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– A REVIEW

PRODUCTION OF BIODIESEL FROM SPENT COFFEE GROUNDS BY TRANSERTIFICATION AND ITS BYPRODUCTS AS FUEL ADDITIVES

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ABSTRACT

With the rapid increment in demand of energy, precise emissions standard and with the depletion of petroleum reserves and oil resources worldwide, it necessitates the researchers to search an alternative fuel for the fossil fuel. Biofuel is the most trusted, renewable one and is biologically degradable fuel which reduces the emission of exhaust gases. The biofuel is extracted from the lipids of plants and animals. This paper cites a brief review about using spent coffee ground for the production of biodiesel and can be used for the running of IC Engines. The spent coffee ground is also used as fertiliser to improve the fertility of the soil.

Key words: Biodiesel, Waste coffee grounds, Coffee ground oil, Transertification, methyl ester.

INTRODUCTION

Biodiesel

Biodiesel is one of the most promising alternative fuel, which can be utilised as a fuel for the automotive engines. The energy demands are increasing in the world but the fossils fuels are quite limited. The decrease in fossil fuels, emission, pollution caused by them and increasing fuel prices makes energy sources more attractive. Biodiesel is a fuel that is manufactured from fats of animals and plants with the help of catalyst and can be directly used in diesel vehicles with less or no modification[9]. It is biodegradable and non-toxic. Compared to petroleum diesel, biodiesel has more favourable combustion emission profile, with lesser emissions of carbon monoxide (CO), particulate matter and hydrocarbons[3].

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The conversion process of biodiesel through transertification process is shown in Fig. 1. Transertification is the process by which biodiesel is produced[1]. Various factors affect this process like reaction time, molar ratio, type of catalyst used and temperature

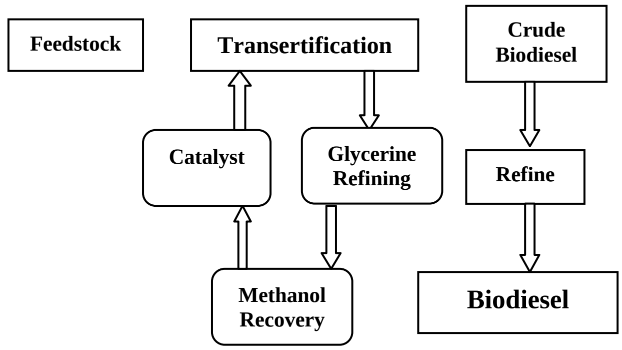

Fig. 1: Conversion process of biodiesel production.

Spent coffee grounds

Coffee is a drink which is prepared from roasted coffee beans, which are the seeds of berries from the Coffee plant. It is slightly acidic in nature and has a stimulating effect on humans because of its caffeine content[1]. It is one of the largest agricultural products that are mainly used as beverages throughout the world[2]. Brazil and Vietnam are the largest coffee producer in the world.

Used coffee grounds are waste from brewing coffee. Used coffee grounds are used for composting or as much as they slowly release Nitrogen (N) into the soil. The composition of coffee grounds is very complex as a wide variety of chemical compounds are present in it.

The literature reviews

(A. Deligiannis et al., 2011) has tried to carry out the study of oil extraction from spent coffee grounds. He collected the coffee grounds and dried it in an oven at around 105^{o}C, so that the moisture content can be reduced in it (around 18-45%). The extraction was done applying a Soxhelet process and the Soxhelet device temperature is maintained at (60-75^{o}C). An organic solvent such as n-hexane was used.

The transertification of coffee oil was carried out in a 500 mL spherical flask. The molar ratio of methanol to oil was 9:1. The catalyst used was sodium hydroxide (NaOH) with amount 1% (w/w). At the end of the reaction, the mixture is transferred to a decanter for glycerol and methyl ester separation with the help of gravity for 24 H. As the two phases get separated, the excess alcohol in each phase was removed by flash evaporation at 90^{o}C. The methanol which is removed can be reused again. The oil content from spent coffee grounds has 15% on dry weight basis. It results in low operation cost compared to other oil seeds. FFAs and water content are two major parameters which influence production of biodiesel. The oil from coffee grounds has 0.62% FFAs measured and 795.4 mg g^{-1}. The density limit of any biodiesel must be between 860 & 900 g m^3. The results obtained were within the specified limit. The spent coffee ground oil has a viscosity of 5.6 $mm^2\,s^{-1}$. The oil extracted possesses better stability due to its high anti-oxidant nature. The fatty acids profile of oil showed that it composed of palmitic acid and linolic acids with 33.93 wt % and 23.27 wt %. The coffee oil was extracted and chemically converted via transertification reaction and the solid waste can be utilized as compost.

(Mebrahtu Haile et al. 2014) has aimed to study the extraction of biodiesel from spent coffee grounds by a two step biodiesel production process. He collected the spent coffee grounds (SCGs) and then allowed to dry in air for several days. Then the moisture content was evaluated by oven drying at 105^{o}C. 300 g of the dried sample of SCG was used for extraction. It was done in 2L round bottom flask of Soxhelet apparatus and extracted for 4-8h using n-hexane, ether and mixture of isopropanol to hexane ratio (50:50) as solvent. The oil was separated from solvents using a rotary evaporator. The two step biodiesel production processes are Acid-catalyzed esterification & Base-catalyzed transertification.

In acid-catalyzed esterification a 1L round bottom flask is used to perform the reaction. To homogenize, the SCG oil was heated to 54^{o}C and mixed with methanol (molar ratio alcohol to fatty acids of 20:1) and quantities of HCl (10 wt%). The reactor was stirred at 600 rpm and temperature of about 54^{o}C for 90 min. The mixture was poured to a separating funnel and allowed to settle for 24h. the unreacted methanol and water was removed from the mixture. In the base- catalyzed transertification, the process is done in a 1L two-necked round bottom reactor equipped with thermometer. The reaction was performed at a temperature of 54^{o}C for about 90 min with 1 wt% of KOH and methanol to oil water ratio of 9:1. The final mixture was cooled at room temperature and then transferred to a separating funnel for glycerol and methyl ester separation. It was kept idle for 24h to get separated by gravity and then excess alcohol was removed from both the phases using vacuum evaporator operated at 80^{o}C. The oil extracted has relatively higher oil content. The final results of the oil from spent coffee grounds has the properties like density of 0.88(g/cm^3), kinematic viscosity of 5.4(mm^2/s), calorific value of 39.6 (MJ/Kg), flash point of 22^{o}C, cloud point of 13^{o}C and water content of 0.01 (% volume).The fatty acids components investigation was done by Gas Chromatography which showed the presence of

C16-C20 methyl esters of fatty acids. The composition of linolic acid (37.3%), palmitic acid (35.7%), and stearic acid (8.1%) are determined. The oil was extracted mixing hexane and isopropanol (50:50 vol/vol) which allowed oil recovery of (21.5%) with comparatively lower cost.

(Nidia S. Caetano et al. 2012) has tried to carry the experiment collecting coffee grounds and allowed by oven drying at 105 ± ^{o}C followed by cooling in desiccators. 10 g of oven dried SCG (at 105^{o}C) and 200 mL of solvent was used in Soxhlet extractor for 2.5 h to 9.5 h of contact time. The oil extraction rate were determine for hexane, isopropanol and mixtures of both in volume ratios of (50:50, 60:40, 70:30, 80:20) The acidic value of oil was lowered by esterification with methanol and acid catalyst. The esterification was performed at 60^{o}C and 500 rpm in an orbital acclimatized shaker for 2.5 h. At the end of the step both phases of methanol and water were separated.

The transertification is performed by adding 40% (w/w) of methanol, with 1% (w/w) of NaOH catalyst for 2 h at 60^{o}C and 500 rpm. The biodiesel is then separated in a separatory funnel, washed with acidified hot water and followed by distilled water until neutral pH. The final biodiesel, which was being obtained from the oil recovered from SCG has a density of 911 (Kg/m^3) at 15^{o}C, kinematic viscosity of 12.88 (mm^2/s) at 40^{o}C, acid value of 2.14 [(mg KOH/g fuel)]. The iodine value is 46.5 [(g I_2/100g fuel)], which is quite low and means the oil is very saturated. The viscosity of the oil is too high to use in direct combustion engine chamber. The water content is 2004 (PPM). The oil was extracted with isopropanol and mixture of hexane/isopropanol (50:50, vol/vol) for higher oil recovery of (21% & 21.5% respectively) at a relatively lower cost.

(Mano Misra et al. 2008) has tried to study the extraction of biodiesel from spent coffee grounds (SCG) and the kinetics of transertification and purification by HPLC (High Performance Liquid Chromatography) was also discussed. He collected the coffee grounds and dried it overnight in an oven at 50^{o}C to remove moisture and then refluxed for 1h with n-hexane to extract the oil from the coffee particles. 300ml of solvent was used for 100g of dried spent coffee grounds for the extraction of oil. The solution was separated by filtration from coffee grounds and oil was separated from solvent using rotary evaporator. The crude oil was quantified using HPLC and the free fatty acids (FFA) were converted into soap by mixing caustic water with the oil extracted. Soap was removed by centrifuging the crude oil for 30min at 5000 rpm and the purified oil was used for biodiesel production through transertification.

The transertification was done by adding methanol and KOH (potassium hydroxide) to the TG (Triglycerides). The reaction mixture was refluxed for 2 h each time. A glass column of 150× 3.2 mm packed with C18 was used. The two phase A (methanol) and B (ispropanol:hexane = 4:5 by volume) was set. The reaction was stopped when the TG peaks in the HPLC analysis disappeared. The mixture was cooled at room temperature overnight and the bottom layer (i.e. glycerine) was separated. The top layer biodiesel was then washed twice with hot water (50^{o}C) and acidified water (0.5 wt% tannic acid) to take of the excess methanol and the traces of catalyst. For the complete conversion of oil to biodiesel 1.5 wt% catalyst and 40 vol% methanol was used. The presence of linolic acid (40.4%), palmitic acid (51.4%) and stearic acid (8.3%) was also determined. The %c and %N after the processing of oil was found to be 41.16% and 7.62% respectively. The C/N ratio was 15.7:1, indicating the processed coffee grounds can still be used as compost for gardens. The major composition of methyl esters in coffee biodiesel are from palmitic and oleic acid.

(G. Cholakov et al. 2013): has aim to study a better procedure for the extraction of coffee residues suitable for production of biofuel and adsorbents. The spent coffee grounds (SCG) and coffee husks (CH) were collected and dried in a laboratory oven at 105^{o}C for removal of water content. 300g of sample were performed on at least two Soxhlet laboratory extractors. Methanol and n-hexane was used as extragents. In a typical batch, about 60g of dried sample of SCG or CH was used for extraction in a Soxhlet extractor with 480ml (8 cm^3 solvent/g dry mass) solvent under refluxed for 20h. After extraction the solvent with the extract was filtered and distilled off. The use of sequences of solvents increases the amount of extracted liquid product both from SCG and from CH. The property of the extracts of SCG has C (69.10%), N (0.50%), O (20.40%) and H (10%), respectively with a yield of 12.2%. The coffee husk has C (51.99%), N (6.39%), O (33.86%) and H (7.76%).

The surface area of the active carbons (AC) prepared from CH-H by carbonization and chemical activation is 820 m^2/g and the active carbon prepared from CH-H/M by carbonization and chemical activation is 513 m^2/g. The surface area of both the active carbons from husks are relatively low and has much better adsorbing capacity. The extraction of SCG with methanol-n-hexane as binary solvent provides more flexibility in extraction and also minimise the extraction time.

(Tomasz Ciesel Czuk et al. 2015) has aim to study the use of spent coffee grounds (SCG) in energy recycling using a combustion process. The SCG which is a left over from coffee made is neutralized and dried in room temperature. This SCG was then mixed with grinding dust, from beech wood processing with SCG additive waste of 10 and 25% (m/m). Using SCG as an additive has some difficulties such as high humidity of waste prevented from briquetting. A product with 10 and 25% addition of SCG was characterized by lower density, lower hardness, and uneven surface to a product made without any addition.

Beech wood calorific value is high and SCG addition is making it even higher. The calorific value with 10% and 25% SCG additive is 19.12 (MJ/Kg) and 20.32 (MJ/Kg) respectively. The additive is worth considering due to a number of factors. It requires no additional investment while applying SCG as a biofuel component. It has high calorific value compared to other briquettes made from pure wood and hence it contributes to an increase of profit to use as an energy source.

RESULTS AND DISCUSSION

The various parameters which plays a vital role in the production of biodiesel are tabulated in the table below. The catalyst used like NaOH, and KOH for the extraction of oil by maintaining a reaction temperature of about 60-80^{o}C. N-hexane is also used as organic solvent. The reaction time is about 2-5 h with molar ratio of 5:1 to 9:1.

Table 1: Process parameters of biodiesel production from SCG

Molar ratio	Type of catalyst used	Amount of catalyst used (wt %)	Reaction time	Operating temperature
5:1 to 9:1	KOH, NaOH HCl	1-3	2 to 5 h	60-80^{o}C

CONCLUSION

- The conversion process of coffee grounds to biodiesel is quite easier and economical too.
- The various parameters, which is discussed above effects the conversion process of SCG to biodiesel.
- The various properties like density, kinematic viscosity, calorific value, flash point, cloud point, etc. is also being discussed.
- It can be the new alternative and potentially a low cost fuel. To improve the process of extraction and conversion to obtain even more higher amount of oil at comparatively low cost.

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