The Homogeneous Conversion Mechanism of Cellulose Pyrolysis Tar Under the Effect of Steam

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Abstract

Biomass accounts for the largest proportion of rural solid waste with high moisture content, which affects the thermal treatment process. This paper studied the effect of steam on the pyrolysis tar of microcrystalline cellulose (MCC) by a two-stage fixed bed. The experiments had been carried out under different steam/feedstock mass ratios ($S/F = 0, 0.8, 1.2, 1.6$) when the first stage was at 600°C , and the second stage was at 800°C . The tar content in the syngas was reduced effectively from 6.68% to 2.30% when the S/F was from 0 to 1.6. Under the four S/F conditions, aromatic compounds accounted for more than 80%, which was the largest proportion of tar products. Significantly, formic acid phenyl ester (FAPE) decreased obviously with the growth of S/F . Besides, when the steam content was excessive, the MAHs, such as phenols and indenenes, could be further cyclized and aromatized to form PAHs. To further study the removal mechanism of tar, the FAPE was investigated by density functional theory (DFT). It was concluded that the O3-C4 bond of FAPE was most likely to be attacked by the H_2O molecule to form phenol, CO_2 , and H_2 directly, among the four possible paths.

Statement Of Novelty

This paper is based on the MCC pyrolysis tar, which provided more reliable tar compositions than using a few representatives. Moreover, the experiment focuses on the effect of steam content without considering the potential role of char. To further understand the conversion mechanism, Gaussian is also used to investigate the possible tar reaction paths.

Introduction

Nowadays, there are still many agricultural-oriented countries and regions. Besides the kitchen garbage commonly found in municipal solid waste (MSW), there are abundant agricultural and wood residues in these places. Since these wastes are always different in various compositions and complex structures, it is meaningful to study the thermochemical reaction mechanism of biomass based on three major biomass components (cellulose, hemicellulose, and lignin). Among them, cellulose is the most abundant, accounting for 40-60%[1], and there have been many studies on it. For example, MCC(crystallinity index is approximately 80%[1]), a typical model compound, is always used to research cellulose pyrolysis characteristics [2–5].

For the thermal treatment of biomass waste, tar production can not be neglected, especially the high tar yield when biomass pyrolysis. To further reduce the adverse impact of tar on equipment and the environment, there have been many fruitful studies on adding catalysts[5–9] and introducing steam [10–12]. In contrast to catalysts, adding steam is a more convenient method, whose calorific value of syngas[13] is usually $10\text{--}18 \text{ MJ/Nm}^3$. Hence, the steam is often applied to promote tar cracking, although the steam could increase equipment heat loss [14].

On the other hand, the moisture content of biomass also impacts the operation of the facility. Compared with typical thermal treatment equipment, such as batch reactors, fluidized beds, the fixed bed has the advantages of simple design and operation with low investment and operating costs. However, the fixed beds running in towns and villages have some shortcomings due to the limited investment cost and simple design. For example, these devices do not have a drying system in front of the furnace because the moisture content of rural waste is lower than that of MSW. Nevertheless, the moisture in the garbage is heated and volatilizes into steam, which will stay in the furnace long enough and affect the whole reaction process. For biomass wastes with large moisture content, it is a non-negligible factor in the reaction process.

Some previous studies have shown that the reforming reaction between steam and pyrolysis/gasification products was conducive to increasing H_2 yield[15, 16] and reducing the yield of tar[10, 11]. Feng et al. [12] found that biomass gasification was optimal at 700-900°C. And under an inert atmosphere, thermal cracking of biomass tar had no apparent influence when the temperature was less than 700°C. Moreover, some views suggested that tar can be cracked effectively by contact with coal char at temperatures above 800° C [11, 17, 18].

These results are encouraging, but the role of steam in the pyrolysis of biomass tar needs to be further confirmed in the absence of char, especially when the tar yield is the highest at 600 °C[19, 20].

Gaussian is a comprehensive quantum chemistry package, which has been widely used in researching the molecular mechanism. The cellulose pyrolysis mechanism has been studied by using the Gaussian to analyze possible pyrolytic pathways[21–24]. Lu et al. [24] described this process as that the indigenous interior units, reducing end (RE end) and non-reducing end (NR end), initially form various characteristic chain ends and dehydrated units, which then evolve into different pyrolytic products. Huang et al. [25] used phenethyl phenyl ether (PPE) as a dimeric lignin model compound to investigate possible pyrolytic pathways by density functional theory methods at B3LYP/6-31G(d) level. Based on the unimolecular decomposition mechanism of lignin pyrolysis studies, Jiang et al.[26] proposed a new intermolecular interaction mechanism of lignin pyrolysis.

This paper studied the yield and composition of tar formed from cellulose pyrolysis with the effect of steam. In particular, this experiment was based on the MCC pyrolysis tar instead of a few representative modelling tars [27, 28], which provided a more reliable result. Moreover, the experiment focused on the effect of steam content without considering the potential role of char. To further understand the conversion mechanism, Gaussian was also used to investigate the possible tar reaction paths.

Materials And Methods

2.1. Model compounds

To simulate the combustible biomass fraction of rural waste, the feedstock used here is MCC, a purified and partially depolymerized cellulose and accounts for about 70% of plant cellulose. The proximate and

ultimate analysis of the feedstock is shown in **Table 1**, which were determined by 5E Series-MAG6700 Proximate Analyzer and 5E Series-CHN2000 Ultimate Analyzer, respectively. Before the experiment, MCC had been sieved to an average diameter of about 0.4 mm and then dried at 105 °C for 24 hours to reduce the interference of moisture content on the experimental results.

2.2 Experimental equipment and conditions

A scheme of the bench-scale plant used for the biomass wastes treatment process is shown in **Fig 1**. The apparatus mainly consists of a reverse L tubular reactor made of steel (outer diameter: 40 mm, inner diameter: 30 mm). There are two stages, with each length of 500mm. The feedstock was delivered into the pyrolysis reactor through a screw feeder installed in the tubular channel. After about 25 minutes of stirring and moving at a low rate, the raw material was absolutely pyrolysis in an inert atmosphere. Then, the remaining residue was sent into the slag hole. Simultaneously, the gaseous products (including syngas and tar) entered the second stage and reacted with saturated steam, as the suction of the vacuum pump at the end. After entirely react, all the gas components were pumped into a condenser to separate the moisture. The tar in the produced syngas could be absorbed entirely by the dichloromethane absorption in the scrubbing bottle after passing through a tar trap. The rest non-condensate gas was also treated safely by other means. As a note, the connection area was covered with electric heating belts (set at 180 °C) to avoid condensation of gas products and steam. Besides, all of these electric heating furnaces are equipped with thermocouples, which could quickly respond the wave to the temperature controller that could adjust it in time to maintain the temperature stability during the experiments.

The experimental conditions are shown in **Table 2**. After carried out for 60 min of every continuous operation, stopped the feed and maintained the steam flow for another 20 min. Each experiment was repeated at least three times to ensure the reproducibility of the results.

2.3 Tar pretreatment and analysis

Before the tar analysis, there were a series of pretreatments: 1) transferred the mixture solution collected from the tar trap and washed it with 50 ml dichloromethane each time, repeating three times; 2) poured all the collected solutions, including the washing solution, into a separation funnel to separate moisture and organic solvents; 3) added anhydrous sodium sulfate to the organic solution to further remove the moisture; 4) separated the tar from the filtered organic solvent (a mixture of tar and dichloromethane) by rotating evaporators following the European standard (CEN/TS15439: 2006). In this process, dichloromethane is an efficient solvent that can absorb the heavy components of tar well. Many studied used it to wash and collect tar formed from the thermal treatment of solid waste[29–31].

The composition of tar was measured by a GC-MS analyzer (7890B-5977A, Agilent Technologies Inc.) The injector and the transfer line were set at 270 and 250 °C, respectively. After 5 min at 50 °C, the oven raised to 270 °C at a rate of 15 °C/min and then maintained at 270 °C for 10 min. In the mass spectrometer, electron ionization (EI) energy was used for ionization. The ion source temperature was maintained at 200 °C. The volume of each injection was 0.2 µL, and the split ratio was 10:1. Identification

of compounds was performed according to library data. There are three parallel samples of each experiment condition, and the average results are shown in **Table S1**.

2.4 Calculation methods

The optimizations of all the geometries of compounds (reactants, products) were performed at the DFT/B3LYP level using the 6-31G(d) basis set. According to the possible reaction paths, the initial guess structure of transition states was located by TS/QST2 with semi-empirical molecular orbital methods/PM6. Then, the transition states were calculated again by the TS method and were confirmed by exactly one imaginary frequency and IRC, whose calculations were employed at the same basic set of the DFT/B3LYP method. Based on all the stable structures (reactants, intermediates, and products), using the 6-311G++(d,p) basis set to complete the frequency and thermochemical analysis at 800 °C. After the zero-point energy correction (ZPE) and thermodynamic correction, the thermodynamic parameters, such as activation energy (reaction barrier), could be used to estimate the possible reaction paths.

Above all, the calculations were performed by Gaussian 09[32]. Furthermore, the Multiwfn3.8 [33] was also used to calculate the frontier orbital and Laplacian [34] to analyze the active sites.

Results And Discussion

3.1 Properties of tar

As shown in **Table 3**, the yield of tar cuts down with steam increasing. It is consistent with earlier reported results on biomass pyrolysis gasification with steam[10–12]. However, the cracking rate of tar is not further improved with the increase of steam: the cracking rate reaches the maximum at S/F=0.8 and gradually slows down with the S/F ratio rise. When it comes to the element change of tar, the transform of components plays a critical role. For example, because the chain compounds are cracked absolutely, and the proportion of aromatic compounds increase, the H/C atomic ratio of tar reduces after the addition of steam. Moreover, compounds with oxygen-containing radicals, such as the FAPE, is cracked by H₂O to form more stable compounds make the oxygen element in tar reduces significantly with the growth of steam, which indicates better tar quality in terms of calorific value and stability[35, 36].

3.2 Effect of steam on tar components

The detectable tar products were identified according to chromatographic peaks, and their proportions were determined from the peak area in GC–MS chromatograms (shown in **Fig S1**). According to the detailed distribution of tar products listed in **Table S1**, the major compositions had been quantified and summarized in **Table 4**. It should be noted that the detectable compound was that whose concentration was above the detection limit, while the identifiable compound was that whose peak area was comparatively large and were identified by the NIST library in this work.

As shown in **Table 4**, o-heterocycles are formed by the polysaccharide structure of MCC after a series of reactions, such as decarboxylation, decarboxylation, and so on[37, 38], and these oxygenated compounds are highly corrosive to boilers, engines, and other equipment[37, 39]. Generally, the o-heterocycles are mainly influenced by temperature. When the temperature at 500~600 °C, There are more o-heterocycles in the primary tar[40] (such as furan, pentose, etc.), and then the o-heterocycles decrease distinctly with the rise of temperature. Moreover, the o-heterocycles are also affected by steam. As seen in **Table 4**, the o-heterocycles increase to 9.42% at S/F=0.8, compared with this proportion is 6.24% during pyrolysis (S/F=0). However, when the steam continues to be added, the proportion of o-heterocycles decreases to about 6-7%. The increment of o-heterocycles at S/F=0.8 can be attributed to the fact that steam can facilitate the crack of the primate tar. With the increase of S/F, the o-heterocycles can be further transformed into more stable aromatic compounds through Diels alder reaction[41–43], which is a critical factor to the decrease of o-heterocycles. Under the effect of steam, the kinds of o-heterocycles in tar also become more abundant. Except for furan, which can also be produced at pyrolysis, there are two new o-heterocycles (including 2-furancarboxaldehyde,5-methyl- and furan,2,5-dimethyl-) since the steam addition.

As presented in **Table 4**, the total proportion of chain compounds is low and gradually decreases to complete disappearance with the rising of S/F. At the same time, the proportion of alicyclic compounds increased after steam addition. The main reason is that the steam promotes the cracking of chain compounds; the productions (such as dienes and dienophiles) can be further cyclized and aromatized by the Diels-Alder reaction. It should be noted that with the continuous increase of steam, the proportion of alicyclic compounds decrease to 5% around which is closely related to the decrease of cycloalkenes. On the one hand, some cycloalkenes can also be further aromatized. On the other hand, O/H/OH active radicals generated by steam can adhere to tar fragment[12, 44], which provides abundant H radicals for the cycloalkenes to form cycloalkanes through the hydrogenation reaction.

Aromatic compounds accounted for the largest proportion of tar products, and the total proportion is always more than 80% under the four S/F conditions of the experimental setup. **Fig 2** shows the proportion of monocyclic aromatic compounds (MAHs) comes to decrease from 78.61% (S/F = 0) to 73.08% (S/F = 1.6) with the increase of steam; while polycyclic aromatic compounds (PAHs) decrease from 5.31% (S/F = 0) to 3.68% (S/F = 0.8) and then increase to 14.43% at S/F = 1.6. Specifically, benzene and alkylbenzenes (including toluene, xylene, and other alkylbenzenes) had little change, and the total proportion remained at about 30%. When S/F is 0.8, the proportion of alkenylbenzenes is twice as much as that of pyrolysis. But with the continued increase of steam, the proportion of alkenylbenzenes does not further increase and remains about 18%. It is worth noting that the proportion of FAPE decreases from 19.16% (S/F = 0) to 5.54% at S/F = 0.8. With the proceeding increase of S/F, the proportion of FAPE keeps on decreasing until it disappears completely. Therefore, the significant cut down of FAPE is the key to affect the overall proportion of MAHs. With the increase of steam, the change of FAPE is shown in **Fig 3**. In this process, the steam stimulates the FAPE to transformed into phenols that increased from 13.38% (S/F = 0) to 15.02% (S/F = 0.8). Nevertheless, it also shows in **Fig 3** that the proportion of phenols turns to decrease with the further addition of steam. According to the conversion paths of phenols (**Fig 4**), the

phenols could be a precursor to form PAHs[45, 46]. Besides, indenenes also present the same change that increases first and then turns around with the addition of steam. It illustrates that steam is conducive to the formation of indenenes, but excessive steam will promote indenenes to further cyclization and aromatization.

Similarly, the change of PAHs in **Fig 2** also proves the above conclusion. Like naphthalenes, as the most representative and lightest PAHs component in biomass tar[47], it plays a decisive role in the composition of PAHs. There is a slight decrease in naphthalenes when the S/F rises from 0 to 0.8. But the sustained growth of S/F makes the proportion of naphthalenes increase significantly, reaching about 11-12%. At the same time, phenanthrene appears at S/F = 1.2 (1.51%) and increases to 3.4% when S/F is 1.6. Therefore, when the steam is excessive, it could promote the aromatic compounds further cyclized and aromatized to form PAHs.

3.3 The reaction mechanism of tar

Given the experimental results in **3.2**, the Gibbs free energy of main tar components (yield > 5%) under pyrolysis conditions is listed in **Table 5**. The FAPE (accounted for 19.16%) has the lowest Gibbs free energy (-420.973 Hartree), and the reaction activity is vigorous. It is also consistent with the experimental result that FAPE is likely to be cracking and completely disappeared with the effect of steam, as shown in **Fig 3**.

The CDD is widely used to predict the reaction sites[48], and the electrophilic reaction is more likely to happen when the value of CDD is smaller. As shown in **Table 6**, the C7 and O3 are the most vulnerable to participate in the nucleophilic reaction, and C1 and O2 are the most vulnerable to electrophilic attack. Besides, there is a direct correlation between LBO and bond dissociation energy, which is also instrumental in predicting reaction sites[49]. The LBOs between atoms are listed in **Fig 5**. Small LBOs of C1-O3 and O3-C4 indicate that the -OCHO radical linked to C4 in the benzene ring can be attacked in two ways. The following analysis will focus on the removal mechanism of the -OCHO radical.

Combined with the analysis of active sites, the possible reaction pathways are shown in **Fig 6**. Path 1 and Path 2 are the reactions of H₂O attacking the 1C-3O bond on the FAPE, and the reaction products are phenol and formic acid (Path 1) and phenol, CO₂, and H₂ (Path 2), respectively. Path 3 has the same reactants and products as path 1, but H₂O attacks the O3-C4 bond of FAPE. Similarly, there are also different attack bonds of Path 2 and Path 4, although the reactants and products are consistent.

The Gibbs free energy of each possible reaction path is listed in **eq. (1)-(2)**, all of these values are negative. It indicates that the reactions of different ways can be spontaneous. In particular, the Gibbs free energy of Path 2 and 4 are -197.267kJ/mol, which means that H₂O is most likely to react with FAPE to product phenol, CO₂, and H₂.

Based on the above analysis, the characteristics of reactants and products greatly affect the Gibbs free energy of the whole reaction. However, the reaction processes between FAPE and H₂O molecules are also influenced by the different attack sites. The molecular structures (including reactants, transition states, and products) of the four paths are shown in **Fig 7**.

Path 1 is the reaction about H₂O attacking the C1-O3 bond of FAPE and substituting the -OCHO radical. During attacking the bond orbital, the H₂O molecule gradually approaches the C1-O3 bond, and the length of the C1-O3 bond increases gradually. Due to the mutual attraction between O16 and C1 atoms, the -OCHO radical still deviates from the benzene ring plane along the direction closed to the H₂O molecule. At the same time, owing to mutual attraction between H18 and O3 atoms, the molecular angle of H₂O increases, and then the O16-H18 bond is stretched to broken. After that, the H18 atom moving towards the O3 atom, the O16-H17 radical approaching the C1 atom. When the FAPE transforms to the transition state (TS1), the C1-O3 bond forms an angle of 86.82° with the benzene ring plane. Besides, the bond of O16-H18 is broken, resulting in the distance between O16 and H18 being enhanced from 0.894Å to 1.147Å. However, the distance between O3 and H18 atoms is reduced to 1.299Å, which is benefited the formation of the O3-H18 bond. After that, the C1-O3 bond of the FAPE breaks, and the distance between C1 and O3 atoms is 1.818Å. The produced H10-C1-O2 radical tends to move away from the benzene ring, and the length between C1 and O16 shrinks to 1.752Å getting ready for bonding. Subsequently, the O3-H18 bond and the C1-O16 bond were formed under the attack of atoms and radicals. The corresponding bond lengths are reduced to 0.972Å and 1.498Å, respectively. Moreover, the H18 atom gradually returns to the benzene ring plane. Thus, the final product system is composed of phenol and formic acid.

Path 2 is the reaction on H₂O attacking the C1-O3 bond of the FAPE and then producing phenol, CO₂, and H₂. When H₂O approaches the FAPE, the -OCHO radical gradually deviates from the benzene ring plane and approaches the H₂O molecule due to the mutual attraction between C1 and O16 atoms. In this process, the attraction between H10 and H18 atoms gradually increases, resulting in the increase of H₂O molecular angle, while the O16-H18 bond is broken and the C1-H10 bond length enlarges to 1.001Å. When the FAPE transforms to the transition state (TS2), the C1-O3 bond forms an angle of 82.19° with the benzene ring plane, and the bond length is slightly stretched from 1.376Å to 1.400Å. Meanwhile, the molecular angle of H₂O is extended from 104.68° to 111.56°, and the distance between H18 and H10 atoms shrinks from 1.832Å to 0.996Å, all of these changes lay a foundation for the formation of H₂ molecule and C1-O16 bond. Then H18 and H10 gradually bond with each other, the bond length shrinks to 0.900Å, and the produced H₂ molecule moves away from the reaction system. In

addition, the C1-O16 bond is formed, and the bond length shrinks to 1.495 Å. On this basis, H17 attacks O3, leading to the formation of the O3-H17 bond and the breaking of the C1-O3 bond and O16-H17 bond, finally forming a stable product system of phenol, CO₂, and H₂.

Path 3 is H₂O molecules attacking the O3-C4 bond of the FAPE to replace -OCHO radical s. As the H₂O molecule gets close to the FAPE, the O3-C4 bond deflects away from the attack direction of H₂O, which drives the whole -OCHO radical away from the benzene ring plane and makes room for substitution reaction. Under the attack of H₂O molecules, the O3-C4 bond is stretched to break. Meanwhile, since the attraction between O16 and C4, H18 and O3, the molecular angle of H₂O increases, while the O16-H18 bond is broken by stretching. In addition, the benzene ring plane gradually coincides with the plane of the hydroxyl radical (O16-H17). When the transition state (TS3) is formed, the O3-C4 bond breaks, and the distance between C4 and O3 atoms is 1.963 Å. Meanwhile, the length between C3 and H18 is shortened to 1.616 Å, and the distance between C4 and O16 shrinks to 1.726 Å. Besides, the O16-H18 bond slightly enlarges from 0.970 Å to 1.006 Å, and the H₂O molecular angle extends from 106.28° to 109.77; these preparing steps make for the O16-H18 bond breaks and forms phenol. In the status of TS3, the O3-C4 bond forms an angle of 78.68° with the benzene ring plane. Then, the O16-H18 bond breaks so that the H18 atom and hydroxyl radical (produced by O16 and H17) attack O3 and C4, respectively. Furthermore, the O3 atom combines with the H18 atom to form the formic acid, and the C4 atom connects with the O16 atom to form the phenol molecule. Finally, the products of phenol and formic acid are obtained through Path 3.

Path 4 is the reaction process of H₂O attacking the O3-C4 bond of FAPE to produce phenol, CO₂, and H₂. Firstly, the H₂O molecule approaches the O3-C4 bond from the side of the -OCHO radical. In the process of attacking the bond orbital, the O16-H17 bond and the O3-C4 bond are gradually stretched to break, and the -OCHO radical moves away from the benzene ring plane. When reaching the transition state TS4, the C4-O16 bond is formed under the attack of the O16 atom to the C4 atom, and the hydroxyl radical (O16-H18) returns to the benzene ring plane to form the phenol molecule. Meanwhile, the H17 atom moves towards the O3 atom, and the distance between both atoms is 1.575 Å. In addition, due to the mutual attraction between H17 and H10 atoms, the C1-H10 bond stretches from 1.093 Å to 1.367 Å, and the angle of O2-C1-O3 extends from 110.73° to 142.41°. And then, because of the instability of the -OCHO radical, the C1-H10 bond breaks under the attraction of H17 and H10 atoms. Owing to the small mass of the H atom, H17 and H10 atoms are preferentially bonded instead of forming the O3-H17 bond, resulting in the stable product system phenol, CO₂, and H₂.

In the above four paths, H₂O molecules are more likely to attack the C1-O3 bond and O3-C4 bond of the FAPE. However, the activation energies of reactions are also diverse in view of the different transition states. For example, it needs 303.482 kJ/mol activation energy to form the transition state (TS1) after H₂O attacks the C1-O3 bond of the FAPE, while the formation of TS2 requires more activation energy (466.673 kJ/mol). to achieve the process. Thus, when H₂O attacks the C1-O3 bond of the FAPE, it is more likely to form phenol and formic acid before the possible subsequent reaction rather than directly

generate phenol, CO₂, and H₂. Similarly, the activation energies are different when H₂O attacks the O3-C4 bond of the FAPE to form the transition states(TS3 and TS4) by Path 3 and Path 4, respectively. In particular, among the four paths, the minimum activation energy is demanded to form TS4 through Path 4. Therefore, when H₂O attacks the O3-C4 bond of the FAPE, it is conducive to the direct formation of phenol, CO₂, and H₂, which is the easiest to achieve among the 4 paths above.

Conclusions

In summary, this paper addressed the effect of steam on cellulose pyrolysis tar in a two-stage fixed bed. The primary findings are summarized as follows:

- (1) Adding steam can reduce the yield of tar contained in syngas from 6.68% to 2.30% availably. With the increase of steam, the element of oxygen in tar decreases while carbon increases.
- (2) FAPE is an important tar product during cellulose pyrolysis, which is the key to affect the overall proportion of MAHs. But with the addition of steam, the FAPE can be effectively decomposed into phenols and other more stable compounds. When the steam content is excessive, the MAHs, such as phenols and indenenes, can be further cyclized and aromatized to form PAHs.
- (3) There are various valid reaction paths between FAPE and H₂O molecules because of the diverse products and the different attack sites. Among the four possible paths, the H₂O molecules are most likely to attack the O3-C4 bond of the FAPE and form phenol, CO₂, and H₂ directly.

Declarations

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Conflicts of interest

The authors have no conflicts of interest to declare.

References

1. Wang, S., Dai, G., Yang, H., Luo, Z.: Lignocellulosic biomass pyrolysis mechanism: A state-of-the-art review. *Progress in Energy and Combustion Science*. 62, 33–86 (2017). <https://doi.org/10.1016/j.pecs.2017.05.004>
2. Suriapparao, D.V., Ojha, D.K., Ray, T., Vinu, R.: Kinetic analysis of co-pyrolysis of cellulose and polypropylene. *J Therm Anal Calorim*. 117, 1441–1451 (2014). <https://doi.org/10.1007/s10973-014-3866-4>

3. Sánchez-Jiménez, P.E., Pérez-Maqueda, L.A., Perejón, A., Pascual-Cosp, J., Benítez-Guerrero, M., Criado, J.M.: An improved model for the kinetic description of the thermal degradation of cellulose. *Cellulose*. 18, 1487–1498 (2011). <https://doi.org/10.1007/s10570-011-9602-3>
4. Dai, G., Wang, S., Zou, Q., Huang, S.: Improvement of aromatics production from catalytic pyrolysis of cellulose over metal-modified hierarchical HZSM-5. *Fuel Processing Technology*. 179, 319–323 (2018). <https://doi.org/10.1016/j.fuproc.2018.07.023>
5. Dai, G., Wang, K., Wang, G., Wang, S.: Initial pyrolysis mechanism of cellulose revealed by in-situ DRIFT analysis and theoretical calculation. *Combustion and Flame*. 208, 273–280 (2019). <https://doi.org/10.1016/j.combustflame.2019.07.009>
6. Patwardhan, P.R., Satrio, J.A., Brown, R.C., Shanks, B.H.: Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresource Technology*. 101, 4646–4655 (2010). <https://doi.org/10.1016/j.biortech.2010.01.112>
7. Hwang, H., Oh, S., Cho, T.-S., Choi, I.-G., Choi, J.W.: Fast pyrolysis of potassium impregnated poplar wood and characterization of its influence on the formation as well as properties of pyrolytic products. *Bioresource Technology*. 150, 359–366 (2013). <https://doi.org/10.1016/j.biortech.2013.09.132>
8. Carvalho, W.S., Cunha, I.F., Pereira, M.S., Ataíde, C.H.: Thermal decomposition profile and product selectivity of analytical pyrolysis of sweet sorghum bagasse: Effect of addition of inorganic salts. *Industrial Crops and Products*. 74, 372–380 (2015). <https://doi.org/10.1016/j.indcrop.2015.05.020>
9. Banks, S.W., Nowakowski, D.J., Bridgwater, A.V.: Impact of Potassium and Phosphorus in Biomass on the Properties of Fast Pyrolysis Bio-oil. *Energy Fuels*. 30, 8009–8018 (2016). <https://doi.org/10.1021/acs.energyfuels.6b01044>
10. Min, Z., Asadullah, M., Yimsiri, P., Zhang, S., Wu, H., Li, C.-Z.: Catalytic reforming of tar during gasification. Part I. Steam reforming of biomass tar using ilmenite as a catalyst. *Fuel*. 90, 1847–1854 (2011). <https://doi.org/10.1016/j.fuel.2010.12.039>
11. Sueyasu, T., Oike, T., Mori, A., Kudo, S., Norinaga, K., Hayashi, J.: Simultaneous Steam Reforming of Tar and Steam Gasification of Char from the Pyrolysis of Potassium-Loaded Woody Biomass. *Energy Fuels*. 26, 199–208 (2012). <https://doi.org/10.1021/ef201166a>
12. Feng, D., Zhao, Y., Zhang, Y., Sun, S.: Effects of H₂O and CO₂ on the homogeneous conversion and heterogeneous reforming of biomass tar over biochar. *International Journal of Hydrogen Energy*. 42, 13070–13084 (2017). <https://doi.org/10.1016/j.ijhydene.2017.04.018>
13. Basu, P. ed: Dedication. In: *Biomass Gasification, Pyrolysis and Torrefaction (Second Edition)*. p. v. Academic Press, Boston (2013)

14. Franco, C., Pinto, F., Gulyurtlu, I., Cabrita, I.: The study of reactions influencing the biomass steam gasification process. *Chem. Eng. Sci.* 58, 8 (2003)
15. Effendi, A., Hellgardt, K., Zhang, Z., Yoshida, T.: Optimising H₂ production from model biogas via combined steam reforming and CO shift reactions. *Fuel*. 84, 869–874 (2005).
<https://doi.org/10.1016/j.fuel.2004.12.011>
16. Ren, J., Cao, J.-P., Zhao, X.-Y., Wei, F., Zhu, C., Wei, X.-Y.: Extension of catalyst lifetime by doping of Ce in Ni-loaded acid-washed Shengli lignite char for biomass catalytic gasification. *Catal. Sci. Technol.* 7, 5741–5749 (2017). <https://doi.org/10.1039/C7CY01670K>
17. Abu El-Rub, Z., Bramer, E.A., Brem, G.: Experimental comparison of biomass chars with other catalysts for tar reduction. *Fuel*. 87, 2243–2252 (2008). <https://doi.org/10.1016/j.fuel.2008.01.004>
18. Hosokai, S., Kumabe, K., Ohshita, M., Norinaga, K., Li, C., Hayashi, J.: Mechanism of decomposition of aromatics over charcoal and necessary condition for maintaining its activity. *Fuel*. 87, 2914–2922 (2008). <https://doi.org/10.1016/j.fuel.2008.04.019>
19. Fagbemi, L.: Pyrolysis products from different biomasses: application to the thermal cracking of tar. *Fuel and Energy Abstracts*. 43, 279 (2002). [https://doi.org/10.1016/S0140-6701\(02\)86434-7](https://doi.org/10.1016/S0140-6701(02)86434-7)
20. Li, X.T., Grace, J.R., Lim, C.J., Watkinson, A.P., Chen, H.P., Kim, J.R.: Biomass gasification in a circulating fluidized bed. *Biomass and Bioenergy*. 26, 171–193 (2004). [https://doi.org/10.1016/S0961-9534\(03\)00084-9](https://doi.org/10.1016/S0961-9534(03)00084-9)
21. Huang, J., Liu, C., Wei, S., Huang, X., Li, H.: Density functional theory studies on pyrolysis mechanism of β -D-glucopyranose. *Journal of Molecular Structure: THEOCHEM*. 958, 64–70 (2010).
<https://doi.org/10.1016/j.theochem.2010.07.030>
22. Zhang, X., Yang, W., Dong, C.: Levoglucosan formation mechanisms during cellulose pyrolysis. *Journal of Analytical and Applied Pyrolysis*. 104, 19–27 (2013).
<https://doi.org/10.1016/j.jaap.2013.09.015>
23. Dai, G., Wang, K., Wang, G., Wang, S.: Initial pyrolysis mechanism of cellulose revealed by in-situ DRIFT analysis and theoretical calculation. *Combustion and Flame*. 208, 273–280 (2019).
<https://doi.org/10.1016/j.combustflame.2019.07.009>
24. Lu, Q., Hu, B., Zhang, Z., Wu, Y., Cui, M., Liu, D., Dong, C., Yang, Y.: Mechanism of cellulose fast pyrolysis: The role of characteristic chain ends and dehydrated units. *Combustion and Flame*. 198, 267–277 (2018). <https://doi.org/10.1016/j.combustflame.2018.09.025>
25. Huang, X., Liu, C., Huang, J., Li, H.: Theory studies on pyrolysis mechanism of phenethyl phenyl ether. *Computational and Theoretical Chemistry*. 976, 51–59 (2011).
<https://doi.org/10.1016/j.comptc.2011.08.001>

26. Jiang, X., Lu, Q., Hu, B., Liu, J., Dong, C., Yang, Y.: Intermolecular interaction mechanism of lignin pyrolysis: A joint theoretical and experimental study. *Fuel*. 215, 386–394 (2018).
<https://doi.org/10.1016/j.fuel.2017.11.084>
27. Li, Q., Wang, Q., Kayamori, A., Zhang, J.: Experimental study and modeling of heavy tar steam reforming. *Fuel Processing Technology*. 178, 180–188 (2018).
<https://doi.org/10.1016/j.fuproc.2018.05.020>
28. Meng, J., Zhao, Z., Wang, X., Zheng, A., Zhang, D., Huang, Z., Zhao, K., Wei, G., Li, H.: Comparative study on phenol and naphthalene steam reforming over Ni-Fe alloy catalysts supported on olivine synthesized by different methods. *Energy Conversion and Management*. 168, 60–73 (2018).
<https://doi.org/10.1016/j.enconman.2018.04.112>
29. Hu, B., Huang, Q., Buekens, A., Chi, Y., Yan, J.: Co-gasification of municipal solid waste with high alkali coal char in a three-stage gasifier. *Energy Conversion and Management*. 153, 473–481 (2017).
<https://doi.org/10.1016/j.enconman.2017.10.026>
30. Lu, P., Huang, Q., (Thanos) Bourtsalas, A.C., Chi, Y., Yan, J.: Synergistic effects on char and oil produced by the co-pyrolysis of pine wood, polyethylene and polyvinyl chloride. *Fuel*. 230, 359–367 (2018). <https://doi.org/10.1016/j.fuel.2018.05.072>
31. Lu, P., Huang, Q., Chi, Y., Wang, F., Yan, J.: Catalytic cracking of tar derived from the pyrolysis of municipal solid waste fractions over biochar. *Proceedings of the Combustion Institute*. 37, 2673–2680 (2019). <https://doi.org/10.1016/j.proci.2018.06.051>
32. Frisch, M.J., Trucks, G., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J., Hada, M., Fox, D.: Gaussian 09 Revision A.1. Gaussian Inc. (2009)
33. Lu, T., Chen, F.: Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem*. 33, 580–592 (2012). <https://doi.org/10.1002/jcc.22885>
34. Lu, T., Chen, F.: Bond Order Analysis Based on the Laplacian of Electron Density in Fuzzy Overlap Space. *J. Phys. Chem. A*. 117, 3100–3108 (2013). <https://doi.org/10.1021/jp4010345>
35. Park, H.J., Heo, H.S., Yoo, K.-S., Yim, J.-H., Sohn, J.M., Jeong, K.-E., Jeon, J.-K., Park, Y.-K.: Thermal degradation of plywood with block polypropylene in TG and batch reactor system. *Journal of Industrial and Engineering Chemistry*. 17, 549–553 (2011). <https://doi.org/10.1016/j.jiec.2010.11.002>
36. Çepelioğullar, Ö., Pütün, A.E.: Products characterization study of a slow pyrolysis of biomass-plastic mixtures in a fixed-bed reactor. *Journal of Analytical and Applied Pyrolysis*. 110, 363–374 (2014).
<https://doi.org/10.1016/j.jaap.2014.10.002>

37. Mohan, D., Pittman, C.U., Steele, P.H.: Pyrolysis of Wood/Biomass for Bio-oil: A Critical Review. *Energy Fuels*. 20, 848–889 (2006). <https://doi.org/10.1021/ef0502397>
38. Li, X., Li, J., Zhou, G., Feng, Y., Wang, Y., Yu, G., Deng, S., Huang, J., Wang, B.: Enhancing the production of renewable petrochemicals by co-feeding of biomass with plastics in catalytic fast pyrolysis with ZSM-5 zeolites. *Applied Catalysis A: General*. 481, 173–182 (2014). <https://doi.org/10.1016/j.apcata.2014.05.015>
39. Brebu, M., Ucar, S., Vasile, C., Yanik, J.: Co-pyrolysis of pine cone with synthetic polymers. *Fuel*. 89, 1911–1918 (2010). <https://doi.org/10.1016/j.fuel.2010.01.029>
40. Baldwin, R.M., Magrini-Bair, K.A., Nimlos, M.R., Pepiot, P., Donohoe, B.S., Hensley, J.E., Phillips, S.D.: Current research on thermochemical conversion of biomass at the National Renewable Energy Laboratory. *Applied Catalysis B: Environmental*. 115–116, 320–329 (2012). <https://doi.org/10.1016/j.apcatb.2011.10.033>
41. Carpenter, D.L., Bain, R.L., Davis, R.E., Dutta, A., Feik, C.J., Gaston, K.R., Jablonski, W., Phillips, S.D., Nimlos, M.R.: Pilot-Scale Gasification of Corn Stover, Switchgrass, Wheat Straw, and Wood: 1. Parametric Study and Comparison with Literature. *Ind. Eng. Chem. Res.* 49, 1859–1871 (2010). <https://doi.org/10.1021/ie900595m>
42. Göransson, K., Söderlind, U., Zhang, W.: Experimental test on a novel dual fluidised bed biomass gasifier for synthetic fuel production. *Fuel*. 90, 1340–1349 (2011). <https://doi.org/10.1016/j.fuel.2010.12.035>
43. Lopez, G., Erkiaga, A., Amutio, M., Bilbao, J., Olazar, M.: Effect of polyethylene co-feeding in the steam gasification of biomass in a conical spouted bed reactor. *Fuel*. 153, 393–401 (2015). <https://doi.org/10.1016/j.fuel.2015.03.006>
44. Futamura, S., Gurusamy, A.: Effects of temperature, reactor type, and voltage properties on the plasma reforming of aliphatic hydrocarbons with CO/sub 2/. In: *Fortieth IAS Annual Meeting. Conference Record of the 2005 Industry Applications Conference*, 2005. pp. 1833–1839. IEEE, Hong Kong, China (2005)
45. Sharma, R.K., Hajaligol, M.R.: Effect of pyrolysis conditions on the formation of polycyclic aromatic hydrocarbons (PAHs) from polyphenolic compounds. *Journal of Analytical and Applied Pyrolysis*. 66, 123–144 (2003). [https://doi.org/10.1016/S0165-2370\(02\)00109-2](https://doi.org/10.1016/S0165-2370(02)00109-2)
46. Font Palma, C.: Modelling of tar formation and evolution for biomass gasification: A review. *Applied Energy*. 111, 129–141 (2013). <https://doi.org/10.1016/j.apenergy.2013.04.082>
47. Fuentes-Cano, D., Gómez-Barea, A., Nilsson, S., Ollero, P.: Decomposition kinetics of model tar compounds over chars with different internal structure to model hot tar removal in biomass gasification.

48. Rong F., Tian L., Fei-Wu C.: Comparing Methods for Predicting the Reactive Site of Electrophilic Substitution. *Acta Physico-Chimica Sinica*. 30, 628–639 (2014). <https://doi.org/10.3866/PKU.WHXB201401211>

49. Lu, T., Chen, F.: Bond Order Analysis Based on the Laplacian of Electron Density in Fuzzy Overlap Space. *J. Phys. Chem. A*. 117, 3100–3108 (2013). <https://doi.org/10.1021/jp4010345>

Tables

Table 1

Proximate and ultimate analysis of raw materials.

Proximate analysis/%				Ultimate analysis/%					Qb,ad(kJ/kg)
M _{ad}	A _{ad}	V _{ad}	FC _{ad}	C _{ad}	H _{ad}	N _{ad}	S _{ad}	O _{ad} ^a	
5.83	-	88.12	6.05	41.92	4.59	0.08	0.19	47.39	16561

^a by difference.

Table 2

Operation parameters of the experiments.

NO.	1	2	3	4
Steam to feedstock ratio (g/g)	0	0.8	1.2	1.6
Nitrogen flow rate[L/min]	3.0	1.7	1.0	0.4
Total feedstock[g]	80			
Fuel feeding rate[g/min]	1.33			
First stage temperature (°C)	600°C			
Second stage temperature (°C)	800°C			
Connecting section temperature (°C)	180°C			

Table 3

Yield and elemental properties of tar.

	S/F=0	S/F=0.8	S/F=1.2	S/F=1.6
Tar yield (g/g)	6.68±0.46	4.51±0.82	3.01±0.85	2.30±0.54
Ultimate analysis [wt.%]				
C	62.72	69.31	76.37	74.53
H	5.34	5.75	5.29	5.62
N	0.36	0.33	0.37	0.35
O ^a	31.58	24.61	17.97	19.5
H/C ^b	1.022	0.996	0.831	0.905

^a by difference; ^b atomic ratio.

Table 4

The distribution of main compounds at different S/F.

		S/F=0	S/F=0.8	S/F=1.2	S/F=1.6
Main types of compounds % area					
Chain compounds ^a		5.39	2.26	1.00	0
O-heterocycles ^b		6.24	9.42	6.24	7.25
Alicyclic compounds		4.45	6.33	4.79	5.24
Aromatic compounds		83.92	81.99	87.97	87.51
Alicyclic compounds % area					
Cyclane ^c		1.71	3.06	4.79	5.24
Cycloalkene ^d		2.74	3.27	-	-
Aromatic compounds % area					
MAHs	Benzene	5.56	5.67	4.66	5.89
	Toluene	16.03	14.49	9.21	11.10
	Formic acid phenyl ester(FAPE)	19.16	5.54	3.75	-
	Benzofuran, 2-methyl-	0.93	0.94	2.24	1.84
	Xylenes ^e	7.74	9.75	10.07	8.66
	Other alkylbenzenes ^f	0.95	1.84	5.62	5.69
	Alkenylbenzenes ^g	9.87	18.60	16.49	20.73
	Indenes ^h	3.94	4.78	9.04	6.75
	Phenols ⁱ	13.38	15.02	13.34	12.42
	Aromatic alcohols ^j	1.05	1.68	-	-
PAHs	Naphthalenes ^k	5.31	3.68	12.04	11.03
	Phenanthrene	-	-	1.51	3.40

^a Chain compounds (n-Hexane; 1,5-Hexadiyne)

^b O-heterocycles (Furfural; 2-Furancarboxaldehyde,5-methyl-; Furan,2,5-dimethyl-)

^c Cyclane (cyclopentane,methyl-; cyclohexane)

^d Cycloalkene (1,3-cyclopentadiene,5-methyl-; 1,3,5,7-Cyclooctatetraene)

- ^e Xylenes (p-Xylene; o-Xylene; Benzen,1,3-dimthyl-)
- ^f Other alkylbenzenes (Ethylbenzene; Benzene,1-ethyl-3-methyl- Benzene,(1-methylethyl)- Benzene,1,2,3-trimethyl-; Benezen,1,2,4-trimethyl-)
- ^g Alkenylbenzenes (Styrene; 2-Propenal, 3-phenyl-; Benzene,1-ethenyl-2-methyl-; Benzene,1-propenyl-; Benzene,2-propenyl-;)
- ^h Indenes (Indene; 1H-Inden,3-methyl-; 1H-Indene, 1-ethylidene-)
- ⁱ Phenols (phenol,2-methyl-; phenol,3-methyl-; phenol,2,4-dimethyl-; phenol,2,5-dimethyl-; Phenol,4-(3-hydroxy-1-propenyl-))
- ^j Aromatic alcohols (Benzyl alcohol; 2,5-dimethylphenyl methyl carbinol)
- ^k Naphthalenes (Naphthalene; Naphthalene,1,2-dihydro-; Naphthalene,1-methyl-; 1,8-Naphthalenedimethanol)

Table 5

The Gibbs free energy of main tar components (yield > 5%) formed from MCC pyrolysis at 800 °C.

NO.	Components	Free energy [Hartree]	NO.	Components	Free energy [Hartree]
1	Formic acid phenyl ester(FAPE)	-420.973	5	P-Xylene	-310.982
2	Naphthalene	-386.022	6	Styrene	-309.773
3	Phenol,3-methyl-	-346.926	7	Toluene	-271.668
4	Furfural	-343.522	8	1,5-hexadiyne	-232.002

Table 6

The electron density of FAPE by CDD.

NO.	$f_A^{(2)}$	NO.	$f_A^{(2)}$	NO.	$f_A^{(2)}$
C1	0.099	C6	0.039	H11	-0.010
O2	0.035	C7	-0.053	H12	0.008
O3	-0.050	C8	-0.023	H13	-0.008
C4	-0.043	C9	0.026	H14	-0.006
C5	-0.039	H10	0.022	H15	0.003

Figures

Figure 1

Schematic representation of the laboratory scale apparatus. (1)Screw feeder (2)Tubular furnace(first)
 (3)Tubular furnace (second) (4)Steam generator (5)Electronic flowmeter (6)Injection pump (7)nitrogen cylinder
 (8)Condenser (9)Tar trap (10)Vacuum pump)

Figure 2

The distribution of MAHs and PAHs at the different S/F.

Figure 3

The distribution of phenols and FAPE at the different S/F.

Figure 4

A process of PAH formation from phenol[46].

Figure 5

The LBOs of FAPE.

Figure 6

The possible reaction pathways of FAPE.

Figure 7

The energy barriers of possible reaction paths.

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