Sustainable Energy & Fuels

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Journal:	*Sustainable Energy & Fuels*
Manuscript ID	SE-ART-03-2020-000419.R1
Article Type:	Paper
Date Submitted by the Author:	06-May-2020
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A novel production of phase-divided jet-fuel-ranged hydrocarbons and phenols-enriched chemicals from catalytic co-pyrolysis of lignocellulosic biomass with low-density polyethylene over carbon catalysts

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Abstract: The catalytic co-pyrolysis of Douglas fir and low-density polyethylene with commercial activated carbon catalysts was investigated for the first time. Six types of activated carbon catalysts were tested and compared. The obtained liquid product contained physically separated parts being in the oil and water phases, where the percentage of the oil phase ranged from 10.10 to 64.4 wt.% depending on various co-pyrolysis conditions. The oil phase of bio-oil was rich in C_8-C_{16} aromatics and aliphatics (up to 98.6 area.%) that were compatible with transportation jet fuel. In addition, the main components of the bio-oil in water phase comprised of phenols and guaiacols, in which the high phenols selectivity (up to 92.9 area.%) and phenol concentration (up to 26.4 mg/mL) were achieved. Hydrogen, methane, carbon dioxide, and carbon monoxide were the main fractions of gaseous products, where a high concentration of methane (23.6 vol.%) and carbon monoxide (39.1 vol.%) could be obtained. The process was optimized based on an overall consideration of bio-oil yield, C_8-C_{16} hydrocarbons selectivity, and phenol concentration. Further, the reaction mechanism involving the production of phenols and hydrocarbons were proposed. Our findings may provide a novel, green, and cost-effective route to produce phase-divided phenols-enriched chemicals and transportation jet fuels.

Introduction

The diminishing supply of fossil-based petroleum and the destructive influence on natural environments has spurred tremendous interests in the exploitation of renewable resources for developing high-value-added chemicals and green biofuels [1-2]. As one of the sustainable sources, lignocellulosic biomass, which consists of cellulose, hemicellulose, and lignin, exhibits greatly promising potential in the fabrication of universal chemicals and renewable hydrocarbon biofuels [3-4]. The lignocellulosic biomass is plentiful mainly in the form of waste streams, energy crops, wood, and agricultural residues, which as the feedstock to produce chemicals and biofuels is much cheaper than edible biomass and crude oil from the perspective of economic[5-6]. Fast pyrolysis has been demonstrated as a facile and eco-friendly conversion technology to acquire bioenergy from lignocellulosic biomass over the past two decades, which is on the verge of commercialization [7-9]. Fast pyrolysis is always performed at 400-600 ºC in the oxygen-free conditions. A high yield of liquid product that is known as bio-oil, which can be a potential alternative to conventional fossil fuel resources [10-11].

Phenol, an important chemical intermediate, is indispensable to manufacture various chemicals and materials, such as phenolic resins and alkylphenols, et al. However, the current technology to produce phenol is mainly through the industrial conversion by cumene process from benzene, at the cost of plentiful consumption of fossil fuels and environment contamination [12-13]. Fortunately, phenols can be obtained from the bio-oil produced by lignocellulosic biomass pyrolysis, which provides a new pathway to manufacture phenols from the renewable natural resources [14]. The phenols are thought to be mainly generated from the lignin decomposition. However, the content of phenols in bio-oil is very low, which causes the down-stream expensive extraction and purification of phenols. Therefore, producing phenol-rich bio-oil from the conversion of lignocellulosic biomass still faces a huge challenge [15]. Numerous efforts have been performed to enhance the phenols formation by using catalysts during the pyrolysis process. Activated carbon catalyst (ACC) has been recognized as an effective catalyst in selectively converting lignocellulosic biomass into phenols

[16-17]. Due to its interesting properties, such as high surface area, tunable surface functional groups and pore volume, ACC exhibits excellent catalytic performance in converting the volatiles from lignocellulosic biomass pyrolysis into phenols [17]. According to our previous studies, ACC was demonstrated to hold a good performance in phenolic-rich bio-oil production during the lignocellulosic biomass pyrolysis process [18-19]. High-purity production of phenol can be achieved when H_3PO_4-activated carbon employed as a catalyst during the glucose pyrolysis process. However, the absolute content of phenols in bio-oil was still not high, which was only around 50 mg/mL [15]. Therefore, the practical fulfillment of lignocellulosic biomass claims effective technologies to achieve the mass production of high-value-added chemicals.

In addition, the conversion of lignocellulosic biomass into transportation biofuels, such as jet fuels, gasoline, and diesel has also attracted great attention worldwide [20-21]. The typical chemical compositions of bio-oil prepared from lignocellulosic biomass are small carbonyl compounds, sugar-derived compounds, and lignin-derived compounds, mainly include acids, ester, sugars, alcohols, aldehydes, ketones, phenols, furans, and aromatic hydrocarbons [22]. Among them, aromatic hydrocarbons are recognized as satisfying products for biofuel because they do not only have good volumetric energy content but also have a large positive influence on seal-swell, O-rings, self-sealing bladder, adhesives, etc. in jet engine systems [23]. However, it is found that the oxygen-enriched intrinsic nature and hydrogen deficiency of lignocellulosic biomass are not conducive to the aromatic generation. The low hydrogen/carbon effective (H/C_{eff}, <0.3) of biomass always results in a low carbon yield and much formation of coke [24]. To mitigate these problems, it is very necessary to co-feed of lignocellulosic biomass with other feedstock with a high H/C_{eff} ratio during catalytic pyrolysis process to enhance the aromatic yields and lower the coke generation [3, 25]. Previous studies have indicated that catalytic co-pyrolysis of lignocellulosic biomass and plastic materials was conducive to decrease oxygen content and improve the aromatic compounds in bio-oil due to the modified reaction mechanism [3, 26-27]. Our previous study found that ACC during catalytic pyrolysis process gave rise to decarboxylation, dehydration, aromatization, oligomerization and Diels-Alder reaction, which caused the conversion of C5 and C6 compounds into phenols [15]. Therefore, we speculated that under the existent of hydrogen donor conditions, ACC could lead to the hydrogenation and deoxygenation of phenol in bio-oil produced from lignocellulosic biomass pyrolysis and simultaneously resulted in the facilitation of aromatics generation.

On the other side, although our previous studies unveiled the good performance of home-made activated carbon catalyst in biomass catalytic pyrolysis processes, the lab-scale production of ACC could not meet the industrial usage and usually comes with less energy efficiency, which will impede the development of such promising carbon-based catalysts. Alternatively, traditionally activated carbons, which have been used for several decades, play important roles in many aspects of domestic and industry, especially as the adsorbent. Fortunately, with the advanced technology, commercial activated carbons are produced by a mature production line with minimum energy input and thus can be obtained cost-effectively at the industrial scale. Therefore, a successful attempt to commercial activated carbons employed as catalysts in biomass catalytic conversion will dramatically drive further development of renewable biomass utilization. According to the aforementioned consideration, the catalytic co-pyrolysis of Douglas fir (DF) and low-density polyethylene (LDPE) over several typical commercial activated carbons (CACs) as the catalysts in a facile fixed bed reactor was performed for the first time. The main purpose of this study was to investigate the simultaneous generation of renewable high-purity phenol and aromatics in bio-oil by fast pyrolysis technology over commercial available ACC. The influence parameters included the CAC category, pyrolytic temperature, catalyst/feedstock ratio and LDPE/DF ratio were discussed in detail on the production of phenols and jet fuel range aromatic hydrocarbons. In addition, the lifetime and performance of CACs during the pyrolysis process were also investigated to provide a comprehensive evaluation. The current study will provide a cost-effective, eco-friendly and convenient route to simultaneously produce hydrocarbon-rich bio-oil and phenols-rich chemicals, ultimately achieving the high-efficiency conversion of lignocellulosic biomass into valuable products.

Experimental

Materials

CAC1 to CAC6 were purchased from Cabot Norit Activated Carbon Americas (Marshall, TX, USA), namely, PETRODARCO 8X30, NORIT GAC 1240, MRX, NORIT GCN 1240 PLUS, NORIT C GRAN, and GAC 830 PLUS. Douglas fir (DF, diameter: 7 mm) was purchased from Bear Mountain Forest Products Inc.

Co-pyrolysis setup

The catalytic co-pyrolysis of LDPE and DF with ACC were performed in a facile fixed bed reactor, and the detailed experimental device was exhibited in Fig. 1. Ex-situ catalytic pyrolysis has been demonstrated to be a promising process to achieve better catalytic performance, however, this process causes the cost increase because of the utilization of additional heating facilities on the separated heating area [28]. In the current study, a handy means was employed to divide the catalyst and feedstock in the same tube furnace, which was not only conducive to enhance the heating efficiency but retrench the economic depletion [15, 29]. The effects of ACC categories (CAC1, CAC2, CAC3, CAC4, CAC5, and CAC6), pyrolytic temperatures (425 ºC, 450 ºC, 475 ºC, 500 ºC, 525 ºC and 550 ºC), catalyst/feedstock ratios (0.4, 0.7, 1.0 and 1.2), and LDPE/DF ratios (only LDPE, 0.3, 0.5, 0.7, 1.0 and only DF) on product prepared from catalytic co-pyrolysis of LDPE and DF were investigated as shown in Table 1. For all runs, a fixed 3 g of DF was used. The usage of LDPE and catalyst was calculated related to the mass of DF. Before each run, the feedstock and catalyst were simultaneously placed into the quartz tube. The quartz wool was used to divide the feedstock and catalyst. The high purity nitrogen was introduced to the reactor at 160 mL/min for 15 min to provide an oxygen-free inert environment. Then the quartz reactor was transferred into the oven after the oven (Thermo Scientific) temperature reached the target value. The high-pure nitrogen at a rate of 70 mL/min was used as the carrier gas to drive the volatiles produced by feedstock pyrolysis passing through the catalyst. Each run was carried out at the target temperature for 10 min to accomplish the pyrolytic reaction. The condenser was employed to collect the non-condensable part in the form of liquid. The yield of bio-oil was based on the difference of collector with or without bio-oil. The solid residue was also collected and weighed after each run. The coke, which deposited on the catalyst, was calculated by the mass difference of the catalyst before and after the experiment. The gas fraction was collected in the Tedlar gas bag. The yield of gas was calculated by difference based on the mass balance of feedstock.

Analysis of bio-oil and gas products

The obtained bio-oil consisted of two parts, namely the water and oil phases. The oil and water phases were stratified due to their natural characterization. The mass of oil and water phases was calculated by their actual weight. The organic phase was analyzed by GC-MS (GC, Agilent 7890A; MS, Agilent 5975C) with a DB-5 capillary column. Before analyzing, the ethyl acetate (HPLC grade, 99.5+%, Alfa Aesar, USA) was used to extract the organic phase from the water phase. The ratio of ethyl acetate/bio-oil was 10:1 (v/v). Then the resulted organic phase was filtered by a 0.22 μm organic syringe membrane. On the other side, the obtained bio-oil in oil-phase was also diluted directly by using ethyl acetate before conducting further analysis. The GC was first heated to 55 ºC for 5 min and elevated to 280 ºC at a rate of 5 ºC/min, which was maintained for 2 min. The high pure helium with a constant flow rate of 0.6 mL/min was used as the carrier gas. The ion source temperature was 230 ºC. The compounds were recognized by comparing the spectral data with those in the NIST data library. The product selectivity was determined by the area percent of compounds obtained from GC/MS results. The phenol concentration in the organic phase was quantified by injecting different standard solutions with various concentrations of phenol into GC/MS.

The components of gas fraction were analyzed by Micro-GC (INFICON INC, Santa Clara, CA, USA) system with a thermal conductivity detector (TCD). The calibration gases include H_2, N_2, CH_4, and CO. In this study, the chemical compounds of the gas fraction with more than 2 carbon atoms were not tested or a very small amount without calculation.

Results and discussion

Catalytic co-pyrolysis of DF and LDPE over various ACs

As shown in Table 1, the various commercial ACs (CAC1, CAC2, CAC3, CAC4, CAC5, and CAC6) were used as catalysts during catalytic co-pyrolysis of DF and LDPE. Detailed descriptions of these activated carbons were listed in supporting information. The products prepared from catalytic co-pyrolysis of DF and LDPE included bio-oil, coke, gas, and char. As shown in Fig. 2A, the yields of bio-oil and gas varied from 47.1 to 59.7 wt.% and from 21.9 to 34.9 wt.%, respectively. The relatively high bio-oil yield was obtained by using CAC1 and CAC3, indicating that most of the fractions produced from catalytic co-pyrolysis of DF and LDPE were converted into condensable liquid fuel compounds. The coke yield from catalytic co-pyrolysis of LDPE and DF ranged from 3.1 to 9.0 wt.%. The higher coke yield was conducive to suppress the catalytic efficiency of the catalyst due to the fact that the coke always deposited on the catalyst during the catalytic pyrolysis process, causing the blockage of micropores and further decline of activating sites [3, 30]. The result showed that CAC4 caused higher coke yield than other CACs. The char yield produced from catalytic co-pyrolysis of LDPE and DF over various ACCs ranged around 14.0%, suggesting that the formation of char was insensitive to the catalyst category. This was due to that the same pyrolytic temperature was employed, which played a crucial role during the pyrolysis experiment [3, 31].

In the bio-oil produced from the catalytic pyrolysis process of lignocellulosic biomass, the generation of water is always accompanied by pyrolytic bio-oil due to the dehydration reaction of hemicellulose, cellulose, and lignin. The water content usually ranges 15-30%, which varies with diverse starting materials, catalyst categories and heating manners [11-12]. The high content of water is pernicious to bio-oil quality. In the current study, the content of the oil phase in bio-oil produced from catalytic co-pyrolysis of LDPE and DF over various ACCs ranged from 54.1 to 67.5

wt.%. The maximum and minimum oil phase contents were obtained when CAC2 and CAC6 as a catalyst, respectively. To better understand the effect of various CACs on the components of bio-oil produced from the catalytic co-pyrolysis of LDPE and DF, the GC/MS was employed to analyze the organic chemical compositions of the oil phase and water phase in bio-oil, respectively. In general, the components of the oil phase mainly are hydrocarbons, such as aromatics, alkanes, etc., and the components of the water phase mainly are oxygenates, such as acid, ketones, furan, phenolics, aldehydes, etc [19]. The detail organic components of the water and oil phases produced from the current reaction condition were exhibited in Fig. 2B and Fig. 2C. Interestingly, the results showed that the major components in the oil phase were hydrocarbons, and these hydrocarbons can be divided into five parts, namely C_8-C_{16} aromatics and aliphatics (jet fuel fractions), C_{17}-C_{23} aromatics and alkanes (diesel fractions), and others (C_{23+} aliphatics and oxygenates). It can be seen from Fig. 2B, the jet fuel fractions were the dominating components in the oil phase of bio-oil. The selectivity of C_8-C_{16} aromatics and alkanes varied from 15.0 to 51.6 area.% and from 38.5 to 54.6 area.%, respectively. The maximum C_8-C_{16} aromatics (51.6 area.%) and C_8-C_{16} hydrocarbon (90.1 area.%) was achieved when the CAC5 was the catalyst during the catalytic co-pyrolysis process, which also resulted in the minimum selectivity of other components. This may be ascribed to the different activated methods of CACs that only CAC5 was chemically activated by H_3PO_4 and others were produced by steam activation. It reported that activated carbon produced by the chemical activation process always has a large surface area and advanced cellular structure [32]. The components of the water phase predominantly consisted of phenolics (guaiacols and phenols) and other oxygenates as shown in Fig. 2C. Among them, the phenolics included guaiacols and phenols. The selectivity of phenolics in the water phase produced from catalytic co-pyrolysis of LDPE and DF ranged from 30.4 to 92.9 area.% and the maximum was achieved when the CAC5 was used as a catalyst in the current study. More important, the quantified GC/MS showed that the maximum phenol concentration (25.0 mg/mL) can be obtained in the water phase produced from the co-pyrolysis process over the CAC5 catalyst. The results demonstrated that when using CAC5 as a catalyst during co-pyrolysis of the LDPE and DF process, both hydrocarbons-rich and phenols-rich bio-oil can be obtained simultaneously. Therefore, the CAC5 exhibited the optimum catalytic performance when compared with other ACCs. In order to further understand the catalytic performance of CAC5 during the catalytic co-pyrolysis of LDPE and DF process, the effect of important parameters including pyrolysis temperature, LDPE/DF ratio and catalyst/feedstock ratio on pyrolysis products were investigated respectively.

Catalytic co-pyrolysis of DF and LDPE under various pyrolytic temperatures

Fig. 3 shows the product yields and selectivity of representative chemical compounds on the basis of various pyrolytic temperatures with the fixed catalyst/feedstock ratio of 1.0 and LDPE/DF ratio of 0.7. The liquid, coke, char, and gas yields are presented in Fig. 3A. Pyrolytic temperature is the most critical operating argument during the pyrolysis process due to the fact that it regulates the decomposition and cracking of the materials. The obtained bio-oil yield with various pyrolytic temperatures (425-550 ºC) firstly increased from 39.4 to 52.7 wt.% then slightly decreased to 51.2 wt.%, with the maximum value at 525 ºC. The gas yield monotonically increased from 14.1 to 35.5 wt.% with the pyrolytic temperature increased from 425 to 550 ºC. These were ascribed to that the pyrolysis reaction is a kind of endothermic processes, increasing pyrolytic temperature was conducive to the devolatilization and cracking, which caused the increase in the liquid and gas yields. However, further enhancing the pyrolytic temperature from 525 to 550 ºC could accelerate the secondary cracking reaction, resulting in the conversion of vapor into non-condensable gaseous products [33-34]. This was consistent with the increased gas yield by rising temperatures from 525 to 550 ºC. The yields of char and coke showed similar trends, which decreased steadily from 16.9 to 12.9 wt.%, and from 29.6 to 0.4 wt.%, respectively, when the pyrolytic temperature increased from 425 to 550 ºC. Similar results were reported in previous studies [15, 25, 35]. The char is the solid residue left after feedstock degradation, while the coke is deposited on the catalyst during the pyrolysis process. The results demonstrated that higher pyrolytic temperature promoted the decomposition of feedstock in the tube furnace into volatile compounds.

The oil phase in bio-oil produced from catalytic co-pyrolysis at 425 ºC was merely 11.0 area.%. This was due to that the dehydration reaction was the domination under such low pyrolytic temperature. The maximum oil phase of 59.0 area.% was achieved at 450 ºC and finally decreased to 45.7 area.% when the pyrolytic temperature increased to 550 ºC. The effect of pyrolytic temperature on the components of bio-oil produced from the catalytic co-pyrolysis of LDPE and DF was investigated as shown in Fig. 3B. In the oil phase of bio-oil, the selectivity of C_8-C_{16} hydrocarbons showed an increasing trend, and the maximum value of 98.5 area.% was obtained at 550 ºC. On the other hand, the selectivity of C_{17}-C_{23} hydrocarbons decreased from 38.8 to 0 area.% with increase pyrolytic temperature from 425 to 550 ºC. The results showed that high pyrolytic temperature was conducive to improve the bio-oil quality from the perspective of jet fuel. Among of them, the selectivity of C8-C16 aromatics increased from 15.6 to 67.3 area.%, while the C_8-C_{16} alkanes decreased from 44.8 to 31.3 area.% with increased temperature from 424 to 550 ºC. This phenomenon was due to that the aromatics were generated from the deoxygenation of phenols and Diels-Alder reaction of olefins from the cracking of long-chain hydrocarbons [36]. High pyrolytic temperature accelerated the cracking of long-chain hydrocarbons, promoting the conversion of olefins into aromatics through the Diels-Alder reaction, which caused the increase in selectivity of aromatics and the decrease in long-chain aliphatics selectivity. In the meantime, hydrogen radicals can be divulged from the Diels-Alder reaction of olefins, and the high temperature was conducive to accelerate the transformation of hydrogen radicals to biomass-derived oxygenates, ultimately promoting the deoxygenation of phenols to produce aromatics [3, 31]. As shown in Fig. 3C, the quantified GC/MS showed that the phenol concentration increased from 23.5 to 25.5 mg/mL then decreased to 21.7 mg/mL with an increase of catalytic temperature from 425 to 550 ºC. There were no guaiacols in the water phase when the pyrolytic temperature was above 475 ºC. The phenolics selectivity firstly increased from 77.4 to 92.9 area.% and then decreased to 87.2 area.% with the increase of pyrolytic temperature from 425 to 550 ºC. Both the maximum value of phenolic selectivity and the minimum other oxygenates selectivity were obtained at 500 ºC. The phenolics were formed after the aromatization, decarboxylation, and dehydration of oxygenates during the catalytic co-pyrolysis process over ACC [15, 19].

Based on the selectivity of C_8-C_{16} hydrocarbons, the 550 ºC was the optimum pyrolytic temperature for catalytic co-pyrolysis of LDPE and DF. However, the catalytic co-pyrolysis process at 500 ºC resulted in the highest oil phase in bio-oil and the optimum phenol selectivity. In addition, from an economic perspective, 500 ºC was more energy conservation and low consumption when compared with 550 ºC. Therefore, the pyrolytic temperature of 500 ºC was employed for the following research.

Catalytic co-pyrolysis of DF and LDPE under various LDPE/DF ratios

The effect of various LDPE/DF ratios (0, 0.3, 0.5, 0.7, 1.0) on the products produced from catalytic co-pyrolysis of LDPE and DF over CAC5 is exhibited in Fig. 4. The pyrolytic temperature was 500 ºC and the catalyst/feedstock ratio was 1. As shown in Fig. 4A, there was no char formation during the catalytic pyrolysis of LDPE alone, suggesting the LDPE can be converted totally with a high yield of bio-oil (81.7 wt.%) and low yield of coke (2.7 wt.%). On the contrary, the lower yield of bio-oil (39.0 wt.%), higher yields of coke (6.7 wt.%), and char (24.3 wt.%) were observed during catalytic pyrolysis of DF alone. With the increase of LDPE in feedstock during the catalytic co-pyrolysis process, the bio-oil yield increased from 46.2 to 59.5 wt.%, while the yields of coke and char showed an opposite trend, which decreased from 4.9 to 2.0 wt.% and from 18.5 to 11.8 wt.%, respectively. The optimum product yields were achieved at the LDPE/DF ratio of 1.0. The increased bio-oil yield was due to that more loading of LDPE could provide more hydrogen during the co-pyrolysis process, suppressing the polymerization reaction of oxygenates derived from DF pyrolysis and accelerating the conversion of DF. In the meantime, the combination of LDPE derived free hydrogen radicals with DF derived oxygenates could accelerate the cracking of hydrocarbon chains and its derivatives, which was also conducive to promote the conversion of LDPE [37-38]. The decreased yields of char and coke could be attributed to that the transformation of hydrogen from LDPE to DF during co-pyrolysis process suppressed the cross-linking and poly-reaction, reducing the formation of stable macromolecular polymers [31].

It was worth noticing that there was no oil phase in bio-oil produced from catalytic pyrolysis of DF alone, and similarly no water phase in bio-oil produced from merely catalytic pyrolysis of LDPE. The high oil content usually represents the great quality of bio-oil, it can be seen from Fig. 4A, with the increase of the LDPE/DF ratio from 0.3 to 1.0 in the feedstock, the oil phase increased from 10.1 to 59.5 wt.%. The maximum oil phase in bio-oil was obtained when the LDPE/DF ratio was 1.0. The components of oil and water phases in bio-oil produced from catalytic co-pyrolysis of LDPE and DF also significantly affected by various ratios of LDPE/ DF. As shown in Fig. 4B, there were no hydrocarbons in the oil phase produced from catalytic pyrolysis of DF alone. This was due to the fact that ACC was conducive to improve the phenolic selectivity and convert lignocellulosic biomass into phenolics during fast pyrolysis process [17].

The result agreed with the organic compositions in the water phase, which were mainly consisted of phenolics (35.0 area.% guaiacols and 55.5 area.% phenols) as shown in Fig. 4C. The phenols selectivity significantly increased when the LDPE/DF ratio was higher than 0.3 and without guaiacols in the obtained bio-oil. The highest phenols selectivity of 92.9 area.% was reached at the LDPE/DF ratio of 0.7. The results showed that the excessive utilization of LDPE was not conducive to improve the phenols selectivity. In addition, the GC/MS quantification results showed that an increase in LDPE addition caused a decrease of phenol concentration. These were due to the fact that with the increase of LDPE in the feedstock, more hydrogen was provided to DF derived oxygenates, facilitating the deoxygenation reaction during the co-pyrolysis process. It is reported that the oxygen of the methoxy group in guaiacols was more likely to be interrupted than that of phenolic hydroxyl group [39-40]. Therefore, with the increase of LDPE/DF ratio from 0.3 to 0.7, the deoxygenation reaction of methoxy in guaiacols was dominant accompanied with lightly deoxygenation reaction of phenolic hydroxyl group during co-pyrolysis process, causing a large increase in alkoxy phenol and slightly decrease in phenol, which resulted in the significantly improved phenols selectivity and slightly decrease in phenol concentration. With further improved the LDPE/DF ratio to 1.0, the deoxygenation reaction of the phenolic hydroxyl group strengthened, causing a significant decrease in both selectivities of phenols and phenol concentration. The total C_8-C_{16} hydrocarbons in the oil phase produced from co-pyrolysis LDPE/DF decreased slightly, among of them, C_8-C_{16} aromatics decreased from 62.2 to 46.8 area.% with the increase of LDPE in the feedstock. This can be ascribed that the main products from LDPE pyrolysis were alkanes (38.6 area.% of C_8-C_{16} aliphatics and 24.7 area.% of C_{17}-C_{23} aliphatics). The increase in LDPE loading resulted in a decrease in catalyst/LDPE ratio, suggesting that lesser catalytic sites were provided to volatiles produced from LDPE pyrolysis. This prevented the cracking of long-chain hydrocarbons and Diel-Alder reaction of an olefin, leading to less generation of aromatics in bio-oil. It can be verified by the selectivity of C_8-C_{16} aliphatics and C_{17}-C_{23} aliphatics, which increased from 30.5 to 41.2 area.% and from 5.5 to 10.5 area.%, respectively, with the increase of LDPE loading during the co-pyrolysis process.

To better understand the interaction between LDPE and DF during the catalytic co-pyrolysis process, the synergistic effect was studied via bio-oil yield, aromatic selectivity, aliphatic selectivity, and phenolic selectivity, respectively. The calculated value of bio-oil yield and aromatic selectivity were calculated by the following equation:

$$\mathrm{SE} = (Y_e - Y_c)/Y_c \qquad (1)$$

$$Y_c = P_1 \times Y_1 + P_2 \times Y_2 \qquad (2)$$

Where the P_1 and P_2 are the weight percentages of LDPE and DF in the feedstock, respectively; Y_1 and Y_2 are the experimental values of bio-oil yield, aromatic selectivity, aliphatic selectivity and phenolic selectivity produced from LDPE and DF pyrolysis, receptively; Y_c and Y_e are the calculated value and experimental value. As exhibited in Table 2, the experimental value of bio-oil yield was lower than the calculated value, suggesting that there was no synergistic effect between LDPE and DF. However, the experimental value of aromatic selectivity, aliphatics selectivity, and phenolic selectivity dramatically higher than the calculated value under various LEPD/DF ratios. Therefore, from the perspective of aromatic selectivity, aliphatics selectivity, and phenolic selectivity, there was a synergistic effect between LDPE and DF during the catalytic co-pyrolysis process. It can be seen from Table 2, the synergistic effects of aromatic selectivity and aliphatics selectivity between LDPE and DF decreased with increasing addition of LDPE, whereas the phenolic selectivity showed a different trend, which increased from 0.33 to 0.87. From the phenol selectivity, the LDPE/DF ratio of 0.7 was the optimum condition for catalytic co-pyrolysis of LDPE and DF.

Catalytic co-pyrolysis of DF and LDPE under various catalyst loadings

Fig. 5A exhibits the various products yields on the basis of catalyst loadings with a fixed pyrolytic temperature of 500 ºC and the LDPE/DF of 0.7. The coke yield firstly increased from 3.1 to 4.1 wt.% then decreased to 2.9 wt.% with an increase of catalyst loading, and the maximum value was obtained at the catalyst/feedstock ratio of 0.7. The char yield varied from 13.9 to 14.5 wt.% and the minimum yield was achieved at the catalyst/feedstock ratio being 0.4. The relatively low char yield indicated that most feedstocks were degraded during the catalytic co-pyrolysis process. The bio-oil yield significantly decreased with the increase of catalyst addition. It can be seen that the bio-oil yield decreased from 56.5 to 46.1 wt.% with the catalyst/feedstock ratios ranging from 0.4 to 1.3, suggesting that a higher catalyst loading was against to the bio-oil generation. This was ascribed to that more catalyst loading caused longer residence time when the volatiles produced from feedstock degradation passed through the catalyst, which resulted in the more secondary cracking reaction of volatiles into small molecular chemicals [34, 41]. It was in agreement with the gas yield, which increased from 26.5 to 36.5 wt.% with an increase of catalyst/feedstock ratio from 0.4 to 1.3. In addition, the oil phase decreased monotonically from 64.4 to 48.6 wt.% with the increase of catalyst loading. The relatively low oil phase in bio-oil indicated higher water phase content in bio-oil. This was due to that more catalyst addition provided more activated sites and facilitated the deoxygenation in the form of water, resulting in the more generation of the water phase in bio-oil.

Fig. 5B and Fig. 5C show the components of bio-oil produced from catalytic co-pyrolysis of LDPE and DF under various catalyst loadings. The selectivity of jet fuel fractions (C_8-C_{16} hydrocarbons) improved from 69.7 to 93.2 area.% with more catalyst usage, indicating that the bio-oil quality improved obviously. The C_8-C_{16} aromatics and phenols increased significantly from 22.1 to 58.7 area.% and from 43.2 to 94.6 area.%, respectively. This was due to the fact that longer residence time caused by increasing the catalyst loading prolonged the contact between catalyst and volatiles produced from feedstock decomposition, facilitating the cracking reaction of long-chain hydrocarbons derived from LDPE. As a result, more short-chain aliphatics were generated and therefore facilitated the aromatization and Diels-Alder reaction, leading to an increase in aromatic selectivity. In addition, more hydrogen radicals were released during aromatization and Diels-Alder reaction of light aliphatics, and thus accelerated the dehydration reaction of the oxygenates derived from DF, leading to the increase in phenol selectivity. In the meantime, the phenol concentration increased dramatically with the increase of catalyst/feedstock ratio from 0.4 to 0.7 and then maintained at about 25.5 mg/mL with further increasing the catalyst/feedstock ratio to 1.3. It can be seen from Fig.5B, the selectivity of C_8-C_{16} aliphatics, C_{17}-C_{23} hydrocarbons and other oxygenates decreased dramatically. The results demonstrated that more catalyst loading was conducive to improve the bio-oil quality by enhancing the selectivity of aromatics and phenols. However, it prevented the bio-oil yield and the generation of the oil phase in bio-oil. The catalytic co-pyrolysis at catalyst/feedstock ratio of 1.0 caused higher bio-oil yield, and the selectivity of aromatics and phenols was similar to that at 1.3. In addition, from an economic perspective, the cost of the catalyst/feedstock ratio of 1.0 was lower than that of 1.3 due to less consumption of catalysts. Therefore, according to the aforementioned, the catalyst/feedstock of 1.0 was the optimum condition for catalytic co-pyrolysis of LDPE and DF under the current experiment.

Process robustness and the recyclability of the CAC5

The co-pyrolysis of LDPE and DF was investigated in the aforementioned decomposition conditions to assure the generation of miscellaneous levels of jet fuels and phenols. The recyclability and lifetime are critical properties in evaluating a catalyst for practical utilization. Herein, the used CAC5 after one time run with a pyrolytic temperature of 500 ºC, catalyst/feedstock ratio of 1.0, and LDPE/DF ratio of 0.7 as exhibited in Table 1. R21 was reused for the second time and the third time with the same experimental conditions. The catalytic co-pyrolysis results exhibited a low selectivity of aromatics (24.3 area.%) and phenols (37.5 area.%), and the majority of chemicals in the water phase of bio-oil with used CAC5 were oxygenated. The jet fuel fraction in the oil phase also decreased significantly. The results suggested that the activated sites of catalyst were partly blocked by coke deposition in the surface of CAC5 and therefore exhibited lower activities after the second recycling run, indicating that the durability and lifetime of CAC5 were poor. This can be demonstrated by the yield of bio-oil, which increased from 51.4 to 64.3 wt.%. The previous research by our group found that the calcination was an effective and low-cost method to improve the regeneration capacity of biomass-based activated carbon [15]. Maybe it is also a promising way to improve the recyclability of commercial CAC5 in the current study, which needs further verification in a future study. Additionally, Yang et al. proposed deep regeneration approach using H_2O and O_2 as regeneration agents to overcome the catalytic activity deterioration of activated carbon, and the results implied that the regenerated activated carbon could maintain its physical properties within several cycles of reuse [42]. Lately, Jeon et al. regenerated the spent activated carbon by washing with a surfactant followed by drying and calcination aimed to remove the boron from the catalysts. The authors stated that boron might block the catalyst pores leading to the decline of active sites. And it was demonstrated that the activity and surface area of the activated carbon were significantly recovered after the regeneration process [43]. Therefore, although the recyclability of CAC5 was poor, it is still a promising catalyst due to its lower production cost and environmental-friendly properties [44].

The analysis of the chemical composition of non-condensable gas produced from the catalytic co-pyrolysis process under various conditions

CO_2, CH_4, CO, and H_2 were reported as the major components of gas products from catalytic pyrolysis of biomass over ACC [45]. However, the gas fraction is always ignored and not well investigated. In the current study, the components of gas products were analyzed and quantified by Micro-GC, which could afford more knowledge for researching the decomposition pathway in the catalytic co-pyrolysis process. The components of gas (H_2, CH_4, CO, C_3H_8/C_3H_6, and C_4H_{10}/C_4H_8) were identified and quantified in a gas fraction. In general, the concentrations of C_2H_6/C_2H_4, C_3H_8/C_3H_6 and C_4H_{10}/C_4H_8 were very low (< 8.9 vol.%) in a gas fraction, especially for the concentrations of C_3H_8/C_3H_6 and C_4H_{10}/C_4H_8, which lower than 4.7 vol.% in a gas fraction. Here, the syngas was researched as the target components and therefore added the CO_2 into other categories in order to simplify the further analysis. As shown in Fig. 6A, the catalytic co-pyrolysis of LDPE and DF over the CAC5 catalyst caused the highest concentration of target gas. The result was due to that the CAC5 provided the optimum catalytic efficiency than other catalysts, facilitating the decarbonylation and cracking reaction of volatiles into small molecules, which resulted in a high concentration of CH_4 and target gas. This was in agreement with the aforementioned results.

The effect of various pyrolytic temperatures on the gas components at the fixed LDPE/DF ratios of 0.7 and catalyst/feedstock ratios of 1.0 is exhibited in Fig. 6B. In the current study, among the target components, CO was the dominant fraction from 22.7 to 37.6 vol.%. The CO from the co-pyrolysis of LDPE and DF was mainly originated from the decarbonylation reaction due to the catalytic effect of activated carbon. The concentration of H_2 was increased from 1.9 to 23.7 vol.% then decreased to 9.7 vo.l% when the pyrolytic temperature increased from 425 to 550 ºC, and the maximum was obtained at 525 ºC. The concentration of CH_4 showed a similar trend with H_2, which obtained a maximum of 23.6 vol.% at 500 ºC. The results showed that high temperature was conducive to the bonding cracking of volatiles towards small molecules, the relatively low temperatures were appropriate for the demethylation of the volatiles within the CAC5. These were in agreement with previous studies [15, 31, 46]. The gas components under various LDPE/DF ratios at the fixed pyrolytic temperature of 550 ºC and catalyst/feedstock ratio of 1.0 is described in Fig. 6C. It was suggested that the increasing addition of LDPE enhanced the concentration of H_2 from 8.1 to 17.4 vol.%, whereas reduced the CH_4 and CO concentration. The increased concentration of H_2 was due to that H_2 from the co-pyrolysis of LDPE and DF was mainly originated from the cracking reaction of LDPE. When increasing the amount of LDPE, the LDPE/catalyst ratio in reaction system will be increased, resulting in the activated sites of ACC was not sufficient to convert a feedstock, which caused the reduction of demethylation and decarbonylation, and further caused the decrease of CH_4 and CO concentrations. Fig. 6D shows the effect of catalyst/feedstock ratios on gas components with a fixed pyrolytic temperature of 550 ºC and LDPE/DF ratios of 0.7. The results showed that increasing loading of catalyst enhanced the concentrations of H_2 and CH_4, whereas decreased the concentration of CO. This was due to that more catalyst loading accelerated the cracking of long-chain aliphatics in LDPE into light hydrocarbons, meanwhile improved the aromatization reaction of the resulted light olefin, causing more generation of hydrogen. Therefore, the more hydrogen could be provided to oxygenates derived from DF, the more accelerated the formation of water. As a consequence, the decarbonylation was alleviated and resulted in less generation of CO. In the catalyst deactivation experiment, the micropores of catalyst were partly blocked and alleviated the catalyst performance, leading to the yield reduction of CH_4 and target gas (R21-R23).

Real waste plastics vary from one another and also differ with model plastics regarding structures, constitutions, and properties, etc., which may have effects on the catalytic performance of activated carbon and is also an important part of our following co-pyrolysis studies. The previous work of our group performed the catalytic pyrolysis of daily waste plastics including polystyrene (PS), polyethylene (PE), polypropylene (PP), and polyethylene terephthalate (PET) over commercial activated carbons. It was found that the activated carbons could also catalyze the conversion of real waste plastics and showed a good potential on withstanding deactivation. The resulting liquid products had a similar distribution with that from the catalytic pyrolysis of model LDPE, which was comparable to jet fuel range hydrocarbons [47]. Norbert et al. investigated the catalytic pyrolysis of the mixture of real waste plastics LDPE and HDPE over activated carbon and zeolites. The authors declared that the activated carbon showed a better nature in the case of decreasing the sulfur content in liquid oil by comparison with zeolites MCM-41 and HZSM-5 [48].

A proposed mechanism of phenol and renewable jet fuel generation from catalytic co-pyrolysis of Douglas fir and LDPE

In the current study, the production of renewable jet fuels and high-purity phenols can be achieved simultaneously. A plausible reaction mechanism for co-feeding Douglas fir and LDPE was proposed as shown in Fig. 7. Many types of research have revealed that phenols were primarily produced from lignin depolymerization due to its benzene rings structure [16, 49]. During the pyrolysis process, the β-O-4 bond of lignin can be cracked by the energy provided by heating, which resulted in the formation of some free radicals. The resulted free radicals were then depolymerized into some phenols and methoxy-phenols. At the same time, the resulted methoxy-phenols can be converted into phenol and methyl-phenol due to acid catalytic sites provided by activated carbon [50]. In the current study, as a kind of renewable plentiful biomass resources, Douglas fir consists of cellulose, hemicellulose, and lignin. It is reported that some C5 and C6 molecules such as furfural and furan ring were generated from the decomposition of cellulose and hemicellulose by dehydration, arrangement, and decarboxylation [51,52]. On the one hand, the resulted C5 molecules can be converted into benzene ring fraction by catalytic sites of ACC via Diels-Alder, oligomerization, and decarbonylation. In the meantime, CO, CH_4, and H_2O were released. On the other hand, the resulted C6 molecules were via rearrangement reaction by the “phenol pool” of ACC converted into 2-methyl-2-cyclopentene-1-one, a most crucial intermediate in phenol production, which was further converted into phenol by rearrangement reaction and releasing a hydrogen molecule [15].

As for LDPE decomposition, it is reported that the C-C bond of LDPE can be cracked by energy provided by heating during the pyrolysis process. The LDPE was decomposed into long-chain hydrocarbons and low-molecular-weight olefins through random scission and chain-end scission [53,54]. During the co-pyrolysis process, the low-molecular-weight olefins derived from LDPE reacted with partial furan compounds derived from Douglas fir by Diels-Alder reaction and dehydration reaction to form aromatics. At the same time, these olefins also can be converted into aromatics by oligomerization, cyclization, and aromatization reaction. In addition, the H+ produced from LDPE degradation was provided to Douglas fir-derived oxygenates, resulting in the conversion of partial phenolics and oxygenates into aromatics over ACC by the dehydration, oligomerization and cracking reactions. Many previous studies have demonstrated that ACC has excellent performance to catalytic biomass into phenol-rich bio-oil [16,55,56]. However, in the current study, the results revealed that biomass can be converted into aromatics and phenol simultaneously when co-feeding with hydrogen donors. This innovative finding paves a novel and eco-friendly pathway for converting biomass into hydrocarbon-rich bio-oil and phenols-rich chemicals.

Conclusions

The conversion of Douglas fir and LDPE into bio-oil was carried out in the current study. The effects of catalyst category, pyrolytic temperature, catalyst/feedstock ratio, and polyethylene/Douglas fir ratios on the products were analyzed. Among six commercial activated carbons, CAC5 was found to be effective in the conversion of feedstock into jet fuel and phenols. From the perspectives of bio-oil quality, the optimal reaction condition for catalytic co-pyrolysis of feedstock was the pyrolytic temperature of 500 °C, the catalyst/feedstock ratio of 1.0, and the

LDPE/DF ratio of 0.7. The GC/MS results showed that the highest selectivity of jet fuel was 98.6 area.%, in which the high selectivity of aromatics (67.3 area.%) was achieved. The highest phenols selectivity of 92.9 area.% was obtained under the optimal reaction conditions. The phenol concentration up to 26.4 mg/mL can be obtained in the current study. The Miro-GC results indicated that among CH_4, CO_2, H_2 and CO, the high concentrations of CH_4 (23.6 vol.%) and CO (39.1 vol.%) were obtained. The current work paves a promising route to simultaneously produce renewable jet fuels and high-purity phenols under inexpensive and mild conditions.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgment

This study was partially supported by The Agriculture and Food Research Initiative of National Institute of Food and Agriculture, United States Department of Agriculture (Award Number: 2016-67021-24533; Award Number: 2018-67009-27904), The National Natural Science Foundation of China, The Key Research and Development Program of Jiangxi Province, China Scholarship Council (Award Number: 21766019; Award Number: 20171BBF60023; Award Number: 201706820027) and Xcel Energy. We would like to thank Dr. Aftab Ahamed for the help with GC/MS analysis. And we also appreciate Dr. Valerie Lynch-Holm and Dr. Dan Mullendore for the SEM/EDS training and analysis carried out in Franceschi Microscopy & Imaging Center (FMIC) of Washington State University.

Figures:

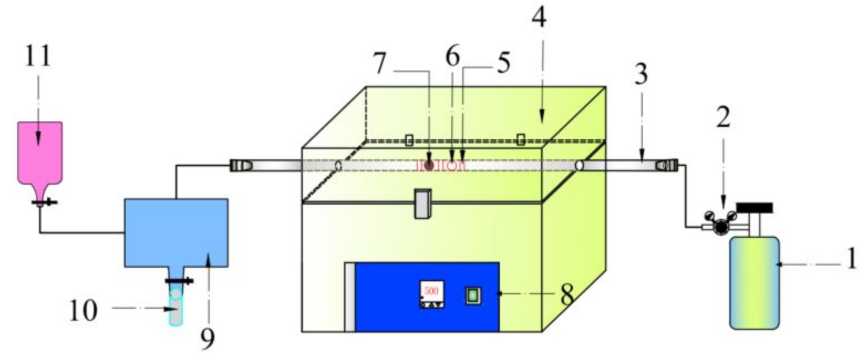

Fig. 1. Schematic diagram of ex-situ catalytic pyrolysis. (1): Nitrogen gas; (2): Gas-flow meter; (3): Quartz tube; (4): Fixed bed furnace; (5): Quartz wool; (6): Samples; (7): Catalysts; (8): Control panel of the furnace; (9): Condenser; (10): Liquid collector; (11): Gas collector.

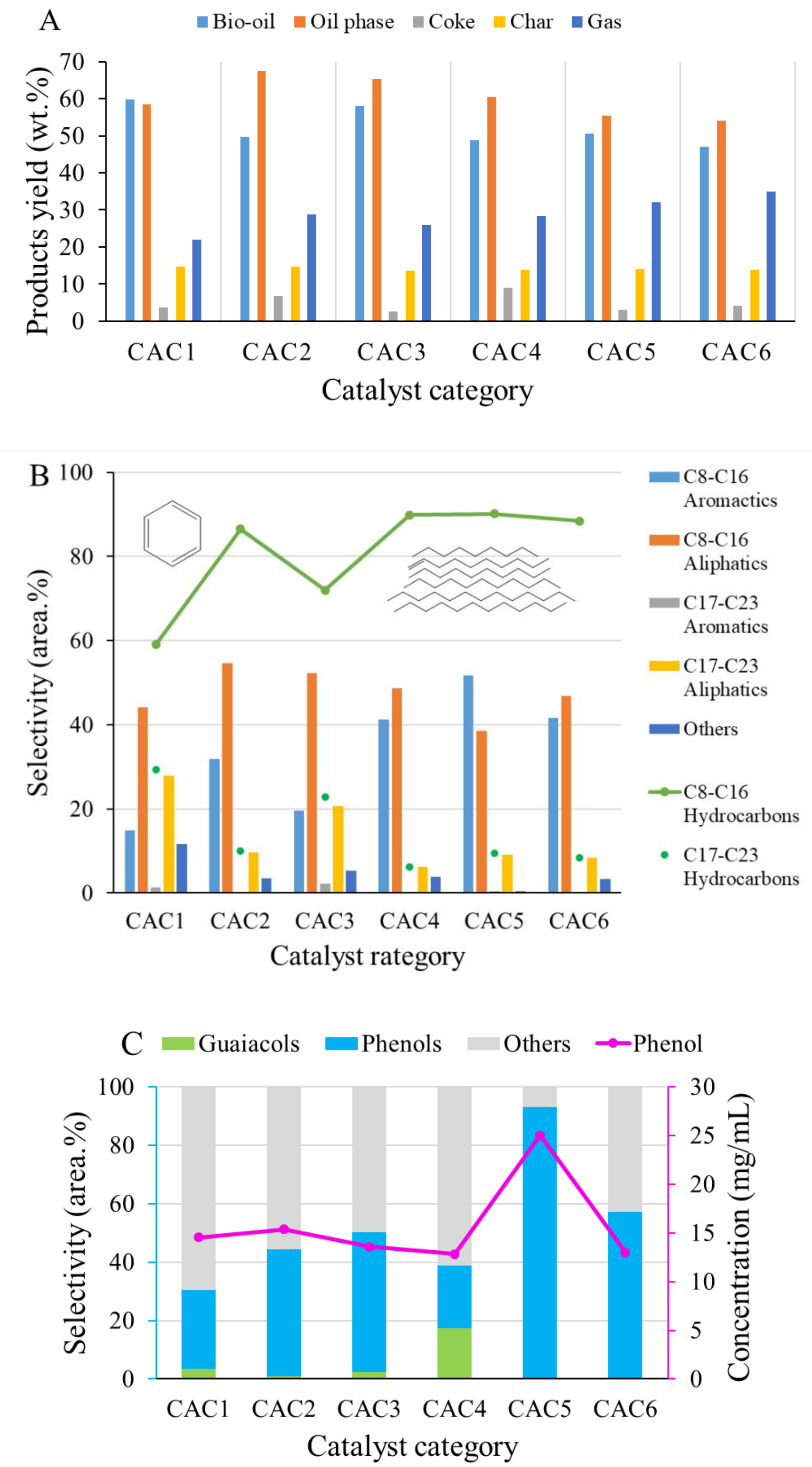

Fig. 2. Product yield distribution and composition of upgraded bio-oils varied with different catalyst categories.

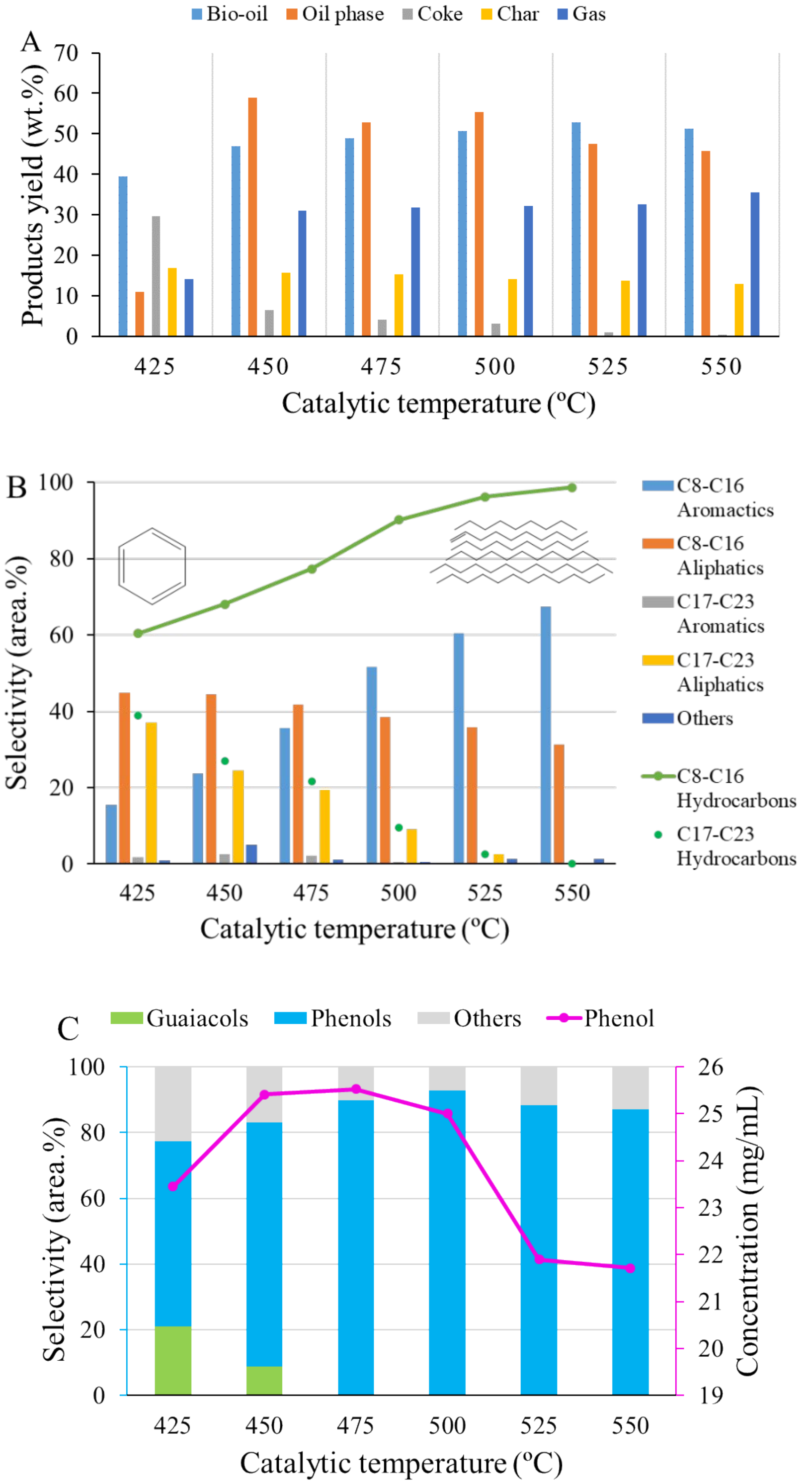

Fig. 3. Product yield distribution and composition of upgraded bio-oils varied with different pyrolytic temperatures over CAC5.

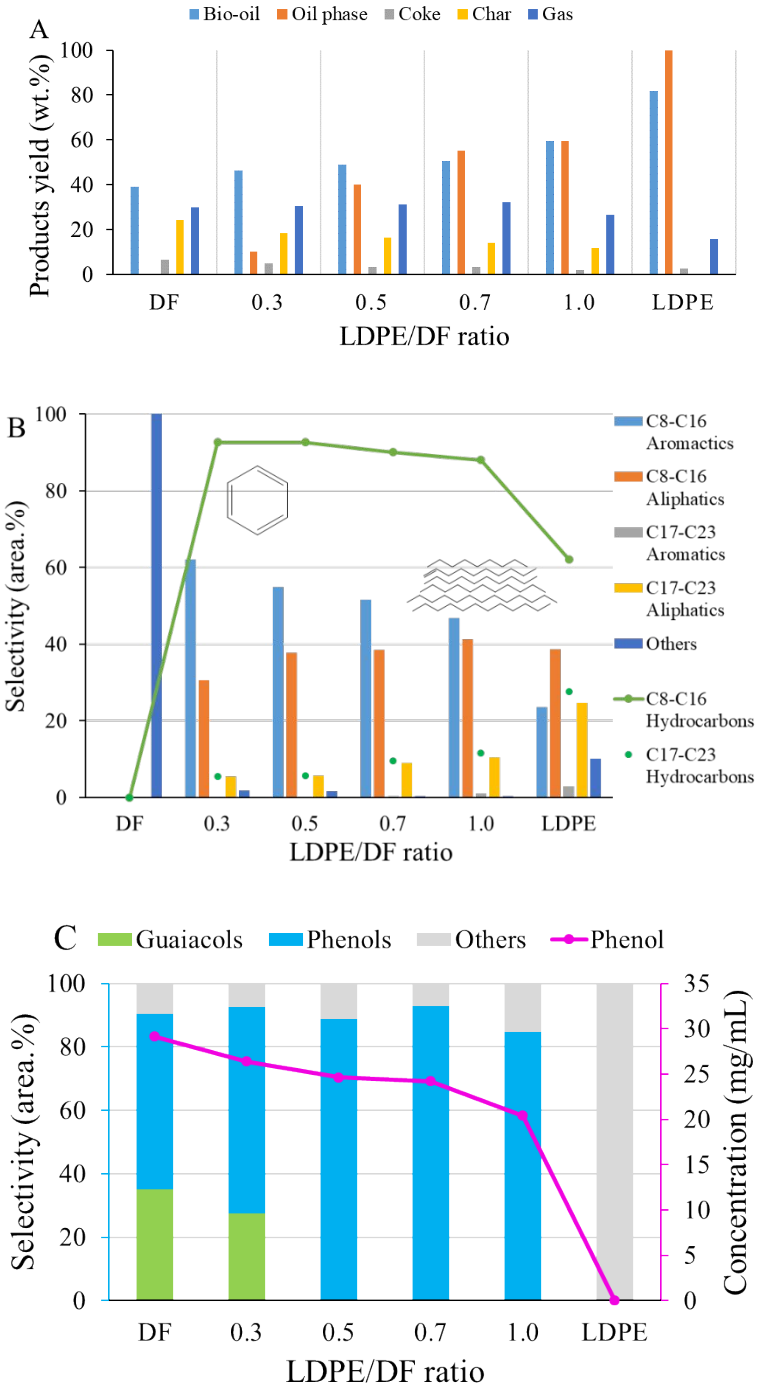

Fig. 4. Product yield distribution and composition of upgraded bio-oils varied with different LDPE/DF ratios. The pyrolytic temperature was 500 ºC and the CAC5/feedstock ratio was 1.

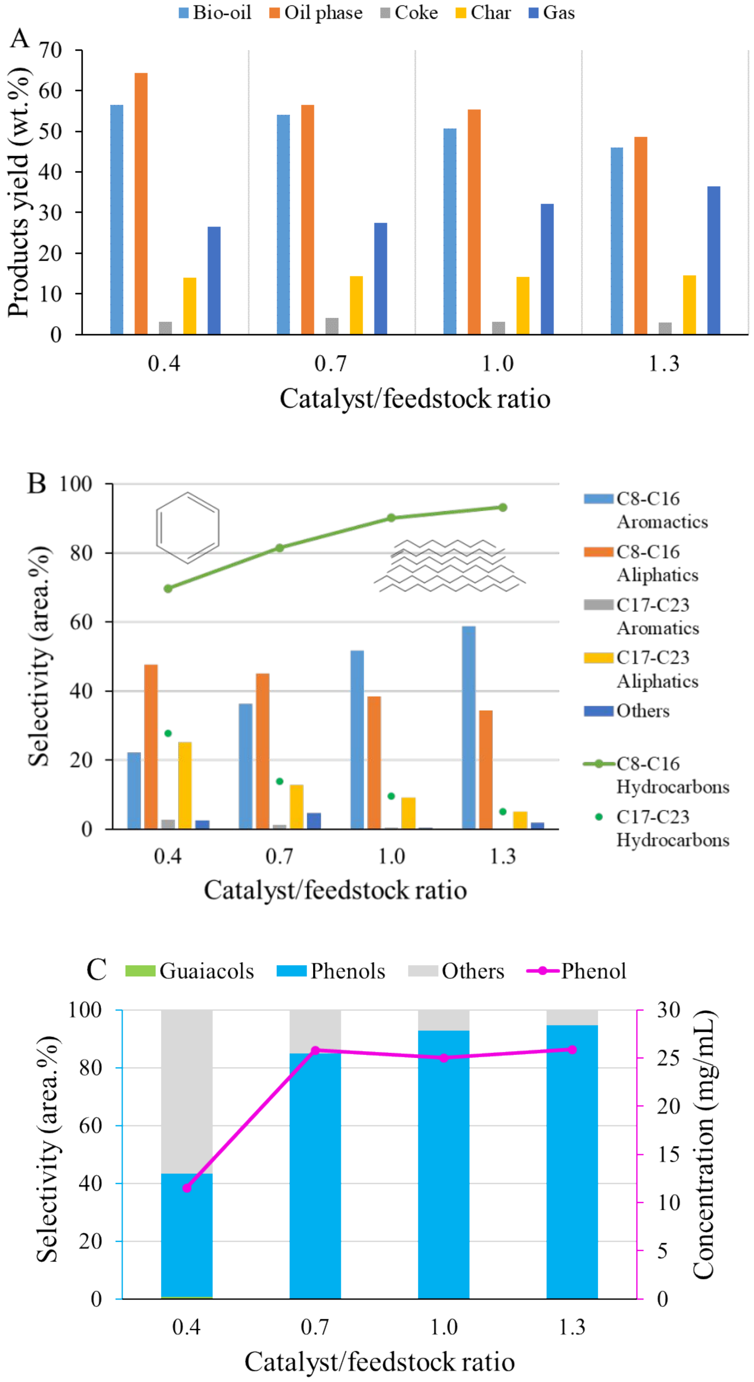

Fig. 5. Product yield distribution and composition of upgraded bio-oils varied with different CAC5/feedstock ratios. The pyrolytic temperature of 500 ºC and the LDPE/DF of 0.7.

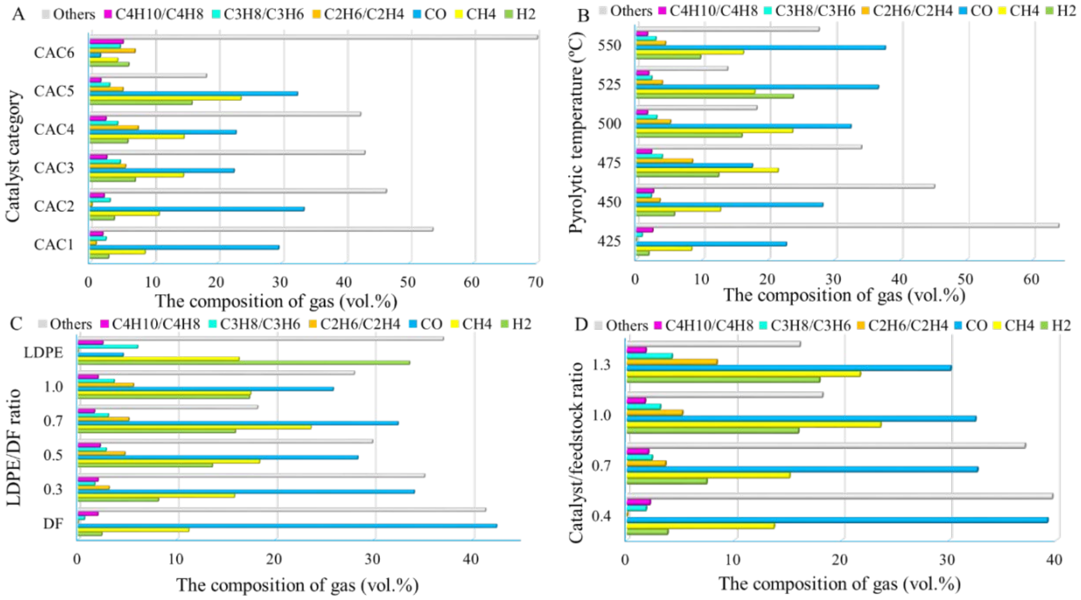

Fig. 6. The composition of gas fraction varied with (A) catalyst categories, (B) pyrolytic temperatures, (C) LDPE/DF ratios, and (D) catalyst/feedstock ratios.

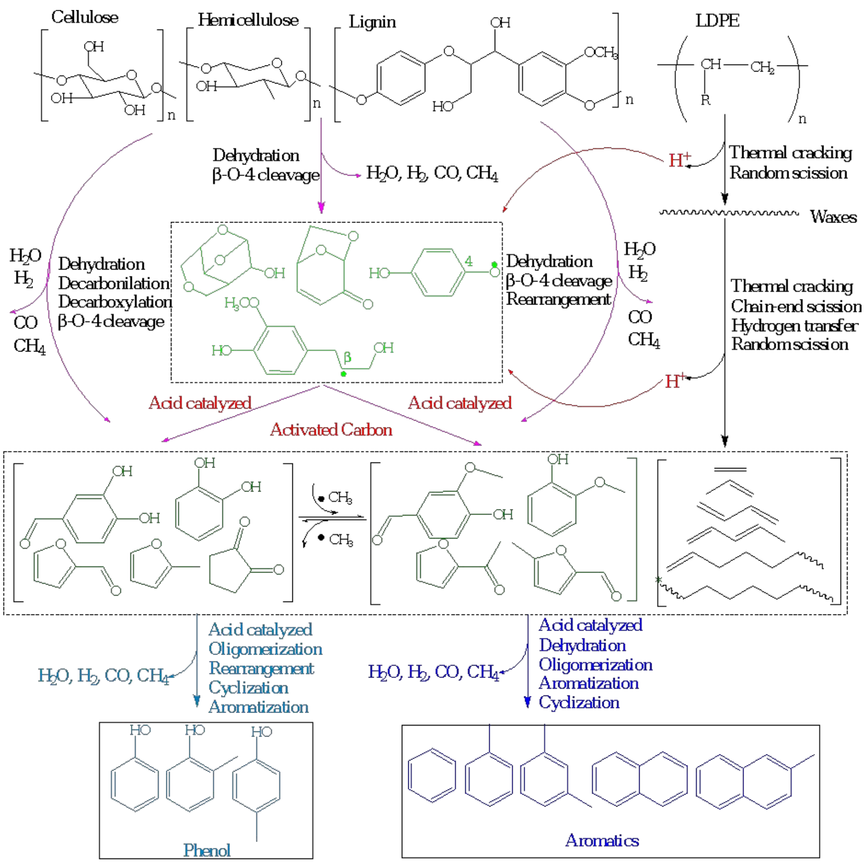

Fig. 7. The proposed reaction pathway of forming phenol and aromatics from the co-pyrolysis of Douglas fir and LDPE over activated carbon catalyst.

Tables:

Table 1 List of reaction condition for each run

Run[a]	Catalyst Category	Pyrolytic Temperature (ºC)	LDPE/DF Ratio	Catalyst/feedstock Ratio
R1	CAC1	500	0.7	1.0
R2	CAC2	500	0.7	1.0
R3	CAC3	500	0.7	1.0
R4	CAC4	500	0.7	1.0
R5	CAC5	500	0.7	1.0
R6	CAC6	500	0.7	1.0
R7	CAC5	425	0.7	1.0
R8	CAC5	450	0.7	1.0
R9	CAC5	475	0.7	1.0
R10	CAC5	525	0.7	1.0
R11	CAC5	550	0.7	1.0
R12	CAC5	500	DF	1.0
R13	CAC5	500	0.3	1.0
R14	CAC5	500	0.5	1.0
R15	CAC5	500	1.0	1.0
R16	CAC5	500	LDPE	1.0
R17	CAC5	500	0.7	0.4
R18	CAC5	500	0.7	0.7
R19	CAC5	500	0.7	1.3
R20	CAC5	500	0.7	1.0
R21	CAC5	500	0.7	1.0
R22	CAC5	500	0.7	1.0
R23	CAC5	500	0.7	1.0

[a] R5, R20, and R21 were conducted under the same condition three times. R22 and R23 were tested for the reused catalyst for two times from R21.

Table 2 Synergistic effects between LDPE and DF during the catalytic co-pyrolysis process under various LDPE/DF ratios over CAC5.

		LDPE/DF ratios					
		DF	0.3	0.5	0.7	1.0	LDPE
Yield of Bio-oil (wt.%)	Y_c	-	48.9	53.2	56.6	60.4	-
	Y_e	39.0	46.2	48.9	50.6	59.5	81.7
	SE	-	-0.06	-0.08	-0.11	-0.01	-
Selectivity of aromatics (area.%)	Y_c	-	6.1	8.8	10.9	13.2	-
	Y_e	0.0	62.2	54.9	52.1	47.9	26.4
	SE	-	9.20	5.24	3.78	2.63	-
Selectivity of aliphatics (area.%)	Y_c	-	14.6	21.1	26.1	31.7	-
	Y_e	0.0	36.0	43.5	47.5	51.7	63.4
	SE	-	1.47	1.06	0.82	0.63	-
Selectivity of phenolics (area.%)	Y_c	-	69.6	60.3	53.2	45.3	-
	Y_e	90.5	92.5	88.7	92.9	84.8	0.0
	SE	-	0.33	0.47	0.75	0.87	-

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Graphical Abstract: