

PRODUCTION OF BIOESTER THROUGH SOLID-CATALYZED TRANSESTERIFICATION OF *STERCULIA FOETIDA* OIL USING AN OPTIMIZED PROTOCOL

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Abstract: The transesterification reaction of *Sterculia Foetida* oil with methanol using natural fiber solid-catalyst was investigated. Various experimental variables, such as the natural oil and methanol molar ratio (1:3, 1:6, and 1:9), temperature (45, 65 and 80 °C), rate of stirring (200, 400 and 600 rpm), and solid-catalyst concentration (1.0, 3.0 and 5.0 %) were adopted. Natural oil and methanol molar ratio of 1:9 with solid-catalyst concentration 5.0 %, mixing intensity of 600 rpm, and reaction temperature 80 °C offered the best *Sterculia Foetida* oil fatty acid methyl esters (FAMES) was accomplished by gas chromatography (GC). The bioester were characterized for their physical and main fuel properties including density, specific gravity, kinematic viscosity, high heating value, cetane number, flash point and cloud point. The chemical structure of bioester oil products were studied by nuclear magnetic spectroscopy (NMR) and Mass spectrometry (MS) techniques. The result showed our solid acid catalyst from sulfonate natural fiber could be used as transesterification catalyst.

1. Introduction

Biofuels are liquid or gaseous fuels made from biomass materials such as agricultural crops, municipal wastes, and agricultural and forestry by products via biochemical or thermo chemical processes. They can replace conventional fuels in vehicle engines, either totally or partially in a blend [1]. Vegetable oil methyl esters, commonly referred to as "biodiesel", are prominent candidates as alternative diesel fuels. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel [2]. Vegetable-oil fuels have not been acceptable because they are more expensive than petroleum fuels. However, with recent increases in petroleum prices and uncertainties surrounding petroleum availability, vegetable oils have become more attractive recently because of their environmental benefits and the fact that they are made from renewable resources [3,4].

Studies with the oil from seeds of *S. Foetida* have reported high content of cyclopropenoids fatty acids (CPFA) [5-7]. Compounds containing cyclopropenoid ring are associated with several biological properties, such as: insecticide, antifungal, antibiotic, antiviral, hormonal, carcinogenic or antitumoral activities and enzyme inhibitor [8,9]. The effects of CPFA in

animals have been the subject of several investigations, including cocarcinogenic and carcinogenic activities [10-12]. Sterculic acid is an inhibitor of Δ^9 -desaturase which converts stearic acid into oleic acid and is potentially noxious to man, since it can alter the cellular membranes permeability and inhibit the cellular reproduction [13].

Transesterification is the reaction of vegetable oil or animal fat with an alcohol to form esters and glycerol. A catalyst is used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is used to shift the equilibrium to the products side [14]. The liquid acid-catalyzed transesterification process does not enjoy the same popularity in commercial applications as its counterpart, the base-catalyzed process. The fact that the homogeneous acid-catalyzed reaction is about 4000 times slower than the homogeneous base-catalyzed reaction has been one of the main reasons. However, acid-catalyzed transesterifications hold an important advantage with respect to base catalyzed ones: the performance of the acid catalyst is not strongly affected by the presence of FFAs in the feedstock. In fact, acid catalysts can simultaneously catalyze both esterification and transesterification. Thus, a great advantage with acid catalysts is that they can directly produce biodiesel from low cost lipid feed-stocks, generally associated with high FFA concentrations (low-cost feed-stocks, such as used cooking oil and greases, commonly have FFAs levels of $\geq 6\%$) [15].

2. Materials and Methods

2.1 Materials

The seeds of *Sterculia foetida* were collected on April 2011 at Naresuan University in Phitsanulok, Thailand and *Sterculia foetida* oil was purchased from department of Chemistry, Faculty of Science, Naresuan University. Analytical reagents using as standards for gas chromatograph (GC) were purchased from Sigma-Aldrich Chemical Corporation, USA. Other chemical were analytical reagents (AR) and purchased Wako Chemical Corporation, Japan.

2.2 Oil extraction methods

Sterculia foetida seeds (400 g) were ground, homogenized and oil was extracted with hexane by cold solvent and soxhlet extraction. The organic extract was filtered and dried with anhydrous sodium sulfate. The hexane was removed under vacuum. The oil obtained was transesterified to determine fatty acids composition by gas chromatography mass spectrometry (GC/MS, Model Agilent 7890/5973). The oven temperature of GC was held at the initial temperature of 140 °C for 1 min and then heated at 8 °C min⁻¹ to 210 °C, 2 °C min⁻¹ to 260 °C, and then to a final temperature of 280 °C at a rate of 30 °C min⁻¹, held for 1 min. The total run time was 36.42 min. The injector temperature was 250 °C and that of the detector was 230 °C. Helium gas was used as the carrier at a flow rate of 1 ml min⁻¹. The analysis with mass detector was carried out at the following conditions: helium as carrier gas, electron energy of 70 eV and mass range from 40 to 500.

2.3 Preparation of solid catalyst

The carbon material with SO₃H groups was prepared from dried bamboo cellulose. The starting material (20 g) was heated for different temperatures (300-500 °C) and carbonize times (15 h) under N₂ flow to produce a black solid, which was then ground by ball mill for 6 h (particle size, <90 μm). The powder (5 g) was then boiled in 50 ml of sulfuric acid (H₂SO₄) at 150 °C under N₂. After heating time for 18 h and then cooling to room temperature, the suspension was filtered to yield a black precipitate, with was washed repeatedly with distilled water until impurities such as sulfate ions were no longer detected in the wash water (detect pH by universal indicator). Dry and determine all acids content by back titration.

2.4 Methylation procedure

The procedures of transesterification were designed to 1, 3 and 5 wt% catalyst concentration (Catalyst (%wt) is relative to the total weight of oils) at the reaction times 1, 3, 6, 12 and 24 h and 1:9 molar ratio of oil to methanol at temperature 80 °C. After cooling, the reaction mixture was filtrated for cleave solid catalyst then poured into a collecting tube and then was centrifuged at 2,000 g for 10 min, which resulted in the phase separation of the methyl esters and the glycerol. The glycerol phase (bottom layer) was removed, and the methyl esters biodiesel phase (top layer) was evaporated with a thermostatic bath at 65 °C to remove the methanol. Then the biodiesel product was analyzed % conversion with ¹H NMR spectrometer.

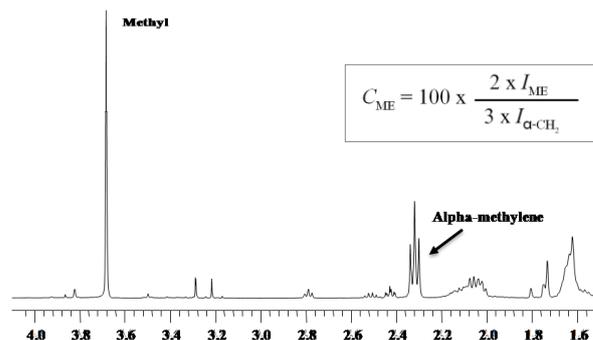


Figure 1. ¹H NMR spectra of 97.8% methyl ester from *Sterculia foetida*.

In the ¹H NMR spectrum of methyl esters is shown in Fig 1., methyl groups were observed singlet spectra at δ 3.678 and triplet spectra of alpha-methylene at δ 2.349. The conversion percentage of methyl ester were determined by ratio of intrigration value between methyl and alpha-methylene spectra.

3. Results and Discussion

3.1 Lipid content

The reference in several extraction oils were found 70-15 percentage and *Sterculia foetida* was 26.15 percentage. The extracted oil (soxhlet extraction) was found among moderate yields, that show in table 1.

Table 1: Yield of vegetable oils [16].

Oil	Oil content (%)
Soybean	15-20
Sunflower	25-35
Rapeseed	38-46
Palm oil	30-60
Peanut oil	45-55
Olive oil	45-70
Corn (Germ)	48
Coconut	63-65
Castor	45-50
Jatropha	30-40
Tung	16-18
<i>Sterculia foetida</i> *	26.15

*Soxhlet extraction from 25 g sample seed.

3.2 Methyl ester properties

The present study introduced a process for biodiesel production through high effective acidic transesterification catalyzed by cellulose sulfonic acid.

Table 2: Fatty acids composition from *Sterculia foetida* seed oil

Peak	Fatty acid	Sample	Ref [5]
		Mean (%)	Mean (%)
1	C _{16:0}	18.77	15
2	C _{16:1}	0.42	0.13
3	C _{18:0}	4.11	1.66

4	Mavalic acid	-	5.4
5	C _{18:1} cis	10.93	5.6
6	Sterculic acid	-	54
7	C _{18:2} cis/cis	10.85	7.7
8	C _{18:3}	-	0.20
9	C _{20:0}	0.95	0.15

Gas chromatography mass spectrometer showed the fatty acids composition in Table 2. The mass spectra of mavalic acid and sterculic acid were not shown up because their structures decompose in high temperature reaction. The mass spectra of other fatty acid were as same as previous work.

¹H NMR analysis showed no artifact formation when acid catalyzed process was used. ¹H NMR spectra of the methyl esters obtained in basic catalyzed process showed no signals for triacylglycerols (δ 4.1–4.3) indicating that the transesterification was quantitative. These spectra showed an additional signal at δ 3.678, characteristic for methyl esters hydrogens and signal at δ 0.900, characteristic for cyclopropene hydrogens of methyl mavalate or methyl sterculate. Thus peaks at δ 3.678 (OCH₃) and at δ 0.910 (terminal CH₃ groups) showed the same area indicating a complete methylation.

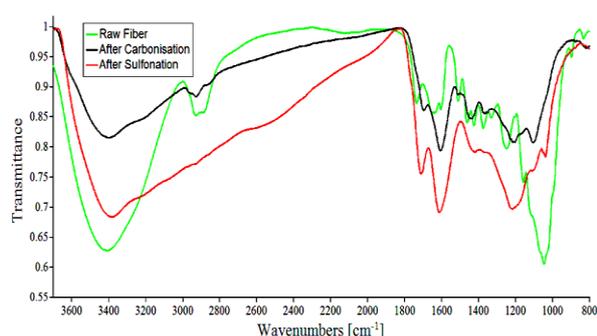


Figure 2. FTIR spectrum label : (Green) Raw material, (Black) Carbonized material, (Red) Sulfonated material.

The FTIR spectra of the carbon catalyst before and after sulfonation showed the vibration bands at 3400 cm⁻¹ (-OH stretching), 1713 cm⁻¹ (C=O bending), 1615 cm⁻¹ (-OH stretching), 1040 cm⁻¹ (SO₃⁻ stretching) and 1365 cm⁻¹ (O=S=O stretching in SO₃H) as showed in (Fig. 2). The material is carbonization at 300°C, 5 h.

3.3. Solid acid catalyst properties

The sample carbonized at lower temperatures presented smaller carbon sheets and therefore have high acids densities because the SO₃H groups are attached only to the edges of the carbon sheets (Polycyclic Aromatic Hydrocarbon). The all acid value have shown in Table 3.

Table 3: Determination of acid value on solid catalyst

Carbonization Temperatures (°C)	All acid content (mmol/g)
300	7.9970
400	5.8351
450	4.3719
500	3.7938
550	3.3267

3.4 Effect of catalyst concentration

The concentration of trifluoroacetic acid catalyst used in the process was varied as 1, 3 and 5 % wt based on the volume of the reaction solution. An appropriate concentration of solid acid catalyst was 5%wt as it gave the higher amount of the methyl ester content (98.4%) after 12 h of reaction time. Therefore, 5 % wt catalyst concentration was suggested in the acidic transesterification catalyzed by solid acid catalyst. The changes of the product specific gravity and the methyl ester content with reaction time under the conditions of 9:1 M ratio of methanol to oil and 80 °C with 5 % wt catalyst concentration were further investigated.

3.5 SEM analysis of prepared catalyst

Scanning electron microscopy images of the solid acid catalyst were shown in Fig. 3. The catalyst is comprised from the union of many crystals. There are many cracks with sizes of micrometers and relatively large pores among these agglomerates. Therefore, triglyceride and methanol may fully contact with the surface of the catalyst to synthesize biodiesel. This solid acid catalyst can be effectively and easily separated from the products by filtration and centrifugation after the reaction.

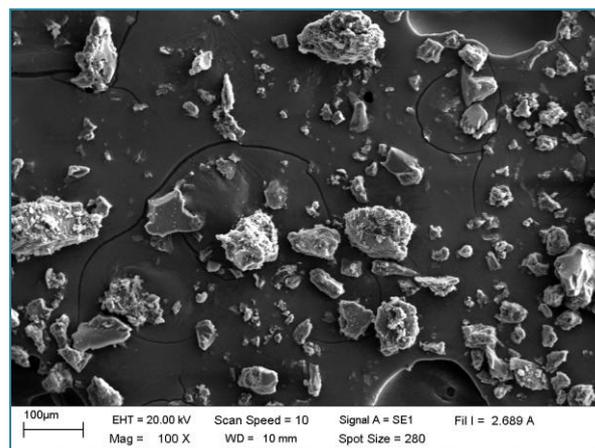


Fig. 3. SEM images of the new prepared solid acid catalyst.

4. Conclusions

The present study introduced a process for biodiesel production through high effective acidic transesterification catalyzed by cellulose sulfonic acid. A range of methanol to oil ratios, acid catalyst

concentrations, reaction temperatures and reaction times were established. The research indicated that the oil could be converted to biodiesel directly by one-step cellulose sulfonic acid catalyze process without extreme temperature and pressure conditions. The best process combination was 5%wt catalyst content with 9:1 M ratio of methanol to oil at temperature of 80 °C. The methyl ester content reached as high as 98.5%. The present procedure represents a simple and mild method for bioester production in short reaction time and with high conversion rate, which would offer potential for an industrial process.

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