants such as, *Thevetia neriifolia Juss*, Amari (*Amoora Wallichii King*), *Ailanthus excelsa*, *Schleichera oleosa L*, *Hodgsonia macrocarpa*, *Citrus limetta*, and *Swietenia mahagoni* are being carried out as an advancement in many countries. The feasibility of biodiesel production from *Thevetia neriifolia Juss* oil (TNO) was studied by Mathirasi and Partha [6]. Results showed that a product yield of 98.7% was achieved in the presence of 0.9 wt.% sodium hydroxide (NaOH) with 9:1 molar ratio at temperature of 65 °C for 20 min. The fuel properties of TNO biodiesel was assessed and found within the limits of ASTM standards. Furthermore, they concluded that TNO was a propitious feedstock for biodiesel industries. Kakati et al. [7] studied the Amari tree seed oil (ATSO) based biodiesel production. ATSO had 16% of free fatty acid (FFA) composition, therefore two stage transesterification process was utilized for biodiesel production. In first stage, acid esterification was achieved with molar ratio (oil: methanol) of 4:1 and 0.80% (v/v) sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) within 3.5 h. Then, base (NaOH) catalyzed transesterification was performed for acid treated ATSO with 30% (v/v) methanol in the presence of 1% (w/v) NaOH for 2.5 h and which yielded 88.5% of methyl ester. Furthermore, biodiesel properties were analyzed and observed to be tantamount with the ASTM D6751 and EN 14214 standards. The preparation and characterization of

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Nomenclature		DI	Direct injection
		EGT	Exhaust gas temperature (°C)
ASTM	American society for testing and materials	GC	Gas chromatography
BBD	Box-Behnken design	HC	Hydrocarbon (ppm)
BP	Brake power	HRR	Heat release rate (KJ/m <sup>3</sup> -deg)
BSFC	Brake specific fuel consumption (kg/kW h)	NOx	Oxides of nitrogen (ppm)
BTE	Brake thermal efficiency (%)	P.dulce	Pithecellobium dulce
CA	Crank angle (degrees)	PDSO	Pithecellobium dulce seed oil
$CO_2$	Carbon dioxide (vol.%)	PDSOME	Pithecellobium dulce seed oil methyl ester
CO	Carbon monoxide (vol.%)	RSM	Response surface methodology

biodiesel from Ailanthus excelsa (A. excelsa) seed oil was carried out by Anjaneyulu et al. [8]. Additionally, biodiesel fuel properties were determined, and when compared with international standards the obtained values were found to be within the limits. Finally, they proposed that A. excelsa seed oil could be a valuable alternative source for bio based fuel production and applications. Silitonga et al. [9] examined the practicability for production of biodiesel from Schleichera oleosa L oil. The influential effect of temperature, molar ratio, catalyst concentration, time and type of catalyst on biodiesel yield were studied. An average yield of 96% was obtained at 8:1 methanol/oil molar ratio, 1 wt.% potassium hydroxide (KOH) catalyst with the time period of 90 min at 55 °C temperature. The properties of the produced biodiesel was also evaluated and are comparable to ASTM D6751 standards. They suggested that, the Schleichera oleosa L oil based biodiesel can be utilized as an alternative to diesel fuel without any extensive modification in engine design. The classical base-catalyzed transesterification process was used to prepare the biodiesel from Hodgsonia macrocarpa (HM) oil. 95.46% of yield was achieved from HM. The fuel properties of HM based biodiesel met with international standards and hence HM oil could be a high quality raw material for biodiesel [10]. Citrus limetta (C. limetta) biodiesel was extracted by simple transesterifcation process. The reaction was executed using 1:6 oil to methanol molar ratio at 60 °C for 120 min with 1 wt.% of KOH and it yielded 92% of methyl ester. Furthermore, physicochemical properties were determined and analyzed. They described that the C. limetta biodiesel might be a feasible alternative to diesel fuel [11]. Similarly, Mohan et al. [12] identified Swietenia mahagoni seed oil as an alternative biodiesel feedstock. In their study, the biodiesel was produced through a two-stage transesterification process. Further, the biodiesel properties were determined and found within standards.

Catalyzed transesterifcation is the most preferable and suitable chemical reaction for biodiesel production, in which oil consists of triglycerides react with alcohol (methanol or ethanol). For fastening the reaction and improving the process yield, acid or alkali catalysts were used in the chemical reaction. Alkali catalyzed transestrerification in the existence of methyl alcohol is preferable for the oils containing lower free fatty acids. This method is advantageous due to its effectiveness, low cost, lower concentration and minimum heat requirement for the reaction. The rate of reaction is influenced by many elements including molar ratio (oil: methanol), catalyst loading, stirring speed, reaction temperature and time [13]. Optimization study of biodiesel synthesis is important so as to facilitate the researchers in the evolution of mass production of biodiesel in the future. Generally, the optimization was actualized by transforming one factor at a time and the response is a function of single factor (one-variable-at-a-time). This is time consuming technique, an outrageous in cost and excludes interactive effects among the selected factors. Furthermore, it does not portray the integral effect on the response of the process. Response surface methodology (RSM) in multivariate system is adopted to provide a research approach in analyzing the interaction of the variables using statistical methods [14]. There are a few reports on the application of RSM in the optimization of biodiesel synthesis from various feedstocks [15-17].

DI	Direct injection
EGT	Exhaust gas temperature (°C)
GC	Gas chromatography
HC	Hydrocarbon (ppm)
HRR	Heat release rate (KJ/m <sup>3</sup> -deg)
NOx	Oxides of nitrogen (ppm)
P.dulce	Pithecellobium dulce
PDSO	Pithecellobium dulce seed oil
PDSOME	Pithecellobium dulce seed oil methyl ester
RSM	Response surface methodology

Recently, biodiesel has been magnetizing the world as a direct fuel or mixing component in diesel vehicles. Kakati and Gogoi [18] produced and characterized the biodiesel from Kutkura fruit seed oil and subsequently the engine performance was evaluated with blends ranging from 10 to 20%. From the characterization studies, they found that the seed oil from Kutkura fruits could be a promising feedstock for biodiesel. 1000 ml of oil yielded 70% of fatty acid methyl esters (FAME) with 300 ml methanol and 8 g (NaOH) for 2 h at 63 °C and 600 rpm. Furthermore, the blending of the FAME with diesel up to 20% provided better performance and reduced smoke emissions on the tested engine. Prospects of biodiesel yielding from Aphanamixis polystachya (A. polystachya) oil have been conferred by Palash et al. [19]. The A. polystachya methyl esters (APME) produced through esterification (1:24 molar ratio, 1% (v/v oil) of hydrochloric acid (HCl) at stirring speed of 600 rpm for 3 h and 60 °C) is followed by transesterifcation with 1:6 molar ratio, 1% (m/m oil) diluted KOH in methanol at 60 °C for 2 h and 600 rpm. The performance and exhaust emissions of APME5 and APME10 fuels in diesel engine were determined. Based on the experimental results, they resolved that APME and their blended fuels can be utilized as a substitute for diesel without any engine adjustments. Naik and Balakrishna [20] used Balnites aegyptiaca (L). Del seed oil and produced 89% of biodiesel through a base-catalyzed esterification at 8:1 molar ratio, 1.26 wt.% KOH, 65 °C for 2.5 h. Furthermore, they conducted experiments on diesel engine powered with biodiesel blends in the ranges of 10 and 20% which resulted in enhancing the engine performance and reduced emissions of carbon monoxide (CO), hydrocarbon (HC) and oxides of nitrogen (NOx) at peak loads in comparison with diesel fuel. They found that the biodiesel blends up to 20% with diesel conceivably used as an alternate fuel in a compression ignition (CI) engines. The Argemone mexicana methyl ester (AMME) production and impact of 20% and 40% blends on direct injection (DI) diesel engine performance and emissions was investigated by Parida and Rout [21]. AMME was produced by two-step transesterification process because of its higher acid value of argemone oil. Initially, oil was mixed with sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and methanol in the volume of 50:10:1 (oil: methanol:  $H_2SO_4$ , (v/v/v) and stirred at 200 rpm for 3 h at 60 °C. The two layers were separated after 3 h of reaction time. Then, the separated oil was mixed with NaOH and methanol in the ratio of 25:0.2:5 and mechanically stirred at 250 rpm at 50 °C for 4 h. Nearly, 86% yield of AMME was obtained. From the engine outcomes, they discerned that the biodiesel blends up to 20% showed superior results than that of diesel fuel. Hence, they deduced that the blends of AMME could be a potential source of fuel for diesel engines in the future. Mofijur et al. [22] reported on crude moringa oleifera oil (CMOO) based biodiesel production and effect of its 10 and 20% volume blends in diesel engine. In their study, two step biodiesel production process was selected to prepare biodiesel. In acid catalyzed step, the CMOO was treated with a molar ratio (methanol: CMOO) of 12:1 and 1% (v/v oil) H<sub>2</sub>SO<sub>4</sub> for 3 h at 60 °C and 600 rpm in order to reduce free fatty acids. After that an alkaline catalyzed process was accomplished with 6:1 molar ratio, 1% (w/w oil) of KOH at 60 °C and 600 rpm for 2 h, which yields 90% of biodiesel. Further, the engine test findings revealed that B10 and B20 CMOO biodiesel blends had higher BSFC than diesel fuel. Similarly,

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