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BIODIESEL PRODUCTION FROM SOME BIOMASS SOURCES AVAILABLE IN VIETNAM

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ABSTRACT

Fossil fuels are being depleted at an alarming rate. Alternative fuel sources such as biofuels seem to offer a promising solution to meet the energy demands. This research focuses on: (Phase 1) extracting oils from some biomass sources available in Vietnam, namely, Cashew nut, Castor seed, Makapuno coconut kernel, Calophyllum inophyllum seed, and Terminalia captappa seed, (Phase 2) converting oils to biodiesel using a transesterification process, and (Phase 3) evaluating the properties of resultant biodiesels and blends. Analysis of the physiochemical properties showed that the produced biodiesels can be the potential candidates for the feedstock in biodiesel production in Vietnam as they exhibited fuel properties within the limits prescribed by the latest American Standards for Testing Material (ASTM), European standards (EN) and Japanese Industrial Standard (JIS). However, Castor oil biodiesel is unsuitable in pure state for its direct use as fuel in internal combustion engines because its kinematic viscosity at 40°C is extremely high (20.76 mm^2/s), exceeding by far the international standard upper limit (5.0 mm^2/s). Thus, Castor oil biodiesel was blended with diesel at 5%, 10% and 20% on a volume basis (B5, B10, B20), respectively, and the quality was evaluated in terms of kinematic viscosity as well as the density at 18℃, gross heating value, and copper strip corrosion for 3 hrs at 50°C. The results showed that physicochemical properties of the blends of Castor oil biodiesel and reference diesel were satisfactory according to international standards such as ASTM, EN and JIS.

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1 INTRODUCTION

Use of renewable energies is now being widely promoted as a countermeasure for global warming. Bioenergy, an environmentally friendly form of energy using organic materials generated as waste byproducts, is attracting especially widespread attention as a primary energy resource ideal for a sustainable society. Biodiesel is an alternative diesel fuel consisting of alkyl monoesters of fatty acids prepared from vegetable oils and animal fats. It has been the focus of a considerable amount of recent research because it is renewable, reduces the emission of some pollutants, and is also readily biodegradable in the environment (Zhang *et al.*, 1998). Here we chose Cashew nut, Castor seed, Makapuno coconut kernel, *Calophyllum inophyllum* seed, and *Terminalia captappa* seed for biodiesel production.

Objective of the present work is to investigate the physicochemical properties of biodiesel fuels produced from some feedstocks that have not yet been utilized widely, i.e. Cashew nut oil (CSO), Castor oil (CTO), Makapuno coconut oil (MCO), *Calophyllum inophyllum* oil (CIO) and *Terminalia catappa* oil (TCO). Besides, data of biodiesel–fuel diesel blends (B5, B10, and B20) prepared from CTBDF were also presented in this work.

2 MATERIAL AND METHODS

2.1 Material

CSO was obtained from Bien Hoa industrial zone, Dong Nai province. The seeds of Castor, *C. inophyllum*, and *T. catappa* were collected in some provinces of Mekong Delta, whereas Makapuno coconut kernels were collected from Tra Vinh Province where they are cultivated in the large area. These oils were extracted with hexane using a Soxhlet apparatus. Thereafter, hexane was removed by rotary evaporation to provide oils. All chemical reagents used for oil extraction as well as for chemical analysis experiments were of analytical grade.

2.2 Methods

2.2.1 Conversion of oil into biodiesel

CSO, CTO, MCO and TCO were converted to methyl esters using a transesterification process in methanol by the use of alkaline catalyst KOH. The procedure details have been described previously by Dat (2009). CIO has the high level of acid value compared to other oils as shown in Table 3. High acid value (AV) is due to the presence of more amount of free carboxylic acid in the oil. The crude oil of CIO was methyl esterified in the presence of sulfuric acid catalyst prior to the methyl esterification in order to prevent the damage of alkaline catalysts (Dat, 2010).

2.2.2 Fatty acid profile

Fatty acid methyl ester contents were analyzed by gas chromatograph mass spectrometer, equipped with the TG–SQC GC column (15m × 0.25mm × 0.25µm) (Thermo scientific). The carrier was helium gas with a flow rate of 1.2 mL/min. The following temperature program was employed: initial temperature was 60°C, heating at a rate of 10°C/min up to 260°C and holding at that temperature for 1 min. Identification of fatty acid methyl esters and the relative amount were defined by use of the computer program installed in the GC–MS system.

2.2.3 Physicochemical properties

The oils and biodiesels derived from selected species were analyzed and characterised for various biodiesel properties such as ***viscosity,*** i.e. the resistance of a fluid to flow through a tube. The kinematic viscosity was determined at 40°C by multiplying the viscometer tube constant with the measured efflux time. The efflux time is the time taken for a known volume of liquid measured at room temperature to pass through a calibrated glass capillary viscometer tube. In this study, the kinematic viscosity of raw oils and their esters were measured with a Viscosity Measuring unit ViscoClock (Schott Instrument), according to the standard method ASTM D445–6. All measurements were replicated three times. In this study, AV of extracted oil and biodiesel was determined by volumetric titration according to the standard method ASTM D664–07 (2007). Data of density at 18°C, flash point, gross heating value and copper strip corrosion value for 3 hrs at 50°C were obtained by the Center of Analytical Services and Experimentation (CASE) in Can Tho, Vietnam.

3 RESULTS AND DISCUSSION

3.1 Fatty acid profile of raw materials to produce biodiesel

The fatty acid identification was carried out by the use of gas chromatographic method as described previously in the experimental section. The fatty acid profile and composition of the oils used for biodiesel production in the present work is summarized and shown in Table 1. In Cn:x, n represents the number of carbon chain and x is the number of unsaturation in the fatty acid.

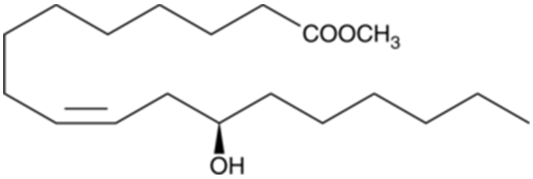
Table 1: Fatty acid composition of the oils derived from various species

Structure	Fatty acid	CKO	CTO	MCO	CIO	TCO
C8:0	Octanoic	–	–	6.13	–	–
C10:0	Decanoic	–	–	9.14	–	–
C12:0	Lauric	–	–	34.95	–	–
C14:0	Myristic	–	–	22.52	–	–
C16:0	Palmitic	8.54	–	14.11	15.54	33.79
C18:0	Stearic	6.77	–	4.11	13.75	7.47
C18:1	Oleic	66.84	–	9.04	41.19	33.62
C18:2	Linoleic	17.37	4.61	–	29.07	24.93
C20:0	Arachidic	0.28	–	–	0.45	–
C20:2	Eicosadienoic		4.65	–	–	–
Others		0.2	90.75*	–	–	–
∑Sat		15.59	–	90.96	29.74	41.26
Monounsaturated		66.84	90.75	9.04	41.19	33.62
Polyunsaturated		17.37	9.26	–	0.45	24.93
$\overline{M}_{oil}$		875.26	932.34	696.32	872.74	872.74
APE		168.42	9.22	18.08	140.52	117.1
BABE		17.37	4.61	0	29.07	24.93

APE = 2 × ($C_{18:1}$ + $C_{18:2}$ + $C_{18:3}$): Allylic Position Equivalent. Calculated from Eq (4) in Ref. (Demirbas, 2007)

BAPE = C18:2 + 2C18:3: Bis–Allylic Position Equivalent. Calculated from Eq (6) in Ref. (Demirbas, 2007)

Methyl ricinoleate (C18:1 OH):



$$\overline{M_{oil}} = 3\overline{M_{FFA}} + M_{glycerol} - M_{water}$$

$\overline{M_{oil}}$: the average of oil moleular weight

$M_{glycerol}$: the glycerol molecular weight

M_{water} : the water molecular weight

The average of oil molecular weight was calculated using equation (1), according to Ref. (Filliéres et al., 1995) and Ref. (Halvorsen et al., 1993)

∑Sat = C8:0 + C10:0+ C11:0 + C14:0 + C16:0 + C17:0 + C18:0 + C20:0

∑Monounsat = C18:1 + C20:1

∑Polyunsat = C18:2 + C18:3 + C20:2 + C20:3

** ricinoleic acid*

It can be seen that TCO is composed of 40% saturated fatty acids and 60% unsaturated fatty acids with one or two double bonds. CSO is mainly composed of 66.84% oleic component (C18:1) in a triglyceride with various other fatty acids just like other vegetable oils. In CTO, the fatty acids consist of approximately 90% ricinoleic acid, which contains hydroxyl (–OH) group. This contains also 4% linoleic acid (C18:2) and 4% eicosadienoic acid (C20:2). The high content level of ricinoleic acid is the reason for the versatile value of CTO in technology. At a glance, MCO is characterized by a high content of saturated fatty acids (90.96%) as a result of its solid form at room temperature. Oleic acid (C18:1) and linoleic acid (C18:2) were the major components of CSO and CIO according to the GC–MS analysis. Generally, there exists a clear dependence of the type and percentage of fatty acids in the oil on the plant species and the growth conditions. High saturated fatty acid alkyl esters in general lead to increasing the cloud point, cetane number, and stability.

It is also important to remark that the low content of allylic methylene carbon on the fatty acid chains and the absence of linolenic acid of the MCO may provide advantages in terms of the oxidation stability of MCO.

3.2 Key characteristics of biomass sources

The physicochemical properties of different oils in the present study was summarized and shown in Table 2.

Table 2: Key characteristics of biomass sources for biodiesel used in the present work

Properties	Raw materials to produce biodiesel				
	CSO	CTO	TCO	CIO	
Color	Brown	Transparent	Yellow	Greenish yellow	
Kinematic viscosity at 40°C, mm^2/s	29.35	165.10	24.05	60.24	29.05
Acid value, mg KOH/g	2.5	4.06	0.5	52.5	0.65
Oil content, %	–	40	60	65	49
Conversion, %	87	98	92	90	90

The color of CSO, CIO and TCO were yellowish or brownish, while CTO and MCO were transparent. Other important difference between these oils is the kinematic viscosity, and CTO showed 165.1 mm^2/s, which was much bigger than those of other vegetable oils.

The values of kinematic viscosity at 40°C are several times higher than that of petro diesel of about 3.15 mm^2/s. As a result, these crude oils cannot be used as fuels for diesel engines directly. Several ways have been considered to reduce their high viscosity, and transesterification is the best choice, as the physical characteristics of fatty acid esters (biodiesel) are close to those of diesel fuel. Among all oil parameters studied, viscosity of the oils of these species differed the most markedly. It ranged from 24.04 mm^2/s to 165.10 mm^2/s, with CTO having very high viscosity. The extraordinarily high viscosity of CTO (165.1 mm^2/s) is attributed to the presence of this hydroxyl group of ricinoleic acid, which is an unsaturated fatty acid occurring in natural vegetable oils with a function of secondary hydroxyl group. The chemical structure is shown in the bottom of Table 1.

Biodiesels are produced from CSO, CTO, MCO, and CO by alkaline-catalyzed methyl esterification. However, this process is not suitable for production of biodiesel from CIO having acid values of 52.5 mg KOH/g. If the feedstock contains a significant percentage of free fatty acid (FFA), typical homogenous base catalysts such as sodium or potassium hydroxide or methoxide will not be effective for transesterification, but an unwanted side reaction in which the catalyst react with FFA to form soap in the form of sodium or potassium salt of fatty acid should take place. Thus the reaction irreversibly quenches the catalyst, and it results in the formation of undesirable mixture of FFA, unreacted triacylglycerols, soap, diacylglycerols, monoacylglycerols, glycerol, water, and/or methanol. A further complicating factor of high FFA content is the production of water upon reaction with homogenous base catalysts. Water can participate in hydrolysis with biodiesel to produce additional FFA and methanol. Hence, the two–step esterification method, i.e. an alkaline–catalyzed transesterification followed by the acid–catalyzed pretreatment, was employed for biodiesel production from these FFA rich bioresoueces.

C. inophyllum seeds contain 60.24% oil which is greenish yellow in color and the oil has very high acid value of 52.5 mg KOH/g. Despite its high acidity level, the oil can be converted to biodiesel with a conversion efficiency of 90%. Oil content was in the range of 40–65% in other species. As can be seen also from the Table 2, there are not so much differences in the conversion rate of oil to biodiesel. They range was from 87–98% depending on the procedures adopted and the source of oil used. The higher acid value seemed to have not so much effect on biodiesel conversion by transesterification.

3.3 Biodiesel characterization

Table 3: Physicochemical properties of biodiesel

Specification	CSBDF	CTBDF	MCBDF	CIBDF	TCBDF	Diesel Nº2
Acid value (mg KOH/g)	0.37	0.14	0.12	0.3	0.31	–
Kinematic viscosity at 40ºC (mm^2/s)	4.81	20.76	3.33	4.82	4.19	3.15

Acid value, mg KOH/g : ASTM (0.5 max.), EN (0.5 max.), JIS (0.5 max.)

Kinematic viscosity at 40°C, mm^2/s : ASTM (1.9–5.0), EN (3.5–5.0), JIS (3.5–5.0)

MCBDF: Makapuno coconut biodiesel fuel; CSBDF: Cashew nut biodiesel fuel; CTBDF: Castor biodiesel fuel; CIBDF: Calophyllum inophyllum biodiesel fuel; TCBDF: Terminalia catappa biodiesel fuel

The use of vegetable oil in the form of triglycerides directly as a fuel is not recommended mainly due to their high viscosity. Conversion of triglycerides into the methyl esters through the transesterification process reduces the molecular weight to one–third and leads to reducing the viscosity, allowing the use of biodiesel in existing engines without any modification.

The biodiesel samples were tested for their fuel properties. The results of acid value and kinematic viscosity at 40°C of biodiesels are summarized in Table 4, compared with those of petrodiesel Nº2. The acid values were within the limits prescribed in the latest ASTM, EN and JIS standards for all of these biodiesels.

Viscosity is the major reason why fats and oils are transesterified biodiesel. The viscosity of biodiesel is approximately an order of magnitude lower than that of the starting oil or fat, leading to better ionization of the fuel in the combustion chamber of the engine. The kinematic viscosity of Castor biodiesel fuel (CTBDF) is about 21 mm^2/s at 40°C, whereas those remains from 3.33 mm^2/s to 4.82 in other biodiesels. Generally, viscosity increases with respect to the number of CH groups in the FAME chain and decreases with the increasing unsaturation of the oil (Demirbas, 2007). However, the high kinematic viscosity of CTBDF should result from the intermolecular hydrogen bond association of the methyl ricinoleate molecules, leading to the main obstacle for the use of pure CTBDF as fuel in internal combustion engines.

3.4 Physicochemical characterization of the CTBDF and its blends

CTBDF has high value of kinematic viscosity, the level of which is fur beyond the limit of standards for biodiesel fuels. CTBDF, therefore, will not be used for fuel as itself in the conventional diesel engines. Some conventional biodiesel fuels have been often used in the blended form with petro diesel fuel globally, and the utilization of the blends of biodiesels will be recommended in order for the effective performance as a fuel.

Biodiesel and diesel are not so much similar in the chemical structure i.e. biodiesel is composed of long-chain fatty acid methyl esters, whereas petro diesel is a mixture of aliphatic and aromatic hydrocarbons that contain approximately 10 to 15 carbons. Biodiesel and diesel have chemical structure and compositions different from each other, and therefore they show some different fuel properties. Once mixed, the blend will exhibit properties different from neat biodiesel or diesel fuels. In the present work, CTBDF was blended with diesel at 5%, 10% and 20% on a volume basis (B5, B10, B20), respectively. Although CTBDF contains the chemical structure composed of not only the methyl ester but also –OH, CTBDF is miscible completely with petro diesel in these blending ratios and forms the stabilized blend fuels.

The blends with less than 20 volume % of CTBDF could meet the specification of the EN 590 standard (<4.50 mm^2/s) with respect to kinematic viscosity. Although the density of pure CTBDF is out of the range of the EN 14214 standard, the blends with reference diesel up to 20 volume % of CTBDF enter the technical specification EN 590.

Table 4: Analysis of the mixtures of CTBDF and reference diesel

Specification	Diesel N°2	B5	B10	B20	B100	EN 590
The density at 18ºC (g/cm^3)	0.84	0.84	0.85	0.85	0.96	0.82–0.85
Kinematic viscosity at 40°C (mm^2/s)	3.15	3.37	3.65	4.43	20.76	2.00–4.50
GHV (MJ/kg)	45.68	45.20	44.78	43.54	35.34	–
Copper strip corrosion at 50°C	1a	1a	1a	1a	1a	–

The gross heating value (GHV) is not specified in the EN 14214 and in the ASTM D6751 biodiesel standard. However, a European standard for using biodiesel as heating oil (EN 14213) specifies a minimum GHV of 35 MJ/kg. GHV is proportional to the chain length of a fuel molecule, but decreases when the unsaturation increases. This parameter is important for estimating the fuel consumption, i.e. the greater the GHV the lower the fuel consumption. The GHV of the pure CTBDF and its blends with reference diesel is summarized in Table 4, and all are above 35 MJ/kg. These values are lower than 45.68 MJ/kg, the typical value for the diesel fuel of fossil origin, and decrease linearly with the amount of diesel in the blend.

The copper strip corrosion at 50°C of the blends of CTBDF and reference diesel is within specification (class 1a).

4 CONCLUSIONS

The production of biodiesel from different cultivars, namely, Cashew nut, Castor seed, *C. inophyllum* seed, Makapuno coconut kernel and *T. catappa* seed has been investigated. Most of values of parameters, i.e. acid value, and kinematic viscosity of biodiesels synthesized met the requirement of JIS K2390: 2008, EN 14214: 2003, ASTM D6751-08. Among the biodiesels investigated in this work, CTBDF made from castor oil showed the unusually high kinematic viscosity of 20.76 mm^2/s that is far beyond the international standard for biodiesel fuel, e.g. 4.50 mm^2/s of EN 14214. Therefore, the blends of CTBDF and reference petro diesel (B5, B10, and B20) were prepared to examine the quality. It was found that these blend up to 20 vol% met the specifications of the EN 590 standard for automotive diesel fuel, e.g. kinematic viscosity 2.0–4.5 mm^2/s.

Use of vegetable oils has become necessary to substitute diesel fuel in order to reduce the impact on the environment and import burden on petroleum products. For a developing country like Vietnam, locally available feedstock or vegetable oils should be used. The right choice of raw materials for biodiesel production must always be based on technical and economic aspects. Economic viability of a species depends very much upon oil content and several other parameters, such as the fruit yield, the ease of harvest, the ease of separation of seed/kernel from the fruit, the ability to store the fruits after harvest, the ease at which the oil can be extracted, conversion efficiency of the oil into biodiesel. It is very important to find adaptable cultures that are suitable to promote a sustainable agriculture, to produce biodiesel with competitive prices.

The study will be helpful for decision–making regarding the production of biodiesel from some feedstocks that have not yet utilized widely, i.e. CSO, CTO, MCO, TCO and CIO. However, further assessment needs to be done for their conversion to biodiesel.

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