

Biodiesel Production from *Sterculia foetida* Oil by Using Solid Support Catalyst

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Abstract. In the present work, the properties of bioester from Samrong oil (*Sterculia Foetida*) and characteristics of cellulose solid catalyst are described. Heterogeneous catalyst was prepared via carbonization, sulfonation and purification giving solid catalyst as brown powder. Control parameters were time and temperature of carbonization and sulfonation reaction, ratio of sulfuric acid to solid material and weight of solid material. The optimized carbonization condition was 300 °C for 15 h. The sulfonation temperature was 150 °C for 18 h under N₂ producing 7.99 mmol/g of acid concentration on solid catalyst. The acidity in water of solid catalyst after purification and drying was decreasing. The results of biodiesel production showed that the triglyceride could be converted to biodiesel directly by one-step sulfonic acid catalyzed process. The experimental condition of reaction process was 3.0 M of catalyst concentration with 9:1 M ratio of methanol to triglyceride at the temperature of 80 °C. This catalysts provided high reactivity of transesterification. The present procedure represents a simple method for biodiesel production with a short reaction time and with moderate conversion rate.

Introduction

Biodiesel are liquid or gaseous fuels made from biomass materials such as agricultural crops, municipal wastes, and agricultural and forestry by products via biochemical or thermochemical processes. They can replace conventional fuels in vehicle engines, either totally or partially in a blend [1]. Vegetable oil (m)ethyl 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 cyclopropanoid fatty acids (CPFA) [5-7]. Compounds containing cyclopropanoid 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 co-carcinogenic 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 feedstocks, generally associated with high FFA concentrations (low-cost feedstocks, such as used cooking oil and greases, commonly have FFAs levels of $\geq 6\%$) [15].

Experimental Section

Sample. The seeds of *Sterculia foetida* were collected on November 2015 at Naresuan University in Phitsanulok, Thailand.

Oil Extraction. Seeds (200 g) were ground, homogenized and oil was extracted with hexane by cold solvent and soxleth 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.

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 (300-600 °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 for 18 h and then cooling to room temperature, the suspension was filtered to yield a black precipitate, which 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.

Methylation procedure. The reaction Experiments were designed to determine effects of 1, 3 and 7 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 9:1 molar ratio of methanol to oil at temperature 80 °C. After cooling, the reaction mixture was filtered to 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 with ¹H NMR spectrometer.

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

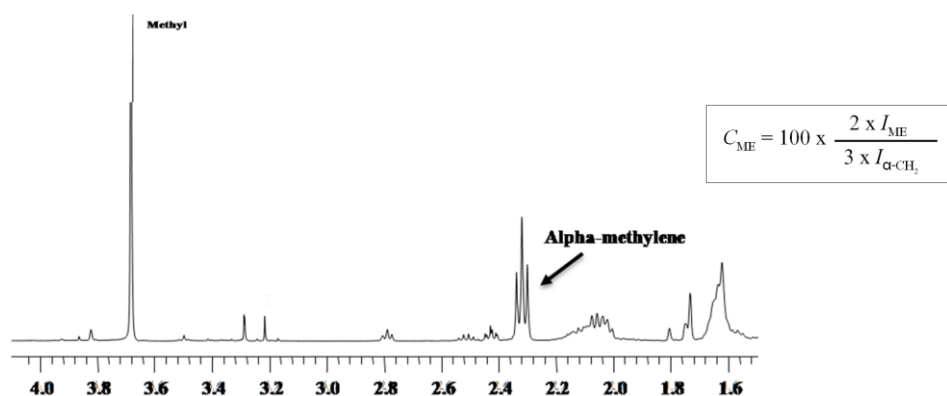


Fig. 1 ¹H NMR Spectra of 97.8% methyl ester from *Sterculia foetida*

Results and Discussion

Lipid content. All lipid content from *Sterculia foetida* seed by soxleth extraction about 26.15%. The extracted oil was found among moderate yields, that show in table 1.

Table 1 Yields of vegetable oils extraction [16]

Oil	Oil content (%)
Soybean	15-20
Sunflower	25-35
Rapeseed	38-46
Plam oil	30-60
Peanut oil	45-55
Olive oil	45-70
Corn (Germ)	48-52
Coconut	63-65
Castor	45-50
Jatropha	30-40
Tung	16-18

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	15.0
2	C _{16:1}	0.42	0.13
3	C _{18:0}	4.11	1.66
4	Mavalic acid	-	5.40
5	C _{18:1} cis	10.93	5.60
6	Sterculic acid	-	54.0
7	C _{18:2} cis/cis	10.85	7.70
8	C _{18:3}	-	0.20
9	C _{20:0}	0.95	0.15

Gas chromatography massspectrometer showed the fatty acids composition in Table 2. The mass spectra of mavalic acid and sterculic acid has'n shown because error technique about retention times. 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.

Solid Acid Catalyst Properties. The sample carbonized at lower temperatures have smaller carbon sheets and therefore have hight acids densities because the SO₃H groups are attached only to the edegs of the carbon sheets (Polycyclic Aromatic Hydrocarbon). The acids density show 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
600	3.1746

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 1:9 M ratio of oil to methanol and 80 °C with 5 %wt catalyst concentration were further investigated.

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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