

CARBON CRYOGEL MICROSPHERE FOR ETHYL LEVULINATE PRODUCTION: EFFECT OF CARBONIZATION TEMPERATURE AND TIME

MUZAKKIR M. ZAINOL, MOHD ASMADI, NOR A. S. AMIN*,
KHAIRUDIN AHMAD

Chemical Reaction Engineering Group (CREG), Faculty of Chemical and Energy
Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia

*Corresponding Author: noraishah@cheme.utm.my

Abstract

The side products of biomass and bio-fuel industry have shown potential in producing carbon catalyst. The carbon cryogel was synthesized from lignin-furfural mixture based on the following details: 1.0 of lignin to furfural (L/F) ratio, 1.0 of lignin to water (L/W) ratio, and 8M of acid concentration. The lignin-furfural sol-gel mixture, initially prepared via polycondensation reaction at 90 °C for 30 min, was followed by freeze drying and carbonization process. Effects of carbonization temperature and time were investigated on the total acidity and surface area of the carbon cryogel. Furthermore, the effects of these parameters were studied on the ethyl levulinate yield through esterification reaction of levulinic acid in ethanol. The esterification reaction was conducted at reflux temperature, 10 h of reaction time, 19 molar ratio of ethanol to levulinic acid, and 15.0 wt.% carbon cryogel loading. Based on the carbonization temperature and time studies, the carbon cryogel carbonized at 500 °C and 4 h exhibited good performance as solid acid catalyst. Large total surface area and acidity significantly influenced the catalytic activity of carbon cryogel with 80.0 wt.% yield of ethyl levulinate. Thus, carbon cryogel is highly potential as acid catalyst for the esterification of levulinic acid with ethanol.

Keywords: Carbon cryogel, Esterification, Ethyl levulinate, Levulinic acid, Lignin-furfural.

1. Introduction

The development towards sustainability and green technology has increased drastically through research by many countries. This includes the production of new materials or products such as catalysts and chemicals derived from bio-based

materials and waste. The carbon cryogel derived from lignin and furfural, the by-product of biomass and bio-fuel processing, has shown the potential as catalyst. Previously, phenol has been commonly used with formaldehyde to produce gels [1-3]. The alternative to substitute phenol was made by using lignin [4-6] to produce organic gels with formaldehyde. Instead of using formaldehyde, its derivative such as furfural are possible to be applied for gel production in the presence of acid medium [7]. Carbon gel may be prepared through different types of drying process such as supercritical, freeze and evaporative drying to produce aerogels, cryogels, and xerogels, respectively. Carbon cryogel was produced through freeze drying followed by carbonization.

Lignin-furfural mixture may be classified as furan resin that is synthesized via poly-condensation reaction in the presence of acid catalyst. The synthesized furan resin resulted in linear oligomers through the furan rings linkage by methylene and methylene-ether bridges [8]. The use of lignin and furfural in the synthesis of the carbon gel as catalyst is an alternative and opportunity for improving the sustainability in bio-fuel industry. The carbonization process of cryogel is important to prepare the carbon cryogel. Thus, the study on the carbonization temperature and time is required in order to obtain the optimum carbonization conditions. In addition, the energy used for the process can also be optimized.

Producing bio-fuel based chemical products from derivation of renewable sources such as biomass is an alternative to replace petroleum resources due to the depletion of fossil fuel. Levulinic acid (LA) is one of the organic acids that show high potential to be derived from lignocellulosic biomass. LA is suitable fuel additive such as ethyl levulinate via esterification with ethanol. The synthesized ethyl levulinate may be used as an oxygenate additive in fuels [9] and diesel miscible biofuel (up to 5 wt.%) [10]. The function as additive is to improve the engine performance, fuel handling and stability, and fuel quality which help in reducing the production of carbon monoxide. Besides, the ethyl levulinate can also be used as flavouring agent and precursor for production of γ -valerolactone (GVL) [11].

The esterification reaction of LA was carried out in the presence of acid catalyst to produce ethyl levulinate. The use of homogeneous acid catalyst shows some disadvantages although high yield of product may be achieved. Therefore, the application of heterogeneous catalyst is required to improve the synthesis of ethyl levulinate. Fernandes et al. [12] has stated that the heterogeneous catalyst is required for easier catalyst separation and is reuseable for several times, instead of using mineral acid that is corrosive to the equipment and further neutralization process is required [12]. Therefore, the performance of carbon cryogel through the effect of carbonization was studied on the LA catalytic esterification reaction.

Accordingly, the objectives of this study are to determine the effects of carbonization temperature and time on carbon cryogel production. The carbon cryogel was characterized using surface area analyzer (BET), temperature programme desorption (TPD), thermogravimetric analyzer (TGA), Fourier transform infrared spectroscopy (FTIR), and Field Emission Scanning Electron Microscopy (FESEM). Besides, the study of the esterification of LA to produce

ethyl levulinate was carried out using carbon cryogel with different carbonization temperatures and time to observe the reaction performance.

2. Materials and Methods

Lignin (Sigma-Aldrich, USA) and furfural (Merck, Germany) were used as the main materials for carbon cryogel production. The lignin-furfural mixture was mixed with ethanol (C₂H₆O, 95%) and sulphuric acid (H₂SO₄, 95–97%) that were purchased from QRec, New Zealand in the gel synthesis. Levulinic acid (Merck, Germany) was used with absolute ethanol (Merck, Germany) for the synthesis of ethyl levulinate in the presence of carbon cryogel.

The method of gel synthesis followed the previous study [13]. Lignin and furfural was mixed in the ratio of 1:1 in the presence of 8M of H₂SO₄ as the acid catalyst. Distilled water and ethanol with the ratio of 1:1 were used to dilute and homogenize the mixture. The reaction was conducted at 90 °C for 30 min to synthesis the gel. The gel was immersed with *t*-butanol for solvent exchange. Then, the product was pre-frozen for 24 h and freeze dried for 8 h to form cryogel. Finally, the carbon cryogel was prepared through the carbonization of cryogel in the inert atmosphere. As for carbonization, the various range of temperatures (between 300 to 700 °C) and time (between 1 to 5 h) were studied.

The performance of carbon cryogel was tested on the esterification reaction of levulinic acid. The esterification reaction of LA was conducted in a reflux condenser at reflux temperature (~70 °C) for 10 h with 19:1 molar ratio of ethanol to LA and 15 wt.% catalyst loading to produce ethyl levulinate. GC-FID 7820A gas chromatograph system (Agilent Technology) was used to characterize ethyl levulinate (EL) and the yield was calculated based on the standard concentration. The GC condition was followed by using HP-5 column (length, 30.0 m; diameter, 320.0 µm); injector temperature, 270 °C; column temperature, 80 °C (13 °C/min) → 170 °C (40 °C/min) → 250 °C; carrier gas, nitrogen (1.0 mL/min). The equation below was used to calculate the EL yield.

$$\text{EL yield (wt. \%)} = \left[\frac{C_p \times V_p}{1000} \right] / W_i \times 100 \quad (1)$$

where, C_p is final product concentration (mg/L), V_p is final volume of product (L), and W_i is weight of levulinic acid (g).

The surface area of the carbon cryogel was evaluated using Micromeritics 3Flex 3.01 instrument based on nitrogen adsorption and desorption at -196 °C and calculated by using Brunauer Emmett Teller (BET) method. The NH₃-TPD was conducted to analyse the acidity of the carbon cryogel by using thermal conductivity detector (TCD) with 10% NH₃/He gas passing up to 900 °C. The selected carbon cryogel was further characterized with TGA to study the stability and the main composition, FTIR to observe the chemical bonding of the product, and FESEM to observe the surface morphology. TGA was conducted using Perkin Elmer TGA 7 instrument using ramp temperature of 10 °C/min from 30 to 900 °C under nitrogen flow. The FTIR was analysed using Perkin-Elmer Spectrum with KBr pellet for spectra obtained at IR range of 650 to 4000 cm⁻¹. The morphology of cryogel and carbon cryogel was observed at 1000x, 10 kV by using FESEM (JSM-6701F).

3. Results and Discussion

3.1. Carbonization studies

The effect of carbonization temperature and time were studied on carbon cryogel surface area and acidity. The results are depicted in Figs. 1 and 2, respectively. As for the effect of carbonization temperature, the result shows that the surface area increases when carbon cryogel was heated from 300 to 600 °C but the surface area slightly decreased at 700 °C (Fig. 1a). The carbonization process affects the formation of pores on carbon cryogel surface, thus increasing their surface area. Besides, the increase in surface area was also caused by the reduction of particles size due to the weight decomposition of carbon cryogel through the carbonization at high temperature. High surface area is required for carbon cryogel to be applied as catalyst since it can give high space availability for reaction to occur.

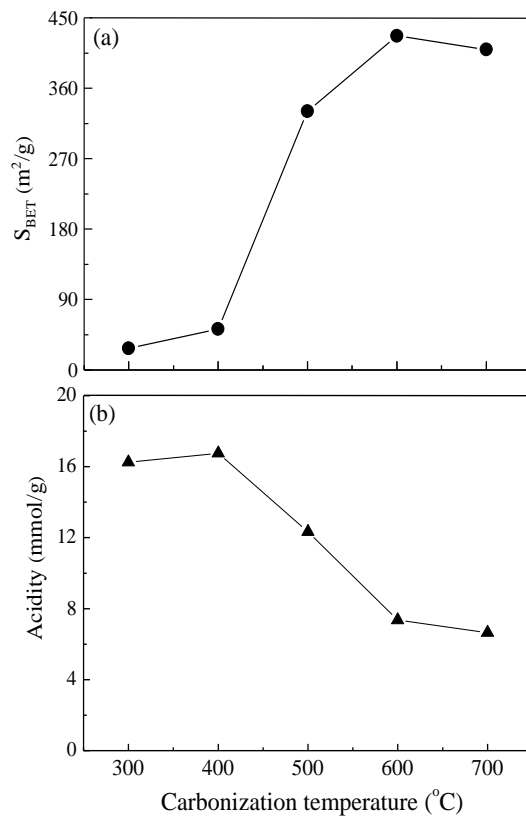


Fig. 1. Effect of carbonization temperature on (a) surface area and (b) total acidity of carbon cryogel (4 h).

The active sites available on the carbon cryogel surface are important and need to be considered. Thus, the carbon cryogel was analyzed to estimate the total acidity of acid site on its surface. The total acidity of carbon cryogel (Fig. 1b) shows a contrasting result where the reduction in their acidity occurs as the carbonization temperature was increased. Although the total acidity was reduced,

their total acidity observed was retained at high value due to the strong acidity of carbon cryogel. The reduction of acidity was mainly influenced by the decomposition of acid site contributed by low and moderate acidity which are decomposed between 100 to 300 °C and 300 to 600 °C, respectively. The high acidity remaining in the carbon cryogel was refers to the strong acidity that was fully decomposed above 700 °C. The carbon cryogel produced at 600 °C was obtained high surface area but low acidity compared to carbon cryogel produced at 500 °C. Therefore, the carbonization temperature was selected at 500 °C as the carbon cryogel have high surface area and high acidity. In addition, the carbon cryogel also was tested for esterification reaction as another response in carbon cryogel selection that is further discussed.

The selected carbonization temperature of carbon cryogel production at 500 °C was further study for the effect of carbonization time and the result was depicted in Fig. 2. The effect carbonization time shows the significant effect on carbon cryogel surface area as it was increased with increasing heating time. A sufficient carbonization time are required for carbonization of cryogel to obtain high surface area and acidity of carbon cryogel at an optimum carbonization temperature (500 °C). As shown in Fig. 2a, the surface area keeps on increasing up to 5 h, thus the response parameter of total acidity and their testing result on esterification reaction was considered for the selection of carbonization time.

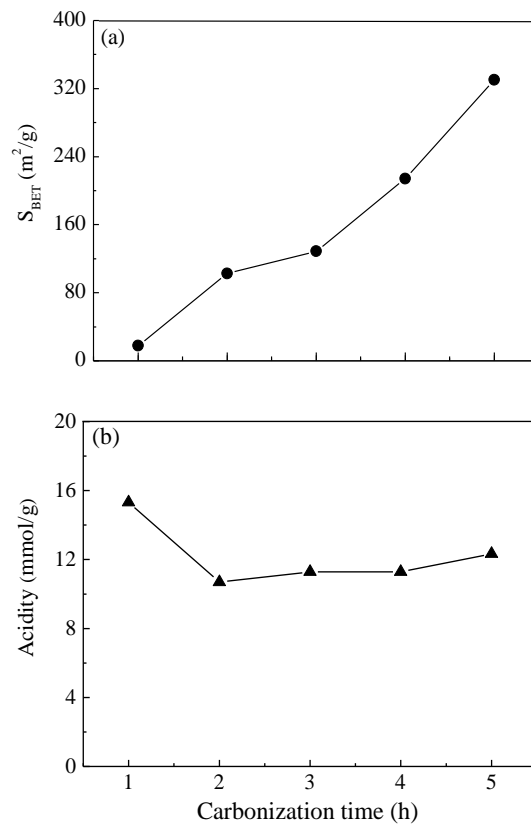


Fig. 2. Effect of carbonization time on (a) surface area and (b) total acidity of carbon cryogel (500°C).

For different carbonization time study, the result for total acidity shows some reduction in the first 2 h and after that the total acidity of carbon cryogel shows small difference in its value up to 5h. The acidity of carbon cryogel was thermally affected due to the decomposition of the organic compounds and their active sites, but the difference in carbonization time presents small changes in acidity. By comparing the result of carbon cryogel in carbonization temperature study, high decomposition of carbon cryogel was influenced by increased temperature. The physical heating shows small influence on total acidity of carbon cryogel at constant temperature possibly due to the low decomposition of acid sites. Since the total acidity remains constant and the surface area keeps on increasing, thus, the response on ethyl levulinate yield was considered to justify the selection. The testing of esterification by using carbon cryogel at different carbonization time will be further discussed later. Based on the carbonization time study, 4 h of heating time was sufficient for the production of carbon cryogel as catalyst in esterification of levulinic acid to obtain the optimum yield. Although carbon cryogel at 500 °C and 5 h produced high surface area (330.35 m²/g) and acidity (12.33 mmol/g) but the optimum ethyl levulinate was obtained by carbon cryogel produced at 500 °C and 4 h. The optimum condition for carbonization of carbon cryogel was selected at 500 °C and 4 h resulted in high surface area of 214.19 m²/g and acidity of 11.29 mmol/g.

The characterization of selected carbon cryogel was conducted to study their physical and chemical properties. The curves of thermal gravimetric (TG) and derivative thermal gravimetric (DTG) as depicted in Fig. 3 was used to determine the thermal stability of cryogel and carbon cryogel. The DTG peak reveals the initial weight loss of cryogel and carbon cryogel which is attributed to the weight of moisture inside the sample between 30 and 100 °C [13, 14]. High volatilization of cryogel was observed due to high moisture content of gel compared to carbon cryogel that contains moisture less than 10 wt.% influenced by the moisture of the environment. Based on DTG peaks of the cryogel, the major decomposition between 150 to 500 °C refers to the decomposition of low molecular weight organic compound such as furfural structure followed by sulfonated group. Singare et al. [15] has stated that sulfonate functional group possibly decomposed at high temperature up to 521°C. The weight of the samples decomposed rapidly with increasing temperature above 600 °C due to the decomposition of heavy organic material including the lignin structures that were linked in the cryogel structure. The high decomposition of cryogel up to 900 °C was shows that cryogels are non-thermally stable and not suitable for application at high temperatures (> 200 °C).

The carbon cryogel exhibits higher thermal stability as TG curve (Fig. 3b) shows mass decomposition of approximately 10 wt.% for temperatures up to 500 °C. High decomposition of carbon cryogel occur above 500 °C up to 900 °C as the carbon cryogel drastically decomposed by approximately 40 wt.%. The decomposition of carbon cryogel presented between 500 to 800 °C is mainly influenced by the lignin in the carbon cryogel structure. The high weight percentage of carbon cryogel can be maintained up to 500 °C since the carbonization of cryogel was performed at the same temperature. The carbon cryogel reduces in stability at temperatures above 500 °C, as the lignin linked to the structures of carbon cryogel was not fully restructured during carbonization. Thus, the organic compound in the carbon cryogel such as functional groups in the lignin structure was not thermally

stable at high temperatures ($> 500^{\circ}\text{C}$) and starts to decompose. The carbonization process has produced complex carbon structure through the restructuring of bonding structure of the cryogel. The result shows that the carbonization process has increased the carbon stability and the decomposition of carbon cryogel occurred at a higher temperature compared to cryogel.

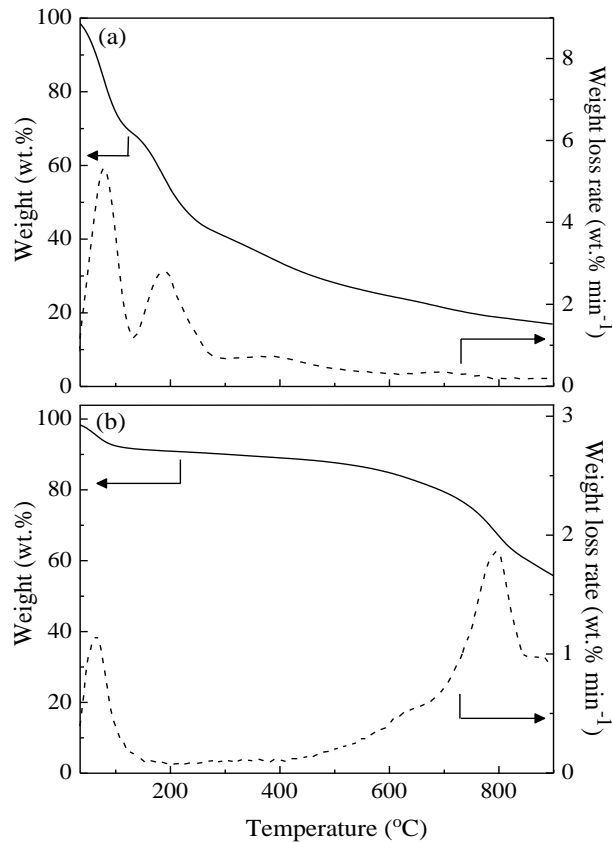


Fig. 3. TGA-DTG curve of (a) cryogel and (b) carbon cryogel.

The related chemical bonding and surface chemistry of cryogel and carbon cryogel are presented through the infrared spectra as in Fig. 4 and summarized in Table 1. The spectra were used to describe the possible bonding structure and functional groups of the cryogel and the effects after carbonization. The cryogel presents the structure of alcohol functional group through detection of broad frequency peak of O-H around $3300\text{--}3600\text{ cm}^{-1}$. The weak frequency around $2850\text{--}2960\text{ cm}^{-1}$ of C-H of alkyl group was detected. The absorption band around 1625 and 1500 cm^{-1} in the spectrum attributed to the presence of C=C aromatic compound and small peak around 750 to 850 cm^{-1} is related to its substituent types. This C=C of aromatic is referred to the aromatic in the lignin structure. The detection of SO_3H functional group (sulfonates) in cryogel and carbon cryogel structure was observed through the band spectra for S=O and S-O stretching between the frequency range of 1250 to 1000 cm^{-1} . The stretching of the functional groups of S=O and S-O was related to SO_3H group [16, 17]. The band

spectra of S=O stretching was detected around 1150-1250 cm^{-1} while the weak band of S-O stretching was appeared around 1050 cm^{-1} . These functional groups are important for the production of cryogel and carbon cryogel as it is related to the formation of active sites. The sulphuric acid used for gels synthesis possibly has bonded to the gel structure during the synthesis and formed an active site on the surface of carbon cryogel to function as catalyst.

In addition, the frequency peak of C-O is also present in the cryogel and carbon cryogel structure at 1260-1000 cm^{-1} . The C-O peak refers to the possible structure of the phenolic group (C-O-H) and ether (C-O-C) especially in the cryogel structure. As stated by Poljanšek and Krajnc (2005), the asymmetric stretch of phenolic C-C-OH was detected around 1237 cm^{-1} and the stretching vibration of C-O-C aliphatic ether was around 1100 cm^{-1} [2]. The bonding structure of C-O is important to explain the linkage structure of lignin and furfural during the gels formation. The C-O-C stretching presented may refer to the dimethyl ether bridge formation. In this regard, the ether bridge linkage in cryogel structure explains the formation of resol type resin.

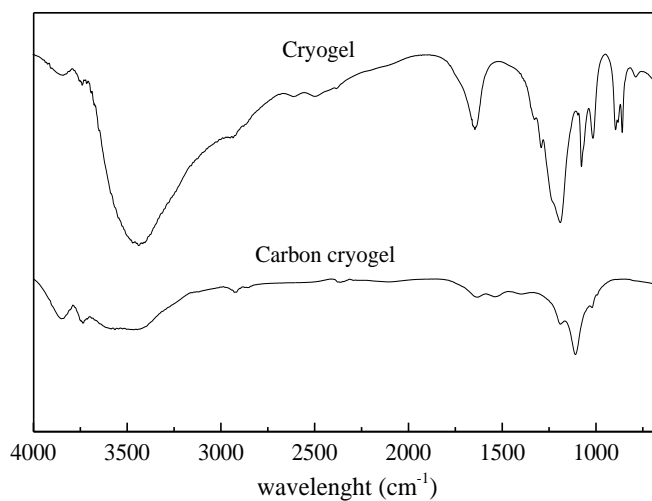


Fig. 4. FTIR spectra of cryogel and carbon cryogel.

Table 1. Functional group of the cryogel and carbon cryogel bonding structure.

Wavelength, cm^{-1}	Functional group
3300-3600	O-H
2850-2960	C-H
~1625 and ~1500	C=C Aromatic (Ar)
~1450 and ~1375	-CH ₃ bending
1150-1250	S=O
1000-1260	C-O
1050	S-O
850-1000	C-C
750-850	Ar constituent type

Based on spectra, the carbon cryogel structure has demonstrated some peak reductions due to the effect of carbonization process. The frequency range of O-H at $3300\text{-}3600\text{ cm}^{-1}$, and C-O and S-O functional groups at $1000\text{-}1300\text{ cm}^{-1}$ was reduced in their intensity. The reduction is related to the decomposition of oxygen bonded in the structure by carbonization.

The reduction of O-H functional group may increase the degree of hydrophobicity of carbon cryogel as the carbonization temperature increases with increasing decomposition of O-H. Yamamoto et al. [18] has stated that the carbon cryogel pore surface are supposed to be hydrophobic where the degree of hydrophobicity increased with increasing pyrolysis temperature. Other peak reductions was occurred at wavelength of $1500\text{-}1700\text{ cm}^{-1}$ and $1000\text{-}650\text{ cm}^{-1}$ possibly due to the decomposition of other organic compounds and the restructuring of the carbon cryogel bonding affected by the carbonization process. Regarding to the FTIR spectra, the cryogel and carbon cryogel has performed good surface chemistry with the available SO_3H functional group referred to the formation of active sites. However, carbon cryogel was applicable as catalyst due to high surface area, high total acidity and thermal stability compare to cryogel.

The surface morphology of cryogel and carbon cryogel are depicted in Fig. 5. The small spherical with micro size (microsphere) particles were observed for both cryogel and carbon cryogel. However, there is a small difference in size as the size of the cryogel particles was reduced after carbonization. Besides, the organic layers on the surface of cryogel also vanished after the carbonization process.

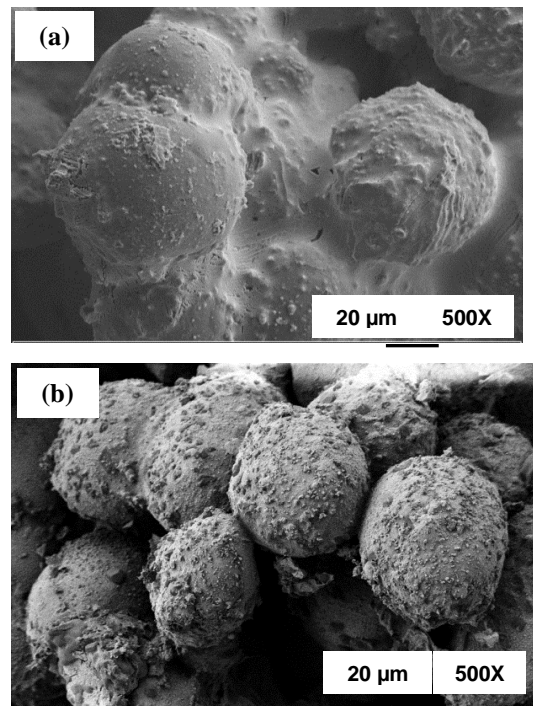


Fig. 5. FESEM images of (a) cryogel and (b) carbon cryogel.

This was caused by the decomposition of organic compound during carbonization at high temperature that gives an effect on the changes of the surface and structure of carbon cryogel. The decomposition of organic compound was possibly lead to the shrinkage of particle caused by the reduction and restructuring of the functional group and carbon bonding. This reduces the particles size and increases the surface area of carbon cryogel microsphere particles with increasing carbonization temperature and time.

3.2. Carbon cryogel catalytic testing

The carbon cryogel prepared through the carbonization study was tested for esterification of levulinic acid and the result is shown in Fig. 6. The ethyl levulinate yield increased from 57.7 wt.% up to 78.7 wt.% with increasing carbonization temperature of carbon cryogel up to 500 °C. Above the carbonization temperature of 500 °C, the yield reduced consistently. The carbon cryogel prepared at 700 °C only obtained 51.9 wt.% of ethyl levulinate yield. The result of ethyl levulinate yield was consistent with the result discussed in Fig. 1 for the total surface of carbon cryogel up to 500 °C. The result of total surface area keeps on increasing but the result of ethyl levulinate yield obtained reduces with increasing temperature. This result revealed the influence of the acidity of carbon cryogel towards the catalytic activity on the esterification reaction. The acidity continuously decreases with increasing carbonization temperature. Thus, the carbon cryogel prepared above 500 °C exhibit low total acidity and possibly reduces the reaction activity and yield of ethyl levulinate.

Fig. 6b shows the result of ethyl levulinate yield by carbon cryogel at different carbonization time. The yield of ethyl levulinate increases with increasing carbonization time up to 4 h. Carbon cryogel prepared at 500 °C and 4 h has produced 80.0 wt.% of ethyl levulinate yield. However, the ethyl levulinate yield was slightly decreased in presence of carbon cryogel at 5 h of carbonization time. This trend is consistent with the result of total surface area but the increase in yield by carbon cryogel at different carbonization time is not obvious as presented by the trend of surface area of carbon cryogel. At carbonization time of 1 h, low surface area of carbon cryogel produced can obtain 63.5 wt.% yield of ethyl levulinate. This yield is possibly contributed by high acidity on carbon cryogel. As for carbonization time of 2 h and above, the total acidity only shows a small change. Thus, the increase in ethyl levulinate yield was contributed by carbon cryogel surface area. This explains that the esterification reaction was influenced by high surface area of carbon cryogel due to the available number of acid site on the carbon cryogel surface. Besides, the study also revealed the importance of total acidity and its effect on the reaction and ethyl levulinate production. Therefore, the relationship between carbon cryogel surface area and total acidity are very important and need to be considered in order to enhance the reaction with high production of ethyl levulinate.

3.3. Comparative study

The result of this study was compared with the result obtained by previous studies as shown in Table 2. The result was compared based on esterification condition in producing ethyl levulinate to observe the ability and performance of carbon

cryogel with other catalyst. Amberlyst-15 is a commercial catalyst which shows high performance to many reactions. As for the levulinic esterification, the moderated yield was obtained using Amberlyst-15 at moderate condition [12]. Besides, SO_4/SnO_2 shows low yield of ethyl levulinate at moderate reaction condition. The Amberlyst-15 and SO_4/SnO_2 may obtain a higher yield of ethyl levulinate if their reaction condition is modified such as the reaction was conducted at longer reaction time and increasing the catalyst loading. High performance was shown by dodecatungstophosphoric acid supported on desilicated H-ZSM-5 (DPTA/DH-ZSM-5) with high yield of ethyl levulinate of 82.0 % at moderate reaction conditions [10]. Catalyst modified using chemical may show high performance due to the active site promoted by the high acidity of chemical compound. Besides, UiO-66 and UiO-66-NH were prepared from terephthalic acid and aminoterephthalic acid, respectively also have shown high performance for esterification reaction of levulinic acid [19]. The reaction have produced ethyl levulinate yield of 94.0 % and 95.0 %, respectively. The long reaction time (8 h) is required to obtain high yield of ethyl levulinate. High performance was shown by catalyst promoted by acid used in the UiO-66 and UiO-66-NH catalyst synthesis.

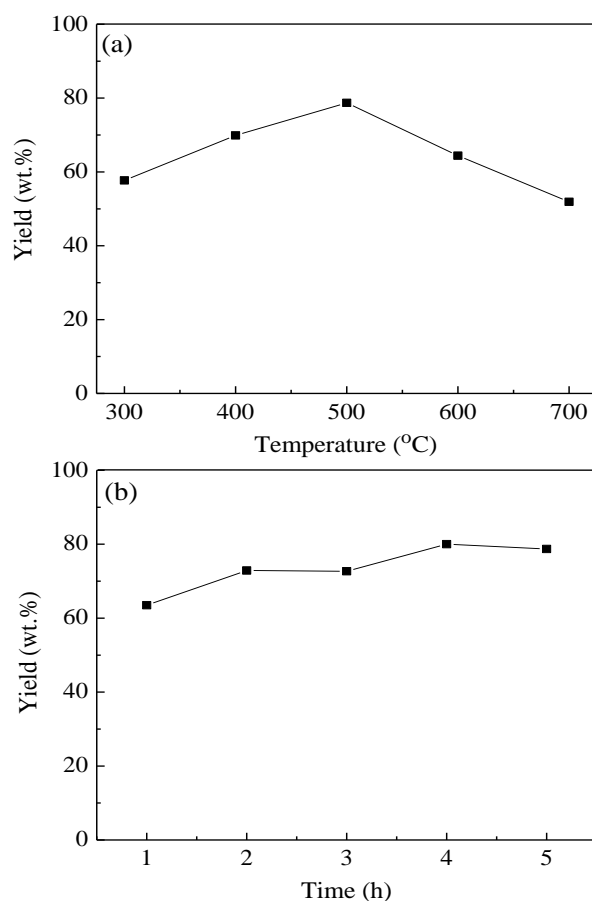


Fig. 6. Effect of carbonization (a) temperature and (b) time of carbon cryogel on ethyl levulinate yield.

Table 2. Comparison study on the levulinic acid esterification via heterogeneous acid catalyst.

Catalyst	Time (h)	Temp (°C)	Catalyst load. (wt.%)	Molar ratio (EtOH to LA)	Yield (mol.%)	Conv. (%)	Ref.
Amberlyst-15	5.0	70.0	2.5	5.0	55.0	50.0	[12]
SO ₄ /SnO ₂	5.0	70.0	2.5	5.0	40.0	44.0	[12]
DPTA/DH-ZSM-5	4.0	78.0	25.0	6.0	82.0	94.0	[10]
UiO-66-NH	8.0	78.0	1.8 ²	15.0	95.0	-	[19]
UiO-66	8.0	78.0	1.8 ²	15.0	94.0	-	[19]
H ₄ SiW ₁₂ O ₄₀ /SiO ₂	6.0	75.0	51.0	18.0	67.0	-	[20]
40WD-S	10.0	78.0	107.7 (0.5 ²)	64.0	76.0	-	[9]
Carbon cryogel	10.0	78.0	15.0	19.0	64.5 (80.0 ¹)	-	This study

¹ the data in wt.%, ² the data in mol.%

H₄SiW₁₂O₄₀/SiO₂ was also applied for the reaction as studied by Yan et al. [20] at moderate reaction temperature and 6 h to produce 67.0 % of ethyl levulinate. However, the reaction was carried out with high loading of catalyst. In addition, the ethyl levulinate was also synthesized in the presence of Wells-Dawson HPA in silica (40WD-S) using a moderate reaction temperature and long reaction time (10 h) to produce 76.0 % of ethyl levulinate. The high yield obtained was also influenced by high loading of catalyst used which is about 107.0 wt% with 64.0 of molar ratio of ethanol to levulinic acid. The high catalyst loading possibly give more surface reaction with active site and higher solvent used will shift the reaction for ethyl levulinate production. However, the high usage of catalyst loading and ethanol may increase the production cost. The long reaction time increases the usage of energy for production. The additional cost of using higher catalyst loading may reduce the production efficiency unless the catalyst used is high catalytic stability. As for carbon cryogel, moderate reaction temperature was also applied for 10 h of reaction time to produce 80.0 wt.% (64.5 mol.%) of ethyl levulinate. Carbon cryogel also has shown good performance of catalytic reaction as obtained by H₄SiW₁₂O₄₀/SiO₂ and 40WD-S. The carbon cryogel produced from lignin and furfural had obtained high surface area and total acidity which has shown high potential for the esterification reaction. Further study or modification on carbon cryogel is possible in order to improve the carbon cryogel production and enhance the reaction with high production of ethyl levulinate. Even though long reaction time was applied in this study using carbon cryogel, the condition used is not the optimum as it was fixed for observation of carbon cryogel performance. Therefore, further study is required to be conducted to obtain the optimum parameter condition on ethyl levulinate production.

4. Conclusions

The carbonization study of carbon cryogel obtained the optimum carbonization temperature and time of 500 °C and 4 h, respectively for ethyl levulinate production. The carbon cryogel was produced with high surface area and acidity as the selected carbon cryogel has obtained the total surface area of 214.19 m²/g and acidity of 11.29 mmol/g. The effect of carbonization temperature and time gave a significant effect on their total surface area and also the total acidity of carbon cryogel. Besides, the effect of carbonization on carbon cryogel also shows an effect on the production of ethyl levulinate from esterification of levulinic acid due to the influence of total surface area and acidity of carbon cryogel. The carbon cryogel has shown the potential as solid acid catalyst for esterification of levulinic acid. The carbon cryogel prepared in this study was applied for the reaction and have produced up to 80.0 wt.% of yield of ethyl levulinate.

Acknowledgments

The funding received from Research University Grant (vote 04H69) and (vote 09H27) which was supported by Ministry of Higher Education (MOHE), Malaysia and Universiti Teknologi Malaysia (UTM) leading to these research findings.

References

1. Scherdel, C.; and Reichenauer, G. (2009). Carbon xerogels synthesized via phenol–formaldehyde gels. *Microporous and Mesoporous Materials*, 126(1–2), 133-142.
2. Poljanšek, I.; and Krajnc, M. (2005). Characterization of phenol-formaldehyde prepolymer resins by in line FT-IR spectroscopy. *Acta Chimica Slovenica*, 52, 238-244.
3. Mukai, S.R.; Tamitsuji, C.; Nishihara, H.; and Tamon, H. (2005). Preparation of mesoporous carbon gels from an inexpensive combination of phenol and formaldehyde. *Carbon*, 43(12), 2628-2630.
4. Çetin, N.S.; and Özmen, N. (2002). Use of organosolv lignin in phenol–formaldehyde resins for particleboard production: I. organosolv lignin modified resins. *International Journal of Adhesion and Adhesives*, 22(6), 477-480.
5. Tejado, A.; Peña, C.; Labidi, J.; Echeverria, J.M.; and Mondragon, I. (2007). Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis. *Bioresource Technology*, 98(8), 1655-1663.
6. Vázquez, G.; Antorrena, G.; González, J.; and Mayor, J. (1995). Lignin-phenol-formaldehyde adhesives for exterior grade plywoods. *Bioresource Technology*, 51(2–3), 187-192.
7. Fink, J.K. (2005). 4 - Phenol/Formaldehyde Resins, in *Reactive Polymers Fundamentals and Applications*, William Andrew Publishing, Norwich, NY.
8. Fink, J.K. (2005). 7 - Furan Resins, in *Reactive Polymers Fundamentals and Applications*, William Andrew Publishing, Norwich, NY.

9. Pasquale, G.; Vázquez, P.; Romanelli, G.; and Baronetti, G. (2012). Catalytic upgrading of levulinic acid to ethyl levulinate using reusable silica-included Wells-Dawson heteropolyacid as catalyst. *Catalysis Communications*, 18, 115-120.
10. Nandiwale, K.Y.; Sonar, S.K.; Niphadkar, P.S.; Joshi, P.N.; Deshpande, S.S.; Patil, V.S.; and Bokade, V.V. (2013). Catalytic upgrading of renewable levulinic acid to ethyl levulinate biodiesel using dodecatungstophosphoric acid supported on desilicated H-ZSM-5 as catalyst. *Applied Catalysis A: General*, 460, 90-98.
11. Maldonado, G.M.G.; Assary, R.S.; Dumesic, J.A.; and Curtiss, L.A. (2012). Acid-catalyzed conversion of furfuryl alcohol to ethyl levulinate in liquid ethanol. *Energy & Environmental Science*, 5(10), 8990-8997.
12. Fernandes, D.; Rocha, A.; Mai, E.; Mota, C.J.; and da Silva, V.T. (2012). Levulinic acid esterification with ethanol to ethyl levulinate production over solid acid catalysts. *Applied Catalysis A: General*, 425, 199-204.
13. Zainol, M.M.; Amin, N.A.S.; and Asmadi, M. (2015). Synthesis and characterization of carbon cryogel microspheres from lignin-furfural mixtures for biodiesel production. *Bioresource Technology*, 190, 44-50.
14. Zainol, M.M.; Asmadi, M.; and Amin, N.A.S. (2014). Impregnation of magnetic particles on oil palm shell activated carbon for removal of heavy metal ions from aqueous solution. *Jurnal Teknologi*, 72(1), 7-11.
15. Singare, P.U.; Lokhande, R.S.; and Madyal, R.S. (2011). Thermal degradation studies of some strongly acidic cation exchange resins. *Open Journal of Physical Chemistry*, 1(02), 45.
16. Hara, M. (2010). Biodiesel production by amorphous carbon bearing SO₃H, COOH and phenolic OH groups, a solid Brønsted acid catalyst. *Topics in Catalysis*, 53(11-12), 805-810.
17. Dawodu, F.A.; Ayodele, O.; Xin, J.; Zhang, S.; and Yan, D. (2014). Effective conversion of non-edible oil with high free fatty acid into biodiesel by sulphonated carbon catalyst. *Applied Energy*, 114, 819-826.
18. Yamamoto, T.; Sugimoto, T.; Suzuki, T.; Mukai, S.R.; and Tamon, H. (2002). Preparation and characterization of carbon cryogel microspheres. *Carbon*, 40(8), 1345-1351.
19. Cirujano, F.G.; Corma, A.; and Llabrés i Xamena, F.X. (2015). Conversion of levulinic acid into chemicals: Synthesis of biomass derived levulinate esters over Zr-containing MOFs. *Chemical Engineering Science*, 124, 52-60.
20. Yan, K.; Wu, G.; Wen, J.; and Chen, A. (2013). One-step synthesis of mesoporous H₄SiW₁₂O₄₀-SiO₂ catalysts for the production of methyl and ethyl levulinate biodiesel. *Catalysis Communications*, 34, 58-63.