Production And Applications Of Biodiesel From High Acid Value Feedstocks

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ABSTRACT

Biodiesel is an oil derived fatty acid methyl esters that is produced through esterification processes. It could be produced from various types of oils including vegetable, animal and waste oils. Depending on the type of feedstocks used, the process of esterification must be tailored to the properties of the raw materials. Depending on the origin of the oils, different pre-treatments are required starting from the extraction of the oil. Two step process must be employed for feedstocks with high free fatty acid (FFA) values (>5%) as opposed to the one step transesterification step for feedstocks of lower FFA values. Crude seed oils (Jatropha and Bintangor Laut) and waste oils (Used Cooking Oils - UCO and Grease Trap Oils-GTO) are usually high in free fatty acid (FFA) values thus requiring further refining and/or a two-step esterification process. Among the most challenging feedstock carried out on FRIM's pilot plant are the grease trap waste oils from effluents and waste cooking oils. Starting from the preparation of the raw material up to the product (biodiesel) applications, smart and sound decision must be made during the production of biodiesel and identifying their end uses. After biodiesel production, identifying the product (biodiesel) applications suitable with their properties is very important due to the environmental and public health contributions of the whole value chain. End use should be identified based on the biodiesel stabilities. The benefits of extracting, conversion and application of the oils and biodiesel are tremendous. This paper will discuss the challenges faced in producing biodiesel of different properties from various feedstocks focusing

ISSN 1823- 5514, eISSN 2550-164X

Received for review: 2017-07-25
Accepted for publication: 2017-07-27
Published: 2018-05-15

on the jatropha, bintangor laut crude seeds oil, grease trap and waste cooking oils and their applications.

Keywords: *biodiesel, properties, seeds oil, waste oils, applications*

Introduction

Biodiesel precursors such as fresh seed oils and waste oils are derived from fruits and industrial activities. Extraction of these types of oils are seen to be contributing to the second generation biofuels that does not compete with food chain. Many types of seeds produces oils that are edible, however Jatropha and Bintangor laut seeds belongs to the non-edible seeds that contain oils up to 30 – 40%. Jatropha (*Jatropha curcas*) and Bintangor Laut (*Callophylum innophylum*) are commonly found growing on idle land and sandy soils especially by the sea respectively. Being a shady tree Bintangor Laut is usually used in landscapes. Used cooking oil are usually collected from home kitchen and eateries. Collection campaigns by municipal councils usually aimed at cleaning the environment. Grease trap oils are derived from the process of servicing grease traps from eateries effluents. Service contractors are usually not properly educated on proper methods of servicing the grease traps and ultimately the oils ends up in the waterway thus polluting the rivers and waterways.

Methodology

Preparation of Raw Material

Extraction of crude oil from the seeds of Jatropha (CJO) and Bintangor laut (CBO) seeds require different procedures since the size and shapes are different. Jatropha seeds oil extracted out from the fruits and the CJO obtained by directly pressing the seeds using rolling pressing machines. On the other hand, extraction of CBO requires the fruits to be steamed first followed by roller pressing. Waste oils such as UCO are being collected from households and eateries must be filtered and allowed to stand for sediments to settle. Grease traps oils (GTO) are extracted from grease traps using methods of heating the residues and allowed to solidify. The solids are then separated from the non-oil components, heated again and filtered. Thus extraction of GTO requires a larger working area

Biodiesel Production

Acid Esterification

The grease trap oil was esterified to triglycerides in a pre-treatment process with methanol using anhydrous H_2SO_4 (acid catalyst). The reaction was conducted at 60 ± 5°C for 60 min. After this time, the mixture was poured into a separatory funnel, where the excess methanol along with impurities moved to the top layer and was removed. The bottom layer was used for the alkali transesterification.

Alkali Catalyzed Transesterification

The bottom layer product of acid esterification was heated to the desired temperature before being synthesized by the catalytic transesterification using methanol as aliphatic alcohol and KOH as base [1]. The mixture was heated under reflux at 60 ± 5° C for 60 min. After this time, the mixture was poured into a separatory funnel and the product was allowed to settle under gravity for 12 h in a separating funnel. The products of the alkali transesterification process result in the formation of two layers viz., an upper layer containing a mixture of small quantities of unreacted oil, glycerol and transesterified products (esters) and a lower layer of glycerol. The lower layer of glycerol was removed.

Post Treatment Process

The transesterified product (methyl esters or raw biodiesel) was mixed gently with distilled water (30% volume of distilled water to volume of biodiesel) at 60± 5°C in order to remove impurities like catalysts. The mixture was allowed to settle under gravity for 8 h. The settled layer of mixture with impurities was drained out. Water wash was repeated till the pH of drained water was measured in the range 6 to 7. After washing, the final product was again heated to 120°C for 3 to 4 hours to remove excess water.

Analysis (Acid number; FFA; calorific value; cetane number; pH; moisture)

The total acid value and free fatty acid (FFA) of the samples were determined according to the ASTM D664 (2011) method, and calorific value was determined using a Bomb Calorimeter Leco AC 500 (Germany). Moisture content of oil and biodiesel was determined by Karl Fisher method using a Metrohm 831 KF Coulometer instrument (Herisau, Switzerland). Density/specific gravity of samples were determined by using densimeter model Alfa Mirage MD 300s (Japan). The colour of the sample determined by visual examination.

Results & Discussions

The initial properties of crude oils were determined and shown in Table 1. Results showed that the extraction yield for seed oils for jatropha and Bintangor laut are in the range of 30-40 % based on the seeds. For waste oils, UCO (85%) gave higher extraction rate compared to GTO (20 –30%). This is because UCO is collected in the form of liquid whereas GTO is extracted from semi solid effluents trapped in the grease trap. The UCO only requires heating followed by filtration whereas GTO requires several heating procedures before filtration can be carried out. . Extraction experiments and analysis carried out showed the average values of crude oil yields extracted from the methods depicted in Table 1. Results showed that all crude oils obtained were of high acid values compared to crude palm oil.

Table 1. Crude oil yield after extraction and properties of oil

Source	CJO	CBO	UCO	GTO	CPO
Crude Oil Yield (%)	30	40	85	20-30	>95
Acid value mg (mgKOH/g)	26.5	38	20.78	132.58	0.31
Free Fatty Acid (FFA) (mg KOH/g)	13	19	10.39	66.29	0.15
Calorific value (MJ/kg)	37-38	38.6	38.16	39.76	36.54
Moisture (%)	<2	7.07	3.21	1.25	2.24
Density/ specific gravity	0.879	0.888	0.834	0.891	0.881
Colour	YB	DG	YB	DB	YB

Legend: CJO: Jatropha — YB: Yellowish Brown
CBO: Bintangor laut — DG: Dark Green
UCO: Used Cooking Oil — YB: Yellowish Brown
GTO: Grease trap Oil — DB: Darker Brown
CPO: Crude palm Oil — YB: Yellowish Brown

Table 2 shows the properties of biodiesel from different type of crude oils with high free fatty acid (FFAs) contents compared to the ASTM 6751-15 [2]. These preliminary results indicated that the properties of methyl esters did not meet the complete "fuel grade" requirements for especially for the acid number and moisture content specification.

Stability Issues of Biodiesel Applications In Engines

Aging and oxidation reactions contributes to the instability of biodiesel after production. These reactions lead to high acid numbers, high viscosity, and the formation of gums and sediments during storage [3]. Thus appropriate stabilizing agents such as must be employed to handle this problem. An increase in MC of biodiesel is due to absorption of moisture at higher surrounding temperatures which then precipitates out when the temperature drops. Water accumulation will occur at the bottom of the storage vessels and the process will repeat [4].

Table 2. Properties of biodiesel from crude oils extracted

Source	CJO	CBO	UCO	GTO	ASTM
Acid number (mgKOH/g)	9.25	5.12	0.92	5	0.5 max
Free Fatty Acid (mg KOH/mg)	4.62	2.56	0.46	2.5	0.25 max
Density (kg/m^3)	0.879	0.888	0.834	0.834	0.860-0.900
Calorific Value (MJ/kg)	37.5	41.4	38.16	39.76	N.S
pH	N.S	N.S	6.54	1.2	N.S
Moisture (%)	0.1	N.S	3.21	1.25	0.05max

N.S: not specified
Legend: CJO: Jatropha
CBO: Bintangor laut
UCO: Used Cooking Oil
GTO: Grease trap Oil
ASTM: ASTM D6751-15

Oxidation stability of biodiesel derived from high acid number waste oils monitored from previous experiment showed that the biodiesel oxidative stability decreased with respect to time during storage. Thus for standard compliance additive must be added. The addition of the antioxidant can improve and maintain oxidative and storage stability of the biodiesel B100 over a 12 weeks period. The binary combination TBHQ: PG and TBHQ: BHT also showed better performance than either individual antioxidant or can improve oxidative and storage stability of grease oil-based biodiesel (B100) for up to 12 weeks [5]

Successful applications

Biodiesel derived from high FFA feedstocks are usually not stable and undergoes oxidation. The options on its application or use must take into account this features. Oxidation is the reaction of the products with moisture and light resulting in rancidity and sedimentation. When this occurs the properties of the biodiesel will not satisfy the stipulated standards. Hence it does not qualify for use as biofuel for engines/vehicle applications.

Nevertheless the biodiesel could be used in none or less strict applications. For example as a fuel in stoves and as replacements for fossil diesel in various green activities such as carriers for active ingredients in mosquito fogging. A complete waste recycling will be achieved with high impact on the environment and minimum cost [6].

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