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

Feng Tang  
Zhejiang University State Key Laboratory of Clean Energy Utilization

Yuqi Jin (jinyuqi@zju.edu.cn)  
Zhejiang University State Key Laboratory of Clean Energy Utilization

Yong Chi  
Zhejiang University State Key Laboratory of Clean Energy Utilization

Jiayu Ma  
Zhejiang University State Key Laboratory of Clean Energy Utilization

Zhongxu Zhu  
Zhejiang University State Key Laboratory of Clean Energy Utilization

Jinhua Gong  
Zhejiang University State Key Laboratory of Clean Energy Utilization

Research Article

Keywords:

DOI: https://doi.org/10.21203/rs.3.rs-247390/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License. Read Full License
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 addition was from 0 to 1.6. The steam could promote craking of compounds to form more stable compounds. To further study the removal mechanism of tar, the main tar component, phosphonic acid, (p-hydroxyphenyl-), was investigated using density functional theory (DFT). It was concluded that intermediate product from cellulose pyrolysis was more likely to react with H2O and made against the production of phosphonic acid, (p-hydroxyphenyl-), consistent with the experimental results.

1. Introduction

Nowadays, there are still many agricultural-oriented countries and regions. Besides the kitchen garbage commonly found in municipal solid waste (MSW), there are also abundant agricultural and wood residues in these places. Given these wastes are always different as the 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, researchers have conducted fruitful studies by 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 10-18 MJ/Nm³. 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 affects 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. But 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 is conducive to increasing H2 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 suggest 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 the cellulose pyrolysis with the effect of steam. In particular, this experiment was based on the MCC pyrolysis tar instead of a few representative modeling tar[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.

2. 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.

Table 1 Proximate and ultimate analysis of raw materials.
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 entirely pyrolysis in an inert atmosphere. Then, the remaining residue was sent into the slag hole. Simultaneously, the gaseous products (including syngas and tar) entered into 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. Furthermore, heating belts (set at 180°C) cover the connecting section to reduce steam condensation before entering the second stage.

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.

| 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 | | | |

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).

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 0.2μL, and the split ratio was 10:1. There are three parallel samples of each experiment condition, which have been measured by GC-MS, and the average results are shown in the Appendix.

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[29]. And the Multiwfn3.8 [30] was also used to calculate the frontier orbital and Laplacian [31] to analyze the active sites.

3. Results And Discussion

3.1 Properties of tar
As shown in Table 3, the yield of tar cuts back with steam increasing. It is consistent with earlier reported results on biomass pyrolysis gasification with steam[10–12]. However, this trend is not maintained: the reduction rate reaches the maximum at S/F=0.8, declined by one third from 6.68% during pyrolysis, and then it is gradually slowing down. Similarly, the H/C atomic ratio of tar reduces after the addition of steam and reaches the minimum at S/F=1.2. And the oxygen element in tar reduces significantly with the growth of steam, which indicates better tar quality in terms of calorific value and stability[32, 33].

| Table 3: Yield and elemental properties of tar. |
|-----------------------------------------------|
| **S/F** | **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                   | 31.58     | 24.61     | 17.97     | 19.5      |
| H/C                 | 1.022     | 0.996     | 0.831     | 0.905     |

by difference; b atomic ratio.

### 3.2 Effect of steam on tar components

According to the measurement result of tar products (shown in the Appendix), the major compositions have been quantified and summarized in Table 4. Generally, O-heterocycles are highly corrosive to boilers, engines, and other equipment. Its yield is influenced significantly by temperature. Baldwin et al.[34] summarized the variation of biomass tar with temperature changing and thought there were more O-heterocycles in the tar at 500~600 °C, such as furan and pentose. They also reported the tar, like the O-heterocycles, cracked distinctly with the rise of temperature. However, the O-heterocycles yield is also affected by steam. After the addition of steam, the proportion of total O-heterocycles increases, and forming two new derivatives (Appendix, 24, 21/43/71). It can be attributed to the fact that steam can facilitate the dissociation of these O-heterocycles, which are formed by the polysaccharide structure of MCC after a series of reactions, such as decarboxylation, decarboxylation, and so on[35, 36]. In the reaction process, the compounds also crack into radical groups like the methyl radical to promote the substitution reaction and generate new derivatives.

Compared with complete pyrolysis, the steam stimulates the decline of open-chain compounds and increments alicyclic compounds in MCC pyrolysis tar significantly. However, the changing trend of alicyclic compounds is inversely proportional to the amount of steam. For example, with the continuous growth of steam, the cycloalkenes almost disappear after reaching the maximum value at S/F=0.8. Moreover, the rising rate of the cycloalkanes also slows down significantly. To be specific, the increase in steam has two effects: some of the olefin, alkyne produced from MCC pyrolysis are further decomposed into non-condensing gases (such as CO, CO₂, C₁-C₄) or may react with aromatic compounds to form new compounds. On the other hand, O/H/OH active radicals generated by steam can adhere with tar fragment[12, 37], and produce many unsaturated open-chain compounds, which are likely to boost the forming of cyclohexene through the Diels-Alder reaction. At the same time, it is also accompanied by the hydrogenation reaction, which can further form cycloalkanes.

After the addition of steam, the proportion of aromatic compounds (the largest of the tar products) reduce slightly. For example, the yield of toluene is still over 10%, the same as during pyrolysis, while phosphonic acid, (p-hydroxyphenyl) reduces and azobenzene disappears completely. In particular, the phosphonic acid, (p-hydroxyphenyl) with multiple hydroxyls decreases by about 10% under the effect of steam; and this trend is more clearly with the increase of steam amount (S/F).

However, as shown in Fig 2, the trend of monocyclic aromatics compounds is enhancing with the amount of steam growing, and the yield of monocyclic aromatics compounds changes from 28.32% (S/F = 0) to 45.73% (S/F = 1.6). The amount of unsaturated monocyclic aromatics, which are the critical products in the pyrolysis-gasification process, is also proportional to steam. For example, alkyl benzene increases significantly and reaches the maximum increments of 18.88% at S/F=1.6. However, it is challenging to generate polycyclic aromatic hydrocarbons (PAH) by the Diels-Alder reaction because the styrene is not a dienophile[38]. And the styrene is more likely to react with hydrogen radicals to form alkylbenzenes rather than cyclization and aromatization. It also can be proved by the increment of xylene and other alkylbenzenes in Fig 2. Significantly, the other alkylbenzenes increase considerably, which comes from 0.95% at S/F=0 to a maximum of 6.40% at S/F=1.2. Besides, monocyclic aromatics compounds, such as phenol, increase with the addition of steam and then slightly decrease at S/F=1.6, but all of these have a little fluctuation. It indicates that phenols and its derivatives are stable, and only a part participates in the reaction[39, 40]. Therefore, there are two possible pathways to reduce the yield of phenols: firstly, the phenols could be a precursor to form PAHs[41, 42] as shown in Fig 3, secondly, the reaction of substitution or polycondensation occurs.

Except for the toluene and phenol, naphthalene is also the most representative aromatic compound in biomass tar, whose molecular amount is the smallest among PAHs[43]. In combination with the previous analysis, naphthalene may be formed through a series of polymerization by the phenol precursor. Naphthalene, unlike benzene, is more likely to participate in electrophilic substitution as its poor stability. Therefore, the naphthalene is inclined to react with the H radical to form naphthalene,1,2-dihydro- Furthermore, steam can facilitate the formation of compounds with caged scaffolds (Appendix, 37/63, 38/90), but their yields are inversely proportional to steam. Furthermore, the anthracene derivatives (Appendix, 68/93) also increases with the amount of steam growing after the first appearance at S/F=1.2.
Based on the above analysis, the transformation path of compounds can be summarized, as shown in Fig 4. In short, steam has two functions: it can promote compounds cracking, especially the compounds with double or triple bonds; on the other hand, it stimulates polymerization, which means the increment of steam leads to the increase of PAHs and facilitates the formation of the caged scaffold.

Table 4 The main compounds distributed at different S/F (the first stage was 600 ℃, and the second stage was 800 ℃)

|                          | S/F=0 | S/F=0.8 | S/F=1.2 | S/F=1.6 |
|--------------------------|-------|---------|---------|---------|
| **Main types of compounds** |       |         |         |         |
| Open chain compounds     | 5.39  | -       | 1.16    | -       |
| Alicyclic compounds      | 3.74  | 10.33   | 8       | 7.36    |
| O-heterocycles           | 4.95  | 9.01    | 6.14    | 8.03    |
| Aromatic compounds       | 85.92 | 80.66   | 84.7    | 84.61   |
| **Open chain compounds** |       |         |         |         |
| n-Hexane                 | -     | -       | 1.16    | -       |
| 1,5-Hexadiyne            | 5.39  | -       | -       | -       |
| **Alicyclic compounds**  |       |         |         |         |
| Cyclane                  | 1.71  | 3.24    | 5.6     | 5.81    |
| Cycloalkene              | 2.03  | 3.61    | -       | -       |
| Other alicyclic compounds| -     | 3.48    | 2.4     | 1.55    |
| **Aromatic compounds**   |       |         |         |         |
| Benzene                  | 3.47  | 8.46    | 5.41    | 6.53    |
| Toluene                  | 12.88 | 15.49   | 10.59   | 12.3    |
| Benzene, (2-nitroethyl)- | -     | 5.76    | 4.74    | 2.85    |
| Phosphonic acid,(p-hydroxyphenyl-) | 15.21 | 5.94 | 4.35 | - |
| Xylenes                  | 6.56  | 8.61    | 8.86    | 9.59    |
| Other alkylbenzenes      | 0.95  | 1.13    | 6.41    | 4.97    |
| Alkenyl benzene          | 7.93  | 15.07   | 7.86    | 18.88   |
| 3-Methylphenylacetylene  | -     | -       | 1       | -       |
| Benzene-alcohol          | 1.04  | 0.74    | -       | -       |
| Indenes                  | 3.12  | -       | 6.39    | 3.83    |
| Phenols                  | 10.93 | 12.98   | 12.41   | 9.38    |
| Naphthalene and its derivatives | 4.1 | 3.92 | 11.18 | 9.6 |
| Azobenzene               | 18.8  | -       | -       | -       |
| Other aromatic compounds | 0.93  | 2.56    | 5.5     | 6.68    |

a O-heterocycles (Furfural;2-Furancarboxaldehyde;5-methyl-;Furan,2,5-dimethyl-)
b Cyclane (cyclopentane; methyl-cyclohexane)

c Cycloalkene (1,3-cyclopentadiene;5-methyl-1,3,5,7-Cyclooctatetraene)
d Other alicyclic compounds (Tetracyclo[5,3,0,0,<2,6>,0<3,10>]>[4,8-diene; 10-Hydroxytricyclo[4,2,1,1,(2,5)]dec-3-en-9-one]

Benzene-alcohol (Benzyl alcohol; 2,5-dimethylphenyl methyl carbinol)
1.488 Å. Besides, the angle between O9-P8 and P8-H19 is 58.93°, and the angle between P8-H19 and benzene ring plane is also 89.41°. All the changes of
from 0.96 Å to 0.981 Å, and the bond distance of the C1-P8 bond is stretched 0.05 Å to 1.85 Å, while the bond length of P8-H19 is lengthened from 1.410 Å to
gradually separates from R-2 due to the offensive OH radical. When R-2 transforms to the transition state (TS5), the bond length of O9-H17 extends marginally
slightly extended due to the mutual attraction between O9 and P8 atoms during the substitution of OH radical for H19 atom. At the same time, the H19 atom
Path 2 is the reaction path of hydroxyl (O9-H17) attacking the P8-H19 bond of R-2 and then substituting the H19 atom. The bonds of O9-H17 and C1-P8 are
radical for R-2 (path 2 and 3).

3.3 The reaction mechanism of tar

Given the experimental results in 3.2, the Gibbs free energy of main tar components (yield > 4%) under pyrolysis conditions is summarized as listed in Table 5. The results show that the phosphonic acid, (p-hydroxyphenyl-), yield =15.21%, has the lowest Gibbs free energy (-875.45883 Hartree), which means it has strong reactivity. And as shown in Table 4, phosphonic acid, (p-hydroxyphenyl-), is likely to react with steam, cracking and completely disappeared.

The CDD is widely used to predict the reaction sites[44], and the electrophilic reaction is more likely to happen when the value of CDD is smaller. As shown in Table 6, the O7 connected with a benzene ring is most likely to be attacked. The other atoms(C1, O11, C4, O10, H16, P8, and O9) are also possibly attacked, but the activity decreases in turn, which is consistent with the experimental results. Besides, there is a direct correlation between LBO and bond dissociation energy, which is also instrumental in predicting reaction sites. The LBOs between atoms are listed in Fig 5. Small LBOs of C4-C7, P8-O9, and P8-O10 indicate that the hydroxyl groups connected with C4 or P8 are probably to break. The following analysis will focus on the removal mechanism of the phosphonic acid group.

Table 5 The Gibbs free energy of main tar components (yield > 4%) formed from MCC pyrolysis at 800 °C

| Components | 1,5-hexadine | Toluene | Styrene | P-Xylene | 1,3-cyclopentadiene,5-methyl- |
|------------|--------------|---------|---------|----------|-----------------------------|
| Free energy[Hartree] | -232.00 | -271.66823 | -309.77283 | -310.98244 | -233.51467 |
| Components | Furral | Phenol,3-methyl- | Naphthalene | Azobenzene | Phosphonic acid, (p-hydroxyphenyl-) |
| Free energy[Hartree] | -343.52177 | -346.92599 | -386.02201 | -572.95485 | -875.45883 |

Table 6 The electron density of phosphonic acid, (p-hydroxyphenyl-) by CDD

| NO. | NO. | NO. |
|-----|-----|-----|
| C1  | -0.0669 | O7  | -0.0875 | H13  | 0.0179 |
| C2  | 0.0611 | P8  | -0.0122 | H14  | 0.0157 |
| C3  | 0.0458 | O9  | -0.0088 | H15  | 0.0211 |
| C4  | -0.0398 | O10 | -0.0177 | H16  | -0.0163 |
| C5  | 0.041  | O11 | -0.0426 | H17  | 0.0058 |
| C6  | 0.068  | H12 | 0.0184  | H18  | -0.003 |

Combined with the analysis of active sites, the possible reaction pathways are shown in Fig 6. R-1 and phosphonic acid may have a substitution reaction to form P-1 and H2O during cellulose pyrolysis (path 1). Moreover, R-2 is produced from cellulose pyrolysis, which can further react with OH radicals to form P-1 and H radical (path 2). But when the steam is added, the R-2 also probably reacts with H2O to form P-2 and phosphonic acid (path 3). Thus, there is the competition of OH radical and H2O to react with R-2. The Gibbs free energy of each possible reaction path is listed in eq. (1)-(3), 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 3 is -61.568kJ/mol, which means that H2O is most likely to set a dominant position in competing with OH radicals for reacting with R-2. It also verifies the experimental result of cellulose pyrolysis tar that phosphonic acid, (p-hydroxyphenyl-) decreases sharply with the addition of steam.

The energy barriers of the three paths are listed in Fig 7, where also shows molecular structures (including reactants, transition states, products) involved in the reaction process. To further analyze the removal mechanism of the phosphonic acid group, this part will focus on the competition between H2O and OH radical for R-2 (path 2 and 3).

Path 2 is the reaction path of hydroxyl (O9-H17) attacking the P8-H19 bond of R-2 and then substituting the H19 atom. The bonds of O9-H17 and C1-P8 are slightly extended due to the mutual attraction between O9 and P8 atoms during the substitution of OH radical for H19 atom. At the same time, the H19 atom gradually separates from R-2 due to the offensive OH radical. When R-2 transforms to the transition state(TS5), the bond length of O9-H17 extends marginally from 0.96 Å to 0.981 Å, and the bond distance of the C1-P8 bond is stretched 0.05 Å to 1.85 Å, while the bond length of P8-H19 is lengthened from 1.410 Å to 1.488 Å. Besides, the angle between O9-P8 and P8-H19 is 58.93°, and the angle between P8-H19 and benzene ring plane is also 89.41°. All the changes of
bond distance and angle promote the breaking of the P8-H19 bond and substitution of OH radical. Then P8 atom and O9 atom gradually form bond 7, the bond length shrinks to 1.61 Å (during the transition state that is 1.97 Å), and P8-H19 bond breaks, H19 gradually deviates from the benzene ring plane, C1-P8 bond also shrinks to 1.79 Å, finally forming a stable product system P-1.

Path 3 is the reaction process of H$_2$O attacking the C1-P8 bond of R-2 and then substituting phosphonic acid. In the process of attacking the bond orbital, the H$_2$O molecule gradually approaches the C1-P8 bond, and the bond length of H19-O18 stretches with the molecular angle expands. When the R-2 converters to transition state (TS3), the bond distance of H19-O18 extends to 1.44 Å, and the molecular angle extends from 109.50° to 113.69°. What is more, the bond length of C1-P8 is stretched from 1.80 Å to 2.08 Å, while the phosphonic acid group deviates from the benzene ring plane, and the C1-P8 bond forms an angle of 40.84 °with the benzene ring plane. All of these make for the substitution of the H atom. After that, the H19-O18 bond breaks to produce the H19 atom and OH radical (O18-H20). The H19 atom further attacks C1, and the P8 is also attacked by OH radical. In this case, the atom distance between C1 and H19, and between O18 and P8 is 1.22 Å and2.03 Å, respectively. Finally, the compound forms a stable structure (P-2).

$$R_1 + H_2PO_4 \rightarrow P_1 + H_2O \quad \Delta G = -31.146 \text{ kJ/mol} \quad (1)$$

$$R_2 + OH \rightarrow P_2 + H \quad \Delta G = -38.663 \text{ kJ/mol} \quad (2)$$

$$R_2 + H_2O \rightarrow P_2 + H_2PO_4 \quad \Delta G = -61.568 \text{ kJ/mol} \quad (3)$$

4. 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) Steam mainly enhances the decomposition to form more stable compounds. When the cellulose pyrolysis, the phosphonic acid, (p-hydroxyphenyl-) can be formed by the further reaction of hydroquinone or intermediate containing a phosphonic acid group. Nevertheless, this intermediate is more likely to react with H$_2$O to form phenol and phosphonic acid after the addition of steam.

Declarations

Acknowledgments

This work was supported by the National Key R&D Program of China [Grant NO. 2018YFD1100602].

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, PE., 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, PR., 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 processq. 8 (2003)

15. Effendii, A., Hellgardt, K., Zhang, Z., Yoshida, T.: Optimising H 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 biomass species: application to the thermal cracking of tar. Fuel and Energy Abstracts. 43, 279 (2002). 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

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. 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)

30. Lu, T., Chen, F.: Multiwfnn: A multifunctional wavefunction analyzer. J. Comput. Chem. 33, 580–592 (2012). https://doi.org/10.1002/jcc.22885

31. 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

32. 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

33. Çepelioğlu, Ü., 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

34. Baldwin, R.M., Magnini-Bair, K.A., Nimlos, M.R., Pepiot, P., Donovan, 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

35. 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

36. 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

37. Futamura, S., Gurusamy, A.: Effects of temperature, reactor type, and voltage properties on the plasma reforming of aliphatic hydrocarbons with CO/sub 2/. In: Fourth IAS Annual Meeting, Conference Record of the 2005 Industry Applications Conference, 2005. pp. 1833–1839. IEEE, Hong Kong, China (2005)
38. Overman, L.E., Freerks, R.L., Petty, C.B., Clizbe, L.A., Ono, R.K., Taylor, G.F., Jessup, P.J.: Diels-Alder reactions of 1-(acylamino)-1,3-dienes. J. Am. Chem. Soc. 103, 2816–2822 (1981). https://doi.org/10.1021/ja00400a054

39. Demirbas, A.: Mechanisms of liquefaction and pyrolysis reactions of biomass. Energy Conversion. 14 (2000)

40. Wang, S., Guo, X., Wang, K., Luo, Z.: Influence of the interaction of components on the pyrolysis behavior of biomass. Journal of Analytical and Applied Pyrolysis. 91, 183–189 (2011). https://doi.org/10.1016/j.jaap.2011.02.006

41. 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

42. 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

43. 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. Chemical Engineering Journal. 228, 1223–1233 (2013). https://doi.org/10.1016/j.cej.2013.03.130

44. 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

Appendix

Supplementary data
| NO. | Compounds                        | Formula | Area % | NO. | Compounds                          | Formula | Area % | NO. | Compounds                        | Formula | Area % |
|-----|----------------------------------|---------|--------|-----|------------------------------------|---------|--------|-----|----------------------------------|---------|--------|
| 1   | Furfural                         | C₅H₄O₂ | 4.95   | 19  | Furfural                          | C₅H₄O₂ | 7.45   | 41  | Furfural                         | C₅H₄O₂ | 4.75   |
| 2   | 1,5-hexadiyne                    | C₆H₁₀  | 5.39   | 20  | Benzene                           | C₆H₆   | 8.46   | 42  | Benzene                           | C₆H₆   | 5.11   |
| 3   | Benzene                          | C₆H₆   | 3.47   | 21  | 2-Fluranacarboxaldehyde,5-methyl  | C₈H₁₀O₂ | 0.95   | 43  | 2-Fluranacarboxaldehyde,5-methyl | C₈H₁₀O₂ | 1.41   |
| 4   | Phosphonic acid, (p-hydroxyphenyl) | C₈H₈O₄P | 15.21 | 22  | Phosphonic acid,(p-hydroxyphenyl) | C₈H₈O₄P | 5.94   | 44  | Phosphonic acid,(p-hydroxyphenyl) | C₈H₈O₄P | 4.12   |
| 5   | 1,3-Cyclopentadiene,5-methyl     | C₉H₁₀  | 2.03   | 23  | 1,3-Cyclopentadiene,5-methyl      | C₉H₁₀O₂ | 0.79   | 45  | Furan,2,5-dimethyl               | C₉H₈O₂ | 0.61   |
| 6   | Cyclopentane, methyl             | C₅H₁₀  | 1.71   | 24  | Furan,2,5-dimethyl                | C₆H₈O₂ | 0.61   | 46  | Cyclopentane, methyl             | C₅H₁₀  | 4.75   |
| 7   | Toluene                          | C₇H₈   | 12.88  | 25  | Cyclopentane, methyl              | C₇H₁₀O₂ | 3.24   | 47  | Cyclohexane                      | C₇H₁₀ | 1.11   |
| 8   | Phenol,3-methyl                  | C₇H₈O  | 9.31   | 26  | Toluene                           | C₇H₈   | 15.49  | 48  | N-Hexane                         | C₇H₈O | 1.11   |
| 9   | Benzyl alcohol                   | C₇H₈O  | 1.04   | 27  | Phenol,2-methyl                   | C₇H₈O  | 7.38   | 49  | Toluene                          | C₇H₈O | 1.11   |
| 10  | Styrene                          | C₈H₈   | 7.93   | 28  | 1,3,5,7-cyclooctatetraene         | C₈H₈O₂ | 2.82   | 50  | Phenol,3-methyl                  | C₈H₈O | 0.77   |
| 11  | Benzen,1,3-dimethyl              | C₉H₁₀  | 2.20   | 29  | Benzen,1,3-dimethyl               | C₉H₁₀O₂ | 5.76   | 51  | Styrene                          | C₉H₈O | 3.41   |
| 12  | P-Xylene                         | C₉H₁₀  | 4.36   | 30  | Benzen,1,3-dimethyl               | C₉H₁₀O₂ | 8.61   | 52  | Benzen,1,3-dimethyl              | C₉H₁₀O₂ | 4.12   |
| 13  | Indene                           | C₉H₆   | 3.12   | 31  | Phenol,2,5-dimethyl               | C₉H₁₀O | 5.60   | 53  | Benzen,1,3-dimethyl              | C₉H₁₀O | 5.60   |
| 14  | Benzfuran,2-methyl               | C₉H₈O  | 0.93   | 32  | 2-Propanol,3-phenyl               | C₉H₈O  | 2.92   | 54  | P-Xylene                         | C₉H₁₀ | 3.41   |
| 15  | Phenol,4-(3-hydroxy-1-propenyl)  | C₉H₁₀O₂ | 1.62  | 33  | Benzen,1-propenyl                 | C₉H₈   | 3.17   | 55  | Ethylbenzene                     | C₉H₁₀ | 2.00   |
| 16  | Benzen,1-ethyl-3-methyl          | C₁₀H₁₂  | 0.95   | 34  | Benzen,2-propenyl                 | C₁₀H₁₀O | 8.98   | 56  | Phenol,2,4-dimethyl              | C₁₀H₈O | 2.00   |
| 17  | Naphthalene                      | C₁₀H₈  | 4.10   | 35  | Benzen,1-ethyl-3-methyl           | C₁₀H₁₀ | 1.13   | 57  | 3-Methylphenylacetylene          | C₉H₈O | 1.11   |
| 18  | Azobenzene                       | C₁₂H₁₀N₂ | 18.80 | 36  | Naphthalene                       | C₁₀H₈O | 3.92   | 58  | Indene                           | C₉H₈O | 3.41   |
|     |                                  |          |        | 37  | Tetracyclo [5,3,0.0, 2,6<0<3,10>dec-4,8-diene | C₁₂H₁₀O | 2.57   | 59  | Benzfuran,2-methyl               | C₉H₁₀O | 2.00   |
|     |                                  |          |        | 38  | 10-Hydroxytricyclo [4,2,1,1,(2,5)dec-3-en-9-one | C₁₂H₁₀O₂ | 0.91   | 60  | Benzen,2-propenyl                | C₉H₈O | 3.41   |
|     |                                  |          |        | 39  | 2,5-Dimethylphenyl methyl carbinol | C₁₀H₁₂O | 0.74   | 61  | Benzen,1-ethyl-3-methyl           | C₉H₁₀O | 3.41   |
|     |                                  |          |        | 40  | Benzocyclopehtatriene              | C₁₁H₁₀ | 2.56   | 62  | Naphthalene                       | C₁₀H₈O | 4.75   |
|     |                                  |          |        |     |                                    |          |        |     |                                  |          |        |
|     |                                  |          |        |     |                                    |          |        |     |                                  |          |        |
|     |                                  |          |        |     |                                    |          |        |     |                                  |          |        |
|     |                                  |          |        |     |                                    |          |        |     |                                  |          |        |
|     |                                  |          |        |     |                                    |          |        |     |                                  |          |        |
|     |                                  |          |        |     |                                    |          |        |     |                                  |          |        |
1,4-Dihydro-1,4-ethanoanthracene

C_{16}H_{14}