Energy Conversion and Management 160 (2018) 364–374

Contents lists available at ScienceDirect

Energy Conversion and Management

journal homepage: www.elsevier.com/locate/enconman

Process optimization, kinetics of production *Jatropha curcus* methyl ester, and its utilization in single cylinder diesel engine

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ARTICLE INFO

Keywords:
Biodiesel
Emission
Heterogeneous catalyst
*Jatropha curcus*oil
Performance
Pseudo-first order kinetics
Transesterification
VCR engine

ABSTRACT

An experimental investigation was conducted on a single cylinder, VCR diesel engine for various biodiesel-diesel blends with varying load conditions (0, 3, 6, 9 and 12 kg). Aim of present work was to examine physicochemical characteristics, performance and exhausts emissions of the engine for various load conditions using biodiesel produced from a non-edible feedstock, *Jatropha curcus linn* and its various blends. *Jatropha curcus* methyl esters (JCMEs) were synthesized by two stage chemical processes i.e. esterification followed by transesterification, as the feedstock comprises high free fatty acid content of 6.16 mg of KOH/g. Sulfuric acid was employed as acid catalyst in esterification stage at optimized molar ratio of 1:6 (oil:methanol), 1.0% v/v H_2SO_4 and 60 min of reaction time at 65 ± 0.5 °C temperature to ensure reduction of initial FFA from 6.16 to 0.3 mg of KOH/g. In second stage, transesterification was performed where 1:20 M ratio (oil:methanol), 1.5 wt% potassium impregnated zinc oxide 60K/ZnO-900 as heterogeneous base catalyst, at a temperature of 65 ± 0.5 °C with 600 rpm agitation speed for time 55 min conditions resulted in 97.00% conversion of JCMEs. Synthesis of biodiesel was ascertained by FTIR and NMR (^{13}C and ^{1}H) techniques. The reusability studies reveled that catalyst can be reused up to five successive reaction cycles with no significant decrease of its catalytic activity. In order to understand, reaction rate constant and activation energy required for the reaction, kinetics of the process was also investigated. Different JCMEs blends were prepared as JB10%, JB20%, JB30%, JB100% and B00% (diesel fuel) on volume basis with diesel fuel. All blends had shown the promising results of important physicochemical properties such as density, calorific value, flash point, fire point and cetane index as per ASTM standards. Furthermore, the influence of these prepared blends on engine performance and exhaust emissions were investigated under various load conditions. As compared with diesel fuel, blended fuel resulted in improved performance of engine as indicated by high brake thermal efficiency (BTE), brake specific fuel consumption (BSFC) and exhaust gas temperature (EGT). In terms of exhaust gas emissions, all blended fuels resulted in lower carbon monoxide (CO) and carbon dioxide (CO_2) as well as higher hydrocarbon (HC), nitrous oxide (NOx), and oxygen (O_2) emissions. The study concludes that the blended fuel can be used as tenacious source of eco-friendly and alternative fuel for commercial engine as it has been observed for better performance and exhaust emissions profile as compared with diesel fuel.

1. Introduction

Intensifying global energy requisition and diminishing resources of fossil fuels have motivated the scientific community to seek alternative energy resources that have least global warming and pollution effects [1]. Under this situation, efforts have been made to adopt new and renewable sources of energy, such as biodiesel as a fuel as alternate to petroleum diesel [2,3]. Biodiesel derived from locally available renewable feedstock has gained attention because it can be applied in existing diesel engines without any modification. It is biodegradable, and is supportive to rural and agriculture economy [4]. In addition, being renewable, it also helps in curbing so called notorious "carbon"

Abbreviations: ASTM, American society for testing and materials; BSFC, brake specific fuel consumption (g/kWh); BTE, brake thermal efficiency (%); B00%, diesel fuel; CO, carbon monoxide (% vol.); CO_2, carbon dioxide (% vol.); CV, calorific value; EGT, exhaust gas temperature (°C); FTIR, Fourier-transform infrared spectroscopy; HC, hydrocarbon (ppm); JO, *Jatropha* oil; JB10%, 10% *Jatropha* biodiesel and 90% diesel fuel; JB20%, 20% *Jatropha* biodiesel and 80% diesel fuel; JB30%, 30% *Jatropha* biodiesel and 70% diesel fuel; JB100%, 100% *Jatropha* biodiesel; JCME, *Jatropha Curcus* methyl ester; ME, methyl ester; ND-IR, non-dispersive infra-red detector; NO_X, oxides of nitrogen (ppm); NMR, nuclear magnetic resonance spectroscopy; VCR, variable compression ratio engine

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https://doi.org/10.1016/j.enconman.2017.12.072
Received 3 September 2017; Received in revised form 21 December 2017; Accepted 22 December 2017
0196-8904/

and other harmful emissions in form of hydrocarbons (HCs), particulate matter (PM), benzene, toluene, ethyl benzene, xylene (BTEX) and other undesirable elements and compounds [5]. The reason behind worldwide acceptance of biodiesel is its superiority over diesel fuel in terms of high cetane number, improved lubricity, no aromatics, almost no sulfur content and 10–12% oxygen by weight which makes it better resulting in emissions of fewer harmful pollutants [6]. However, biodiesel may raise NOx emissions and engine durability issues such as injector cocking and filter plugging in low temperatures environments [7].

Biodiesel is derived from various feedstocks ranging from a variety of edible and non-edible oils, animal fats and waste cooking oils. At present, more than 95% biodiesel is being derived from edible oil sources resulting in higher production cost and food scarcity. Hence, scrutiny of potential feedstock for commercially viable biodiesel production is an important area [8]. India is fourth largest consumer of crude and petroleum products, however, due to limited availability of crude resources, India has to rely on its imports that result in huge outflow of its foreign exchange. It is also expected that the demand of petroleum diesel would hike at the rate of 6–7% over the next couple of decades with expanding vehicle ownership. Therefore, in order to meet such energy crisis and to ensure country's energy security, it has become necessary to focus on some alternative fuels based on indigenously produced renewable feedstock [9]. In order to promote the production of biodiesel, Indian government had initiated blending of 5% of biodiesel till the end of the year 2006–07. Further, this blending percentage was again revised to 20% up to the end of 2011–12. Moreover, in order to meet this 20% blending target, government proposed large scale plantation of *Jatropha* on 11.2 million hectare of land [9]. *Jatropha curcus linn* is considered as most favorable alternate, as it is non-agricultural, non-edible, low cost and sustainable feedstock [10]. It belongs to the *Euphorbiaceaous* family and is mainly found in the region of central and south America, southeast Asia, India and Africa. It is highly drought resistance and can be cultivated in harsh conditions. It has pest resistant and high seed productivity for 30–40 years. Oil content in the *Jatropha* seeds is 35–40% and 50–60% in the kernel. *Jatropha* oil contains some poisonous and purgative chemicals that make it non-edible and suitable for biodiesel production [10]. In Indian prospects, 80–100 million hectare of available wasteland can be used for Jatropha cultivation which can reduce the dependency of imports of crude oil with additional benefits of green belt on wasteland and support to agricultural and rural development. Presently, India has estimated annual production potential of 200 thousand metric tons of *Jatropha* oil [11].

Transesterification is well accepted and best method for biodiesel synthesis which refers to a base-catalyzed consecutive chemical reaction between triglycerides present in oil and alcohol to produce fatty acid alkyl esters [7]. However, this method is limited to lower free fatty acid (FFA) containing feedstocks. The direct transesterification of high FFA containing feedstocks hinders the conversion of triglycerides to methyl ester by soap formation reaction between free fatty acids and base catalysts. The presence of high FFA content in oil ($> 2\%$) requires a pretreatment step, esterification prior to transesterification [12]. Esterification is acid-catalyzed reaction in which FFA present in feedstock are converted into fatty alkyl esters while triglycerides are converted into fatty alkyl ester in transesterification reaction. The technology is commonly based on the use of homogeneous alkaline catalyst (hydroxides and alkoxides of sodium and potassium) for biodiesel production which leads to several complex processes such as washing steps to remove contamination of catalyst from products, undesirable soap formation, toxic waste generation, high cost, etc. [13]. Such problems caused by homogeneous catalyst can be eliminated by application of heterogeneous catalyst for synthesis of biodiesel.

Present work describes biodiesel synthesis from *Jatropha* oil via two stages: esterification followed by transesterification and evaluation of physicochemical properties along with performance and emission characterization of various blends with diesel fuel. Numerous studies have been conducted on the production of biodiesel from *Jatropha* oil. Further, its physicochemical properties as well as performance and emission behavior of the same and its blends with diesel fuel were also investigated. Chavan et al. [14] studied the synthesis of *Jatropha curcus* biodiesel using waste eggshell and 90% yield was attained with 2 wt% of catalyst, 1:8 oil: methanol molar ratio for 2.5 h of reaction time. They found that all the fuel properties of synthesized biodiesel were comparable to diesel fuel. Syam et al. [15] have reported the synthesis of *Jatropha* methyl ester using KOH and NaOH catalysts with 99 and 90% of yield at 60 and 180 min of reaction time, respectively. Kumar et al. [16] reported a study on ultrasonic-assisted synthesis of *Jatropha* methyl ester using Na/SiO_2 catalyst. They reported 98.53% yield at optimal reaction conditions such as molar ratio, oil to methanol 1:9, catalyst conc. 3 wt% and 15 min of reaction time. Sahoo and Das [17] have described the process optimization for biodiesel production from *Jatropha* oil along with other two feedstocks: *Karanja* and *Polanga* oils. They obtained 93% methyl ester yield in case of Jatropha oil at 11:1 volumetric ratio of alcohol to oil, 1.1% of KOH for 2 h of reaction time. Endalew et al. [18] have reported biodiesel production from *Jatropha curcas* oil via single-step simultaneous esterification and transesterification reactions using La_2O_3 based catalyst. Pramanik [19] reported engine performance of crude *Jatropha* oil using C.I. engine and they concluded that blending content up to 50% volume of *Jatropha* oil showed comparable viscosity to diesel fuel and acceptable brake thermal efficiencies and SFCs values and it can be used as substitute for diesel fuel without major operational difficulties. The performance and emissions study of *Jatropha* oil in diesel engine has been reported by Chauhan et al. [20]. Among all the emissions, NOx emissions declines while CO, CO_2 and HC emissions got slightly enhanced throughout the trials. Agarwal and Agarwal [21] studied viscosity, performance such thermal efficiency and brake specific fuel consumption and emission characteristics of crude *Jatropha* oil and its various blends with diesel fuel. They concluded that all these properties were comparable with diesel fuel for lower blend while were marginally inferior for higher blends. Jindal et al [22] investigated the effect of CR and injection pressure on performance and emission properties of *Jatropha* biodiesel using diesel engine, they further negotiated that *Jatropha* biodiesel can be used at higher CR ratio as well as at higher injection pressure. Chavan et al. [23] studied the emission parameters of CO, HC and NOx gases at various CR ratios of *Jatropha curcus* methyl ester blends such as JB10%, JB20%, JB30% and JB100% on single cylinder VCR engine. JB30% blend showed best emission improvement. The emission of CO were reduced up to 43%, while HC and NO_X emissions were reduced up to 50% and 20% respectively. Ramesh and Sampathrajan [24] investigated the performance and emission characteristics of *Jatropha* biodiesel blends B20-B100 at 2, 2.5 and 3.5 kW brake load conditions using Kirloskar made 5.2 kW diesel generators. They found that blended fuel provided significant improvement in engine performance brake thermal efficiency (BTE) and exhaust gas temperature (EGT). Conversely, they found increased NOx emissions by 15–19%, whereas reduced CO emissions by 14–16% as compared to diesel fuel. Rehman et al. [25] showed that the emissions of carbon monoxide (CO) and hydrocarbon (HC) decreased when *Jatropha* biodiesel content in blended fuel increased while emission concentration of NOx increased. Kathirvelu et al. [26] studied, from the perspective of emissions and performance, the effect of brake power (kW) when a CI diesel engine was fueled with *Jatropha* biodiesel blends. They found that the HC, CO and soot emissions was decreased while exhaust gas temperature and NOx was increased due to improved combustion compared to diesel. Tan et al. [27] also found that *Jatropha* biodiesel blends fueled in light duty diesel engine could significantly reduced HC, CO (at high load) and toluene emissions, while NOx emissions were similar at lower load as compared to diesel fuel. Ruhul et al. [28] studied the effect of blends (10 and 20%) of three type of biodiesel *Jatropha, Alexandrian laurel,* and palm in four cylinder turbocharged diesel engine. In the test using