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USE OF COW TALLOW AS A FEEDSTOCK FOR BIODIESEL PRODUCTION

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ABSTRACT

Cow Tallow a by-product of slaughter houses can be used as a viable feedstock for the production of biodiesel due to its high yield capacity, availability, and low cost. Sodium hydroxide and methanol were used as catalyst and solvent respectively. Characterization of oil and biodiesel samples were carried out using Association of analytical chemist (AOAC) and American society of testing and materials (ASTM) respectively. Other characterization methods used were Fourier transform Infrared Spectroscopy (FTIR) and gas chromatography-mass spectrophotometry (GC-MS) techniques. FTIR (Fourier Transform Infrared spectroscopy) was carried out to characterize (identify the constituent elements) of both the feedstocks and their methyl esters. The fatty acid profile of the raw feedstocks and the produced methyl esters were taken to ascertain the % concentration of the different fatty acids and their effect on the quality of biodiesel produced . The physico-chemical properties of the bioiesel produced were also determined and compared with standards. A biodiesel yield of 92.33 wt% was obtained which thus confirms that cow tallow was a viable feedstock for the production of biodiesel.

INTRODUCTION

Rising petroleum prices and concerns raised from environmental pollution caused by its exploration and refining has demanded additional efforts in seeking alternative energy sources. The study of biofuels as an alternative to fossil fuels has gained popularity over the last decade due its reliability as a renewable fuel. Biodiesel production from low-cost feedstocks are needed since biodiesel from food-grade oils are not economically competitive with petroleum-based diesel fuel. Biodiesels are renewable, non-toxic, and biodegradable, and therefore, are a promising alternative to fossil diesel fuel (Chincholkar et al, 2005). In addition to a number of technical advantages of biodiesel, such as prolonged engine life due to better lubricating property, higher flash point that makes them safer during storage and transport, biodegrability, and non-toxicity, it is also environmentally-friendly due to reduced exhaust emissions (Hoda, 2010). Biodiesel are fuels composed of mono-alkyl esters of long chain fatty acids. The long and branched chain triglyceride molecules are transformed into mono-alkyl esters and glycerol through esterification/transesterification reactions. Biodiesel can be prepared from animal fats by the transesterification of triglycerides (TG) with methanol using an alkaline, acid or enzyme catalysts (Taher et al.,2011). Cow/Bovine tallow is however a very promising feedstock because of its low cost, availability without competition with food market, high calorific value, high number of cetanes, and most importantly, because of its high conversion rate (do Santos et al.,2018). Transesterification is performed commonly using a base catalyst, such as sodium hydroxide or potassium hydroxide (NaOH, KOH), and methanol due to their low prices, effectiveness, low concentration, and heat requirements in the reaction.

This study seeks to establish cow tallow as a potent feedstock that can be used for production of high quality biodiesel.

2 Experimental Methods

2.1 Reagents and Materials.

Methanol (Sigma-Aldrich), NaOH flakes, Phenopthalene, Sulphuric acid, Magnesium trisilicate ($MgSi_3$), Sodium Sulphate, Diethyl ether.

2.2 Apparatus and Instruments.

Beakers (20ml, 50ml, 100ml), Centrifuge (Hettich University II), Conical Flasks (20ml, 50ml,100ml, 1000ml), Cuvettes, Electronic Weighing Balance. (B. Bran Scientific, England), Heat drying oven (DHG Series Ocean Med+ England), Electronic Temperature Regulation Heating Mantle (98-I-B Series), HH-S Thermostatic water Bath (DKS Series; Ningbo Biocotek Scientific Instrument Co.,Limited, Measuring Cylinder, Pipette (1ml, 2ml, 5ml, Pyrex), Test tubes (5ml, 10ml, Pyrex), Gas chromatography coupled FID and ECD, Buck Scientific Infra-red Spectrophotometer. Model (M530), Seperating Funnel.

2.3 Esterification.

Equal volume of cow tallow and alcohol (methanol) was mixed in a beaker, Sulphuric acid in the ratio of 1:10 to the solution was added, the solution was then heated and stirred over varied temperatures, time and speed. The Solution was then separated in a separating funnel.

2.4 Biodiesel separation.

After the base transesterification process, the reaction mixture was allowed to settle for 24 hours inside a separating funnel to allow clear separation of biodiesel from glycerine by gravity. The layer on the top was the biodiesel while the bottom layer was the glycerol. Thereafter, the two layers were separated by settling using separating funnel. The biodiesel separation was carried out by decanting as the glycerol was drained off while the biodiesel remained.

2.5 Gas chromatography analysis.

The fatty acid composition of the biodiesel samples was analyzed by gas chromatography coupled with mass spectrometer according to AOCS official method Ce 2-66. The gas chromatographic analysis was made using GC-MS-QP2010 plus, Shimadzu. The GC column used was calibrated by injecting methyl ester standards. Good seperations were achieved by diluting the samples (n-hexane collected) in a small amount of ethyl acetate. The carrier gas used was hydrogen and its flow rate was regulated at 41.27ml/mins while the column flows at 1.82ml/mins. The oven temperature was set at 80°c before rising up at 6°c/min until 340°c. The identification of peaks was done by comparison of their retention time and mass spectra with mass spectra library (NIST05s LIB) (Fu et al., 2008).

2.6 Physico-chemical analysis.

The physico-chemical analysis of the oils were determined by ASTM and AOAC, (2000) standard methods. The kinematic viscosity was determined by ASTM D-445 method, the density was determined by ASTM D-1298 method and the pour point determination was made using ASTM D-97method. The flash point of the fuel was determined by ASTM D-93 the cloud point was estimated according to ASTMD-2500 and acid value was measured following the ASTM D-664 method. The refractive index was determined using AOAC 921.08. the specific gravity was ascertained using AOAC 920.212 and iodine value using AOAC 920:159. The sulfur content and calorific value were determined according to ASTM D-4294 and ASTM D-246 respectively. The moisture content was obtained using air oven method using the rotary evaporator oven (BTOV 1423).

3.0 Results and Discussion.

3.1 Cow Tallow biodiesel composition.

. The ideal mixture of fatty acids has been suggested to be C16:1, C18:1 and C14:0 in the ratio 5:4:1. Such a biodiesel would have the properties of very low oxidative potential (Knothe, 2005: Schenk et al, 2008). Though this ratio is not always realized most of the time, it paints a piture of the ratio of unsaturated to saturated fatty acid profile needed for oxidative stability in a biodiesel fuel. It shows that the unsaturated fatty acid should have a higher ratio to the saturated ones. This was not the case in the cow tallow biodiesel as the unsaturated fatty acid was lower than the saturated fatty acid in the ratio (45:54) as seen in table 3.1 below. This is not ideal as oxidative stability is influenced by unsaturation (Ramos et al, 2009). The high percentage of oleic acid which is a low degree unsaturated fatty acid however compensates for the saturates in stearic and palmitic acid. In view of this, saturated fatty acid could be reduced or unsaturated fatty acids increased by controlling culture conditions.

Table 3.1: Tallow biodiesel fatty acid profile

Component	Name	Concentration (µg/ml)	% Concentration
C18	Stearic Acid	28.2844	31.862
C16	Palmitic Acid	15.5274	17.491
C14	Myristste	3.1727	3.574
C18:2	Linoleic Acid	4.2171	4.75
C20:2		0.7706	0.868
C20:5		2.9883	3.366
C18:1	Oleic Acid	32.5555	36.673
C12	Lauric Acid	1.255	1.413
Total		88.771	

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3.2 Effect of fatty acid profile/ structure on physico-chemical property of biodiesel

The important parameters for a potential biodiesel are viscosity (mm^2/s), oxidative stability (h), cetane number, cold filter plugging point (°C), density (kg/m3), saponification value (mg

KOH/g-oil), iodine value ($mgI_2/100$ g), and high heating value (Kumar and Sharma, 2016).

These biodiesel properties are majorly affected by compositional variations including fatty acids type, chain length, number and position of double bonds. Hoekman et al,(2014), proposed a correlation between unsaturation and biodiesel properties such as viscosity (mm^2/s), cold filter plugging point (°C), cetane number, iodine value ($mgI_2/100$ g), density (kg/m^3), and high heating value. High saturation in fatty acid profile supports the cetane number (CN), kinematic viscosity, and cold flow behavior. The effect of saturation on the cloud point (cp) can be highlighted when the cloud point of fish oil methyl ester (FOME) prepared by Kudre et al (2017) with a lower ratio of saturated fatty acid (30.8) had a low cloud point of -5°c while cow tallow methyl ester with a higher degree of saturation (54) recorded higher cloud point of -3 to 9°c as seen in table 3.2 below. Unsaturation in fatty acid profile supports the density and high heating value of biodiesel (Jakeria et al, 2014). The flash point of highly unsaturated methyl esters such as soyabean oil methyl ester (SME) as studied by Shumaker et al (2007) has higher flash point of 171°c when compared to cow tallow methyl ester (CTME) with lower ratio of unsaturates having a lower flash point of 81°c. It has been observed by several researchers that combustion characteristic of fuel is also dependent on properties of particular biodiesel in which CN play an important role in engine performance (Yusuf et al, 2011). Properties like density and heating value are directly correlated with CN. Due to higher oxygen content, biodiesel has higher CN which provides smoother engine operation (Atabani et al 2012).

CN of biodiesel varies according to different feedstocks utilized in the production of biodiesel. Researchers have shown that biodiesel possesses low viscosity than vegetable oil, so its flow rate is higher than other oils (Sivaramakrishnan and Ravikumar, 2012). The main problem associated with biodiesel is low-temperature performance due to its high cold filter plugging point. Parameters like cold filter plugging point (CFPP), cloud point (CP), low-temperature filterability test (LTFT) which determines the cold flow behavior of diesel fuel are also affected by the compositional changes in fatty acids (Nainwal et al, 2015).

Cow tallow biodiesel recorded a high acid value of 0.984 mgKOH/g as compared to ASTM D6751 standard of 0.5 mgKOH/g. this could be attributed to the high moisture content of the cow tallow (feedstock). Do Santos et al (2018) compared two bovine tallows with moisture contents of 0.2% and 0.8%, and obtained acid values of 0.6 mgKOH/g and 2 mgKOH/g respectively. This thus inferred that high humidity forms additional free fatty acids (FFA) leading to saponification reaction, which cause losses during the biodiesel production. The low peroxide/acid value (1.9) could be attributed to the low percentage of poly unsaturated fatty acids available in cow tallow biodiesel. This is because poly unsaturated fatty acid methyl ester such as linolenic acid (C18:3) which is abundant in some other biodiesel fuels with higher peroxide values oxidize faster than other less unsaturated fatty acids like oleic acid (C18:1) (Yamane et al, 2001). This thus makes biodiesel with less unsaturated fatty acids not easily oxidized thus resulting in lower peroxide values as in the case with cow tallow biodiesel.

Table 3.2 Physico-chemical properties of cow tallow and cow tallow biodiesel

Physico-chemical properties	cow tallow	cow tallow biodiesel
Acid Value (mgKOH/g)	0.22	0.984
Specific gravity (m/v)	0.875	0.842
Ash content	0.081	0.09
Moisture content	1.32	0.61
Viscosity (mpas)	35.6	1.52
Calorific Value (KJ/Kg)	34,032	34,216
Refractive index	1.614	1.4435
Cloud point (°C)	47	-3
Pour point (°C)	-	-9
Flash point (°C)	135	81

Saponification value (mgKOH/g)	200.72	161.5
Iodine value (Wij's)	47.5	33.5
Peroxide value (Meq/Kg)	1.7	1.9
Smoke point (°C)	130	78
Titre (°C)	47	-15
Conductivity (μs/cm)	-	nil
Sulphur (%)	0.1	0.08

3.3 Comparison of cow tallow methyl esters (biodiesel) with other biodiesels and fossil diesel.

Methyl esters obtained from cow tallow (CTME) were compared with other methyl esters namely: soyabean soapstock methyl ester (SSSME), coconut oil methyl ester (CME), soyabean methyl esters (SME), Palm kernel methyl ester (PKME), Rapeseed oil methyl ester (RME), and Palm oil methyl ester (PME). Conventional fossil diesel fuel (JIS #2) and ASTM 6751 biodiesel standards were also used as a reference for comparison. The net calorific values of methyl ester fuels are about 15% lower than that of the diesel fuel as seen in table 3.3 below. Comparing the net calorific values in methyl ester fuels, CTME, the cow tallow biodiesel had a low calorific value of 34.2 MJ partly due to its animal origin whose calory level are naturally lower compared to biodiesels of plant origin. Soyabean methyl ester (SME) had the highest calorific value due to the high calory content of the feedstock (soyabeans). Furthermore, less net calorific value make more fuel consumption for combustion. The calorific value of the methyl esters could be brought to par with the diesel fuels through more efficient separation and purification of the feedstock. Blending with fossil diesel could also help in bridging the calorific value gap. The densities of methyl ester fuels were generally higher than that of the diesel fuel. The density of cow tallow methyl esther (CTME) is 842 kg/m^3 which is lowest of the methyl ester fuels though falling within the range of the standard limits. The kinematic viscosities of the methyl ester fuels are higher than that of the diesel fuel except for the cow tallow biodiesel. This serves as an advantage it has over other methyl esters as although they fall within the standard limits, the high density and kinematics viscosity could cause negative effects on the combustion process such as advance fuel injection timing and poor combustible mixture formation. Cow tallow methyl ester (CTME), Coconut oil methyl ester (CME) and Palm Kernel methyl ester (PKME) though having lower kinematics viscosities compared to the other methyl ester fuels have their viscosity values closer to that of the fossil diesel fuel. The pour points of all methyl ester fuels are higher than that of the diesel fuel. The cow tallow biodiesel pour point falls well within the standard ASTM limits thus making it the most favourable in terms of pour point values. Among the methyl ester fuels, the pour point of cow tallow biodiesel (CTME) was the lowest and Palm oil methyl ester (PME) recorded the highest pour point as seen in table 3.3 below.

Table 3.3: Comparison of Physicochemical properties of methyl esters with fossil fuel and standards.

Physico-chemical properties	CTME	SSSME	CME	PME	PKME	RME	SME	JIS#2 (Fossil diesel)	Standard min	Standard max
Calorific value (MJ)	34.2	30.7	35.22	36.85	35.61	36.55	38.22	43.12	35	

Density (Kg/m^3)	842	870	874	879	877	886	883	826	-	880
Kinematic viscosity (mpas)	1.52	4.1	2.7	4.5	2.9	4.5	4.1	2.5	1.9	6
Pour point (°C)	-9	0	-5	12.5	-5	-7.5	0	-12.5	-15	0

4 Conclusion.

- Cow tallow is a good and viable feedstock for the production of biodiesel.
- Biodiesel obtained from cow tallow compared favourably with methyl esters from other feedstocks and fossil fuels
- Varying of reaction parameters had an effect on the biodiesel yield and quality.
- The fatty acid profile of the methyl esters had an effect on the physico-chemical properties and quality of the biodiesel.

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