Preparation of Cellulose Based Catalyst for Converting Rubber Seed Oil to Biodiesel

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ABSTRACT

Cellulose based catalyst was prepared through a two-step procedure including partial cellulose carbonization at 400°C for 2 h to obtain "black powder" and sulfonation of the black powder using concentrated sulfuric acid at 230°C for 16 h to synthesize the catalyst. The as-synthesized catalyst possessed super acid sites assigned for –SO$_3$H groups located on polycyclic aromatic fragments enhancing its activity on methanolysis of a wide range of vegetable oils and animal fats. In this study, the activity of the catalyst were demonstrated on Vietnam rubber seed oil containing a large amount of free fatty acid in its chemical composition for synthesizing the fatty acid methyl esters (FAMEs) known as biodiesel. The methanolysis were established at 130°C in an autoclave reactor, and the reaction reached a yield of 95.8% after 4 h. The FAME content in the final product was 100% giving favorite characteristics for using in diesel engine according to the ASTM D 6751. Some techniques were applied such as XRD, FT-IR, EDX and TPD-NH$_3$ for characterizing the structure, element composition, functional group vibrations and acidity of the catalyst. The FAME composition was determined by GC-MS method.

Keywords: Carbon based catalyst, partial carbonization, cellulose catalyst, biodiesel, rubber seed oil.

INTRODUCTION

The esterification of higher fatty acids by liquid acid catalysts such as sulfuric acid (H_2SO_4) was a process commonly used for biodiesel production, but it involved high consumption of energy and the separation of the catalysts from the homogeneous reaction mixtures was costly and chemically wasteful. Recyclable solid acids, such as Nafion [1, 4], made better catalysts, although they were also expensive and their activity was less than that of liquid acids. There were some other solid acids described as they possessed great activity on esterification and trans-esterification such as SO_6^{2-}/ZrO_2, acid supported mesoporous materials [2, 3, 5, 6]... However, these catalysts required extreme conditions for well converting feedstocks to methyl esters; even they were categorized as super acids.

Carbon-based or biomass-based catalysts were a relatively new and important class of solid catalysts. The discovery of the sugar catalyst by Toda et al in 2005 had attracted considerable interest because it could be prepared from renewable sources such as sugars, starch and cellulose, using low energy in the pyrolysis

step (carbonization temperature ~ 400°C), and ease of functionalization of the carbon surface by sulfonating in sulfuric acid to produce acid catalysts. Furthermore, the activity of the sugar catalyst was comparable with sulfuric acid for the esterification and trans-esterification reaction [7].

According to Toda et al., in 2005 [7] a glucose based solid acid was prepared through two-step process including partial carbonization of D-glucose followed by sulfonation of the carbonized powder. The catalyst exhibited considerable activity on methanolysis because of the introduction of $-SO_3H$ groups on its surface. However, there was a few information relating to the structure of the catalyst published in that paper, and a conclusion about potential of widening the materials such as starch and cellulose for catalyst preparation was not demonstrated. In the field of our works, we also realized that the catalysts prepared from sugar, starch or cellulose or even natural biomass by the given two-step process also possessed high density of sulfonic acid ($-SO_3H$) groups generating the superacid sites and exhibited great activity in methanolysis of a wide range of feedstock. The catalyst consisted of flexible polycyclic carbon nanosheets with acid groups such as $–SO_3H$, $-COOH$, and phenolic hydroxyl ($-OH$) in a three-dimensional network [7]. For the feedstock aspect, according to the Vietnam Rubber Group, the rubber seed oil was mainly distributed in South area with above 500.000 ha (up to ~ 1.000.000 ha considering to expanded plants growing in Laos and Cambodia) expected to produce 330.000 tons of oil per year for main applications in paint and lacquer industry [12]. The rubber seed oil was considered as the second generation feedstock with favorable chemical components for biodiesel production demonstrated by a lot of publications [13-15]. Some studies considered an appearance of a toxic chemical Linamarin in its component avoiding the uses of the rubber seed oil in food processing [12, 15]. As a consequence the application of the rubber seed oil in biodiesel production was indicated as a sustainable way to develop the production of alternative fuels in Vietnam.

The composition of the rubber seed oil included a large amount of free fatty acids contributed by the oil sources and the existence of lipase catalyzed hydrolysis of the triglycerides, so various base catalysts could not be applied for the conversion because of saponification during the synthesis. As mentioned above the best way in this case was to develop a new solid acid catalyst with high activity and selectivity (superacid). Hence the carbon based catalysts were considered as potential candidates to overcome this challenge.

This paper covered some new approaches including preparation of a carbon based catalyst derived from cellulose, so called cellulose based catalyst, demonstration of the $-SO_3H$ attached on the polycyclic aromatic system and application of the as-synthesized catalyst for converting the Vietnam rubber seed oil to biodiesel.
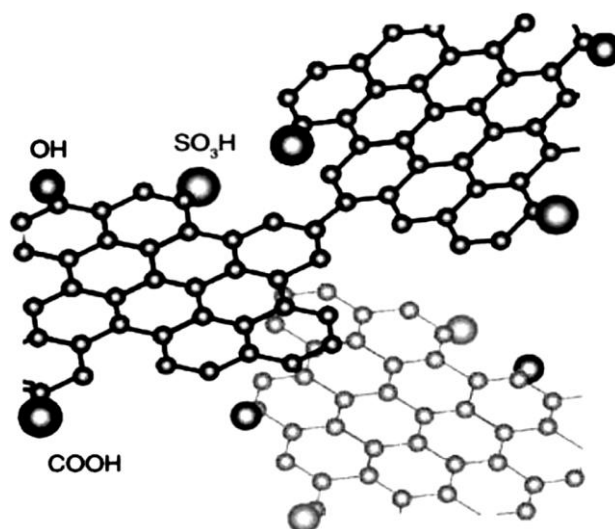

Figure 1. Structure of carbon based catalyst according to Toda [7]

MATERIALS AND METHODS

Chemicals: Cellulose was purchased in local market. H_2SO_4 98%, CH_3OH were purchased from Merck and used directly without any further purification. Distilled water was prepared in our laboratory.

Preparation and characterizations of cellulose based catalyst: The preparation of cellulose based catalyst was established through a two-step process: partial carbonization of cellulose to obtain "black powder" in step 1, and sulfonation of the black powder to get the catalyst in step 2. The procedures were described as follow:

Firstly, the cellulose was partially carbonized in a pyrolysis reactor filled with nitrogen atmosphere. 200 g of the cellulose was added to the reactor at ambient temperature. The nitrogen flow was passed through the reactor for 30 min before the carbonization at volume flow of 100 mL min^{-1} to completely push the air out. Then, temperature was risen up to 300-400°C and kept for 1-5 h. Vapor running out the reactor was condensed in inner shell by cooling water flowing in outer shell of a condenser. After finishing the partial carbonization, the solid in the reactor was withdrawn and rinsed with hot water to separate organic and inorganic acids, salts generated in the process. The solid after water rinsing and drying at 120°C was called "black powder". This powder was sulfonated with concentrated sulfuric acid in the next step.

Secondly, the as-synthesized black powder was ground into uniform for sulfonation procedure. 10 g of the black powder was fed into a 500 mL rounded bottom flask supported magnetic stirrer. A volume of 200 mL of 98% H_2SO_4 was poured into the flask. The flask was put on heater supported magnetism. Then, temperature was risen to 230°C for 16 h with stirring speed of 400 rpm. A water condenser was attached with the flask neck to avoid evaporation of acid. After 16 h of sulfonation, the mixture was cooled down to room temperature followed by diluting the mixture with a large amount of water. The acid was diluted, and the precipitate was obtained through vacuum filter. The water was also used to completely wash the precipitate until the waste water became neutral. The precipitate was dried in an oven at 120°C for 6 h to completely eliminate the rest of water in the sample. The black powder and the catalysts were characterized by XRD, FT-IR, EDX and TPD-NH$_3$ method. Powder XRD of the samples were recorded on a D8 Advance Bruker diffractometer using Cu Kα (λ = 0.15406) radiation with two techniques such as small and wide angle. TEM images were recorded on a JEM1010-JEOL TEM operated at 80 kV. Both TPD-NH$_3$ and TPD-CO$_2$ were measured on a Micromeritics Autocue II 2920 V4.01. FT-IR spectroscopies were measured on Nicolet 6700 FT-IR Spectrometer.

Catalytic activity test on methanolysis of rubber seed oil: Vietnam rubber seed oil was purchased from local market in Dong Nai province. The oil was heated up to 120°C to separate trace water and inhibits *Lipaza* enzyme responded for raising the oil acidity. Then, the oil was used directly for methanolysis without further purification.

The methanolysis was carried out in a batch autoclave supported heater and magnetic stirrer. For the first step, 100 mL methanol was poured into the autoclave with magnetic stirrer; then 10 g of the as-synthesized catalyst was fed in this autoclave followed by adding a volume of 100 mL rubber seed oil; the autoclave was closed and began to start the stirring and raise the temperature; the temperature was set up to 130°C for 5 h with stirring speed of 500 rpm. After the reaction finished, the liquid was separated from the catalyst by decantation; the liquid then was purified by rinsing with hot water to obtain raw biodiesel; water in the raw biodiesel was removed by drying at 120°C for 2 h, and after this procedure, the refined biodiesel could be stored or used. The raw biodiesel yield was calculated by equation:

$$\mu = (m_{bio}/m_{oil}) \times 100\%$$

In which, μ, m_{bio} and m_{oil} were the biodiesel yield, the mass of refined biodiesel and the mass of the rubber seed oil, respectively. The refined biodiesel was also tested its methyl ester composition by GC-MS method. GC-MS techniques was established on an Agilent HP 6890 GC-5898 MS supported capillary HT-

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5MS. A series of specification methods were used to determine the rubber seed oil and the synthesized biodiesel properties such as ASTM D 1298, D 445, D 97, D 464, D 664, D 93, D 95, D 189, D 2015 and E 2583; EN 1411 and 12622.

RESULTS AND DISCUSSION

Investigation of partial carbonization of cellulose: The catalyst preparation consisted of two steps including the partial carbonization and sulfonation consecutively. In which the carbonization obtaining black powder vastly affected the final characteristics of the cellulose based catalyst [7, 16, 17]. According to these reports, the followed sulfonation process could be progressed through two compete reactions including sulfonation and sulfation as major and minor processes respectively. The sulfonation aimed to electrophilic substitution of the $-SO_3H$ onto the "free positions" of the polycyclic aromatic system of the black powder, in contrast to the sulfation which required many free $-OH$ groups belonging to phenolic and carboxylic functions. The sulfonation produced catalyst with strong acidity and high stability while the sulfation did not. Therefore, the black powder structure and characteristic played a crucial role in the next sulfonation through introducing a large amount of the free position on the aromatic rings instead of phenolic or carboxylic groups. The temperature and time of the carbonization were the most important factors, so we focused on investigations of these conditions affecting the chemical group composition in the black powder.

Figure 1 described FT-IR spectra of the black powders obtained at different temperatures such as $300^{o}C$, $400^{o}C$ and $500^{o}C$. The major peaks occurred in the diagram corresponded to $-OH$ phenolic, $-OH$ carboxylic, and $C=C$ aromatic groups 3400-3600 cm^{-1}, 2800-2900 cm^{-1} and 1600-1650 cm^{-1}, respectively [21]. The occurrences well adapted with many studies over the world for the black powder properties [18-21].
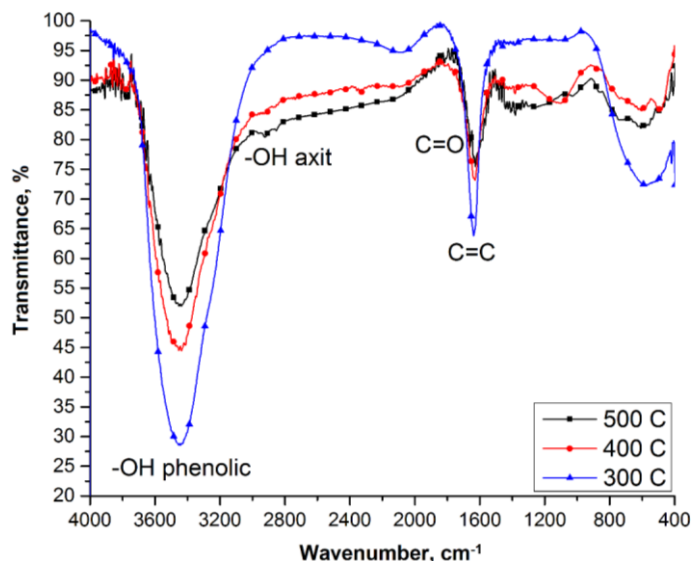

Figure 1. FT-IR spectra of black powder samples at different temperature

By increasing carbonization temperature, the peaks corresponding to the $-OH$ phenolic groups decreased in its intensity demonstrating the deep condensation during the carbonization. The intensity of the $-OH$ carboxylic peaks increased from $300^{o}C$ to $400^{o}C$, but decreased when the temperature reached $500^{o}C$. In contrast the intensity of the $C=C$ groups belonging to polycyclic aromatic system decreased from $300^{o}C$ to $400^{o}C$, but increased when raising temperature to $500^{o}C$. The same phenomenon was also observed when analyzing the peaks of the $C=C$ groups. The conversion of the rubber seed oil when using the catalysts obtained from these black powders at $300^{o}C$, $400^{o}C$ and $500^{o}C$ reached 66.0%, 83.8% and 81.1%, respectively.

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Franklin [22] reported that there were many parallel and continuous processes during the carbonization; in which the most important reactions were condensation and graphitization tending to enrich and inhibit the free position on the aromatic rings, respectively. Therefore the highest conversion of the rubber seed oil using the catalyst derived from black powder at 400°C was adaptable with the medium level of condensation and graphitization. Hence the temperature of 400°C was chosen for investigation of time. Figure 2 described the FT-IR spectra of the black powders at different times at temperature of 400°C.
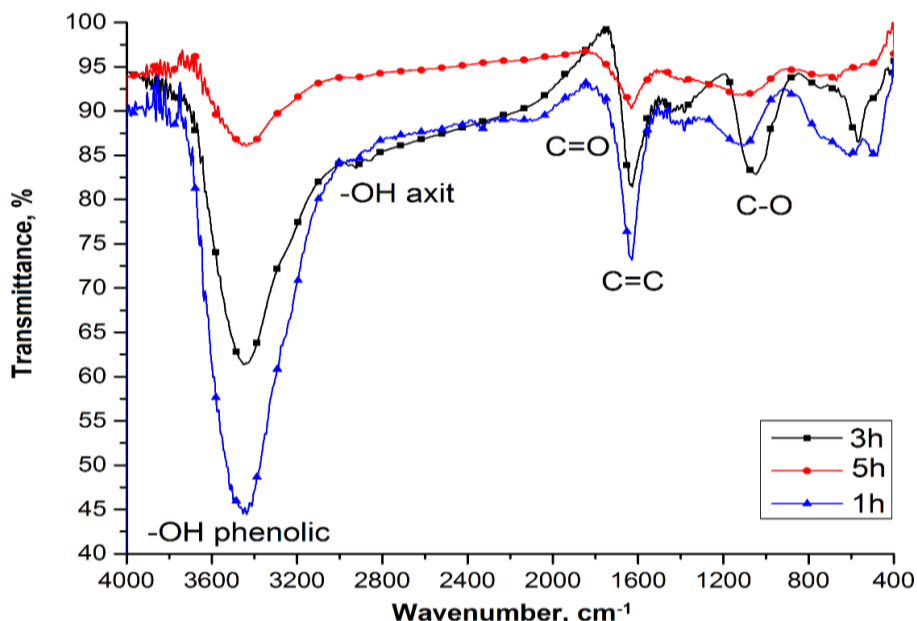

Figure 2. FT-IR spectra of black powder samples at different times

The FT-IR spectra also pointed out the common peaks at 3400-3500cm^{-1}, 2800-3000 cm^{-1}, 1600-1650 cm^{-1} and 1700-1750 cm^{-1} corresponding to the –OH phenolic, -OH carboxylic, C=C aromatic and C=O carboxylic groups [21]. The behavior of different groups at FT-IR diagram during the carbonizations was also investigated. The results showed that the behaviors of the functional groups in the black powders due to times were the same as doing investigations of temperature. The conversion of the rubber seed oil to biodiesel reached 94.1%, 86.8% and 80.5% over the cellulose based catalysts synthesized from the black powder at 1, 3 and 5 hours, respectively.

As a consequence, the black powder carbonized at 400°C for 1 h was chosen as precursor for preparing the cellulose based catalyst. Some of the other characterizations of this catalyst and black powder were studied in the next part of this paper.

XRD pattern: Both the black powder and the catalyst were characterized by XRD method. The results were described in figure 3.

Both the black powder and the catalyst could be assigned for an amorphous structure because of high amorphous background in their XRD patterns. There was a little difference between the pattern of the black powder and the catalyst: the region before 2theta = 25° of the black powder had a higher intensity than that of the catalyst; however, in general there was amorphous phases detected for both the black powder and the catalyst.
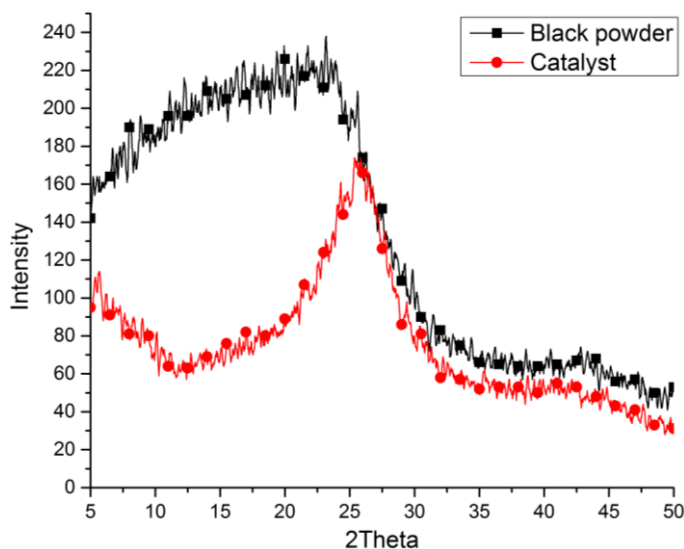
Figure 3. XRD patterns of the black powder and the catalyst

FT-IR spectroscopy: The FT-IR spectroscopies of the black powder and the catalyst were described in figure 4.
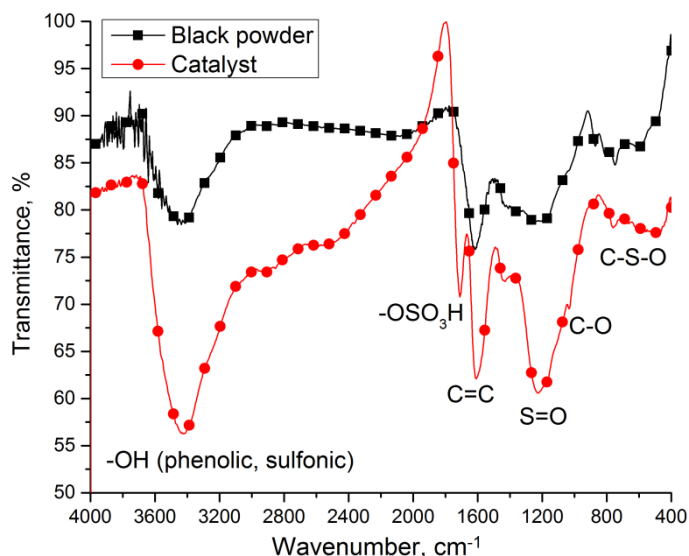

Figure 4. FT-IR spectra of the black powder and the catalyst

The results obtained from FT-IR spectra of the black powder could be described as followed: the phenolic -OH stretching vibration at about 3500 cm^{-1}; the C=C (in polycyclic aromatic rings) stretching vibrations at about 1680 cm^{-1} [10, 11]. In case of the catalyst, beside the same results obtained from the FT-IR spectrum of the black powder, there were some differences such as the stretching vibration of H-bonding relating to –SO$_3$H groups at about 1720 cm^{-1}, the stretching vibration of S=O groups in the –SO$_3$H groups at about 1180 cm^{-1} and a bending vibration assigned for C-S-O groups at 795 cm^{-1} [10, 11]. Those differences illustrated the appearance of -SO$_3$H groups on the catalyst after the sulfonation process.

Toda et al [7] indicated that the partial carbonization at 400°C produced a condensed poly-aromatic system possessed –OH and –COOH groups in the black powder surface. The poly-aromatic system was non-crystal, unordered structure in contrast to graphite structure. Beside, a range of short carbon chain product could be generated such as acids, alcohols, but they also were removed after rinsing with hot water. Therefore, the black powder seem like an intermolecular system, and the sulfonated active groups were located in it [8, 9]. In sulfonation process, the reactions occurred among non-substituted positions in the

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polycyclic aromatic rings and concentrated H_2SO_4 would produce $-SO_3H$ groups. The $-SO_3H$ groups showed very strong acidity greatly strengthens the acidity of the catalyst. In the other aspect, the covalent bonds between the polycyclic aromatic rings surface with the $-SO_3H$ groups strongly stabilized these acid sites and considerably improved the reuse and the regeneration of the catalyst.

EDX spectroscopy: The element compositions of both the black powder and the catalyst were determined by EDX methods. That was to say that the EDX results could clearly confirmed the attachment of the $-SO_3H$ groups on the catalyst surface through the variation of sulfur content before and after the sulfonation. The EDX spectra of the black powder and the catalyst were described in figure 5 and figure 6.
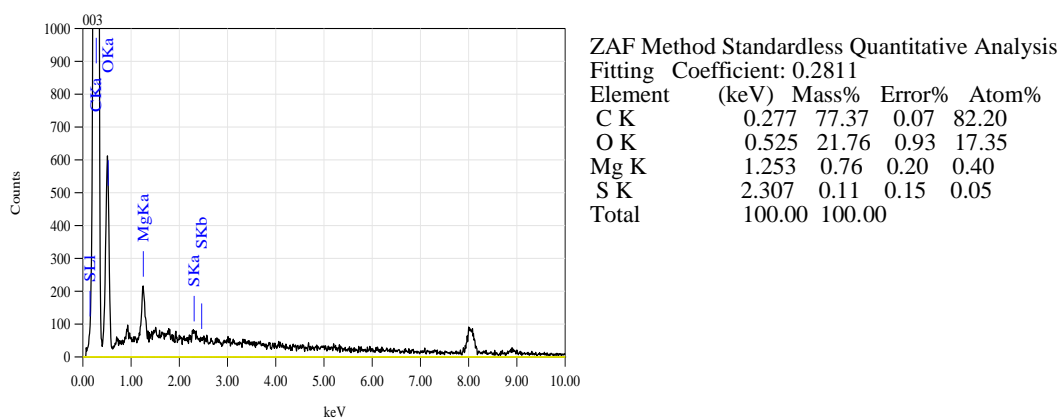

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 0.2811

Element	(keV)	Mass%	Error%	Atom%
C K	0.277	77.37	0.07	82.20
O K	0.525	21.76	0.93	17.35
Mg K	1.253	0.76	0.20	0.40
S K	2.307	0.11	0.15	0.05
Total		100.00		100.00

Figure 5. EDX spectrum and the element composition of the black powder

ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 0.2927

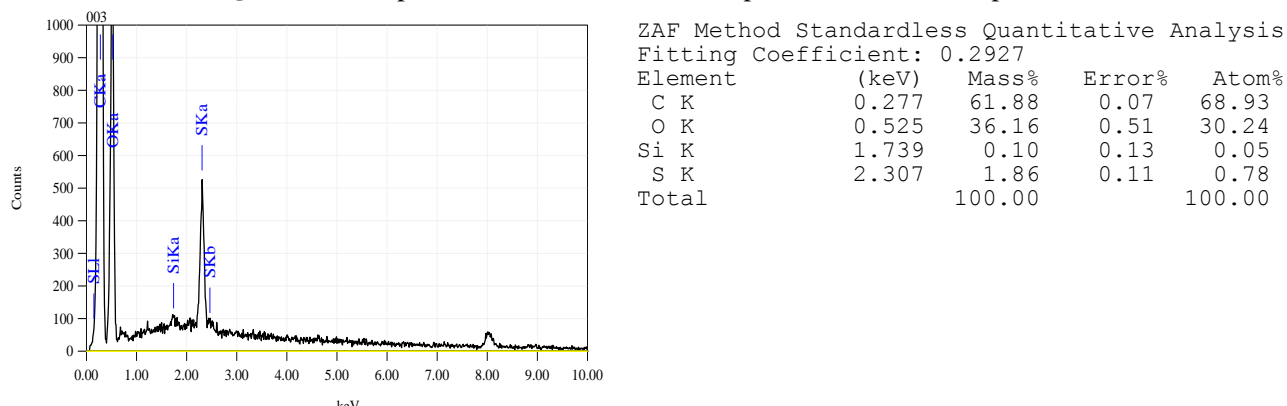| Element	(keV)	Mass%	Error%	Atom%
C K	0.277	61.88	0.07	68.93
O K	0.525	36.16	0.51	30.24
Si K	1.739	0.10	0.13	0.05
S K	2.307	1.86	0.11	0.78
Total		100.00		100.00

Figure 6. EDX spectrum and the element composition of the catalyst

From results, the element compositions of the black powder and the catalyst commonly consisted of C and O as main components. For the black powder, the C, O, Mg and S mass content was 77.37%; 21.76%; 0.76% and 0.11%, respectively. For the catalyst, the C, O, Si and S mass content was 61.88%; 36.16%; 0.10% and 1.86%, respectively. The results indicated a sharp increase of sulfur content from 0.11% in the black powder to 1.86% in the catalyst; namely the sulfur content increased about 17 times after sulfonation demonstrating a high density of the $-SO_3H$ on the catalyst surface. The Mg element appeared in the black powder but disappeared in the catalyst because the water rinsing of $MgSO_4$ salt generated after sulfonation. There was a signal of very small Si content in the catalyst caused by the trace impurity of the acid or the sulfonation reactor.

Acidity quantitation by TPD-NH$_3$ method: The results obtained from the FT-IR and EDX spectroscopies clearly showed an attachment of the $-O-SO_3H$ groups onto the catalyst surface. Because they possessed a very strong acidity in comparison to sulfuric acid, they also considerably strengthen the acidity of the catalyst. Therefore, the TPD-NH$_3$ method was used to demonstrate this conclusion. The

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TPD-NH$_3$ diagrams and the desorption peaks of the black powder and the catalyst were described in figure 7 and table 1.

(a)   (b)
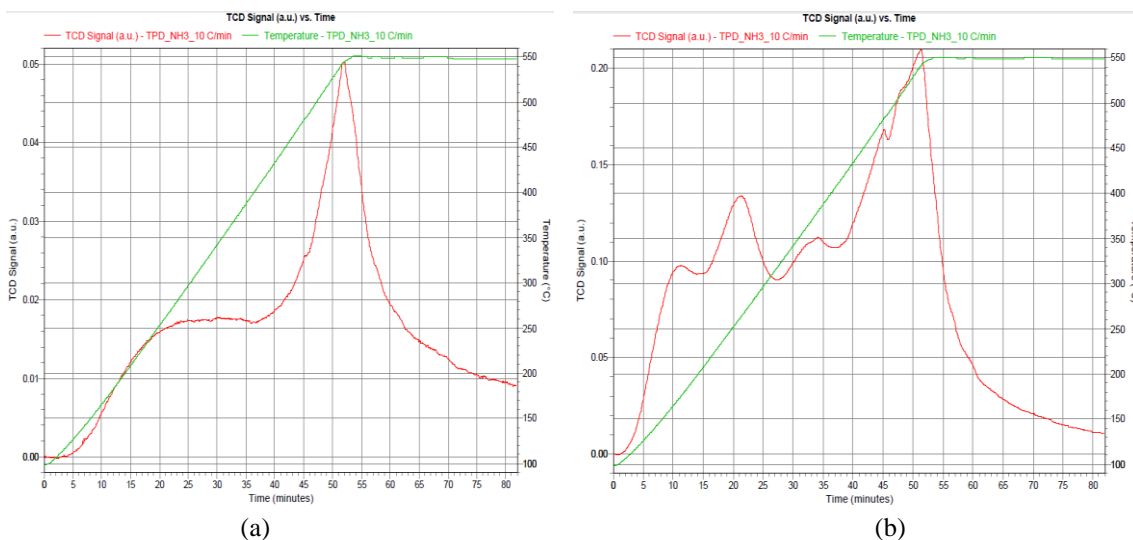
Figure 6. TPD-NH$_3$ diagram of the black powder (a) and the catalyst (b)

Table1. Desorption peaks of the black powder (a) and the catalyst (b)

Peak Number	Temperature at Maximum (°C)	Quantity (cm³/g STP)
1	301.9	24.68434
2	544.2	12.84542

Peak Number	Temperature at Maximum (°C)	Quantity (cm³/g STP)
1	180.6	56.57465
2	261.8	7.14746
3	493.6	78.91750
4	537.1	20.06201

From the desorption peak properties such as temperature, NH$_3$ volume at standard temperature pressure, the acidities of the black powder and the catalyst were summarized in table 2 and 3.

Table 2. Parameters obtained from TPD-NH$_3$ method for the black powder

Acid sites	Desorption temperature peaks, °C	NH$_3$ volumes at STP conditions, ml NH$_3$/g	Acid site contents, %	Desorption NH$_3$ molar, mmol/g	Acid site density, $10^{20}/g^{-1}$
Medium	301.9	24.68	65.76	1.10	6.62
Strong	544.2	12.85	34.24	0.57	3.43

Table 3. Parameters obtained from TPD-NH$_3$ method for the catalyst

| Acid sites	Desorption temperature peaks, ^{o}C	NH$_3$ volumes at STP conditions, ml NH$_3$/g	Acid site contents, %	Desorption NH$_3$ molar, mol NH$_3$/g	Acid site density, g^{-1}
Weak	180.6	56.57	34.77	2.53×10^{-3}	15.24×10^{20}
Medium	261.8	7.15	4.39	0.32×10^{-3}	1.93×10^{20}
Strong	493.6 and 537.1	78.92+20.06 = 98.98	60.84	4.42×10^{-3}	26.62×10^{20}

The results clearly illustrated that the catalyst acidity was much more than that of the black powder, especially the strong acid sites. For a comparison, the strong acid site density of the catalyst was 7.76 times higher than that of the black powder. This result positively affirmed the compatibility of previous techniques. The high acidity density of the catalyst improved its activity in methanolysis of rubber seed oil to produce biodiesel.

Biodiesel synthesis by methanolysis of rubber seed oil on cellulose based catalyst: The rubber seed oil specifications were determined by various standard methods and described in table 4.

Table 4 . The rubber seed oil specifications

Properties	Methods	Values
Density (25°C)	D 1298	0.925
Kinetic viscosity at 40°C, cSt	D 445	60
Pouring point, ^{o}C	D 97	-20
Saponification value, mg KOH/g	D 464	198
Acid number, mgKOH/g	D 664	67
Iodine number, g I$_2$/100g	EN 1411	142.8
Flash point, ^{o}C	D 93	220.2
Water content, mg/kg	D 95	253
Residue content, mg/kg	EN 12622	245
Carbon residue content, mg/kg	D 189	19
High heating value, MJ/Kg	D 2015	35.3
Refractive index	E 2583	1.4712
Color	-	Transparent, heavy brown
Odor	-	Specific

The acid number of the rubber seed oil was very high (67) responding for about 33.5% of free fatty acids, do the base catalysts was unable to use in the methanolysis because of the saponification. The methanolysis on the cellulose based catalyst completely avoided the saponification, so this was a very suitable way to do with various kinds of feedstock. The highest yield of biodiesel was 95.8% after 4 hours of reaction demonstrating a great activity of the catalyst. The refined biodiesel obtained from the methanolysis was analyzed by GC-MS method to determine the fatty acid methyl ester (FAMEs) composition and described in figure 9 and table 5. The FAMEs content reached 100.00% demonstrating a very high purity of the refined biodiesel.
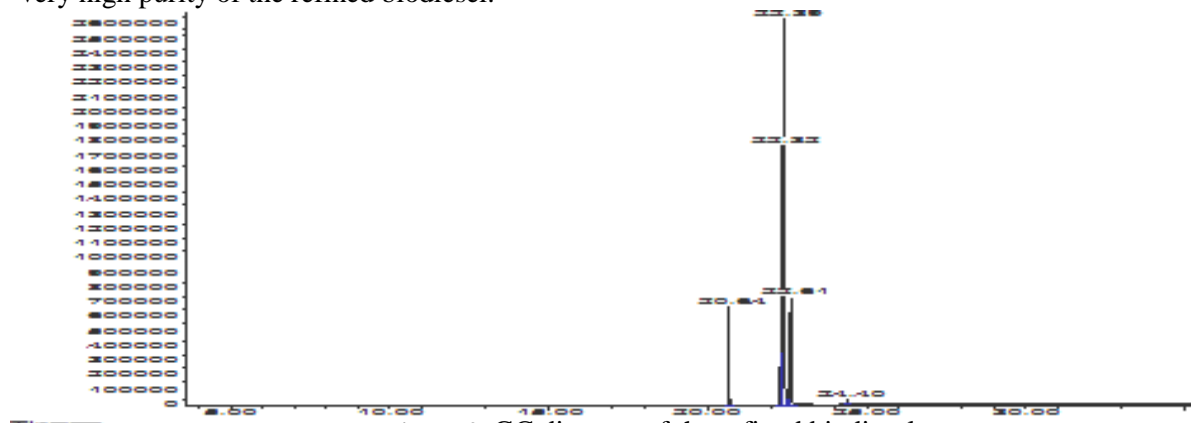
Figure 9. GC diagram of the refined biodiesel

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Table 5. Fatty acid composition in refined biodiesel derived from GC-MS results

No.	Acid names	Components	Formulas	Contents, %
1	Hexadecanoic	C16:0	$C_{16}H_{32}O_2$	10.69
2	9,12-Octadecadienoic	C18:2	$C_{18}H_{32}O_2$	28.90
3	13-Octadecenoic	C18:1	$C_{18}H_{34}O_2$	47.79
4	Octadecanoic	C18:0	$C_{18}H_{36}O_2$	12.12
5	Eicosanoic	C20:0	$C_{20}H_{40}O_2$	0.50
Sum				100.00

APPLICATIONS

The prepared Cellulose based catalyst had favorable activity when applied to the methanolysis of the Vietnam rubber seed oil.

CONCLUSIONS

Cellulose based catalyst was successfully prepared through partial carbonization of cellulose followed by sulfonation of the as-synthesized black powder. Both the black powder and the catalyst possessed amorphous structure with main element compositions of C and O. Through the sulfonation of the black powder, the -SO_3H groups were rigidly located on the catalyst surface by covalent bonds with the poly-aromatic rings enhancing the catalyst activity and stability. The acidity of the catalyst also sharply increased after the sulfonation of the black powder.

The catalyst revealed favorable activity when applied to the methanolysis of the Vietnam rubber seed oil. The FAMEs content in refined biodiesel reached 100% while the methanolysis yield was up to 95.8% affirming the wonderful potential of the catalyst in biodiesel synthesis with various kinds of feedstock, even with rich free fatty acid feedstocks.

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