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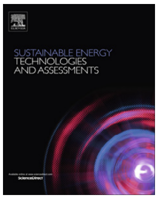

Original article

Anaerobic digestion of the inedible oil biodiesel residues for value addition

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ABSTRACT

Biodiesel from inedible oil seeds is a sought after renewable energy resource, however, per kg of biodiesel production from *Pongamia pinnata* (*PP*) and *Jatropha curcas* (*JC*) generates 7.88 and 5.83 kg residues, respectively in the form of pods, deoiled cakes (DC) and impure glycerol (IG). The pods and DC are lignocellulosic whereas IG contained 18–30% glycerol along with methanol, water, oil, soap, etc. The presence of inhibitory compounds in the residues such as lipids in DC; acid insoluble lignin in pods; methanol, lipids and soap in IG reduces the overall volume and rates of biogas production. The removal of methanol from IG enhanced the biogas volume by 10–20% and simultaneously reduced the lag phase by 50% at (S/I) ratio of 0.25. The co-digestion of IG with lignocellulosic residues at 1:1 ratio also increased the biogas yield and reduced the lag phase by over 50% without any need for supplementary nutrients. The total biogas yields from *PP* residues was 2–3 times higher than *JC* residues, offering relatively faster returns on investments. The biogas generation from the residues and its reuse as an energy source was estimated to reduce the biodiesel manufacturing costs by 40–80% and 19–40% in PP and *JC*, respectively.

Introduction

The biodiesel manufacturing across the globe has gained momentum due to various factors such as, (i) Unavailability of fossil fuels due to demographics and political instability (ii) Modern methods of biodiesel production and new catalyst formulations yielding higher biodiesel (iii) The breeding and cultivation of new varieties of oil crops with higher yields of lipid (iv) Increase in the cultivation of inedible oilseed plants on waste land (v) New engine designs that can utilize biodiesel and its admixtures as fuel (vi) Stringent regulations for reducing the GHG emissions [1,2]. The shortages of food across the globe have often led to policies that prevent the food-fuel conflicts and hence convert agricultural land to grow fuel crops. Therefore, research efforts have been towards identification, breeding and plantation of non-edible oil seed crops and trees such as *Pongamia pinnata*, *Jatropha curcas, Simarouba glauca, Madhuca indica* etc. on non-agricultural and wastelands. These plants can be grown on less fertile lands (wastelands) that are considered unfit to grow cash crops, have comparatively lower water and nutrient demand and similar lipid yields as edible oil seed crops.

Biodiesel is the final product that interests the industries and users; however, its processing leads to the production of various residues such as, (i) Seed cover/pod/husk (ii) Deoiled cakes (iii) Waste glycerol (iv) Biodiesel wash water, etc. The above said residues are distributed across the farmers, oil expellers and biodiesel processing industries therefore their cumulative energy potential remains unrecognized. The drive for replacing Petro-diesel with biodiesel has already created a supply chain that links the farmers with the oil expellers and subsequently to the biodiesel processing industries. Moreover, the same supply chain can be utilized to trade the residues making the energy recovery process more holis-

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Abbreviations: JC, *Jatropha curcas*; JDC, *Jatropha* deoiled cake; JP, *Jatropha* pods; JDCW, *Jatropha* deoiled cake without oil; IJG, Impure *Jatropha* glycerol; MJG, Methanol free IJG; SMJG, Water extracts of MJG by saponification; Gm, Modified Gompertz model; Ap, Experimental gas yield (ml); Ag, Gas yield estimated from Gm; λ, Initial lag phase in days; μ_m, Specific gas production rate (d^{-1}); PP, *Pongamia pinnata*; PDC, *Pongamia* deoiled cake; PP, *Pongamia* pods; PDCW, *Pongamia* deoiled cake without oil; IPG, Impure *Pongamia* glycerol; MPG, Methanol free IPG; SMPG, Water extracts of MPG by saponification; BMP, Biological methane potential; S/I, Sludge/Inoculum ratio; DC, Deoiled cake; AD, Anaerobic digestion; □, Indian National Currency, Indian Rupee.

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tic, economic and environment friendly and can augment incomes from the biodiesel plants. In the current collection system, seed pods are left behind to the farmers as residue during the separation of kernels from the pods; while the deoiled cake from mechanical oil expelling processes remains as a residue with the 'oil mills' or expellers. Finally, the biodiesel industries generate waste glycerol during the biodiesel processing and manufacture, often oil expelling and biodiesel manufacturing are clubbed together in many industries. The hard and woody nature of the pods and the presence of toxic compound in deoiled cakes makes them unfit for consumption by livestock. These are therefore burnt in conventional wood stoves and sometimes traded as a low value biomass fuel. Similarly, the high costs of glycerol purification from impure glycerol has reduced its demand in the market as well as due to the reduction in the cost of petroleum derived glycerol to less than \$20 per barrel [3].

Multiple options to maximize energy recovery and derivation of value added products from the residues have been reported. Options include direct combustion and gasification of the deoiled cakes and husk, waste glycerol as a binder for pelletization of agro-residues, AD of deoiled cake to biogas, extraction of saccharides from deoiled cakes and then subjecting the saccharides to ethanol fermentation, extraction and purification of pure glycerol from waste glycerol, AD of waste glycerol to biogas, fermentation of glycerol to hydrogen, methanol, ethanol, citric acid, 1,3-propanediol, polyhydroxyalkanoates (PHA) etc [4–7]. Most of the attempts had been for discrete pathways and have focused on the reuse of a single residue, but not operated for optimizing the overall process from 'farm to fuel'. These earlier approaches focusing on single pathways always lead to a lower level of harvestable energy and/or economic potential of the residues. The objective of this research was therefore to characterize the various residues and estimate the mass and energy flow during the processing of biodiesel from *PP* and *JC*. In addition, it presents the data in multiple forms and pathways to enable evaluation of the overall process efficiency from both agronomic and industry viewpoints. Secondly, it assesses the physico-chemical properties and inhibitory effects of the residues on AD and methods to overcome these challenges. Thirdly, it studies the impact of impure glycerol on biomethanation process and evolves a strategy to improve its degradability. Finally, an assessment of the capital gains of converting residues to biogas over the direct sale of residues in both *PP* and *JC*.

Materials and Methods

Sample collection

The samples were collected from the biofuel division present at University of Agricultural Sciences, Dharwad, University of Agricultural Science, Bengaluru and RV College of Engineering, Bengaluru, India.

Physico-chemical analysis

The total solids (TS), volatile solids (VS) and total lipids were determined as per the Standard Methods [8]. The composition of lignocellulosic biomass such as non-structural carbohydrates, structural fibers, pectin (calcium pectate) and cellulose were determined [9–11]. Calorific value was estimated using a bomb calorimeter in the Bangalore Test House. The C, H, N, O and S of the samples were estimated in Leco True Spec analyzer set at a temperature range of 850-1000 °C using helium as a carrier gas and oxygen for combustion. The IG samples were analyzed by following methods commonly used in the water content [12], soap and catalyst [13], glycerol [14]. The total lipid content in IG was estimated by acidifying the sample to pH 1 using Hydrochloric-acid followed by the addition of distilled water and extraction of the separated lipids using hexane as per the Standard Methods [8].

Biological methane potential

The BMP experiments were conducted in a 125 ml serum glass bottle fitted with an airtight butyl rubber stopper, held in its position with an aluminium crimp camp. The total biogas volume (ml) generated during the AD processes was measured weekly by downward displacement of an acidified solution [15,16]. All the BMP experiments were carried out in duplicates. The BMP of the PDC, PP, JDC, JFS was estimated at substrate to inoculum S(VS)/I (VS) ratio of 0.125, 0.25, 0.5 and 1. The methanogenic inoculum was collected from a large-size biomass fed biogas plant at our centre. The PDC and JDC were subjected to BMP in its crude form, e.g. with lipids and lipid-free form depicted as PDCW and JDCW. The lipids were removed from PDC and JDC by hexane extraction as per the Standard Methods [8]. Similarly, the impure glycerol was subjected to BMP in three different forms such as, (i) Crude/unchanged form of *Pongamia* (IPG) and *Jatropha* (IJG) glycerol (ii) Crude glycerol, free from methanol for both *Pongamia* (MPG) and *Jatropha* (MJG) (iii) Water soluble compounds (glycerol etc.) extracted from MPG and MJG via saponification method is named as SMPG and SMJG, respectively. Additionally, the above forms of crude and pure glycerol were also subjected to BMP by adding nutrients at various S (TS) /I (VS) ratio depicted as IPG-N, IJG-N, MPG-N, MJG-N and PG-N, SMPG-N, SMJG-N. The PDC and JDC were also co-digested with their respective three forms of glycerol (crude, methanol removed and water extractive) as described above. The BMP of co-digestion was performed at an S/I ratio of 0.25 at various mixture ratios of deoiled cakes (VS) and glycerol (TS) (w/w) at 1:1, 1:2, 1:4, and 1:8. The S/I ratio of 0.25 was chosen based upon its comparatively lower inhibition towards anaerobic bacteria while digesting oilcakes and waste glycerol. Additionally, co-digestion of pure glycerol (99% analytical grade) with PDC was also performed for comparison.

Data analysis

The kinetic parameters of the experimental BMP data, such as Ag, μ_m and d^{-1} were estimated using Gm [17]. The curve fitting of Ap values using Gm showed an $R^2 \geq 0.99$ for most of the samples, however the inhibition of AD was synonymous with a poor fit of $R^2 < 0.99$, lower Ag, μ and longer λ; similar results were also reported earlier [18]. In order to make the data comparable and comprehensive, the S/I ratio of each experimental sample displaying highest Ag, lower λ, and $R^2 \geq 0.99$ were selected and shown in the results. The BMP performances of a few residues at various S/I ratios, however, have been included in the Supplementary data 1 and Supplementary data 2 to aid the reasoning.

Results and discussion

Mass and energy flow

The mass flow analysis of biodiesel processing (Fig. 1) reveals that per kg of biodiesel production from *PP* and *JC* generates 7.88 and 5.83 kg of residues respectively. The total energy of these residues amounts to 128.61 and 103.13 MJ, which is 3.46 and 2.63 times higher than the energy of 1 kg biodiesel derived from *PP* and *JC* respectively. In case of *PP* nearly 50% of the total residues by weight existed in the form of pods and 37.5% as deoiled cakes whereas in *JC* nearly 35 and 48.75% exited in the form of pods and deoiled cakes, respectively. The processing of *PP* biodiesel thus