

INTRODUCTION

1. The topic's necessity

Ethyl lactate is one of the biology solvents which can replace traditional solvents from oil in more than 80% of industrial applications such as printing, painting, producing detergents and plant protection products ... because of its good properties such as: good solubility, low volatility, flame retardancy, little effect on human health, no cancer, biodegradability, use of renewable material source, and especially not participating in the process of creating photochemical ozone causing bad impact on the environment.

Ethyl lactate is formed by the thermodynamic balance reaction between lactic acid and ethanol. In addition to measures to improve the yield of ethyl lactate's production such as providing excess ethanol, continuously removing the water by equilibrium distillation with another solvents ..., the incorporation of using acid catalysts is an effective and necessary solution to shift the equilibrium and accelerate the reaction speed to produce ethyl lactate.

Effective catalysts for the esterification of lactic acid into ethyl lactate in the liquid phase are usually homogeneous acids such as sulfuric acid, phosphoric acid, anhydrous hydrochloride. However, these catalysts can corrode the equipment, which are difficult to be separated from the reaction mixture, low selectivity and causing the environment large amounts of waste. Thus heterogeneous catalytic acids such as zeolite, Amberlyst 15 ion exchange resin, Nafion NR 50, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{SO}_4^{2-}/\text{ZrO}_2$, ... have been studied and used instead of homogeneous acids for easy separation from the mixture, the higher the selectivity, the less side effects, the recyclability, reuse and less equipment corrosion. Recently, a new trend is to use sulfonated carbon-based catalysts for the synthesis of ethyl lactate from lactic acid and ethanol. This catalyst is environmentally friendly, not soluble in most acids, bases or organic solvents, strong affinity with organic matter, having phenolic ($-\text{OH}$) functional groups, carboxylic acid ($-\text{COOH}$) and the strong sulfonic acid ($-\text{SO}_3\text{H}$) group, made from different carbonaceous materials and especially from agricultural by-product. With these superior properties, solid acid catalysis based on sulfonated carbonate promises to be an effective catalyst for esterification.

In addition, another type of carbonaceous material containing the strong sulfonic acid ($-\text{SO}_3\text{H}$) group, known as graphene oxide prepared

by graphite oxidation with the Hummers method has attracted the attention from scientists because beside typical carbon feature, this material bears some special characteristics include: thin-film, multi-layered porous structures, oxygen-containing functional groups, fast electron transfer, and good dispersion in water. Therefore, this material is considered to be a potential acid catalyst.

2. The thesis's objective and content

The objective of the thesis is to find suitable conditions for the synthesis of carbon -based solids from biomass (CS) and graphene oxide (GO), catalyzing the lactic acid esterification reaction to ethyl lactate, and applied to make biological solvents in processing plant protection drug.

The dissertation shall include following research contents:

- Systematic study of the synthesis and characteristics of sulfonated carbon - based catalysts from common biomass sources.
- Synthetic and characteristics of graphene oxide - based catalysts.
- Evaluating the activity of the catalysts synthesized in the lactic acid esterification reaction to ethyl lactate.
- Research on regeneration and reuse of catalysts.
- Study on the application of ethyl lactate in the preparation of biological solvents in processing plant protection drugs.

3. The thesis's scientific and practical significance

Contributing to the knowledge of synthesizing carbon sulphonates from biomass, graphite oxidation with the Hummers method, forming the sulfonic acid group $\text{-SO}_3\text{H}$, making the material a solid acid catalyst Bronsted with high effect for esterification.

Meeting the practical demand for environmentally friendly solvents and contributing to the efficient use of agricultural byproducts and reducing environmental pollution.

4. The thesis's new contribution

Identifying the appropriate condition for the synthesis of solid acid catalysts based on sulfonated carbon (CS) from various biomass by-products: sawdust, straw, bagasse, rice husk, water hyacinth, corn stalks, cassava stalks, through two phases of biomass pyrolysis and sulfonation of pyrolysed coal from biomass. It has been shown that catalysts derived from sawdust exhibit the best performance for lactic acid esterification to ethyl lactate, thus studying the catalytic rates, assessing the recyclability, reuse of catalysts on the basis of sawdust biomass.

Graphene oxide (GO) and graphene oxide catalysts on activated

carbon (GO/AC) have been applied to lactic acid esterification with GO catalytic exhibiting the best activity, GO/AC has similar activity to CS.Mc catalyst. The advantage of GO/AC over GO is that it is easy to be separated from the reaction mixture, increasing the practical application of GO.

Preparing biological solvents containing ethyl lactate and applying biological solvents to process plant protection drugs Biosol-D 2.5EC (containing deltamethrin) and Biosol-Ch 20EC (containing chloropyrifos ethyl). Results showed that the biological efficiency of Biosol-D2.5EC product was equivalent to that of Videcis 2.5EC with the use of fossil solvents.

5. The thesis's construction

The thesis consists of 126 pages: Introduction (2 pages); Overview (33 pages); Experiment (26 pages); Results and Discussion (47 pages); Conclusion (2 pages); New contributions (1 page); List of published works (1 page); References including 118 references (14 page). The thesis has 31 tables and 45 charts.

CHAPTER 1. OVERVIEW

1.1. Lactic acid esterification of ethyl lactate

1.1.1. Characteristics and application of ethyl lactate

1.1.3. Mechanism of reaction

1.1.4. Factors affecting lactic acid esterification

1.1.5. Solid acid catalysts for lactic acid esterification

1.2. Solid acid catalysts based on sulfonated carbon

1.2.1. Introduction of sulfonated carbonate - based catalysts

Carbon sulfonated (CS) based-catalysts with the carbonate construction are arranged in layers consisting of a system of aromatic rings in the amorphous form, on the surface containing functional groups linked to the aromatic ring system. In this group, there is the group $-OH$, $-COOH$ and especially the strong-acid group Bronsted $-SO_3H$.

1.2.2. Method to prepare sulfonated carbon-based catalyst

1.2.2.1. Polymer pyrolysis containing sulfonic precursors

1.2.2.2. Synthesis by special sulphonation agents

1.2.2.3. Sulfoisation and biochar of aromatic compounds

1.2.2.4. Sulfoisation of carbon material obtained from the saccharide pyrolysis process

1.2.2.5. Sulfoisation of carbonaceous material obtained from biomass

pyrolysis

1.2.3. Application of catalysts based on carbon sulphonation

1.3. Lignocellulosic biomass and biomass pyrolysis

1.3.1. Chemical composition of biomass

1.3.2. The pyrolysis process of biomass

1.3.3. Potential and reserves of biomass resources in Vietnam

1.4. Solid acid catalyst based on graphene oxide

1.4.1. Activated carbon

1.4.2. Introduction and application of graphene oxide

Graphene oxide (GO) was synthesized by Hummers method with the presence of concentrated H_2SO_4 , in addition to the catalyst $-\text{COOH} - \text{OH}$ group and $-\text{SO}_3\text{H}$ group

1.4.3. Method to prepare graphene oxide

1.5. Researches in Viet Nam

1.6. Conclusions from the literature review

CHAPTER 2. EXPERIMENT

2.2. Compounding the solid acid catalyst on solid carbon-sulphosated basis

CS catalysts from biomass including: sawdust (Mc), straw (Ro), bagasse (Bm), rice husk (Vt), water hyacinth (Be), conr stalks (Tn), cassava stalks (Ts) is modulated through two phases: biomass pyrolysis and sulfonation of pyrolysed coal.

2.2.1. Stage of biomass pyrolysis

40g of the material is put into the pyrolysis equipment, conducting heating at $10^\circ\text{C} / \text{min}$, in N_2 environment at $100\text{mL} / \text{min}$. Pyrolysis conditions: pyrolysis temperature of 300°C ; 400°C ; 500°C ; 600°C , in the time of 1-7 hours. The black solid obtained is the product of pyrolysis.

2.2.2. Stage of sulfonation of pyrolysed coal

15 g of the pyrolysed coal is stirred with H_2SO_4 98% by volumes from 75mL; 150mL; 300mL (corresponding to volume rates of H_2SO_4 98% (mL) /pyrolysed coal mass (g) of 5/1, 10/1, 20/1), in a 3-neck glass flask of 500mL capacity with reed welding. Sulphonation conditions: temperature of 80°C ; 120°C ; 150°C ; 170°C , in the time of 8 hours; 15 hours; 20 hours; 24 hours. Cool the reaction for 30 minutes, then dilute the mixture with 1 liter of distilled water twice. Filter, rinse the solid with hot distilled water (80°C) until the ion SO_4^{2-} is not detected in the

washing water (testing with 10% BaCl₂ solution). Dry the solid at temperature of 105°C for 8 hours, the black material obtained is sulphonated carbon.

2.2.3. Reuse and regeneration of sulfonated carbon catalysts

After each cycle of esterification, the CS catalyst is filtered and rinsed several times with hot distilled water ($\geq 80^{\circ}\text{C}$) until the ion SO_4^{2-} is not detected in the washing water (testing with 10% BaCl₂ solution). Then, dry the solid at temperature of 105°C for 8 hours.

Sulphonated carbon catalyst regenerated with H₂SO₄ 98% in conditions: at temperature of 150°C, in the time of 15 hours and the ratio of regenerated catalyst mass (g) / H₂SO₄ (mL) volume at 1:10

2.3. Modulating solid acid catalyst on graphene oxide basis

2.3.1. Modulating graphene oxide catalyst

Graphene oxide is compounded with the improved Hummers method: 1g of graphite powder and 500mg of NaNO₃ are mixed at 0°C, then gradually add 50 mL of H₂SO₄ 98% to the mixture. After stirring for 30 minutes, add 3g of KMnO₄. The mixture is stirred at 35°C for 2 hours. Gradually put 50 mL of ionised water to the mixture and put the heat to 90°C, and then stir the mixture for 2 hours. Finally add 5mL of H₂O₂ 30%. The final product was washed with HCl 3.7% by centrifugation, and then wash with ionised water until pH = 7.

2.3.2. Modulating graphene oxide catalyst on activated carbon

Commercial activated carbon (AC) is washed with distilled water several times until removing black dust, then dry at 105°C for 48 hours. The dried sample is crushed to a size under 0.063 mm.

The GO / AC catalyst is modulated: 5.2 g of the activated charcoal of the size under 0.063 mm is dried, 104 mL of the GO solution of 5 mg/L (GO dispersed in ion distilled water) is stirred in a 250mL glass for 5 hours at room temperature. Then dry at 85°C for 48 hours. The powder obtained is graphene oxide catalyst on activated carbon (GO / AC) at a mass ratio of 1:10.

2.4. Method of determining the composition, characteristics of material

Use modern methods such as TGA, XRD, SEM, BET, elemental analysis, ...

2.5. Evaluating catalytic activity in lactic acid esterification

2.5.1. Building standard route and analysis of ethyl lactate content with GC-FID method

2.5.2 Evaluating catalytic activity in lactic acid esterification

51g of the lactic acid 50%, 52.087g of the ethanol (corresponding to 4: 1 molar ratio of ethanol /lactic acid) in a 3-necked flask with the volume of 250 mL is put in the oil pot. Put the reaction system heat to 82°C. Put 1,275 gam of catalyst (corresponding to a catalytic ratio of 5% of the lactic acid mass) to the reaction system, start counting the reaction time immediately after putting the entire catalyst. Maintain a reaction system temperature at 82°C. Collect and analyze the sample on gas chromatographs over time.

2.6.2. Evaluating the quality of biological solvents

2.6.3. Processing plant protection drugs

2.6.4. Evaluating the application efficiency of biological catalyst in the preparation of plant protection drugs

2.6.4.1. Evaluating the quality of plant protection drugs

The technical requirement of the product BVTV containing the corresponding deltamethrin and chlorpyrifos ethyl ester is evaluated according to the standard of TCVN 8750: 2014, TCCS 30: 2011 / BVTV and compared to commercial products on the market.

2.6.4.2. Testing 2.5EC deltamethrin BVTV product on the large scale

The 2.5EC deltamethrin BVTV product is selected for the large scale testing, evaluating the effect of rice leaf insect pest control (*Cnaphalocrocis medinalis*) and affecting post-spraying plants. The test is conducted in the field in Hai Quang commune, Hai Hau, Nam Dinh: rice plant, Bac Thom seed number 7; stage of stand-up; use concentration of 0.5L/ha.

CHAPTER 2. RESULTS AND DISCUSSION

3.1. The solid catalyst based on sulfonated carbon

3.1.1. Synthesis and charaterics of sulfonated carbon catalyst

3.1.1.1. Study on the pyrolysis process of biomass

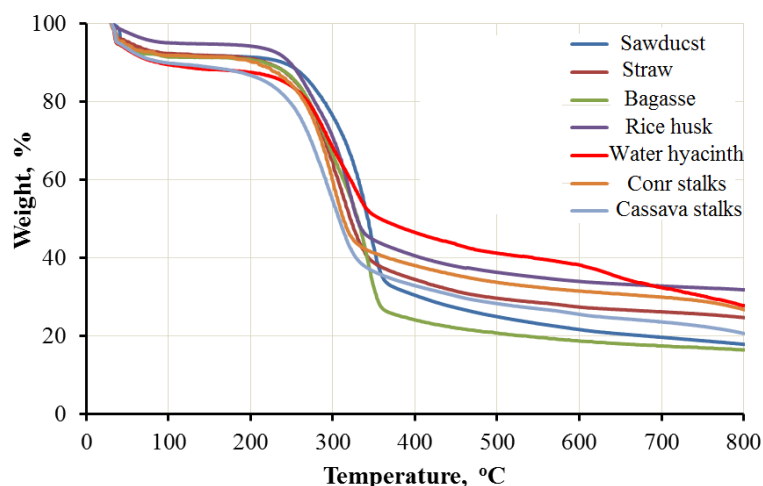
a. Chemical composition and thermal properties of biomass

The ash amounts of straw, rice husk and water hyacinth, which are quite high, are 10.34%, 15.60% and 11.06%, respectively. It can be guessed that efficiency of getting solid products is low for bagasse because it contains high amount of hemicellulose. Contrary, this efficiency for straw, rice husk and water hyacinth are high.

Table 3.1. Chemical composition of biomass

Samples	Moisture content (%)	Ash amount (%)	Lignin (%)	Extracted composition (%)	Celullose (%)	Hemicellulose (%)
Sawdust	9.01	2.51	24.89	4.74	49.02	9.83
Straw	9.96	10.34	25.55	4.98	40.02	9.15
Bagasse	6.49	2.00	21.95	3.09	45.13	21.34
Rice husk	7.30	15.60	32.79	1.69	35.56	7.06
Water hyacinth	7.08	11.06	14.46	4.12	37.10	26.18
Corn stalks	6.33	5.83	26.18	7.24	43.89	10.53
Cassava stalks	7.87	3.97	25.84	6.42	42.61	13.29

Thermal properties show that the losing wt of the biomass samples is highest around 250-350°C. In which, the highest losing wt is 80% for bagasse and the lowest one is 60% for husk and water hyacinth around 200-500°C. In temperature over 350°C to 600°C, the losing wt is slow and reach 80% at 600°C. Then, the condensation of aromatic compounds is happened to form the amorphous structure of carbon. Therefore, the pyrolysis temperature of materials around 350-600°C.

**Fig. 3.1. Thermal analysis diagram TGA of samples in N₂ environment**

b. Effects of temperature on properties of the biochar

Raman spectrums of biochar from sawdust over temperatures do have G band at 1607 cm⁻¹ corresponding to the vibrations at E_{2g} of sp² hybrid carbon atoms in graphite structure. At 400, 500 and 600°C, the samples also have a band at 1389 cm⁻¹ and the shoulder of a peak at 1465 cm⁻¹ corresponding to the system of aromatic compounds in the amorphous carbon materials. This band is not appear at 300°C, proving that the amorphous carbon structure do not form. Besides, the total of peak areas of samples at 400°C is higher than at 500 and 600°C. So, the appropriate pyrolysis temperature is 400°C.

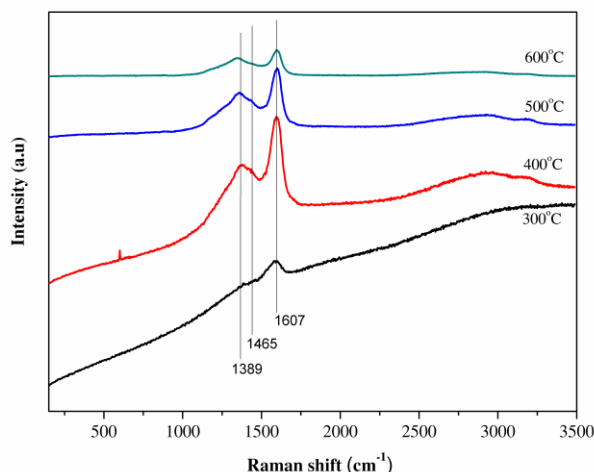


Fig. 3.2. Raman spectrums of biochar from sawdust over temperature

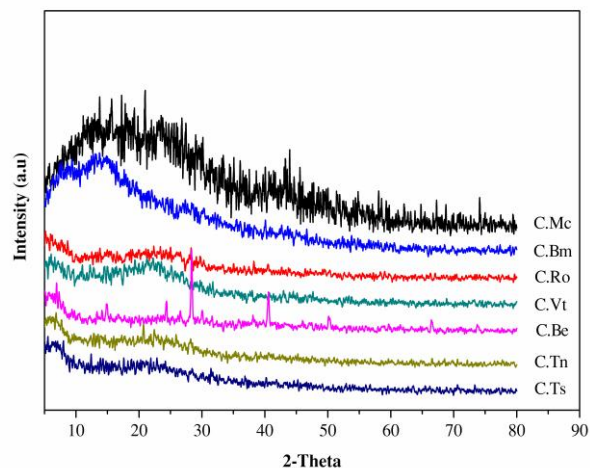


Fig. 3.3. XRD patterns of biochars from biomass (N_2 environment, time of 5h, temperature of 400°C, rate of heat of 10°C/min)

XRD patterns in Fig.3.3 show that the biochars have the amorphous structure. For samples made from water hyacinth, there are several peaks corresponding to such heavy metals as Pb, Cd, Te... with quite high amount.

Amounts of the biochars made from sawdust, Corn stalks and cassava are equal and this amount for bagasse is quite low (about 25%). For straw, this amount is 34.52% and the highest amount is around 41-42% for husk and water hyacinth.

Table. 3.2. Amounts of biochar made from biomass
(N_2 environment, time of 5h, temperature of 400°C, rate of heat of 10°C/min)

Materials	%wt of biochar	Materials	%wt of biochar
Sawdust	30.09	Water hyacinth	42.35
Straw	35.17	Corn stalks	31.88
Bagasse	24.45	Cassava stalks	30.54
Rice husk	41.41		

S_{BET} of biochars are low, from 0.59 to 3.30 m²/g while one of CS is quite high, from 150.2 to 423.4 m²/g (except one of CS.Be). Therefore, the pyrolysis temperature for water hyacinth is continuously studied. Table 3.4 shows that the increase of S_{BET} follows the increase of temperature from 400 to 600°C. However, S_{BET} is not prioritized in the

esterification reaction of acid lactic, so the appropriate pyrolysis temperature for water hyacinth is 600°C.

Table. 3.3. Specific surface areas of biochar and CS catalysts (N_2 environment, time of 5h, biochar temperature of 400°C, rate of heat of 10°/min, sulfonated temperature of 150°C, time of 15h)

Biomass	Biochar		CS sample		
	Samples	S_{BET} (m ² /g)	Samples	S_{BET} (m ² /g)	D_{pore} (nm)
Sawdust	C.Mc	0.59	CS.Mc	423.4	3.8
Straw	C.Ro	3.30	CS.Ro	275.4	5.5
Bagasse	C.Bm	1.80	CS.Bm	244.6	4.4
Rice husk	C.Vt	1.83	CS.Vt	335.9	3.8
Water hyacinth	C.Be	3.22	CS.Be	8.5	6.1
Corn stalks	C.Tn	2.15	CS.Tn	208.5	5.5
Cassava stalks	C.Ts	3.16	CS.Ts	150.2	5.6

Table. 3.4. Specific surface areas of biochars and CS.Be catalyst made from water hyacinth at various pyrolysis temperatures (N_2 environment, time of 5h, temperature of 400°C, rate of heat of 10°/min)

Pyrolysis temperatures, (°C)	S_{BET} of biochars, (m ² /g)	S_{BET} of CS.Be catalyst, (m ² /g)
400	3.2	8.5
500	4.5	60.8
600	3.1	177.6

So, the appropriate pyrolysis temperature of sawdust, straw, rice husk, bagasse, corn stalks and cassava stalks is 400°C but this temperature of water hyacinth is 600°C.

c. Effects of the pyrolysis time

Table. 3.5. Effects of the pyrolysis time on amounts of biochar made from sawdust (N_2 environment, rate of heat of 10°/min)

Pyrolysis time (h)	amounts of biochar, %
1	79.45
2	60.85
3	46.13
4	36.50
5	30.73
6	30.50
7	27.98

When the pyrolysis time increases from 1 to 5 h, amounts of biochar decreases and then stable. Therefore, the appropriate pyrolysis time is 5h for sawdust and others.

So, the appropriate conditions for the pyrolysis process of biomass: temperature of 400°C (600°C for water hyacinth, rate of heat of 10°/min, time of 5h, N₂ environment, N₂ flow rate of 100 mL/min.

3.1.1.2. Study on sulfonation process of biochar

a. Effects of compounds ratio in the reactions

The various compounds ratio in the reaction do not change %S. However, %O slightly increase with the increase of sulfuric acid. On the other hand, the H₂SO₄/amount of biochar ratio changes but the number of acid grounds –SO₃H of catalysts is stable. Therefore, the H₂SO₄/amount of biochar ratio was chosen to be 10 mL/1g.

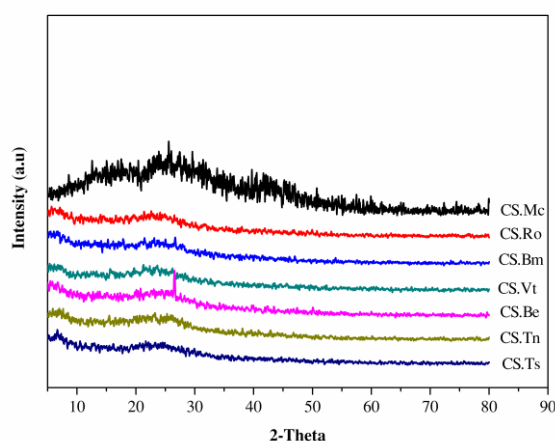
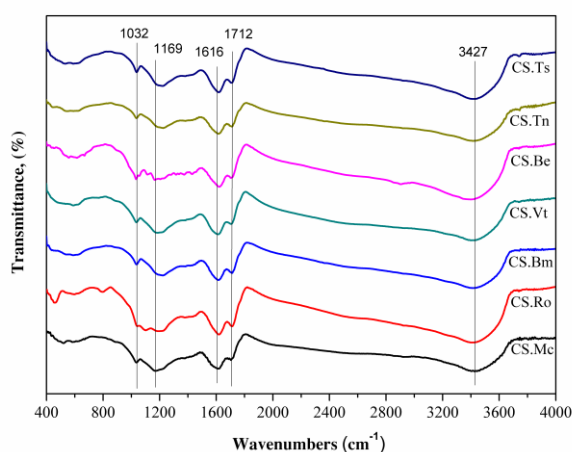
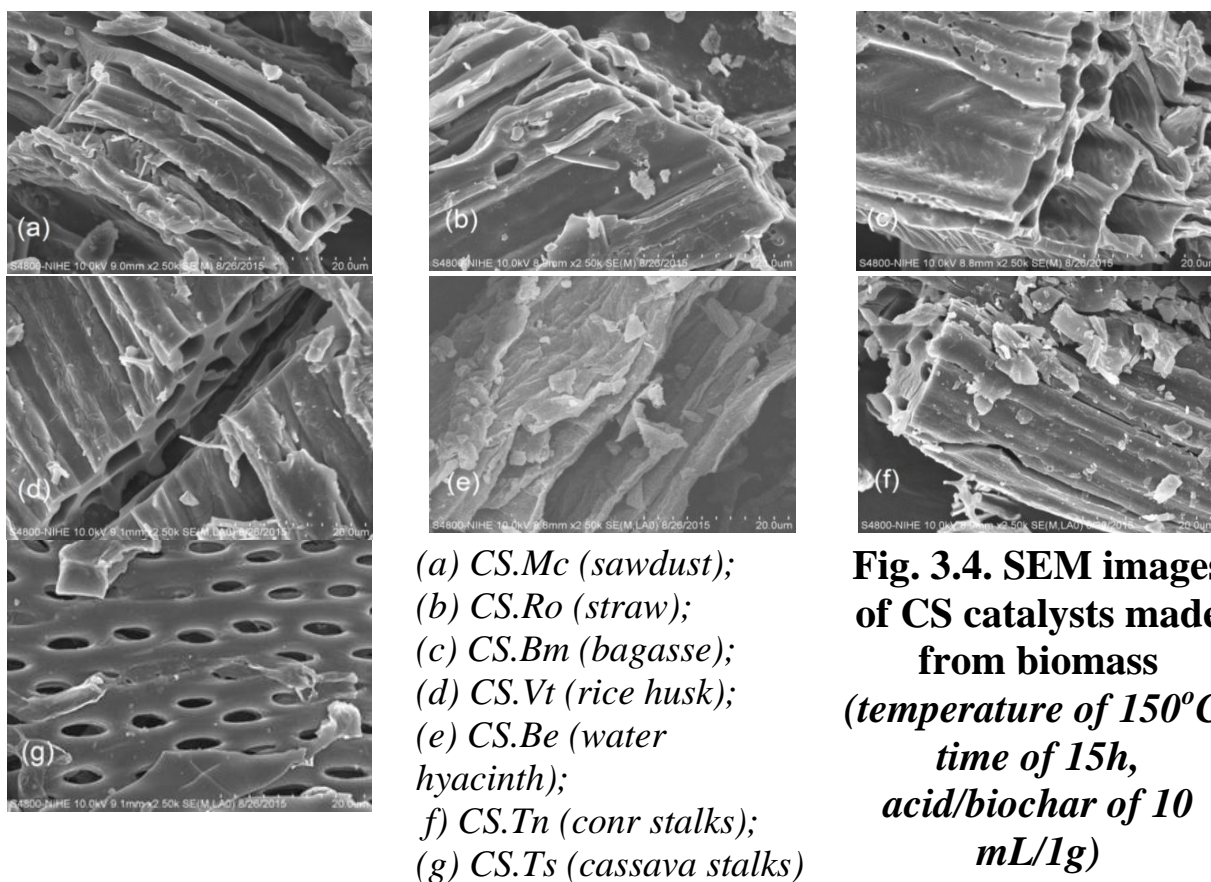
Table. 3.6. The atom composition of CS.Mc catalyst made from sawdust (temperature of 150°C, time of 15h)

Samples		The atom composition (%)			
		C	S	O	H
The pyrolysis biochar made from sawdust		87.5	< 0.2	8.3	3.0
CS catalyst made from sawdust with various H ₂ SO ₄ /amount of biochar ratios	5/1	63.41	1.68	30.13	2.65
	10/1	62.63	1.70	31.22	2.84
	20/1	63.12	1.69	31.78	2.76

Table. 3.7. Effects of compounds ratio in sulfonated period of the reaction (temperature of 150°C, time of 15h)

Biomass	Samples	The amounts of acid group –SO ₃ H (mmol.g ⁻¹) of catalysts with various H ₂ SO ₄ /amount of biochar ratios		
		5/1	10/1	20/1
Sawdust	CS.Mc	1.13	1.14	1.15
Straw	CS.Ro	0.82	0.84	0.83
Bagasse	CS.Bm	1.05	1.07	1.05
Rice husk	CS.Vt	0.81	0.81	0.80
Water hyacinth	CS.Be	0.70	0.69	0.67
Conr stalks	CS.Tn	0.97	0.96	0.96
Cassava stalks	CS.Ts	1.02	1.04	1.03

SEM images show that almost CS samples have the porous structure with the large, uneven, capillary and vertical capillary. However, in the case of CS.Be (fig. 3.4e), not observe so.



IR spectras of CS catalysts show that there is the vibration of –OH bond of phenolic and carboxyl groups at 3427 cm^{-1} on the surface of sulfonated carbon. There are the peak at 1712 cm^{-1} corresponding to C=O groups of –COOH and the peak at 1616 cm^{-1} corresponding to C=C one of aromatic compounds. There are also the peaks at 1032 cm^{-1} , 1169 cm^{-1} corresponding to the balanced and unbalanced stretching vibrations of O=S=O groups of –SO₃H, proving that –SO₃H groups were successfully added to the aromatic compounds of biochar.

XRD patterns of CS catalysts have band including peaks at $2\theta = 20\text{--}30^\circ$, indicating that the catalysts have the amorphous structure. For Cs.Be, there is a clear peak at $2\theta = 26^\circ$, it may be the peak corresponding to graphite structure but there is no peak corresponding to heavy metals as the case of biochar materials. This is caused by the dissolution of heavy metals in sulfonated process.

b. Effects of sulfonated temperature

Table. 3.8. Effects of sulfonated temperature on acid property of catalysts (time of 15h, acid/biochar of 10 mL/1g)

Material	<div style="text-align: center;">Temperature Samples</div>	Amount of -SO ₃ H group (mmol.g ⁻¹)			
		80°C	120°C	150°C	170°C
Sawdust	CS.Mc	1.46	1.19	1.14	1.15
Straw	CS.Ro	1.18	1.04	0.84	0.83
Bagasse	CS.Bm	1.32	1.12	1.07	1.08
Rice husk	CS.Vt	1.20	0.96	0.81	0.82
Water hyacinth	CS.Be	0.91	0.80	0.69	0.66
Conr stalks	CS.Tn	1.21	1.07	0.96	0.95
Cassava stalks	CS.Ts	1.29	1.08	1.04	1.02

The amount of –SO₃H group decrease following the order: –SO₃H (80°C) > –SO₃H (120°C) > –SO₃H (150°C) ~ –SO₃H (170°C). In which, The amount of –SO₃H group is highest in the case of CS.Mc catalyst made from sawdust and lowest one belongs to CS.Be catalyst made from water hyacinth.

On the other hand, the results show that the “leaching” of –SO₃H groups decreases when the increase of temperature. At 150°C, the “leaching” of –SO₃H groups is just 33%. So, it can be considered that 150°C is the appropriate temperature for process of CS synthesis.

Table. 3.9. Effects of sulfonated temperature on the “leaching” of –SO₃H groups of CS catalysts (time of 15h, acid/biochar of 10 mL/1g)

T° Catalysts	80°C			120°C			150°C			170°C		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
CS.Mc	1.46	0.97	66.4	1.19	0.39	33.3	1.14	0.35	30.7	1.15	0.33	28.7
CS.Ro	1.18	0.63	53.4	1.04	0.45	43.3	0.84	0.26	30.9	0.83	0.24	28.9
CS.Bm	1.32	0.76	57.6	1.12	0.43	38.4	1.07	0.33	30.8	1.08	0.30	27.8
CS.Vt	1.20	0.66	55.0	0.96	0.41	42.7	0.81	0.27	33.3	0.82	0.25	30.5
CS.Be	0.91	0.54	59.3	0.80	0.37	46.2	0.69	0.22	31.9	0.66	0.20	30.3
CS.Tn	1.21	0.69	57.0	1.07	0.41	38.3	0.96	0.29	30.2	0.95	0.29	30.5
CS.Ts	1.29	0.71	55.0	1.08	0.42	38.9	1.04	0.32	30.8	1.02	0.30	29.4

(1) Initial density of –SO₃H groups (mmol/g)

(2) Density of leached –SO₃H groups (mmol/g)

(3) the “leaching phenomenon” of –SO₃H groups (% mol)

The atoms' amounts of CS.Mc catalyst (table 3.10) are quite fit with –SO₃H groups' amounts (in order to make it easier, the thesis only analyzes the composition of the sample made from sawdust as a representative one). The amount of sulfur of CS at 80°C and 120°C is higher than at 150°C and 170°C. Yet, BET method (Table 3.11) indicate that the best results were gained at 150°C. As a result, 150°C is the appropriate temperature for sulfonated process of biochar.

Table 3.10. Effects of sulfonation temperature on the atom composition of catalysts made from sawdust (time of 15h, acid/biochar of 10 mL/1g)

Samples	The atom composition (%)			
	C	H	S	O
Biochar made from sawdust	87,5	3,0	<0,2	8,3
CS.Mc (80°C)	64,55	3,36	2,65	30,30
CS.Mc (120°C)	63,89	3,12	2,03	30,27
CS.Mc (150°C)	63,33	2,73	1,67	30,32
CS.Mc (170°C)	63,48	2,59	1,68	29,80

Table 3.11. Effects of sulfonation temperature on the specific surface area of CS.Mc catalysts made from sawdust (time of 15h, H₂SO₄/biochar of 10 mL/1g)

Sulfonation temperature, (°C)	The specific surface area BET, (m ² /g)
80	22,2
120	159,9
150	423,4
170	151,3

c. Effects of sulfonated time on acid property of the sulfonated carbon catalyst

When time increase from 8 to 15 h, the amount of the acid group increases and still increases at time of 24 h, then being stable. Therefore, the appropriate time of sulfonated process is 15 h. For this time, the highest amount of $-\text{SO}_3\text{H}$ groups is 1.14 mmol/g for catalyst made from rawdust and the lowest amount of $-\text{SO}_3\text{H}$ groups is 0.69 mmol/g for one made from water hyacinth.

Table 3.12. Effects of sulfonated time on the amount of $-\text{SO}_3\text{H}$ groups (temperature of 150°C , $\text{H}_2\text{SO}_4/\text{biochar}$ of 10 mL/1g)

Biomass	Catalysts	The amount of $-\text{SO}_3\text{H}$ groups over various reaction time (mmol/g)			
		8 h	15 h	20 h	24 h
Sawdust	CS.Mc	0.99	1.14	1.15	1.14
Straw	CS.Ro	0.77	0.84	0.82	0.85
Bagasse	CS.Bm	0.95	1.07	1.07	1.06
Rice husk	CS.Vt	0.71	0.81	0.83	0.80
Water hyacinth	CS.Be	0.61	0.69	0.67	0.68
Corn stalks	CS.Tn	0.84	0.96	0.98	0.96
Cassava stalks	CS.Ts	0.93	1.04	1.04	1.06

The results show that the total of the acid group of CS catalysts is around 3.98- 5.56 mmol/g, in which, the amount of $-\text{SO}_3\text{H}$ groups is around 0.69 -1.14 mmol/g.

Table. 3.13. The acid property of CS following the acid-base titration method (temperature of 150°C , time of 15h, $\text{H}_2\text{SO}_4/\text{biochar}$ of 10 mL/1g)

Material	Catalysts	The amount of $-\text{SO}_3\text{H}$ groups (mmol/g)	The total of amount of acid groups (mmol/g)
Sawdust	CS.Mc	1.14	4.53
Straw	CS.Ro	0.84	3.98
Bagasse	CS.Bm	1.07	4.95
Husk	CS.Vt	0.81	4.00
Water hyacinth	CS.Be	0.69	4.56
Corn stalks	CS.Tn	0.96	5.56
Cassava	CS.Ts	1.04	4.07

The amount of $-\text{SO}_3\text{H}$ groups of the catalysts also characterized by TPD- NH_3 method. The best result is 1.16 mmol/g for CS.Mc catalyst. The lowest result is only 0.20 mmol/g for CS.Be catalyst. This results fit with the acid-base titration method.

Table. 3.14. The amount of $-\text{SO}_3\text{H}$ groups following TPD- NH_3 method

Material	Catalysts	The total of amount of acid groups (mmol/g)			
		$\leq 200^\circ\text{C}$	200 – 400 $^\circ\text{C}$	$\geq 400^\circ\text{C}$	Tổng
Sawdust	CS.Mc	1.16	0	13.71	14.87
Straw	CS.Ro	1.10	0	17.79	18.89
Bagasse	CS.Bm	0.43	1.74	6.89	9.06
Rice husk	CS.Vt	0.52	0	21.53	22.05
Water hyacinth	CS.Be	0.20	2.45	12.57	15.22
Corn stalks	CS.Tn	0.39	3.55	21.13	25.06
Cassava stalks	CS.Ts	0.27	0	27.59	27.86

So, the results of biomass pyrolysis and sulfonated biochar processed to prepare sulfonated carbon catalysts are summarized:

- Pyrolysis process : temperature of 400°C (600°C for water hyacinth), time of 5 h, N_2 environment, %wt of biochar of 30-33%, highest 40% for water hyacinth and rawdust, lowest 24% for bagasse.
- Sulfonated process : temperature of 150°C , standard pressure, time of 15h, H_2SO_4 98% as the sulfonated agent, $\text{H}_2\text{SO}_4/\text{biochar}$ of 10 mL/1g.
- The catalysts made from sawdust have the highest amount of SO_3H groups (1.14 mmol/g) and the catalysts made from water hyacinth have the lowest one (0.69 mmol/g).
- S_{BET} of all catalysts is over 100 m^2/g . In which, the catalysts made from rawdust is 423.4 m^2/g . For water hyacinth, S_{BET} is affected so much by pyrolysis temperature.

In all materials, rawdust is the most appropriate one for preparing the sulfonated carbon catalyst because in the esterification reaction of acid lactic, the amount of $-\text{SO}_3\text{H}$ groups is the most important.

3.1.2. The catalytic activity of the sulfonated carbon for the esterification reaction of lactic acid

3.1.2.2. The catalytic activity of the sulfonated carbon for the esterification reaction

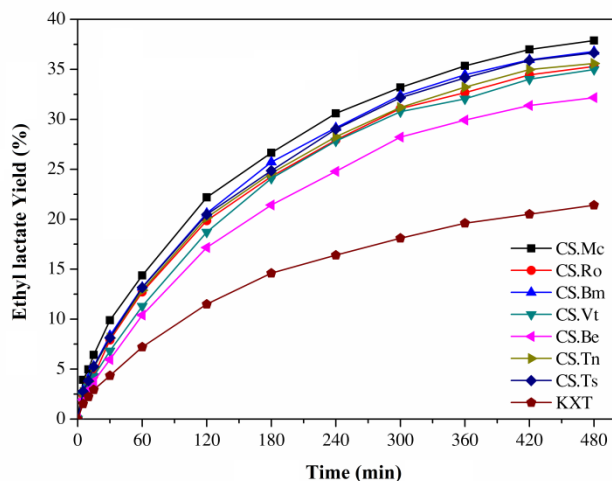


Fig. 3.7. Ethyl lactate forming efficiency after 8h (temperature of 82°C, lactic acid 50%, ethanol/acid of 4/1, 5% wt of catalysts)

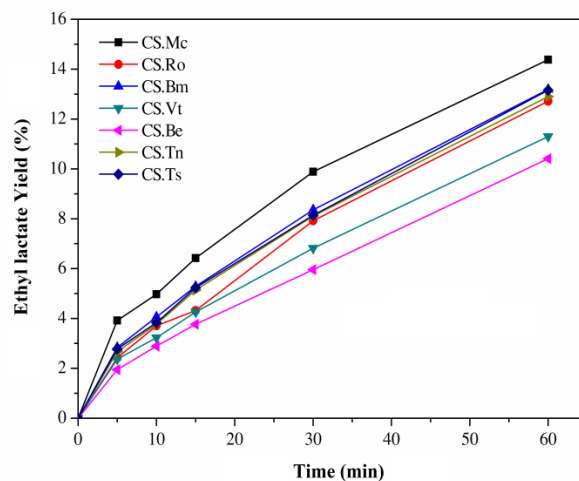


Fig. 3.8. Ethyl lactate forming efficiency after 1h (temperature of 82°C, lactic acid 50%, ethanol/acid of 4/1, 5% wt of catalysts)

Ethyl lactate forming efficiency is highest to be 38% for CS.Mc catalyst and lowest to be 32% for CS.Be one after 8h. This results fit with the amount of $-\text{SO}_3\text{H}$ groups but not the total of amount of acid groups. This also shows that the amount of $-\text{SO}_3\text{H}$ groups plays so important a role for Ethyl lactate forming efficiency. Therefore, CS.Mc was chosen for the next studies.

3.1.3. Effects of the amount of catalysts on efficiency of esterification reaction of lactic acid

When the amount of catalysts increases from 5 to 10%, ethyl lactate forming efficiency also increases from 38 to 49% after 8h. Continuing to increase the amount of catalysts to 12%, it seems that ethyl lactate forming efficiency insignificantly increases in comparison to the amount of catalysts of 10%. So, the amount of catalysts was chosen to be 10%.

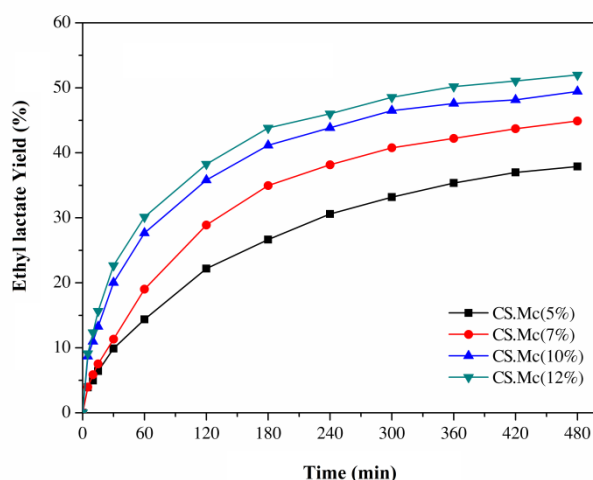


Fig. 3.9. Ethyl lactate forming efficiency over time with various the amount of catalysts after 8h (temperature 82°C, lactic acid 50%, ethanol/acid of 4/1, CS.Mc catalyst)

3.1.4. Reusing and recycle ability of the catalysts

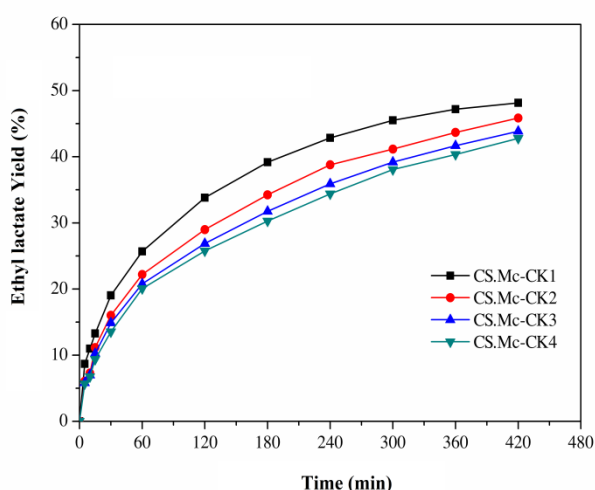


Fig. 3.10. Ethyl lactate forming efficiency after 4 reaction cycles (temperature 82°C, lactic acid 50%, ethanol/acid of 4/1, CS.Mc catalyst, 10% wt of catalyst)

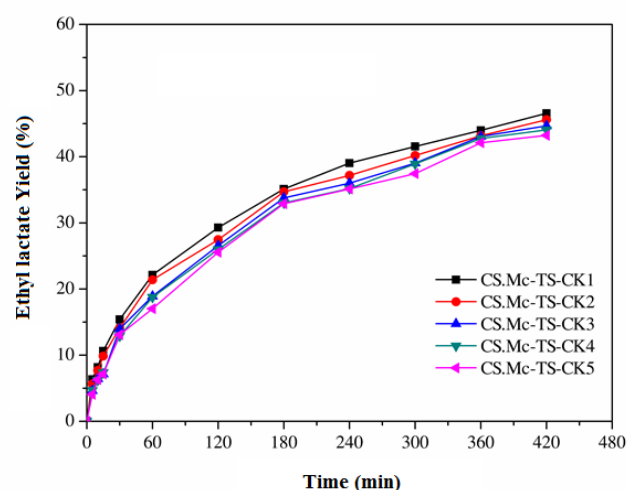


Fig. 3.11. Ethyl lactate forming efficiency of recycled CS.Mc catalyst after 5 reaction cycles (temperature 82°C, lactic acid 50%, ethanol/acid of 4/1, recycled CS.Mc catalyst, 10% wt of catalyst)

After every reaction cycle, the conversion of lactic acid into ethyl lactate decreases: the first cycle of 48,14% after 420 minutes, next cycles of 45,85%, 43,8% and 42,78%. After 4 cycles, ethyl lactate forming efficiency decreases 5,40%.

The catalytic activity of recycled catalysts shows that recycled CS.Mc catalysts after 2 cycles are equivalent to the initial catalysts (46,56% in comparison to 45,85%) and the efficiency is 43,23% after 420 minutes and 5 cycles. The results indicate that the decrease of the catalytic activity of recycled catalysts is lower than the initial catalyst.

The stable catalytic activity after recycling was proved by the results of acid property characteristics and FT-IR spectra in Table 3.15 and Fig. 3.16.

SEM images (Fig. 3.17) and the amount of acid groups (Table 3.15) of recycled CS.Mc catalyst is almost similar to the initial catalyst.

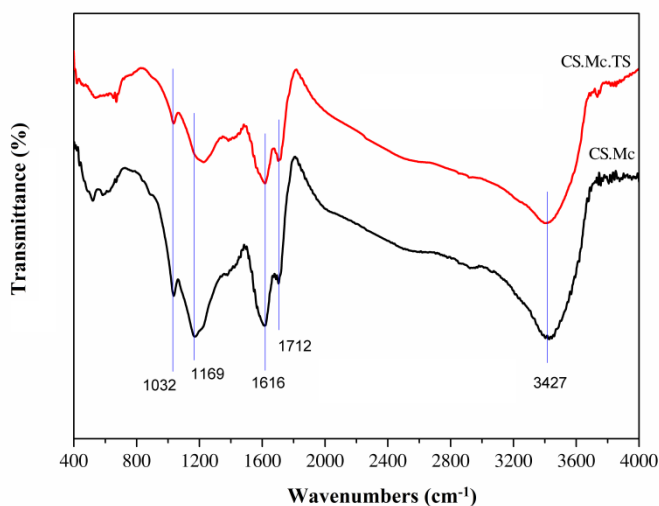
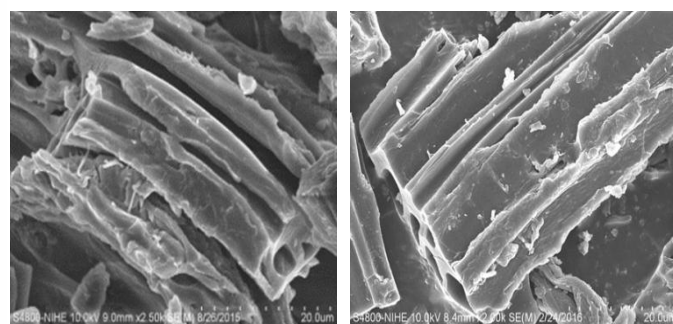


Fig. 3.12. FT-IR spectras of the initial catalyst (CS.Mc) and recycled catalyst (CS.Mc.TS) (*sulfonated time of 15h, temperature of 150°C, H_2SO_4 /CS.Mc of 10 mL/1g*)



(a)

(b)

Fig. 3.13. SEM images of the initial catalyst (a) and recycled catalyst (b) (*sulfonated time of 15h, temperature of 150°C, H_2SO_4 /CS.Mc of 10 mL/1g*)

Table. 3.15. The amount of acid groups of recycled CS.Mc catalyst (*sulfonated time of 15h, temperature of 150°C, H_2SO_4 /CS.Mc of 10 mL/1g*)

Catalysts	The amount of -SO ₃ H groups (mmol/g)	The total of the amount of acid groups (mmol/g)
CS.Mc	1.14	4.53
CS.Mc.TS	1.12	4.58

It can be said that CS catalyst can be reused and recycled many times but keep stable activity for the esterification reaction of lactic acid into ethyl lactate.

3.2. Solid acid catalyst based on graphene oxide

3.2.1. Catalyst characteristics based on graphene oxide

3.2.1.1. XRD patterns

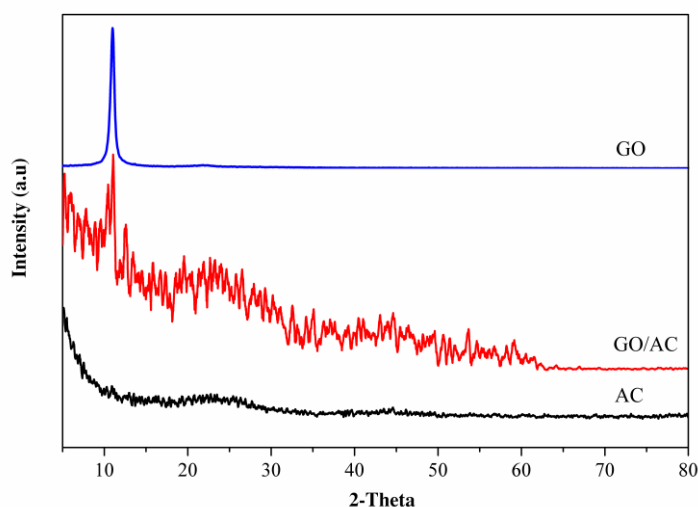


Fig. 3.14. XRD patterns of activated carbon (AC) ; graphene oxide (GO) ; GO/AC (wt ratio of 1:10)

XRD pattern of GO have a sharp peak at $2\theta = 11^\circ$ corresponding to featured peak of GO. This peak is also observed in the case of GO/AC, showing that GO was added on the surface of AC in GO/AC catalyst.

3.2.1.2. SEM and EDX images

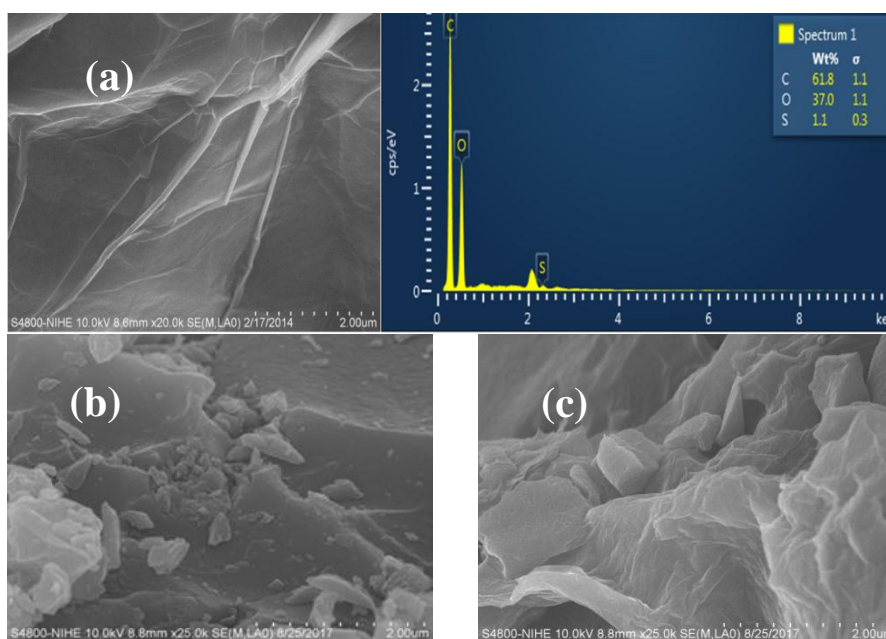


Fig. 3.15. SEM-EDX images of GO (a), SEM image of AC (b), GO/AC (c) (wt ratio of 1 :10)

SEM-EDX images of GO indicate that GO have the layer structure and the peak of sulfur (Fig. 3.19a). While the activated carbon have the rough structure (Fig. 3.19b). There is a structure in which the activated carbon is covered by GO, proving the successfully preparing of GO/AC.

3.2.1.3. FT-IR spectra

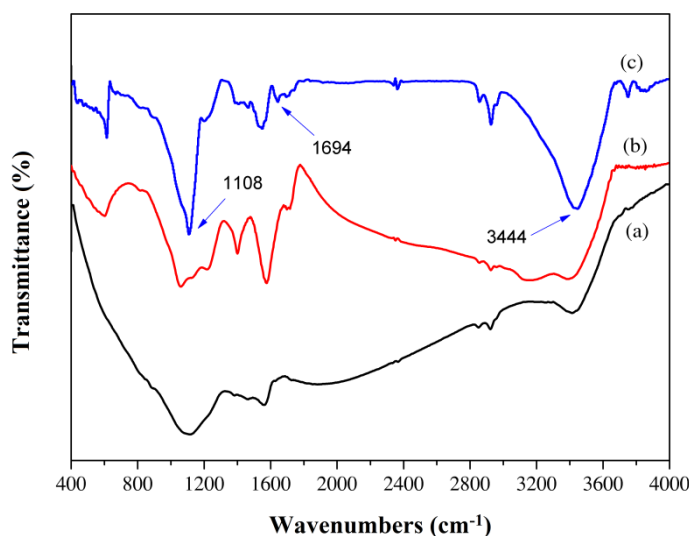


Fig. 3.16. FT-IR spectras of AC (a), GO (b), GO/AC (c) (wt ratio of 1:10)

FT-IR of GO and GO/AC have vibrations at 3444, 3387 cm^{-1} corresponding to $-\text{OH}$ groups and 1694, 1698 cm^{-1} corresponding to $\text{C}=\text{O}$ groups of $-\text{COOH}$. Besides, there is the valence vibrations at 1108, 1059 cm^{-1} corresponding to $\text{S}=\text{O}$ groups of $-\text{SO}_3\text{H}$. There is no vibrations of $\text{S}=\text{O}$ for activated carbon.

3.2.1.4. The specific surface area and the amount of $-\text{SO}_3\text{H}$ groups

The activated carbon's S_{BET} is quite high (721.1 m^2/g). After added by graphene oxide, GO/AC catalyst's S_{BET} decreased to be 570.3 m^2/g . It is caused by filling the activated carbon's capillaries with GO.

Table. 3.16. The specific surface area and the amount of $-\text{SO}_3\text{H}$ groups of catalysts based on GO

Catalysts	The amount of $-\text{SO}_3\text{H}$ groups (mmol/g)	S_{BET} (m^2/g)
CS.Mc	1.14	423.4
CS.Mc after 4 reaction cycles	0.64	-
Activated carbon	0	721.1
GO	0.92	215.9
GO/AC	0.35	570.3
GO/AC after 6 reaction cycles	0.29	618.9

The amount of $-\text{SO}_3\text{H}$ groups is 0.92 mmol/g and 0.35 mmol/g for GO and GO/AC catalyst, respectively. Table 3.16 also shows that there is no the significantly difference for the amount of $-\text{SO}_3\text{H}$ groups between CS.Mc (1.14 mmol/g) and GO catalyst.

3.2.2. The catalytic activity of the catalysts based on graphene oxide for esterification reaction of lactic acid

The catalytic activity decreases in the following order: GO (51%) > CS.Mc (37%) \approx GO/AC (35.4%) >> activated carbon (20%) but it is

not follow the decrease law of the amount of $-\text{SO}_3\text{H}$ groups. It can be caused by the amount of effective $-\text{SO}_3\text{H}$ groups which is higher in the case of GO than GS.Mc as well as the good dispersion of GO in comparison to CS.Mc in reaction environment. The results also shows that the catalytic activities of CS.Mc and GO/AC catalysts are quite equivalent to reported Amberlyst 15 và $\text{K}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ catalysts.

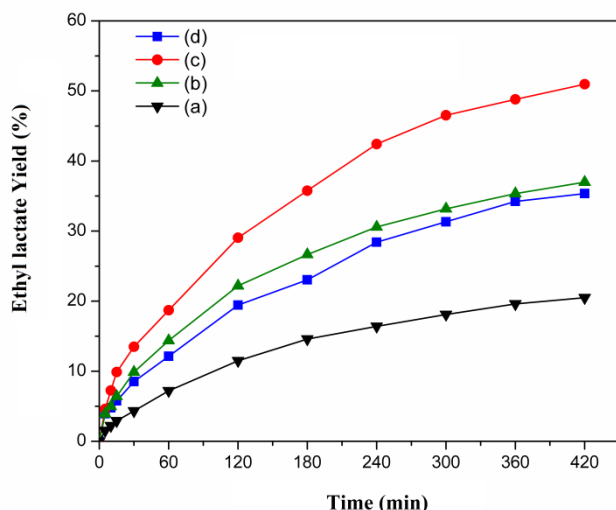


Fig. 3.17. Ethyl lactate forming efficiency over time for activated carbon (a), CS.Mc (b), graphene oxide (c), GO/AC (d) (temperature of 82°C , lactic acid 50%, ethanol/acid of 4/1, 5% CS.Mc; 1% GO and 1% GO in GO/AC in comparison to lactic acid)

3.2.3. Reusing ability of graphene oxide supported on activated carbon catalysts

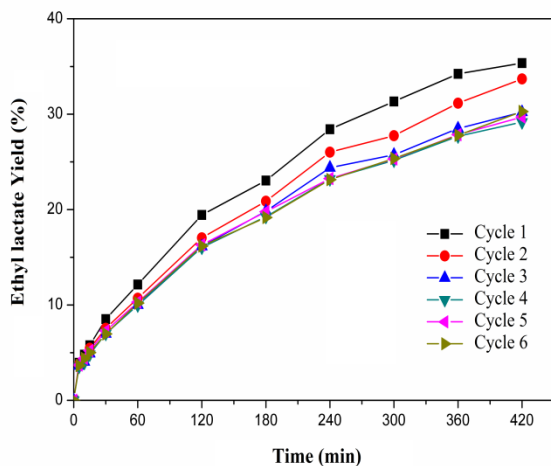


Fig. 3.18. The catalytic activity of GO/AC catalyst after 6 reaction cycles (temperature 82°C , lactic acid 50%, ethanol/acid of 4/1, 1% GO in GO/AC in comparison to lactic acid)

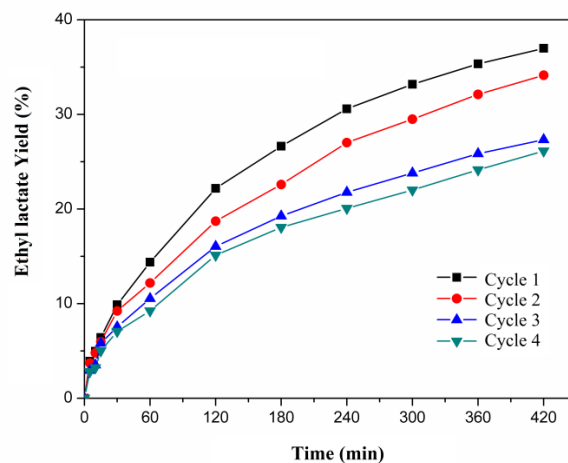


Fig. 3.19. The catalytic activity of CS.Mc catalyst after 4 reaction cycles (temperature 82°C , lactic acid 50%, ethanol/acid of 4/1, 5% wt of CS/Mc in comparison to lactic acid)

The catalytic activity of GO/AC catalyst is stable from 3rd cycle. These results are consistent with the decrease of $-\text{SO}_3\text{H}$ contents in the GO/AC catalyst from 0.35 mmol.g^{-1} to 0.29 mmol.g^{-1} after 6 cycles

(Table 3.16). Ethyl lactate forming efficiency decreases after every cycle (Fig. 3.23). Thus, GO/AC catalyst shows not only a good catalytic activity but also a good stability.

It can be said that GO phase was well dispersed and attached onto activated carbon. The attachment of graphene oxide onto activated carbon surface may be explained by a self-esterification between COOH and OH groups to form a COO- bonding and making the interaction π - π between GO and AC.

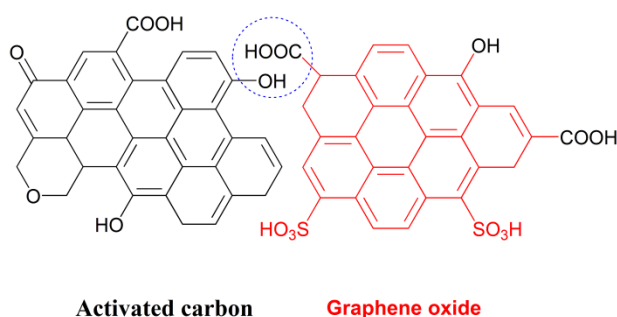


Fig. 3.20. The model of esterification between activated carbon and graphene oxide

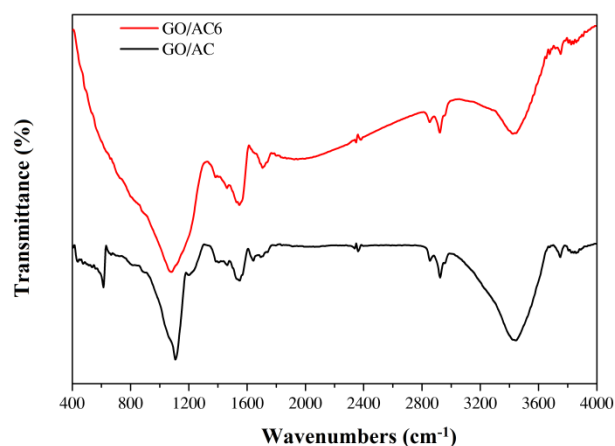


Fig. 3.21. FT-IR spectras of GO/AC catalyst and recycled GO/AC catalyst after 6 cycles

The FT-IR spectra of the GO/AC after 6 cycles of reaction also showed vibrations at 3423 cm^{-1} , 1705 cm^{-1} and 1080 cm^{-1} corresponding to the presence of the groups OH , COOH and SO_3H , respectively. The combination of GO and AC reduces the disadvantage of GO, making the better catalyst GO/AC which makes it easier to remove the catalysts from the reaction mixture by normal methods and has a high specific surface area.

3.3. Bio solvents to produce plant protection products

3.3.3. Evaluate the quality of plant protection products deltamethrin 2.5EC và chloropyrifos ethyl 20EC including DMSH

Deltamethrin 2.5EC và chloropyrifos ethyl 20EC including DMSH follow TCVN 8750:2014 and TCCS 30:2011/BVTV.

Table. 3.17. Technical targets of Biosol-D2.5EC và Biosol-Ch20EC ethyl 20EC chứa DMSH

STT	Technical targets	Unit	Biosol-D2.5EC	Biosol-Ch20EC
1	The amount of active compounds	%	2.3	19.0
2	The stability of emulsion			
2.1	- Initial	mL	Full	Full
2.2	- After 0.5 h	mL	0	0
3	Foam level	mL	9	10
4	pH	-	4.46	3.60
5	The stability at 54°C±2 after 14 days			
5.1	The amount of active compounds	%	2.4	20.3

3.3.4. Investigate the bio activities of Biosol-D2.5EC in high extent

Table. 3.18. The density of leaf and effects of plant protection products in the time of experiment

Samples	The density of leaf before experiment (unit/m ²)	The density of leaf after experiment (unit/m ²)			Efficiency (%)		
		3 days	7 days	14 days	3 days	7 days	14 days
Biosol-D2.5EC	12.6	8.2	5.6	4.8	52.3	61.1	71.4
Videcis 2.5EC	11.6	7.2	5.6	6.0	54.5	57.8	61.2
Water (comparison sample)	12.6	17.2	14.4	16.8	-	-	-

The density of leaf is lower than comparison sample for both Biosol-D2.5EC and commercial product with amount of 0.5 L/ha. After 3 days, the density of leaf for Biosol-D2.5EC is higher than Videcis 2.5EC but after 7 and 14 days, it was the opposite. These results were also fit with the results of efficiency.

CONCLUSION

1. Systematically studied the influence factors and determined suitable conditions for the synthesis of solid acid catalyst on carbon sulfonation basis from various biomass by-products such as sawdust, straw, bagasse, rice husk, water hyacinth, corn stalks, cassava stalks through two phases: incomplete pyrolysis: temperature of 400°C (600 °C for water hyacinth), heating speed of 10 °C / minute , time of

- 5 hours, environment of N₂, N₂ current speed of 100mL/ minute; Sulfonation stage: 98% H₂SO₄, volume ratio of H₂SO₄ 98%/ biochar of 10mL/1g, temperature of 150°C, time of 15 hours.
2. Used modern physic-chemical methods: TGA-DTA, BET, XRD, Raman, FT-IR, SEM, TPD-NH₃, elemental analysis, acid-base titration to characterize synthesized CS properties. From there, the carbon sulphonated catalyst (CS.Mc) was selected from sawdust with the acid concentration of –SO₃H and the highest specific surface area (1.14 mmol / g and 423.4 m² / g, respectively) is the appropriate catalyst for the lactic acid esterification reaction to ethyl lactate.
 3. Evaluated the activity of carbon sulphonated catalyst from sawdust (CS.Mc) in the lactic acid esterification reaction to ethyl lactate. The highest yield to create ethylene lactate reached 49% after eight hours of reaction, with an ethanol / lactic acid molar ratio of 4/1, 50% of lactic acid concentration and appropriate catalyst content of 10% over lactic acid.
 4. Regenerated catalyst CS.Mc: H₂SO₄ 98%, ratio of H₂SO₄ 98%/ biochar equivalent 10mL/1g, temperature of 150°C, sulfonation time of 15 hours. Post-recycle catalysts can be renewable, after 4 reaction cycles, metabolism yield to ethyl lactate reduced by 5.3% at a relatively low rate.
 5. Successful synthesized catalyst on the base of graphene oxide (GO) and graphene oxide on activated carbon (GO/AC) with the acid concentration of Bronsted –SO₃H of 0.92 mmol / g and 0.35 mmol / g, catalyzed the lactic acid esterification reaction to ethyl lactate for the conversion yield to ethyl lactate by 51.0% and 35.4%, respectively. With the same yield to create ethyl lactate, the amount of GO catalyst required is 10 times smaller than that of CS.Mc. The GO/AC activity decreases slightly after the first 3 cycles and is almost unchanged after the third cycle. After 6 cycles, the yield to create ethyl lactate decreases by 5.1%. In particular, the GO dispersion over activated carbon (GO/AC mass ratio of 1/10 in the GO / AC catalyst) increased the separation and was easy to recover the catalyst at normal pressure.
 6. Prepared biological solvents containing 48% of FAME, 48% of EL and 4% of NK 2010, applied to replace the xylene solvents in the preparation of Biosol-D2.5EC and Biosol-Ch20EC. The quality of Biosol-D2.5EC obtained is equivalent to the commercial product of the same type like Videcis 2.5EC to prevent rice leaf rollers.