From Glucose-Based Carbohydrates to Phenol-rich Bio-oil Integrated with Syngas Production via Catalytic Pyrolysis over Activated Carbon Catalyst

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From Glucose-Based Carbohydrates to Phenol-rich Bio-oil Integrated with Syngas Production via Catalytic Pyrolysis over Activated Carbon Catalyst

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Abstract: The catalytic pyrolysis of carbohydrates over phosphoric acid-activated carbon catalyst (ACC) was investigated to obtain phenol-rich bio-oil and syngas production in the facile fixed bed reactor for the first time. The central composite designs (CCD) was adopted to optimize experimental operating conditions of glucose catalytic pyrolysis, where the effects of reaction temperatures and ratios of catalyst to reactant on product distributions were studied. The main chemical components of obtained catalytic bio-oils from glucose were phenols, ketones, and anhydrosugars, in which the selectivity of phenols ranged from 4.8 to 100% depending on various reaction conditions. The highest selectivity of phenol was achieved at the reaction temperature of 450 °C with a catalyst to reactant ratio of 1. Carbon monoxide, carbon dioxide, methane, and hydrogen were the main gas fractions in gaseous products, where high concentrations of carbon monoxide (50.2%) and hydrogen (9.2%) could be attained. Additionally, catalytic pyrolysis of cellulose with different catalyst to reactant ratios at the reaction temperature of 450 °C was also investigated and the results exhibited similar phenomenon to those of glucose. A high selectivity of phenols (96.7%) could also be achieved intergraded with a high concentration of carbon monoxide (42.1%). The mechanism of phenol generation was further discussed and the "phenol pool" was proposed to describe the catalytic function of the ACC in catalytic conversion of volatiles to phenols. Our findings suggest that the catalytic pyrolysis of renewable and earth-abundant carbohydrates over the ACC might provide a novel and viable route to generate high-purity phenols to ultimately advance the utilization of biomass energy.

1. Introduction

The increasing rate of consumption of traditional fossil fuel and consequent environment pollution have triggered seeking renewable and environment-friendly energy resources to alleviate worldwide energy and environment issues.[1] Lignocellulosic biomass, the most abundant and inexpensive renewable feedstock coming from photosynthesis of the plant, has regarded as a promising carbon resource that is of great potential in generating value-added fuels, chemicals, and carbon materials.[2-4] The thermochemical conversion technology, e.g. catalytic fast pyrolysis, has been considered as a facile, efficient and cost-effective route to convert biomass into liquid fuels and value-added chemicals.[5]

Phenol, an important aromatic organic compound, is essential to produce various materials and chemicals, which contain plastics, phenol resins, caprolactam, and pharmaceutical drugs et.al.[6] The production of phenol has increased at an average annual rate of 1.8% since 2010, but still could not meet the world increasing consumption rate. It is predicted that the global phenol consumption will continuously grow at slightly over 2.5% per year in the following five years according to chemical economics handbook 2016, and the worldwide phenol market is estimated to be valued at USD 31.73 billion by 2025. However, most of the phenol is currently synthesized from benzene in industry, consuming large amounts of fossil fuels and accompanying with a low selectivity of phenol production and environmental pollution.[7] Therefore, developing a new route of producing phenol from a renewable feedstock is of critical importance to alleviate the fossil fuels consumption and environmental pollution. Fortunately, phenols can be found in bio-oils obtained from biomass pyrolysis, which offers a fresh method of generating phenols from the renewable feedstock.[8] Extensive efforts have been devoted to the phenol production by the thermochemical conversion of biomass in the past decade. Nascent attempts have concentrated on the catalytic pyrolysis with basic, acidic, and carbonates catalysts together with varying experimental conditions to maximize the yield of obtained phenol.[9, 10] Phosphates such as K_3PO_4, K_2HPO_4, and KH_2PO_4 also showed catalytic activity in phenol production and the selectivity up to 64.2% could be achieved.[11, 12] In addition, the oxidative degradation of lignin induced by transition metal catalysts (e.g. Mn, Fe, Co, and Cu) were also investigated and the results indicated binary catalysts presented a better catalytic performance.[13, 14] The raw and modified zeolites, exhibit effective catalytic activities in bio-oil upgrading for hydrocarbons production, but do not perform well in selective production phenols. Thus, further expensive extraction and

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purification of phenols from bio-oil are needed with a consequence of extra environmental pollution.[15, 16] There is thereby a significant challenge to obtain phenol rich bio-oil from catalytic pyrolysis of lignocellulosic biomass.

Recently, the activated carbons (ACs) have been demonstrated catalytic activity in selectively converting biomass into phenols via catalytic pyrolysis. Previous work in our group revealed that catalytic bio-oils rich in phenols could be obtained through microwave-induced pyrolysis over commercial ACs. By loading a high catalyst to feedstock ratio (3:1), a up to 74.7% selectivity of phenols was achieved with corresponding phenol selectivity of 42.5% at the optimized temperature of 400 °C.[17, 18] The mechanism study indicated that phenols were primarily formed from lignin component of the biomass via a series of reactions including decarboxylation, dehydration, molecule arrangement and so forth.[19] Subsequently, similar experiments were conducted in another research group with different raw biomass being the feedstock and phenol-enriched bio-oils were also collected.[20] A comparative study of different heating methods between traditional and microwave-induced pyrolysis was also investigated to compare phenols harvest. The experiment results revealed that a high but not high enough selectivity of phenol (64.58 area%) was achieved at optimized reaction condition.[21] Additionally, the phenol-enriched bio-oils were also obtained by employing the fluidized bed with the assistance of activated carbons, confirming the method as an alternative way to generate phenols from biomass feedstock regardless of the heating method applied.[22] Generally, activated carbons are currently produced by the physical (steam activation) or chemical activation (react with acid or alkali activation agents) processes and different activation methods will lead to various physical and chemical properties, such as surface area, pore size distribution, and surface functional groups.[23] Given the catalytic activities of phosphates in bio-oil upgrading, we proposed that the activation with a phosphoric acid agent could bring P-containing groups in addition to normal surface groups that act as catalytic sites in obtained activated carbons and our initial experimental results have demonstrated selective phenols production from biomass catalytic pyrolysis.[24] Therefore, the activated carbon activated by phosphoric acid is thought to be a promising catalyst in the catalytic conversion of biomass into value-added phenols.

Aforementioned studies were mainly engaged in topics of phenols production from raw biomass and lignin with commercial activated carbons. Besides, phenols are thought to be generated from lignin decomposition during catalytic pyrolysis with activated carbon catalysts, because lignin is constructed with benzene ring and its further reactions make it possible to form phenols successfully.[18-20, 25, 26] The compounds existing in attained phenol-rich bio-oils, on the other hand, are the mixtures of phenol, methyl-phenol, dimethyl-phenol and so forth, making it challenging to attain high-purity phenol in catalytic bio-oils due to the natural complex of lignin.[27] Besides, the yields of bio-oils from lignin pyrolysis are usually relative low, leaving high yield of less valuable solid residue during thermochemical conversion.[28] Thus, alternative feedstock should be explored and investigated. Glucose-based renewable feedstock like cellulose, the main component of the lignocellulosic biomass, has a worldwide distribution and can be obtained largely from biomass with low costs.[29] Nevertheless, there are relatively rare studies

devoted to the generation of phenol from glucose-based carbohydrates and these possibilities remain to be explored. In addition, the gaseous products from catalytic pyrolysis are also usually paid less attention during phenol. The previous study indicated that hydrogen, methane, carbon monoxide, and carbon dioxide were major constituents in obtained gases,[18] which can be involved in important refinery processes as significant reactants to produce valuable chemicals and fuels. Costly carbon monoxide is an industrial gas that has various applications in bulk chemicals manufacturing, such as aldehydes, methanol, and acetic acid production.[30] Therefore, gas products rich in carbon monoxide should be calculated to reach the goal of price-competitive renewable phenols production during biomass catalytic pyrolysis processes. Unfortunately, there has not been any successful attempt to selectively produce phenol integrated with generation of carbon monoxide-enriched fuel gases. Herein, this study aims to fill these knowledge gaps and systemically investigate the production of renewable high-purity phenol and fuel gases rich in carbon monoxide by catalytic pyrolysis of glucose and cellulose over activated carbon catalyst in the facile fixed bed reactor for the first time. The distinct reaction conditions including catalytic pyrolysis temperature as well as catalyst to feedstock mass ratio were discussed in detail on the production of phenol and carbon monoxide during the catalytic pyrolysis processes.

2. Experimental Section

2.1 Materials

The crop waste, corn stover, was collected from Brookings (South Dakota, USA), which was milled and sieved to a particles size of less than 2 mm prior to use. D-(+) glucose powder (CAS number: 50-99-7) was purchased from Sigma-Aldrich Corporation (USA). Microcrystalline cellulose (CAS number: 9004-34-6) with an average particle size of 50 μm and 85 wt% phosphoric acid aqueous solution (CAS: 7664-38-2) was purchased from Alfa-Aesar corporation (USA). Distilled water was used throughout the experiment except with other statements.

2.2 Activated carbon catalyst preparation

The activated carbon catalyst was produced via thermochemical activation of corn stover with phosphoric acid. First, washed the corn stover with tap water to remove some dust impurities followed by drying in a dry oven at 100 °C until the mass was constant. Mix 100 mL phosphoric acid with 700 mL distilled water in a 1L baker to generate the diluted acid solvent. Impregnate 100 g corn stover in the prepared acid solution for 12 h and then dry for another 12 h at ambient temperature. Subsequently, the mixture was transferred into a 100 °C oven overnight until mass remained constant. The final mass ratio of phosphoric acid to biomass was 0.85, which was selected according to our previous studies.[24, 31] The activated carbon catalyst was then generated by conducting microwave-induced pyrolysis of dried mixtures. Specifically, 100 g mixtures were put in a 500 mL quartz bottle reactor, then inflated nitrogen gas for 15 min to create an oxygen-free condition inner the reactor. The pyrolysis process lasted for 1 h with an input power of 700 W (Sineo MAS-II microwave reactor). More description of this reaction system could refer to reference elsewhere.[16, 31] The obtained catalyst was then collected and washed with room-temperature distilled water until the

pH was around neutral to remove all residual phosphoric acid. Finally, dried the ACC in the oven at 100 °C until mass stayed constant and kept the ACC in the oven in order to keep the lowest water content in ACC before further using as a catalyst.

2.3 Catalyst Characterization

Surface area and pore distribution of the obtained ACC was evaluated by N_2 adsorption/desorption isotherms at 77 K using a physisorption analyzer (Micromeritics R TristarII 3020). Prior to analysis, the ACC sample was degassed at 250 °C overnight to remove moisture and impurities. The specific surface area was calculated according to Brunauer-Emmett-Teller (BET) theory. Micropore volume, micropore, and external surface area were determined using the t-plot method.[32] Fourier Transform Infrared (FTIR) spectra of ACC sample was obtained with an IR Prestige 21 spectrometer in attenuated total reflection (ATR) mode (Shimadzu, Ge crystal). The spectra were recorded at a range of 500-4500 cm^{-1} at a resolution of 8 cm^{-1} using a combined 64 scans. The morphology and element analysis of the ACC surface were viewed and determined using scanning electron microscope and energy dispersive X-ray (SEM/EDX, FEI Quanta 200 F), respectively. The total acidity and acid strength distribution of the catalyst were determined by temperature programmed desorption of ammonia (NH_3-TPD) which was performed using a Micromeritics Autochem 2920 instrument in a quartz reactor coupled with a Mass Spectroscopy (MS) as the detector. Initially, approximate 0.1 g sample was purged at a flow of Ar/He gas (5%/95%, 50 mL/min) at 300 °C for 1 hour. After cooling down to the room temperature, the sample was saturated with 10 % NH_3/He for 1 hour at 100 °C. After saturation, the sample was purged with Ar/He gas (5%/95%, 50 mL/min) until no NH_3 was detected in the outlet gas. The desorption was performed by ramping the temperature up to 400 °C at a heating rate of 10 °C/min. The desorbed NH_3 was detected by MS.

2.4 Catalytic pyrolysis in the fixed bed and products analysis

The catalytic pyrolysis of glucose/cellulose with activated carbon being the catalyst was conducted in a facile fixed bed reactor as shown in Figure 1. The sample was air dry in an 100 °C oven to remove the physically bound moisture, prior to conducting the experiments. Previous studies have indicated that a better catalytic performance could be achieved by using *ex-situ* catalytic pyrolysis (separated catalyst from feedstock), whereas an additional heating facility is usually needed to supply the separated heating area, resulting in the cost rise from the view of economy.[33] Here, we adopted a facile process that the separated catalyst and sample were both placed in the tube furnace, which could cut the cost and simultaneously enhance the heating efficiency.[34] Specifically, 5 g feedstock was placed in a quartz tube with the quartz wool at both ends of the sample. Activated carbon catalyst was also loaded in the same way in the tube. Following the nitrogen flow direction, the carbohydrate sample was the first then followed with the activated carbon. Heated the tube furnace (Thermal Scientific) to target temperatures (429, 450, 500, 550 or 570 °C) and then transferred the quartz tube into the furnace. Each experiment run was conducted at setting temperature for 8 min to complete the pyrolytic reaction. The first 2~3 min was used to heat the sample from the room temperature to the target temperature and then it was kept till the end of the experiment. The details of temperature changes during the heating

process were described in Figure S1†, and results suggested that the fast pyrolysis occurred in the current catalytic pyrolysis. Nitrogen gas was inflated for 15 min with the flow rate of 100 mL/min before the pyrolysis to obtain the oxygen-free pyrolytic condition, after that the nitrogen was used as the carrying gas with the same gas flow rate.

The condensed bio-oil was collected and then weighted after each pyrolytic process. Dichloromethane (HPLC grade, 99.7%, Alfa Aesar, USA) was used to extracted organic components from attained bio-oils before conducting analysis. Chemical compounds were detected and partially quantified by Agilent 7890A GC–MS (GC–MS; GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. The GC was initially maintained at 40 °C for 5 min, and then was heated to 280 °C at a heating rate of 10 °C/min and lasted for 5 min. 1 μL of diluted sample was injected into GC with the flow rate of the carrier gas (helium) being 0.6 mL/min. The ion source temperature was 230 °C for the mass selective detector. Compounds were identified by comparing the spectral data with those in the NIST Mass Spectral library. The area percent of compounds obtained from GC/MS results was utilized to predict product selectivity. In order to determine the concentration of phenol, different standard solutions with various concentrations of phenol were also injected to GC/MS and the obtained data were used to quantify the concentration of phenol in the obtained bio-oils.

The gaseous product was collected in a 1 L Tedlar gas bag and then analyzed by an INFICON 3000 Micro-GC (INFICON inc, Santa Clara, CA, USA) system with a thermal conductivity detector (TCD). A standard gas mixture consisting of H_2, N_2, CH_4, CO, and CO_2 was used to calibrate the yield of non-condensable gases. Gas molecules with more than 2 carbon atoms (>=C2) were either not detected or negligible in this research.

The char, the solid residue from the pyrolysis of glucose/cellulose, was also collected and weighted after the catalytic pyrolysis process ended. During the catalytic pyrolysis of feedstock with the ACC, volatiles generated from glucose/cellulose pyrolysis passed through the ACC for upgrading reactions, on which some coke could be deposited. Here, the coke mass was determined by the mass difference of the ACC before and after catalytic pyrolysis. The weight of the non-condensable gas was calculated using mass balance as shown in equation (1). The liquid, char, gas and coke yields were calculated using their corresponding masses divided by the initial reactant mass.

Weight of gas = initial sample mass – liquid mass – char mass – coke mass   (1)
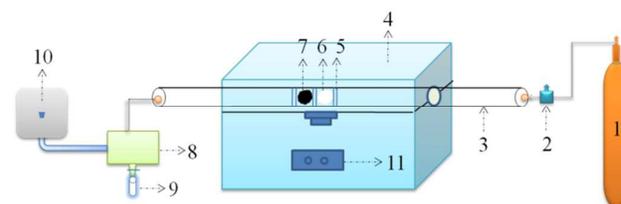
Figure 1. The catalytic pyrolysis system: 1-Nitrogen gas; 2-Gas flow meter; 3-Quartz tube; 4-Fixed bed furnace; 5-Quartz wool; 6-Sample; 7-Activated carbon catalyst; 8-Condenser; 9-Bio-oil collector; 10-Non-condensable gas collector; 11-Control panel of the furnace.

3. Results and discussion

3.1 Catalyst pyrolysis of glucose over ACC

The central composite design (CCD) was adopted to optimize the operating conditions in catalytic pyrolysis of glucose as shown in Table 1. Catalytic pyrolysis temperatures and catalyst to reactant mass ratios played important roles in products distribution based on former studies and thus selected as independent variables.[17] In this experiment, the temperature varied from 429 to 570 °C and the mass ratios of the catalyst related to the reactant varied from 0.27 to 1.13.

Table 1. Experimental design and product yield distribution of catalytic pyrolysis of glucose

Run[a]	Reaction Temperature (°C)	Catalyst/ Glucose ratio	Yield (wt%)			
			Bio-oil	Char	Gas	Coke
R1	429.3	0.7	49.2	18.2	27.8	4.8
R2	450	1	49.6	16.0	30.4	4.0
R3	450	0.4	54.6	16.6	25.4	3.4
R4	500	0.7	48.4	14.7	32.5	4.4
R5	500	1.13	49.4	15.2	32.6	2.8
R6	500	0.7	51.0	15.8	29.4	3.8
R7	500	0.7	49.0	15.2	32.6	3.2
R8	500	0.7	50.4	15.0	31.2	3.4
R9	500	0.7	50.6	14.6	31.6	3.2
R10	500	0.28	59.0	11.6	26.6	2.8
R11	550	0.4	50.8	9.8	36.8	2.6
R12	550	1	48.0	14.2	33.4	4.4
R13	570.7	0.7	53.0	13.4	30.4	3.2
R14	429.3	0.4	50.1	17.4	28.1	4.4
R15	500	0.4	52.2	14.0	30.4	3.4
R16	450	1	55.6	18.4	20.6	5.4
R17	429.3	-	67.4	16.4	16.2	-
R18	450	-	68.4	15.2	16.4	-
R19	500	-	72.8	13.6	13.6	-
R20	550	-	69.6	11.4	19.0	-
R21	570.7	-	71.8	10.8	17.4	-

[a]R1 to R13 was conducted based on the central composite design; R14 and R15 were added as the controls; R16 tested the used catalyst from R2; R17 to R21 are the control in the absence of a catalyst at various temperatures.

Catalytic pyrolysis products yield. Each experiment operating condition and corresponding products yield distributions were presented in Table 1. It can be seen that the yields of bio-oils ranged from 48.0 to 55.6 wt%, which were lower than those in the absence of a catalyst (62.4~72.8 wt%). The lower yield of pyrolytic oil revealed that reforming reactions occurred when volatiles produced from glucose decomposition passed through the activated carbon and further cracking reactions led to the decrease in yield of bio-oils.[20, 21, 35] The yield of gaseous product was in the range of 20.6~36.8 wt%, which was higher than that without a catalyst. The increased gaseous yield can be ascribed to catalytic sites in the ACC favoring the volatiles cracking towards to small gaseous molecules during catalytic processes,[24] which was also in accordance with the inverse trends between yields of bio-oil and gas products along with different catalytic conditions.
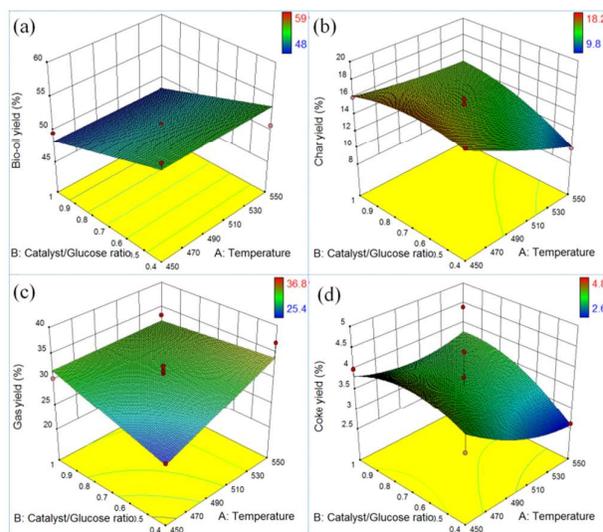
Figure 2. Response surface and contour line for the products yield along with various catalytic pyrolysis temperatures and catalyst to glucose ratios. (a), (b), (c) and (d) for bio-oil, char, gaseous, and coke yield, respectively.

Figure 2 represents the response surface and contour line for the products yields with respect to various catalytic pyrolysis temperatures (A) and catalyst to glucose ratios (B). In Figure 2(a), the yield of bio-oils changed slightly with different operating temperatures when the loaded catalyst to reactant ratio was fixed, which was consistent with the trend of changes in raw bio-oil at the absence of the catalyst. The highest yield of catalytic bio-oil (59.0 wt%) was attained at 500 °C and the ACC to glucose ratio of 0.28:1. On the contrary, the catalyst loading ratio exhibited a critical effect on the yield of bio-oils. Specifically, increasing the ACC to glucose ratio resulted in the decrease of the yield in the upgraded bio-oil as a consequence of enhanced catalytic reactions with more activated carbon used. It was also consistent with the increased yield of the gases produced. As for the yield of gaseous product, both reaction temperature and catalyst/reactant ratio were critical for affecting its yield. The maximum yield of gaseous product (36.8 wt%) was obtained at the catalytic pyrolysis temperature of 550 °C and the ACC to glucose ratio of 1:1. Figure 2(c) depicted that both lower catalytic pyrolysis temperature and less catalyst to reactant ratio resulted in a low gases yield. While the increase of the gases yield was accelerated by increasing operating temperatures and loading more catalysts. These results implied that higher temperature and more activated carbon catalyst favored bond-cleavage reactions of volatiles to generate non-condensable gases. Char and coke were generated from degraded and catalytic processes, respectively. Specifically, char is the solid residue left after glucose decomposition and the coke is formed on the catalyst surface during the ex-situ catalytic processes. The yield of char ranged from 9.8 to 18.4 wt% and the maximum yield was obtained at the reaction temperature of 429.3 °C with the ACC to glucose ratio of 0.7:1. The relative low char yield indicated that the majority of the loaded glucose in the tube furnace was decomposed into volatile compounds. The average yield of char was higher with the assistance

of catalyst, due to that the added catalyst slowed down the speed of volatiles passing through the ACC and therefore increased the retention time of volatile component in the quartz reactor. Longer retention time caused secondary cracking reactions to form a solid residue, which was in accord with the reduced yield of catalytic bio-oil. Coke deposition on catalysts is notorious due to the deactivation of active sites and micropore blockage during catalytic processes.[36] The coke deposition yields variation was depicted in Figure 2(d), varying from 2.6 to 5.4 wt%. The minor coke deposition was affected by short residence time setting at 8 min, which abated the formation of coke precursors.

The formation and deposition of coke were attenuated when the reaction temperature was increased, declining to 2.6 wt% at the temperature of 550 °C with a fixed ACC to glucose ratio of 0.4:1. It was also observed that more coke was formed and deposited with more catalysts applied in the catalytic process. The results indicated that elevated temperatures accelerated cracking reactions of pyrolytic volatiles towards small molecules, forming less coke precursor that would turn out to be the coke ultimately. In contrast, with more catalysts used, more catalytic reaction time would be provided for converting volatiles into more phenols, at the same time generating more coke on the catalyst.

Table 2. Porous structure parameters and acidity of ACC measured by N_2 isotherms and NH_3-TPD analysis.

$S_{BET,total}$ (m^2/g)	1125.6
S_{micro} (m^2/g)	450.3
S_{ext} (m^2/g)	675.3
V_{total} (cm^3/g)	0.71
V_{micro} (cm^3/g)	0.22
V_{ext} (cm^3/g)	0.49
Average pore size (Å)	25.0
Amount of adsorbed NH_3 (mmol/g)	0.398

Characterizations of activated carbon catalyst. The textural and acid properties of the activated carbon catalyst are listed in Table 2. It can be seen that the ACC has a relatively large BET surface area of 1125.6 m^2/g, in which micropore surface area was 450.3 m^2/g. The large surface area of the ACC could provide more reaction surface for the catalytic upgrading reactions inner the activated carbon. The pore distribution result reveals that more mesopores (0.49 cm^3/g) were formed during the activation process with the total pore volume of 0.71 cm^3/g. The average pore size of the catalyst is 25.0 Å, which is larger than the kinetic diameters of phenol and other intermediates during catalytic pyrolysis studied in the present work.[37] Therefore, catalytic reactions would tend to occur in these mesopores. With the aim to further describe the morphology of the ACC surface, SEM was employed to view the image as shown in Figure 3. It can be seen that numbers of cell wall structures of the corn stover were maintained with the development of porous structures induced by acid activation. The obtained ACC also exhibited straight fiber bundles with a tubular structure, which enlarged the catalyst surface area and also let volatiles can pass through smoothly.
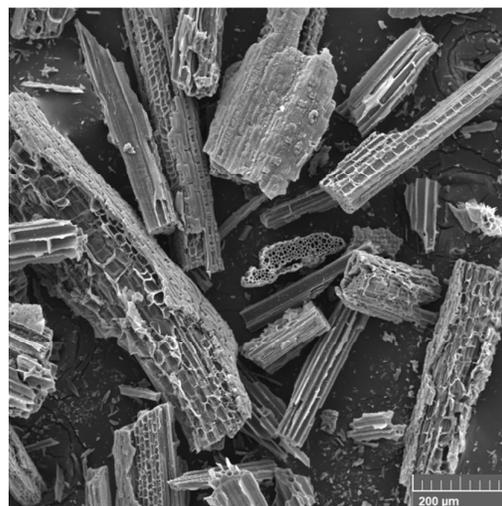
Figure 3. SEM image of the corn stover derived activated carbon catalyst
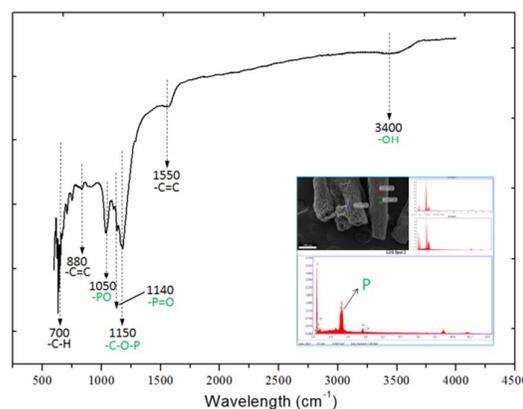
Figure 4. FTIR spectra of the corn stover derived activated carbon via phosphoric acid activation. The insert figure describes the EDX surface analysis.

The surface functional groups were detected by the FTIR spectra since they determine the surface properties of carbons and have significant implications for their behaviours as the catalyst.[38] From Figure 4, one can see that there is a wide absorption band at 3400 cm^{-1} in the spectrum, which indicates the -OH group in hydroxyl groups or absorbed moisture. The absorption peaks at 1550 and 700 cm^{-1} are allocated to -C=C and aromatic ring -C-H, respectively. Another peak at near 880 cm^{-1} can also be assigned to the alkene -C=C group. It should be noticed that phosphoric groups were successfully incorporated into the ACC, evidenced by the appearance of absorption peaks at 1050 cm^{-1} (-P-O), 1140 cm^{-1} (-P=O) and 1150 cm^{-1} (-C-O-P).[38, 39] Besides, further EDX surface analysis also revealed that the P element was introduced to the catalytic surface as shown in the insert figure of Figure 4. Based on these results, we proposed that these P-containing functional groups could be formed and would act as Brønsted acidic sites for acid catalytic reactions occurred in the ACC.[40] The total acidity was further estimated by conducting NH_3-TPD experiment and the NH_3 desorption curves is shown in Figure S2 † . The total acidity

represented by the total NH_3 desorbed from the catalyst was 0.398 mmol/g, which approximates to that of zeolite.[41] The aforementioned analysis indicated that the phosphoric acid activated porous carbon catalyst can be used as the solid acid catalyst due to the embedded P-containing groups acting as Brønsted acidic sites during catalytic pyrolysis processes.
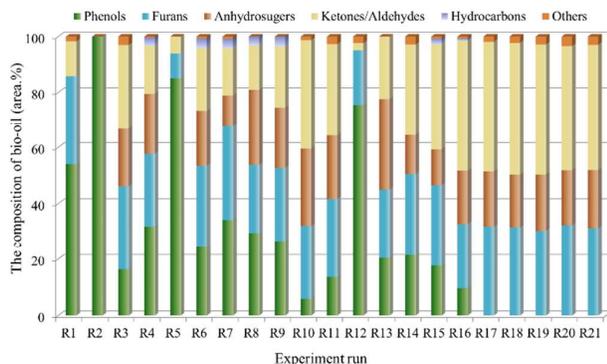
Figure 5. The composition of bio-oil in each experiment run

Chemical compounds analysis of bio-oils. The chemical compositions of bio-oils were further identified and partially quantified by GC/MS to gain a further understand of chemical reactions in *ex-situ* catalytic pyrolysis of glucose. Details of compositions of bio-oils from GC/MS analysis can be found in Table S1†. The components of obtained bio-oils in each experiment run with and without the catalyst were classified and listed in Figure 5. In the absence of a catalyst (R17~R21), the major components consisting of bio-oils were furans, anhydrosugars and ketones/aldehydes. Furans included furfural and its derivatives. Levoglucosenone (LGO) and 1,4:3,6-Dianhydro-.alpha.-d-glucopyranose (LG) were accounted for the most part of anhydrosugars. It should be noticed that no phenols were detected during pyrolysis of glucose at various temperatures without the catalyst because only dehydration, pyran-ring opening, and rearrangement reactions occurred to form oxygenates and anhydrosugars.[42, 43] Besides, there was no significant difference in the compounds distribution of obtained bio-oils without the catalyst in R17 to R21 as presented in Figure 5, which indicates that a similar raw bio-oil could be attained from glucose pyrolysis merely, regardless of various pyrolytic temperature in the current study. The final components of obtained bio-oils were therefore determined primarily by the subsequent *ex-situ* catalytic conversion process, where the ACC acts as the catalyst. Interestingly, when the activated carbon catalysts were introduced into the glucose pyrolysis, the composition of obtained bio-oil varied with various operating conditions and phenols were also detected. Put it in detail, phenols, furans, ketones, and anhydrosugars were the major compounds in catalytic upgraded bio-oils. The selectivity of phenol in obtained bio-oils ranged from 4.8 to 100% (peak area) and the maximum was reached at the catalytic temperature of 450 °C with a catalyst to glucose ratio of 1:1 in the current study (R2). Comparing with fresh catalysts, the catalytic performance of spent catalyst (R16 in Figure 5) exhibited less activity for phenols production due to the deactivation as a result of coke deposition during catalytic processes.

The effects of reaction temperature and ACC to glucose ratio on the chemical composition of bio-oils. Figure 6(a) shows representative chemical compounds distributions on the basis of reaction temperatures with the fixed ACC to glucose ratio of 0.4. In comparison with results from non-catalytic pyrolysis (R18 as the blank), the amount of phenols in upgraded bio-oils significantly increased with the assistance of the catalyst. It can be seen that the selectivity of phenols was in the range from 13.8 to 21.5% at various temperatures and the maximum was attained at the temperature of 429 °C, revealing that a lower catalytic pyrolysis temperature favored the production of phenols.[19] The obtained phenols were predominantly composed of mono-phenol and 2-methyl-phenol, in which the selectivity of mono-phenol was over 90%. These results indicated that a low temperature favored the decarbonylation, decarboxylation, dehydration and oligomerization reactions during volatiles upgrading in ACC which led to the formation of phenol. The quantified results of phenol concentration also showed a similar trend that concentration decreased with the increase of catalytic pyrolysis temperatures. The highest concentration (9.3 mg/ml) of phenol was obtained at the temperature of 429 °C, and increasing temperature resulted in lower phenol concentrations, which were 7.6, 8.2, and 6.1 mg/ml at temperatures of 450, 500, and 550 °C, respectively. The chemical composition of bio-oils from catalytic pyrolysis at 500 °C as a function of ACC to glucose ratios was shown in Figure 6(b). Comparing with the reaction temperature, catalyst to reactant ratio exhibited a notable variation on the chemical compounds distribution.
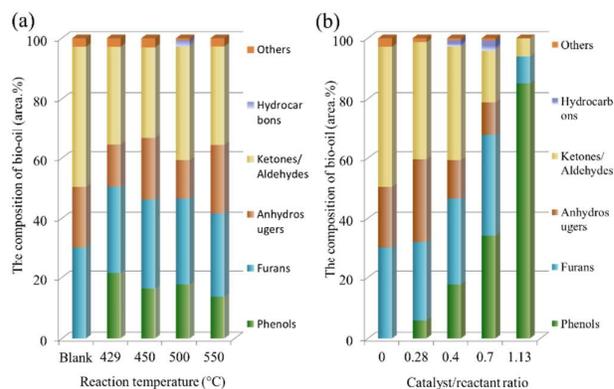
Figure 6. The composition of upgraded bio-oils varied with different reaction temperatures with a fixed catalyst to reactant ratio of 0.4 (a) and catalyst to reactant ratios at the same catalytic pyrolysis temperature of 500 °C (b)

The phenols content increased gradually from 5.9 to 85.1 % with the increased ACC to glucose ratios from 0.28 to 1.13, respectively, which was consistent with a similar trend claimed by other research studies.[19, 20] The concentration of phenol was 3.4 mg/ml with the catalyst to glucose ratio of 0.28 and then increased to 8.2 mg/ml when the catalyst to reactant ratio was 0.4. However, further increasing ACC to glucose ratio has little effect on the phenol concentration, where 8.2 and 8.3 mg/ml of phenol were obtained with ACC to glucose ratios of 0.7 and 1.13, respectively. With the increasing catalyst added (no more than 0.7), the selectivity of phenol increased and reached a high level resulting in the rise of the

concentration. Some generated phenol further reacted with extra catalytic sites to form other phenols or coke precursor on the catalyst with the ratio of 1.13 (R5), and therefore presented less increase in the concentration but with increased selectivity. This phenomenon was also evidenced by the phenol selectivity and concentration in R12, where a lower selectivity was obtained compared with R5, but presented a higher phenol concentration of 12.4 mg/ml. It should be noted that the highest selectivity of phenols could be achieved in R2 at the reaction temperature of 450 °C with the catalyst to reactant being 1 instead of in the experiment of R5 at higher temperature (500 °C) and more catalyst used (1.13) due to relevant low temperature promoting the generation of phenol as discussed aforementioned. Similarly, this high phenol selectivity also came with the concentration that was not high enough. According to former analysis, an excellent selectivity of phenol could be achieved, although the concentration was not high enough. The low concentration of obtained phenol primarily resulted from the high water content of obtained bio-oils (around 90 wt%) due to the nature of the feedstock, which also existed extensively in the relevant studies.[20, 21, 44, 45] Nevertheless, the current study potentially points out a novel and facile route to selectively produce the phenol-enriched bio-oil from the earth-abundant biomass-derived resource.
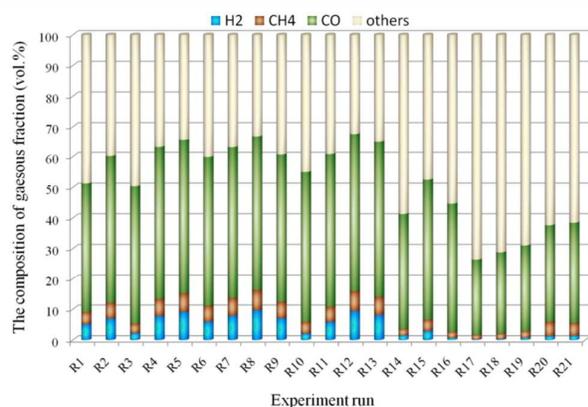
Figure 7. The composition of the gaseous fraction in each experiment run

The effects of catalytic pyrolysis temperatures and ACC to glucose ratios on the chemical composition of non-condensable gases. Previous studies reported that carbon monoxide, carbon dioxide, methane, and hydrogen were the main gaseous products from catalytic pyrolysis of biomass with activated carbon being the catalyst.[35] However, the evolution and changes of these gases were not well investigated. Herein, the compositions of gas fractions were identified and quantified by Micro-GC, which could provide more information for studying the reaction mechanism in the catalytic pyrolysis processes. The gaseous yields varied from 20.9 to 36.8 wt% compared with catalyst-free processes (from 13.6 to 19.0 wt%) as shown in Figure 2(c). The enlarged amount of gases should be attributed to the functional groups chelated in the activated carbon, e.g. -P-O, -P-O-H and -OH,[24] facilitating the bond cracking of volatiles to form more small molecules during catalytic reforming processes. The non-condensed gases mainly contained carbon monoxide, carbon dioxide, methane, and hydrogen. Other light

olefins such as ethylene were either with low concentration (<1 wt%) or not detected. Here, we focused on the syngas production, which was regarded as the target gaseous outcomes and therefore moved the carbon dioxide into the category of other gases in order to simplify the further analysis. The composition of the gaseous fraction in each experiment run was depicted in Figure 7. It can be seen that the concentration of target gases was enhanced with the assistance of catalyst (R1~R16) comparing with none-catalyst pyrolysis (R17~R21), which indicated that the production of these gases was favored during the cracking reactions of volatiles induced by the catalytic sites in the activated carbon. Increasing pyrolysis temperatures also resulted in rising yields of target gases without catalyst (R17~R21), which was in accordance with the phenomenon in previous work.[46]
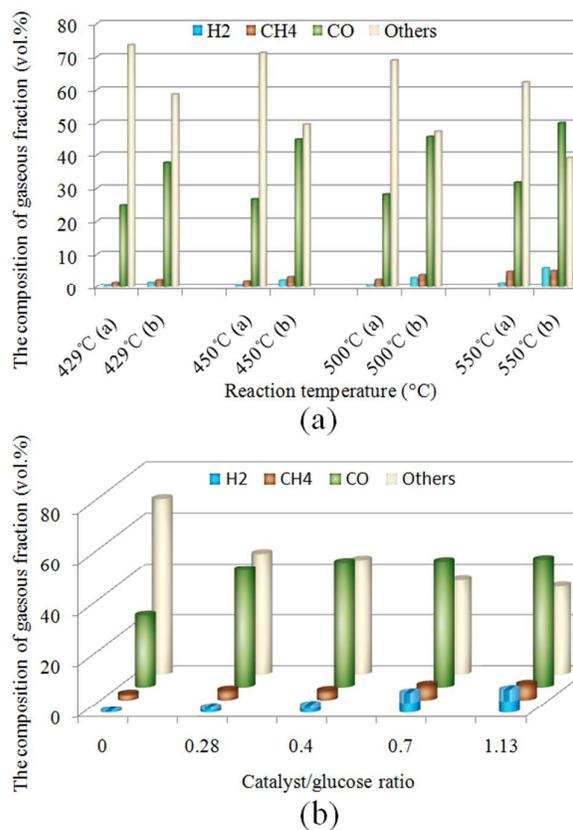
Figure 8. The composition of gaseous fraction varied with (a) reaction temperature without catalyst a and with catalyst b, and (b) catalyst to glucose ratio

The distribution of the gaseous fractions with respect to various pyrolysis temperatures at the fixed ACC to glucose ratio of 0.4 is described in Figure 8 (a). The result indicated that among the target gases carbon monoxide was the dominant composition from 37.7 to 50.2 vol% in the presence of the catalyst. High concentration of carbon monoxide should be attributed to the functional groups in activated carbons that can facilitate the decarbonylation reaction of volatiles towards releasing CO. Increasing catalytic pyrolysis temperatures resulted in the increase of target gases concentration as a consequence of higher temperature favoring the bond creaking of

volatiles towards small molecules.[16] The concentration of hydrogen was also enhanced in the presence of catalyst varying from 1.5 to 5.9 vol%, comparing to that ranged from 0.3 to 1.2 vol% without catalysts. The methane production at the temperature below 500 °C was also accelerated, but the positive effect turned to be slight at a high temperature of 550 °C, which indicated that relatively low temperatures were suitable for the demethylation of the volatiles within the ACC. Figure 8(b) depicts the composition of gaseous fraction varying with increasing AC to glucose ratios at the catalytic pyrolysis temperature of 500 °C. Comparing with obtained gaseous products without a catalyst, target gases generation were dramatically enhanced when the catalyst was applied. The highest concentration of carbon monoxide (50.2 vol%) was obtained with the catalyst to glucose ratio of 1.13. It is noteworthy that increasing catalyst to reactant ratios had little influence on the concentration of carbon monoxide though a slight increase occurred. Specifically, the concentration was 45.9, 49.1, 49.4 and 50.2 vol% with ACC to glucose ratios of 0.28, 0.4, 0.7 and 1.13, respectively. We proposed that the evolution of CO mainly came from furans and anhydrosugar in obtained bio-oil from glucose decomposition. The amount of CO-releasing was therefore determined by the generation of these compounds. A similar trend was also observed in the change of methane concentration. On the contrary, the concentration of hydrogen increased gradually from 0.6 vol% in the absence of a catalyst to 9.2 vol% at the catalyst to glucose ratio of 1.13.

Table 3. Products yield and main compounds in obtained bio-oils from catalytic pyrolysis of cellulose varying with different catalyst to cellulose ratios

	Catalyst to cellulose ratio				
	0	0.28	0.4	0.7	1.13
Products distribution: (wt%)					
Bio-oil	63.3±0.5	52.8±0.5	49.5±0.5	45.8±0.5	44.6±0.5
Gases	17.6±0.6	24.0±0.8	25.6±0.8	29.1±0.8	29.6±0.8
Char	18.8±0.1	18.7±0.1	18.9±0.1	18.8±0.1	18.7±0.1
Coke	/	4.5±0.2	6.0±0.2	6.3±0.2	7.1±0.2
Main compounds in Bio-oils: (area%)					
2-Cyclopentene-1,4-dione	0.6	0.9	0.8		
2-Cyclopentene-1-one, 2-methyl-		2.6	3.5	17.7	2.1
Ethanone, 1-(2-furanyl)-	2.1	4.9	4.7	10.1	
Cyclohexanone	1.4				
1,2-Cyclopentanedione	1.5	5.8	4.3	1.4	
2,5-Furandione, 3-methyl-		1.6			
2-Furancarboxaldehyde, 5-methyl-	6.8	8.8	10.8	24.4	
2,5-Furandione, dihydro-3-methylene-			2.4	7.5	1.2
Phenol		4.7	10.9	34.5	88.4
3-Cyclobutene-1,2-dione, 3,4-dihydroxy-	3.5				
2-Cyclopentene-1-one, 2-hydroxy-3-methyl-	1.5		9.5		
Phenol, 2-methyl-				4.3	8.3
1,2-Cyclopentanedione, 3-methyl-		10.1			
Spiro[3.3]heptane-2,6-dione	4.5		2.6		
Levoglucosenone	29.9	18.8	20.5		
1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	24.6	26.7	23.5		
Maltol		0.3	3.5		
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	6.6	0.7			
1,3-Dioxolane, 2-ethenyl-4-methyl-	5.6				
Bicyclo[2.2.1]heptan-2-ol, 1,3,3-trimethyl-	2.7				
2-Butene, 1-chloro-4-ethoxy-	3.5				
.beta.-D-Glucopyranose, 1,6-anhydro-		3.7			

3.2. Catalytic pyrolysis of cellulose over ACC

In order to provide a valuable extension to obtain phenol-rich bio-oil from the catalytic pyrolysis of glucose-based carbohydrates, cellulose was used as the feedstock to investigate phenol production from earth-abundant renewable resource via catalytic pyrolysis over activated carbons in the fixed-bed reactor for the first time. It is well known that glucose is the monomer of the cellulose and both of them has a similar pyrolytic behavior.[47] Thus, we proposed that the phenol-rich bio-oil could also be achieved by the same procedure as described above. The catalytic pyrolysis temperature of 450 °C was selected in terms of bio-oil yield and phenol selectivity based on studies of glucose. The catalyst to feedstock ratio showed a critical effect on the chemical compounds distribution of glucose catalytic pyrolysis and therefore was regarded as the independent variable here to investigate that of cellulose. Table 3. shows the products yield and main chemical compounds in obtained bio-oils from catalytic pyrolysis of cellulose varying with a different ACC to

cellulose ratio. One can see that the yield of catalytic pyrolysis bio-oils ranging from 44.6 to 52.8 wt.% was lower than that without a catalyst (63.3 wt%), and an inverse trend occurred in the yield of gaseous products, which were consistent with the results presented in glucose catalytic pyrolysis. The yield of gaseous products attained in the presence of a catalyst ranged from 24.0 to 29.6 wt.%, which was higher than that in the absence of a catalyst. The increased gaseous products can attribute to active sites inner activated carbons favoring the cracking reactions of volatiles towards low molecules to finally form the non-condensed gases. A relative low char yield (less than 19 wt.%) indicated that most celluloses were also decomposed into volatiles. The increasing yield of coke deposited on ACC was observed with rising catalyst to cellulose ratios, which had a side effect on the catalytic performance of selective phenol production.
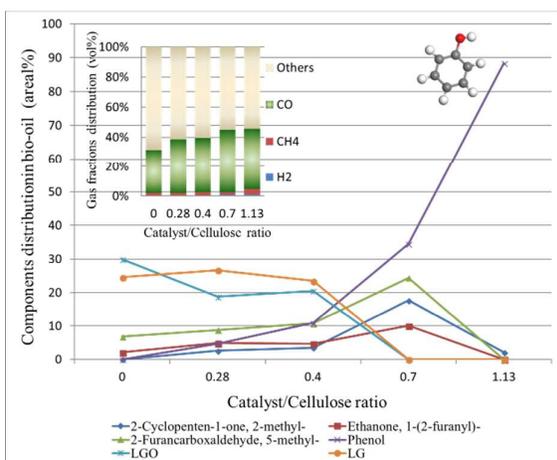
Figure 9. The selectivity of chemical compounds in bio-oils varied with a different catalyst to cellulose ratios. Inserted bar describes the concentration of gaseous with various catalyst to cellulose ratios.

The chemical compounds distribution of obtained bio-oils was also similar to that from glucose, in which anhydrosugars, ketones/aldehydes, phenols, and acid were the main components. Comparing with results from catalytic pyrolysis of glucose, the yield of anhydrosugars was higher in the bio-oil from cellulose, revealing that decomposition and subsequent dehydration of cellulose to form anhydrosugars were kinetically favored during cellulose pyrolysis.[43, 48, 49] The selectivity of phenols in attained bio-oils varied from 0 area% in the absence of ACC to 96.7 area% with a catalyst to cellulose ratio of 1.13, which was also similar to the results obtained from glucose. On the other hand, the selectivity of furans was lower than that from glucose, indicating the production of anhydrosugars rather than furans was favored during cellulose pyrolysis.[43, 48] The evolution of main chemical compounds, 2-Cyclopentene-1-one, 2-methyl; Ethanone, 1-(2-furanyl)-; 2-Furancarboxaldehyde, 5-methyl-; phenol, LGO, and LG, were depicted in Figure 9 with respect to the different catalyst to cellulose ratios so as to elucidate the catalytic pyrolysis mechanism of cellulose. It can be seen that the selectivity of phenol in upgraded bio-oil increased continuously with rising catalyst to cellulose ratio and reached the maximum (88.4 %) at the ratio of 1.13, which indicated that higher amount of loaded catalyst to reactant ratios dramatically enhanced the selectivity of phenol due to more active reaction sites within ACC involved in the volatiles

reforming steps. On the contrary, the selectivity of anhydrosugars decreased with more catalysts added until turned out to be zero with the ACC to cellulose ratio of 0.7, although a slight fluctuation occurred. It revealed that catalytic reaction sites like -P-O-, -P=O and -OH function groups accelerated the cracking reactions of anhydrosugars to form smaller structures like furans, which was evidenced by the increase in the selectivity of 2-Cyclopentene-1-one, 2-methyl-; ethanone, 1-(2-furanyl)- and 2-Furancarboxaldehyde, 5-methyl- when the catalyst to cellulose ratio was less than 0.7. With enough catalyst being used, these furans and ketones would be further converted into phenols and small gaseous products. Besides, the quantified concentration of phenol also increased gradually with rising catalyst to reactant ratios, which were 5.5, 11.5, 25.1, and 53.6 mg/mL with ACC to cellulose ratio of 0.28, 0.4, 0.7, and 1.13, respectively. The obtained phenol concentration from cellulose was higher than that from glucose, indicating that cellulose was a better starting feedstock to produce phenol-rich bio-oil via catalytic pyrolysis with activated carbon catalysts. Carbon monoxide, carbon dioxide, methane, and hydrogen were the major gaseous fractions in the obtained non-condensable products. The concentration of carbon monoxide was 29.3 vol% without catalyst and increased gradually with increasing catalyst to cellulose ratios, resulting in the maximum of 42.1 vol% as shown in the insert bar figure of Figure 9. Hydrogen and methane both had a relatively low concentration (less than 5 vol%), in spite of its increase with more catalyst added.

3.3. The regeneration of the activated carbon and catalytic performance comparison with the zeolite-based catalyst.

The reuse and regeneration are important criterions in determining an effective catalyst for practical usage. Specifically, coke deposition is a notorious process that induces the deactivation of a catalyst and this carbonaceous residue is usually hard to remove with the catalyst being intact.[34] Current solutions to this issue contain two directions: developing catalyst with coke deposition free and removing coke after catalyst deactivation. Combing metal ions with existed catalysts has been an effective attempt to achieve the former solution, whereas the complex synthesis procedure and relevant high cost impede its usage industrially. Calcination is another common way to regenerate catalysts. Based on the later solution, an in-suit catalyst regeneration of the activated carbon was proposed in the current study. Inspired by the fact that the coke is the carbon residue that is similar to the body matrix of the activated carbon and the catalytic performance is mainly determined by surface function groups, we thus speculated that the regeneration of the activated carbon catalyst could be achieved with a similar simple activation step to its production. Herein, processes in ACC production was used to regenerate the catalyst but with the much less phosphoric acid used. Briefly, the used ACC was impregnated in a 40 wt% H_3PO_4 solution for 12 h and then filtrated to remove the liquid solution. Subsequently, dried the sample and then conducted the pyrolysis as described in former ACC generation session. The used ACC after one time run with a catalyst to cellulose ratio of 1.13 as shown in Table 3 was reused for the second time with same operating conditions. The catalytic pyrolysis results revealed that a relatively low selectivity of phenol was obtained (3.5 %) and the main compounds in upgraded bio-oil with used ACC (but not regenerated) were furfural, furans, and

anhydrosugars (Table S2), which was consistent with the result from that of glucose. These phenomena indicated that catalytic sites were tended to be blocked by coke deposition in the ACC and therefore presented less activities. This second used ACC was then underwent regeneration processes as described above and the effective catalytic performance was again obtained as expected that a high selectivity of phenols (85.1%) was attained by catalytic pyrolysis of cellulose at 500 °C with the regenerated ACC to cellulose ratio of 1.15. The regeneration test indicated that the proposed in suit ACC regeneration was an efficient way to reach the catalyst use industrially. It is also worth noting that the deactivated ACCs can be used as the microwave adsorbates in activated carbons production simultaneously with the regeneration of used ACCs, which further lowers the cost and enhances the efficiency of the whole processes.

Comparing with the zeolite-based catalyst which has been demonstrated the effective catalytic performance in bio-oil upgrading to produce aromatics or compounds with high C/O ratio, much more surface area can be achieved in activated carbons that could potentially enlarge the contacting area between reactants and catalyst sites, therefore increasing the efficiency of catalytic activities.[50] The acidity of a catalyst (usually determined by Brønsted and Lewis acidic sites) is thought to have critical effect on the bio-oil upgrading steps such as deoxygenation, decarboxylation, isomerization, and aromatization reactions, whereas strong acidity usually favors the catalyst deactivation by forming large molecular weight aromatics (coke) easily on the catalyst, leaving the challenge of remaining high catalytic activity along with less deactivation after use.[34] As what we introduced at the beginning, the acidity of the activated carbon could be successfully altered by modifying the surface functional groups with simple activation procedures.[23] Thus, activated carbons with tunable physical and chemical properties could have controllable catalytic performance in selectively converting biomass into fuels and chemicals. Recent studies tend to modify zeolites via introducing various metals with the complex and costly process to obtain a better catalyst for bio-oil catalytic cracking, ignoring metal doped bifunctional activity could also be achieved in activated carbons. A successful example can refer to the biochar generated from biomass pyrolysis directly, which has emerged promising catalytic performance in bio-refinery.[51] More important, the cost for activated carbons production is usually less than those of zeolite catalysts and less pollution is generated due to less chemicals are consumed in activated carbons production from renewable biomass resources.[52] In order to make a comparison between the zeolite-based catalyst and the ACC in selective phenol production, the catalytic pyrolysis of cellulose with HZSM-5 being the catalyst was tested in the studied reaction system. HZSM-5 was prepared based on our former study [16] and an HZSM-5 to cellulose ratio of 0.25 at 450 °C was used. Unfortunately, very few phenol compounds were obtained (selectivity < 1%), rather, furfural and anhydrosugars were primary components in reforming bio-oil as shown in Table S2. Based on these results, phosphoric acid activated ACC could show prior catalytic performance in phenol production from catalytic pyrolysis of cellulose in the fixed bed reactor system.

3.4 Mechanism of phenols generation from catalytic pyrolysis of carbohydrates over activated carbon catalysts

Previous studies demonstrated that phenols were mainly generated from the decomposition of lignin component of biomass due to the benzene rings contained in the lignin.[19-21, 53] Cellulose, on the other hand, has received few attentions on benzene-containing chemical synthesis,[54] especially for the phenols generation, and the rare investigation has been devoted to the involved mechanism. Based on the present work, we proposed the mechanism of phenols generation from glucose-based carbohydrates as described in Figure 10. It is well established that anhydrosugars are the main components in bio-oil from cellulose pyrolysis, which was observed in the present work. Besides, some C5 fractions such as furfural and 1,2-Cyclopentanedione were also generated with small concentrations by dehydration, decarboxylation reactions of decomposed cellulose and anhydrosugars. In the meanwhile, some C6 molecules with furan ring (e.g. ethanone, 1-(2-furanyl)- and 2-furancarboxaldehyde, 5-methyl-) were formed through dehydration and rearrangement of anhydrosugars and cellulose decomposition.[55] This chemical step was promoted by activated carbons, evidenced by the increasing selectivity of C6 structures in obtained bio-oils. These C6 components went further rearrangement reactions to form the 2-Cyclopentene-1-one, 2-methyl-, which was considered as the most important intermediate in phenol production. The selectivity of 2-Cyclopentene-1-one, 2-methyl- was also increased with more carbon catalysts being used and the further rearrangement reaction by releasing a hydrogen molecule which converted this C6 structure into a phenol molecule.

On the other side, two generated C5 compounds combined each other through a series of Diels-Alder, decarbonylation and oligomerization reactions occurred on the heterogeneous catalytic sites in activated carbons to form >C6 fractions containing benzene ring, during which some carbon monoxide, methane and water molecules were released resulting in a high CO concentration in upgraded gaseous products. A similar phenomenon has been reported previously in the catalytic reactions of furans to form aromatic hydrocarbons through zeolites catalyst.[56, 57] The "hydrocarbon pool" was employed to elucidate converting methanol and cellulose to aromatics with zeolite catalysts although the exact nature of it has been the subject of many debates.[16, 57, 58] Inspired by this, the "phenol pool" was suggested in the present work to describe the function of activated carbons, where porous carbons filled with catalytic sites such as -OH, -C-P-O, -P=O, and -P-O functional groups composing a comprehensive system that can convert volatiles from glucose-based carbohydrates pyrolysis to phenols rather than aromatic hydrocarbons. With further decarbonylation, demethylation and bond-cleavage reactions, these benzene-containing structures (>C6 fractions) were reformed to phenols. The catalytic function found here in activated carbon extended its application in the phenols synthesis from renewable biomass sources.
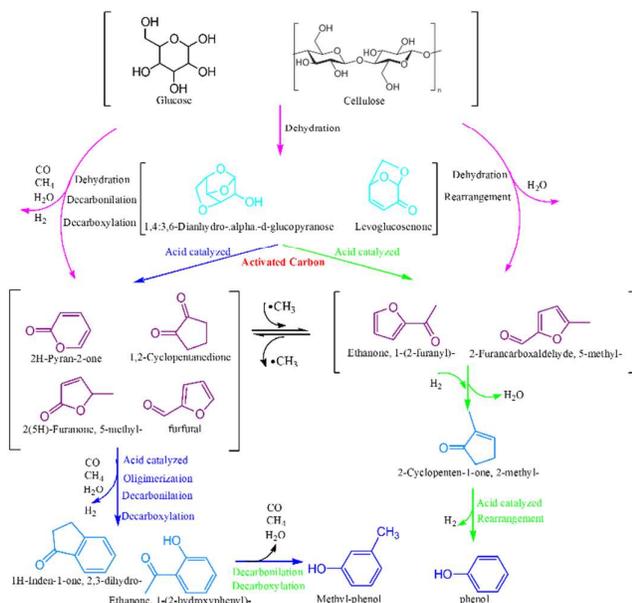
Figure 10. The proposed mechanism of forming phenols from catalytic pyrolysis of glucose and cellulose over activated carbon catalysts

4. Conclusions

In the present study, we investigated catalytic pyrolysis of glucose and cellulose over phosphoric acid-activated carbon catalyst to obtain phenol-rich bio-oil and syngas production in a facile fixed-bed reactor for the first time. Results revealed that catalytic reaction temperatures and catalyst to reactant ratios played important roles in products yield and chemical compounds distribution of bio-oils. High reaction temperature favored the yield of gaseous product with high concentrations of carbon monoxide and hydrogen but resulted in low phenol selectivity in obtained bio-oil. Additional, increasing ACC to glucose ratio could gradually enhance the phenols selectivity and carbon monoxide concentration. The main chemical compounds of catalytic bio-oil were phenols, ketones, and anhydrosugars, in which the highest selectivity of phenol (100 area%) was achieved at a reaction temperature of 450 °C with the catalyst to reactant ratio of 1. Carbon monoxide, carbon dioxide, methane, and hydrogen were the main gas fractions in gaseous products, where high concentrations of carbon monoxide (50.2%) and hydrogen (9.2%) could be attained. The similar phenomenon was observed in catalytic pyrolysis of cellulose with various catalyst to reactant ratios at the reaction temperature of 450 °C. A high selectivity of phenols (96.7%) was achieved intergraded with a high concentration of carbon monoxide (42.1%) in gaseous products. The "phenol pool" was proposed to describe the catalytic function of activated carbons in converting volatiles to phenols. Phenols were generated via two parallel reaction routes: one was directly formed from the rearrangement of C6 compounds and another one was through two furan oligomerization and subsequent acid catalytic reactions. Future work will be conducted to explore an optimized route to maximize the concentration of selective phenol production and obtain a deep understanding of reaction mechanism from the view of molecular scale. The present work might provide a novel and viable route to

generate high-purity phenols from renewable glucose-based carbohydrates.

Abbreviations

ACC: Activated carbon catalyst
LGO: Levoglucosenone
LG: 1,4:3,6-Dianhydro-.alpha.-d-glucopyranose

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Table of entry:

A novel route to selectively produce phenol and carbon monoxide-enriched gas was proposed via catalytic pyrolysis of glucose-based carbohydrates with activated carbon catalyst.