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Article in *Biomass and Bioenergy* · January 2018

DOI: 10.1016/j.biombioe.2017.11.007

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Research paper

Chemical-looping gasification of biomass: Part II. Tar yields and distributions

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ARTICLE INFO

Keywords:

Tar
Biomass
Chemical-looping gasification
Cu-Fe bimetallic oxygen carriers

ABSTRACT

Tar, as a kind of by-product in biomass gasification processes, can adversely affect the efficiency of biomass utilization. Chemical-looping technology has been proposed as a novel way to reduce the tar yield in biomass treatment. As the second part of a two-part series work, the tar evolution characteristic during the biomass-derived chemical-looping gasification (CLG) process using bimetallic Cu-Fe oxides as oxygen carrier (OC) was investigated. The tar collected from batch fluidized bed experiment with Cu₅Fe₅ (50 mol.% CuO + 50 mol.% Fe₂O₃) as OC was first analyzed by Gas Chromatography-Mass Spectrometer (GC-MS) to qualitatively determine the organic compounds contained. It was found that the relative molecular weight of the compounds was mostly concentrated at about 200. Subsequently, the effects of steam to biomass ratio (S/B, in weight), temperature, and oxygen carrier to biomass ratio (O/B, in weight) on tar reforming were investigated. The results indicated that the increase of temperature, S/B and O/B were all favorable for the decomposition and conversion of large molecular compounds in tar into small ones. In addition, quantitative analyses of the tar collected under the optimal conditions with different Cu-Fe mixed metal oxides as OCs were also conducted. It was found that the Cu composition in OC could promote the decomposition of small molecular compounds in tar, while the Fe composition was beneficial to decrease the yield of large molecular compounds in tar. Furthermore, synergistic reactivity of the bimetallic Cu-Fe OC was achieved for tar decomposition during the biomass-derived CLG process.

1. Introduction

The overuse of fossil fuels has resulted in large amount of CO₂ emission into the atmosphere, which eventually incurs serious impact on the global climate [1]. Therefore, the development of clean and renewable energy is of great significance. Biomass, as a kind of carbon-neutral renewable energy resources, holds the advantages of abundant reserves and low pollutants emission. Due to its high contents of hydrogen and volatile, production of syngas (H₂ and CO) via biomass gasification is considered to be a promising way for energy utilization [2]. Tar, which has typical high condensation point, is usually an inevitable byproduct in biomass gasification processes. The generation of tar will not only result in energy waste and reduce the biomass gasification efficiency, but can also corrode the gasification equipment, block the gas pipeline and damage the reactor system seriously [3]. In this sense, investigation on the reduction of tar yield and control of tar composition during biomass gasification processes have attracted extensive attention all over the world [4–6].

Hot gas conditioning by catalytic reforming has been proven as one of the best solutions to mitigate biomass gasification induced tars [7,8]. This method has been realized in different reactors, and a variety of catalytic materials can be used simultaneously. Chemical-looping, as a novel concept for inherent CO₂ capture and sequestration, has been widely investigated for the conversion of different kind of fuels [9]. Simply put, chemical-looping process is achieved by the oxygen carrier (OC) circulating between the fuel reactor (FR) and the air reactor (AR) to provide lattice oxygen and heat sources. In addition, the presence OC can be beneficial to reforming organic compounds (such as tar generated during the biomass pyrolysis process) into syngas, *i.e.*, a gas mixture of H₂ and CO [10]. Generally, the chemical-looping process operates at temperatures well above the condensation point of tar, and the OC with catalytic reactivity can be adopted to decompose the tar content into small organic matters. In this sense, the chemical-looping process should be a promising way to reduce the tar yield during biomass gasification processes.

The suitable OC is one of the key factors for the successful implementation of the chemical-looping reforming technology. The active

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Table 1

A summary of the relative works on chemical-looping reforming of tar.

Tar source	Tar removal efficiency	Reference
Biomass raw gas	Reduce by 95% for the Ni/Al ₂ O ₃ (880 °C); 60% for the ilmenite catalyst (800 °C)	Lind et al. [11]
Biomass raw gas	Reduce by 44.5% at a gas residence time of 0.4 s for M4MgZ1150 (40 wt% Mn ₃ O ₄ ; 60 wt% MgZrO ₃); 35% at a gas residence time 0.4–0.5 s for ilmenite at 800 °C	Lind et al. [12] [18]
C ₂ H ₄	The natural material bauxite and the synthetic bed materials NiO/Al ₂ O ₃ , CuO/MgAl ₂ O ₄ , and La _{0.8} Sr _{0.2} FeO ₃ /γ-Al ₂ O ₃ exhibit high C ₂ H ₄ conversion rates	Martin et al. [13]
C ₂ H ₄ , C ₆ H ₆ , and C ₇ H ₈	La _{0.8} Sr _{0.2} FeO ₃ /γ-Al ₂ O ₃ exhibited a higher catalytic effect than CuO/MgAl ₂ O ₄ ; the presence of C ₆ H ₆ limited the conversion of C ₂ H ₄ with Cu-based catalyst	Martin et al. [22]
Naphthalene	Combination of partial oxidation and catalysis. Conversion of Naphthalene: CSFM + NiO: 97%; ilmenite + NiO is over 95%	M. Ma et al. [15]
Toluene	10Fe/oliv1000 (10 wt% Fe; 1000 °C calcination). Toluene conversion: 91%; hydrogen production (0.066 mol _{H₂} /h/g _{cat})	Virginie et al. [20]
Biomass	Reduce by up to 65% for 10Fe/oliv1000 at 800 °C	Virginie et al. [21]

Table 2

Proximate and ultimate analyses of sawdust.

Proximate analysis (wt.%, ar)				Ultimate analysis (wt.%, daf)					Lower heating value QL (MJ/kg)
Moisture	Volatiles	Ash	FC	C	H	N	S	O ^a	
9.50	75.65	1.02	13.83	44.25	6.36	0.48	0.06	48.85	17.14

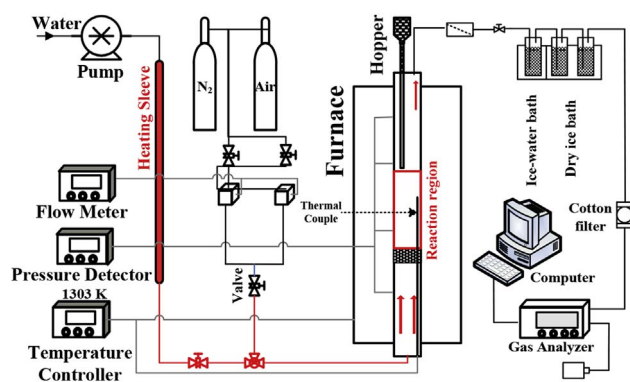
^a by difference.

Fig. 1. Schematic of the fluidized bed reactor system.

metal oxide phase of the OC can promote the fracture of C-C and C-H bonds. At present, transition metal oxides (usually supported by inert supports), such as NiO, Fe₂O₃, MnO₂, CuO et al., are commonly used as OCs in chemical-looping technology [11–13]. In addition, there are some new composite materials such as perovskite based OCs [14,15], which have also been comprehensively investigated. However, the metal oxides may suffer from deactivation due to sintering, coke deposition, and contamination by sulfur, chlorine, and alkali metals [16]. Moreover, some high reactive materials, like supported nickel-based OC, are toxic and expensive, which will increase the burden on the environment and economy.

In the two-part series work, synthetic Cu-Fe mixed metal oxides were investigated as OC in biomass-derived chemical-looping gasification (CLG) process. To be more specific, the first part focused on the optimization of CuO/Fe₂O₃ mole ratio in the bimetallic Cu-Fe OC (Cu₅Fe₅, i.e., 50 mol.% CuO + 50 mol.% Fe₂O₃, was screened out as the most appropriate one) and the identification of the optimal experimental conditions for biomass gasification using Cu₅Fe₅ as OC [17]. As the second part, the aim of this work was to

investigate the performances of Cu-Fe mixed metal oxides in tar reforming.

Actually, plenty of literature on tar reforming with commonly used OCs have been reported. Lind et al. [18,19] conducted the tar catalytic cracking experiment of raw gas from biomass gasification in a circulating fluidized bed with ilmenite (FeTiO₃) as OC. It was found that the addition of 12 wt% of ilmenite reduced the tar yield by about 50 wt %, and the branched tars and phenols were converted to stable aromatic compounds to a large extent. Virginie et al. [20,21] investigated the catalytic effect of Fe/olivine on tar primary reduction during biomass gasification in dual fluidized beds. The results indicated that the use of Fe/olivine instead of olivine contributed to an important decrease in the amount of tar generation, which to be more specific, was reduced by up to 65% at 850 °C. Additionally, the carbon deposition on the catalyst surface was low and can be easily oxidized in the combustion stage.

However, both the catalytic reactivity and oxygen transfer capability of Fe-based OC were limited at low temperatures. Martin et al. [22] investigated a variety of bed materials based on transition metals, like Fe, Mn, Ni, and Cu, in a batch fluidized bed reactor, in which ethylene was chosen as the analogy of tar. The Cu-based materials achieved typical high C₂H₄ conversion, which was close to that of NiO/α-Al₂O₃, while Fe₂O₃/MgAl₂O₄ exhibited a lower catalytic activity. Cu-based materials supported on different inert materials were also used for ethylene reforming [13,23]. All materials exhibited high ethylene conversion in the absence of aromatic compounds in the gasification gas. And Cu modified PURALOX bed material can achieve 90% ethylene conversion in the presence of aromatic compounds [23]. In this sense, Cu-based OC exhibits a higher reactivity when compared with Fe₂O₃. Nevertheless, Cu-based OC presents a tendency to sintering and agglomeration at high temperatures due to its low melting point [24]. The utilization of combined Cu and Fe oxides as OC has then received extensive attention, which exhibits a synergistic effect on improving the reactivity and stability of the OC in chemical looping processes [25–28]. Table 1 just summarizes the research works related to

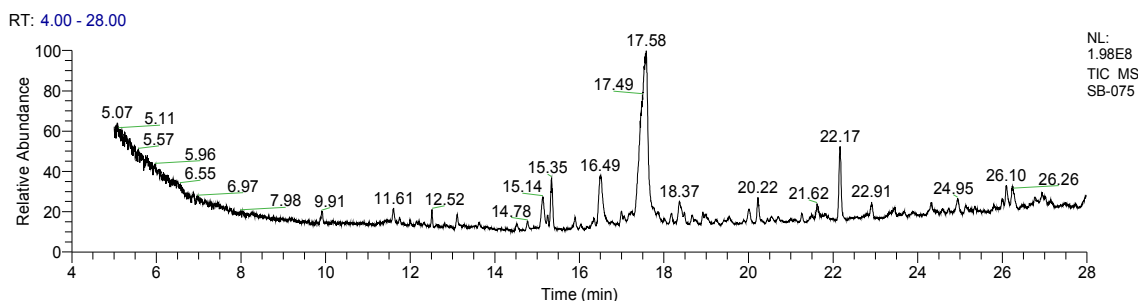


Fig. 2. The ion chromatogram of tar at the optimal condition.

Table 3

The main compounds in tar.

Molecular components	Molecular formula	Relative molecular mass	Composition mass content ratio/%	The main response time (min)
D-Allose	C ₆ H ₁₂ O ₆	180	29.61	17.58
2-Propenal, 3-(4-hydroxy-3-methoxyphenyl)	C ₁₀ H ₁₀ O ₃	178	6.04	22.17
1,16-Cyclocorynan-17-oic acid, 19,20-didehydro-, methyl ester, (16S,19E)	C ₂₀ H ₂₂ N ₂ O ₂	322	5.96	9.91
d-Mannose	C ₆ H ₁₂ O ₆	180	5.95	16.49
D-Glucopyranoside, O-D-glucopyranosyl-(1.fwdarw.3)-D-fructofuranosyl	C ₁₈ H ₃₂ O ₁₆	504	4.95	15.14
Vanillin lactoside	C ₂₀ H ₂₈ O ₁₃	476	3.96	15.35
Phen-1,4-diol, 2,3-dimethyl-5-trifluoromethyl	C ₉ H ₉ F ₃ O ₂	206	3.84	26.26
9,10-Secocholesta-5,7,10 (19)-triene-1,3-diol, 25-[(trimethylsilyl)oxy]-, (3-5Z,7E)	C ₃₀ H ₅₂ O ₃ Si	488	3.73	26.10
9,12,15-Octadecatrienoic acid, 2-[(trimethylsilyl)oxy]-1-[[[(trimethylsilyl)oxy]methyl]ethyl ester, (Z,Z,Z)	C ₂₇ H ₅₂ O ₄ Si ₂	496	2.70	24.32
2-(4-Nitrobutyryl) cyclooctanone	C ₁₂ H ₁₉ NO ₄	241	2.61	18.37
5,8,11,14-Eicosatetraynoic acid	C ₂₀ H ₂₄ O ₂	296	2.38	23.45

chemical-looping reforming. As can be seen, few research was focused on the catalytic reforming reactivity of Cu-Fe based OC towards tar.

In this work, the catalytic effect of Cu-Fe bimetallic OC on the primary reduction of tar during biomass-derived CLG process was investigated. Tar collected from batch fluidized bed experiments under different experimental conditions was analyzed by Gas Chromatography-Mass Spectrometer (GC-MS). The organic compounds of the tar collected under the optimal experimental condition with Cu₅Fe₅ as OC were first qualitatively analyzed. Then, the effects of steam concentration, temperature and oxygen carrier to biomass ratio on the variation of organic compounds in tar were investigated. In addition, the reforming performance of the catalysts with different CuO/Fe₂O₃ mole ratios towards tar was studied under the previously attained optimal experimental condition.

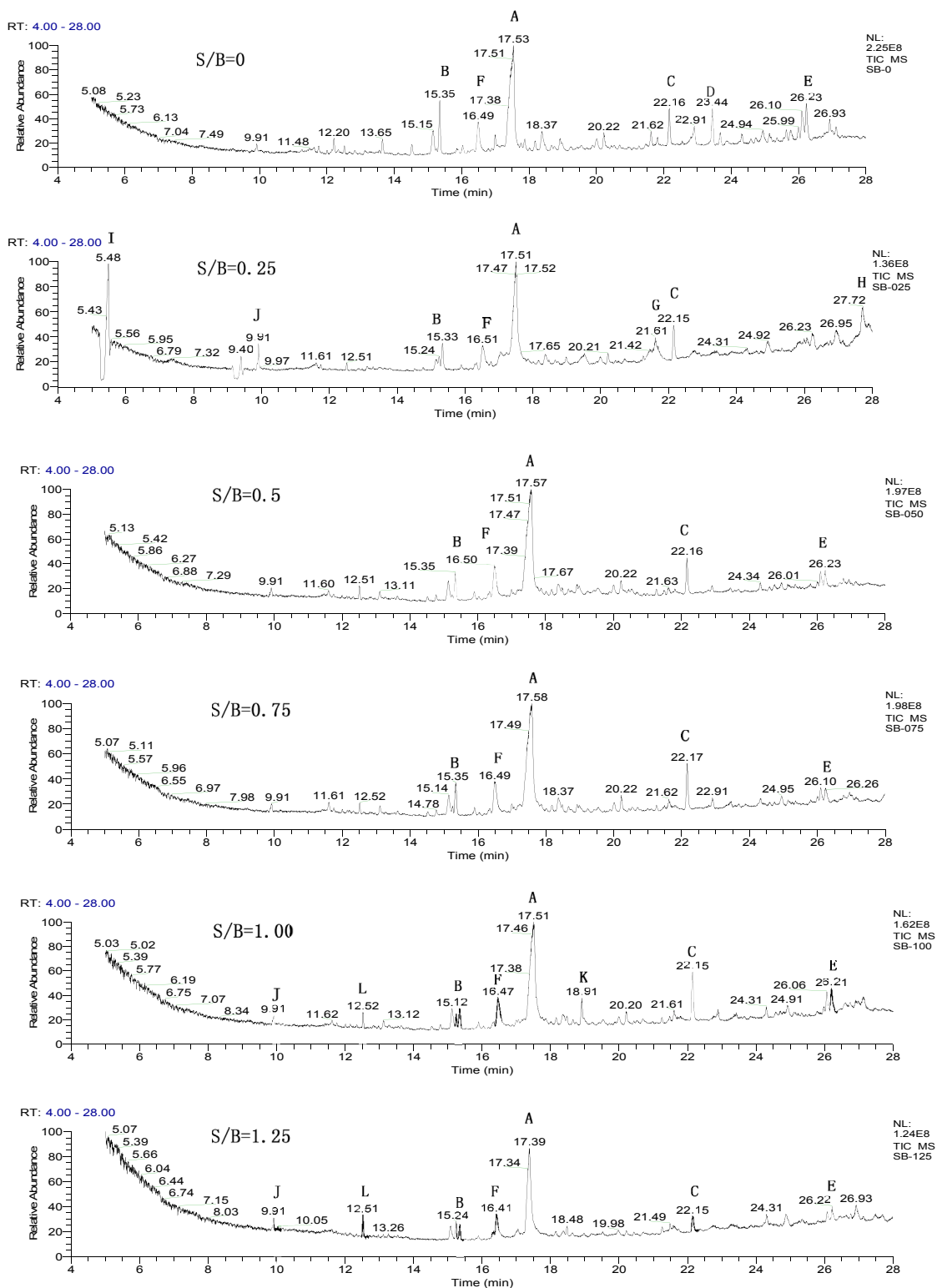
2. Materials and methods

In this paper, five kinds of Cu-Fe OCs were prepared by the sol-gel combustion synthesis method [29]. And the detailed preparation procedure has been introduced in Part I of the two-part series work. The pine sawdust used in this work was crushed and screened to 0.3–0.6 mm then dried at 105 °C in the oven for 18 h. The proximate and ultimate analyses of the sawdust are presented in Table 2.

The biomass-derived CLG experiments were carried out in a batch-operated fluidized bed reactor, as schematically shown in

Fig. 1. A straight stainless steel tube with a height of 890 mm and an inner diameter of 26 mm was used as the reaction chamber, which is electrically heated by a furnace. In the reduction process, a mixture of nitrogen and steam was used as the fluidization agent at a flow rate of 800 mL/min. The steam was generated by heating certain amount of feeding water provided by a constant flow pump. The total duration of steam addition in each test was 5 min, and the mass ratio of steam to biomass (S/B) was changed by adjusting the flow rate of water through the pump. In the oxidation process, the fluidization gas was switched to air and the reduced OC was re-oxidized to be ready for another CLG experiment. Furthermore, sawdust was kept at 2 g for all tests and silica sand with the same particle size was served as the inert bed material if the OC was not enough to balance the total sample weight to 24 g.

Tar produced during gasification was captured by a mixture of HPLC grade methanol and dichloromethane (1:4, in volume) which was stored in three gas bottles with a capacity of 50 ml. In order to achieve the best tar adsorption effect, two of the three gas bottles were placed in a dry ice bath (−78 °C), and the other one was placed in an ice-water bath (0 °C) to remove the steam contained in tail gas. After the experiment, the tar solution was intensively mixed and evaporated at 35 °C for 12 h. Then the residue tar was accurately weighted to determine the tar yield. To attain a more comprehensive understanding of the tar generated in biomass gasification process, especially the compositions and contents of organic matters, the tar collected was further analyzed in a GC-MS (Thermo Scientific: Trace GC Ultra, TM-ISQ). The automatic sampler (Triplus RSH, 1 μL) and



A: D-Allose; B: Vanillin; C: 2-Propenal, 3-(4-hydroxy-3-methoxyphenyl); D: Phenanthrene;
 E: 2,4,7,14-Tetramethyl-4; F: D-Glucopyranoside; G: Cycloheptene, 4-methoxy-2-phenyl-;
 H: Glycine; I: Methylene chloride; J: Nonane, 4,5-dimethyl-; K: 1,4-Benzenedicarboxylic acid, methyl ester; L: 2-Trimethylsiloxy-6-hexadecenoic acid, methyl ester;

Fig. 3. Total ion chromatogram of tar under different S/B conditions.

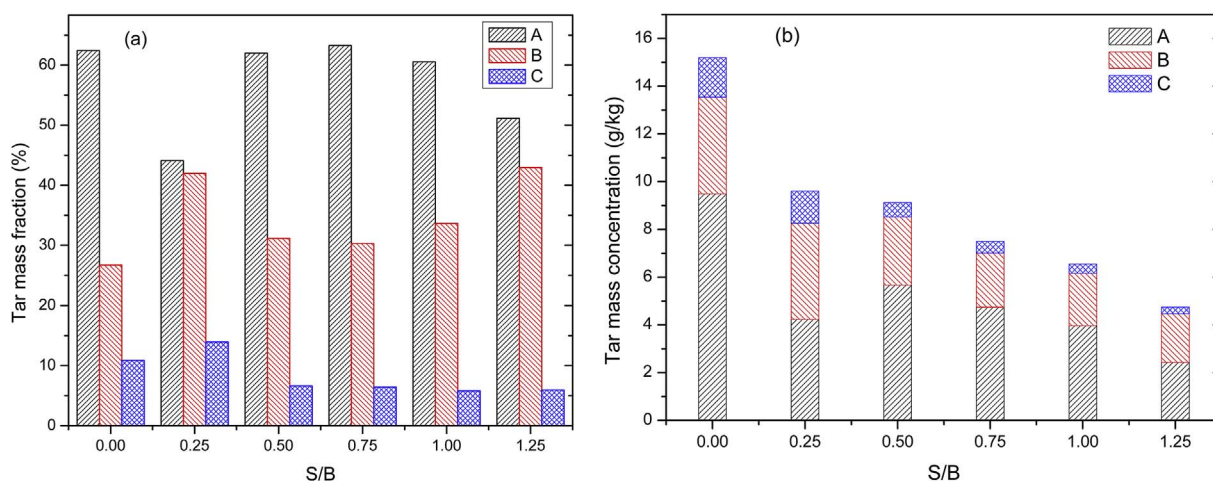


Fig. 4. The effect of S/B on the mass fraction (a) and concentration (b) of three tar components.

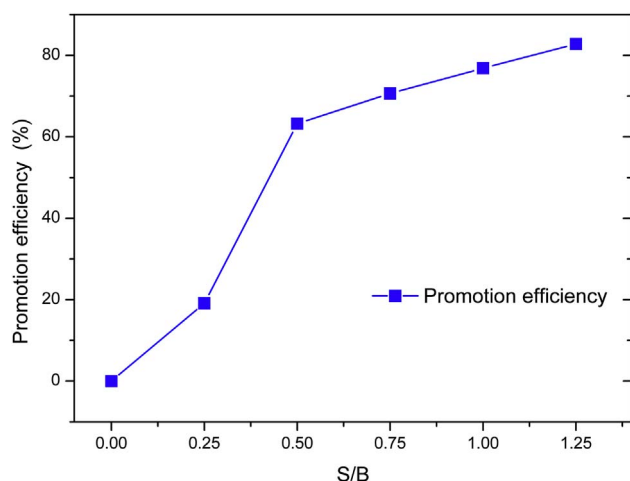


Fig. 5. The efficiency in reducing the original quantity of Class C tars at different S/B ratios.

chromatographic column (TG-WAXMS, 30 m \times 0.25 μ m \times 0.25 μ m) were provided by Thermo Fisher Scientific. The tar was extracted with HPLC grade methanol and dichloromethane (1:4, in volume), and organic compounds in tar were determined in the single quadrupole GC-MS system by ion selective method with helium (> 99.999%) as the carrier gas [30,31]. The temperature in ion source was set at 260 °C.

3. Result and discussion

3.1. Qualitative analysis of the tar

Firstly, qualitative analysis of the tar was conducted to find out the main molecular components in tar, under the experimental condition that the temperature was 800 °C, the O/B (supply oxygen coefficient, defined as the ratio of the active oxygen provided by OC to the oxygen needed to completely convert per unit mass of biomass) was 0.4, the S/B was 0.75 and Cu5Fe5 was chosen as the OC. Fig. 2 presents the ion chromatogram of tar generated under the aforementioned experimental condition. The horizontal coordinate is the detection time, and the

vertical coordinate is the relative abundance of the compound response peak. Each response peak in the diagram corresponds to a particular compound, and the peak area reflects the content of the compound in the tar [32]. As expected, the composition of the tar was rather complex and 49 compounds were detected according to the preliminary statistics. For detailed comparison, 11 main compounds whose mass contents were higher than 2% were listed on Table 3. It can be found that sugars, acids, aldehydes, alcohols, ethers, esters and ketones were the main components in the tar. Notably, the molecular weight of the compounds was mostly concentrated at about 200 and the mass content of D-Allose was the highest, as 29.61%.

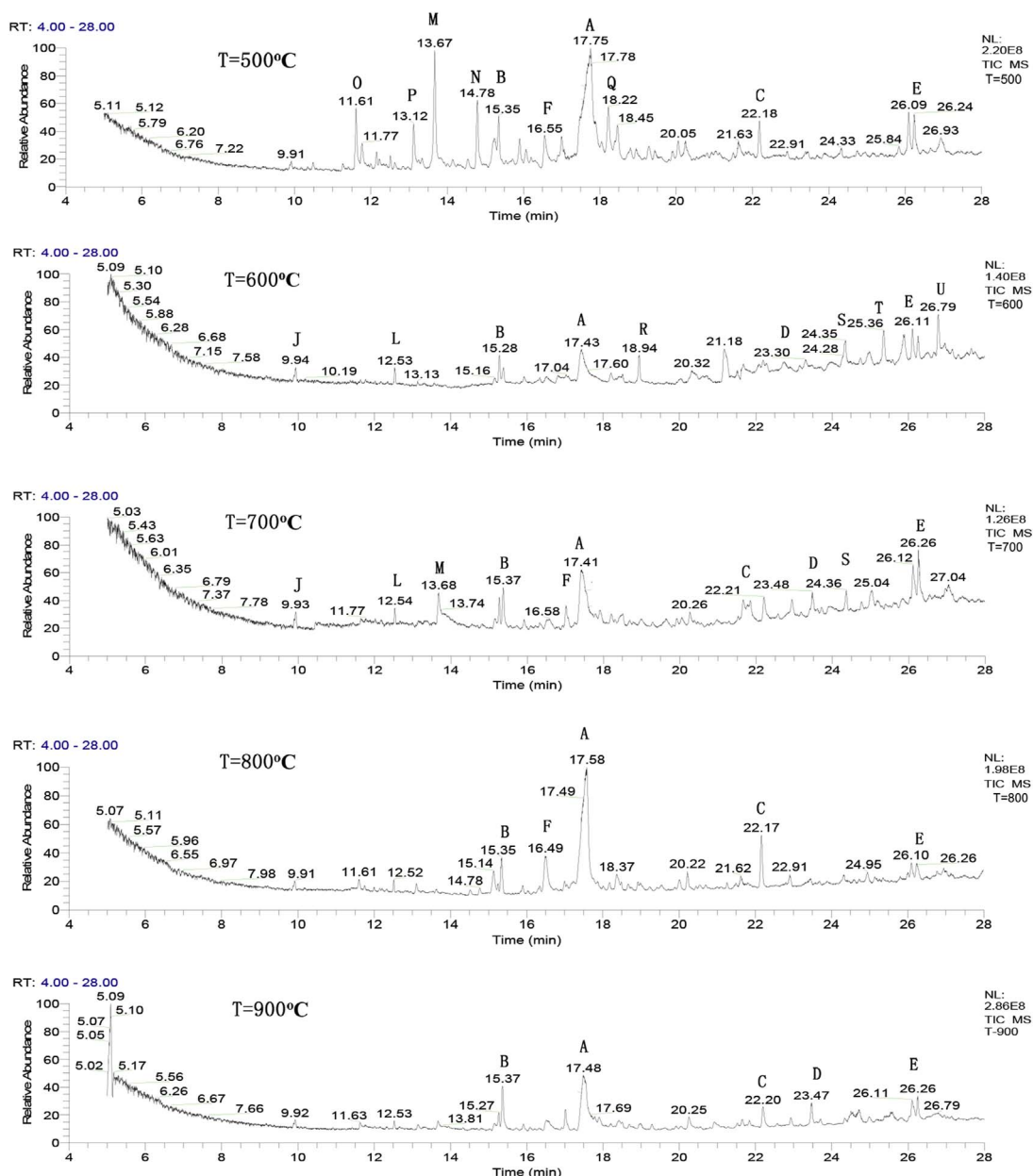
3.2. Quantitative analysis of tar generated under different conditions

Quantitative analysis of tar was carried out in this part. Due to the complexity of tar itself and the variety of tar composition produced under different conditions, the analysis will not be focused on specific compounds. Considering that the relative molecular weight of tar components under different conditions were in the range of 100–700, all compounds in tar were classified into three categories, denoted as A, B and C, which the molecular weights were in the range of 100–300, 300–500 and 500–700, respectively. And the normalized method was used to calculate and analyze the total mass fraction and total mass concentration of each molecular weight segment.

3.2.1. Effect of S/B

In the biomass gasification process, steam can be used as a good medium to increase the H₂ concentration and the gas yield. Moreover, it had been reported that the presence of steam is beneficial for the reduction of tar [33,34]. In this section, the effect of S/B on tar yield was discussed, with Cu5Fe5 as OC under the condition that the temperature was 800 °C and the O/B was 0.4. As shown in Fig. 3, the number of response peaks in the tar decreased obviously after the introduction of water vapor, which indicated that the types of organic matter in tar were reduced. Additionally, with the increase of S/B, the number of the response peak in the tar sample showed a decreasing trend, and the abundance of the response peak also decreased, which demonstrated that the increase of water vapor content can promote the decomposition and transformation of tar.

The effect of S/B on the mass fraction and concentration of the three classes of tar components is shown in Fig. 4. As seen, class A is always



M: Octanoic acid, 6-ethyl-3-octyl ester; N: 4-Ethylcatechol; O: Catechol; P: 1,2-Benzenediol, 4-methyl-; Q: D-Glucopyranoside-; R: 2,4,6-Trimethylmandelic acid; S: 9,12,15-Octadecatrienoic acid; T: Geranyl isovalerate; U: tert-Hexadecanethiol

Fig. 6. Total ion chromatogram of tar under different temperatures.

the main constituent of tar and class C represents the minimum yield. When comparing the tar compositions under conditions of S/B at 0.25 and S/B at 0, it can be found that both the fraction and concentration of class A were significantly reduced when steam was introduced, which decreased from 62.41% to 9.48 g/kg to 44.11% and 4.23 g/kg, respectively, while the decrease of the concentrations of class B and C was not so obvious. It can be speculated that steam addition was more beneficial for the conversion of small molecules when compared to macromolecular substances. With the amount of steam increased to S/B

of 0.5, both the fraction and concentration of class B and C decreased significantly, while the concentration of class A increased. It can be inferred that the increased steam concentration promoted the transformation of class B and C into class A. And when the amount of steam was further increased, the fraction and concentration of class A decreased, while the concentration of class B changed little. It can also be found that the effect of steam on the reduction of larger molecular compounds, *i.e.*, class B and C, was not obvious when the S/B was higher than 0.75.

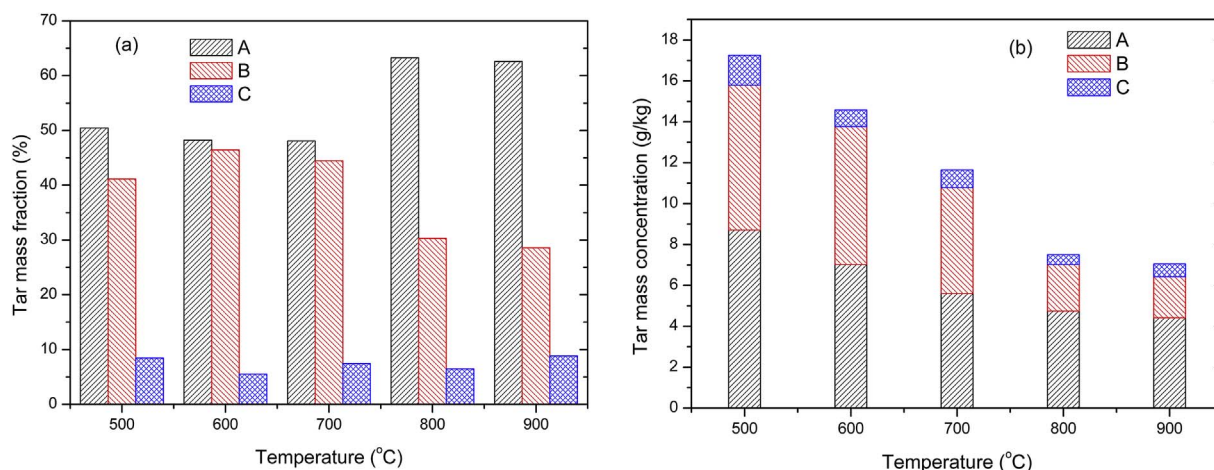


Fig. 7. The effect of temperature on the mass fraction (a) and concentration (b) of three tar components.

To further understand the change of macromolecular tar components with the increase of steam addition, the efficiency in reducing the original quantity of Class C tars as the S/B ratio increases was calculated. As shown in Fig. 5, the promotion efficiencies were obtained by dividing the Class C mass concentration (for each S/B value) by the Class C mass concentration for S/B = 0. It is obvious that the mass concentration of Class C decreased significantly when the ratio of S/B increased from 0.25 to 0.5. And with the further addition of steam, the mass concentration of Class C substances continued to decline, but the decline degree was significantly reduced. In this sense, it can be inferred that the excessive steam addition may result in a decrease of reduction efficiency for macromolecular organic compounds in tar.

From the discussion above, it can be found that the proper amount of steam addition can effectively promote the decomposition of large molecular organic matters into small ones, which would be further converted into syngas. Nevertheless, typical high steam content had no obvious effect on the reduction of large molecules in tar. Moreover, excessive steam addition would consume plenty of heat, which eventually led to a lower gasification temperature in a real auto-thermal operated reactor, and this phenomenon has also been observed by other researchers [35,36]. Lower gasification temperature may affect the reactivity of OC, and inhibit the transformation of large molecular compounds into smaller ones.

3.2.2. Effect of temperature

The effect of temperature on tar yield was evaluated within the temperature range of 500–900 °C, using Cu5Fe5 as OC. The O/B was 0.4 and the S/B was kept at the optimal value of 0.75. Fig. 6 shows the total ion chromatogram of tars collected under different temperatures. As it can be seen, with the increase of temperature, the types of response peak in the sample decreased gradually. The result indicates that the increase of temperature is beneficial to the decomposition and transformation of tar into small molecules.

Fig. 7a shows the mass fraction variation of class A, B and C compounds in tar under different temperatures. The mass fractions of the three kinds of compounds were 50.45%, 41.12% and 8.43%, respectively, at 500 °C. It can be found that the mass fractions variation of the three kinds of compounds in tar was not significant when the temperature was below 800 °C. However, when the temperature was raised to 800 °C, the mass fraction of the class A increased from 48.09% at 700 °C to 63%, while the mass fraction of class B decreased obviously from 44.44% at 700 °C to 30%, and the mass fraction of class C showed

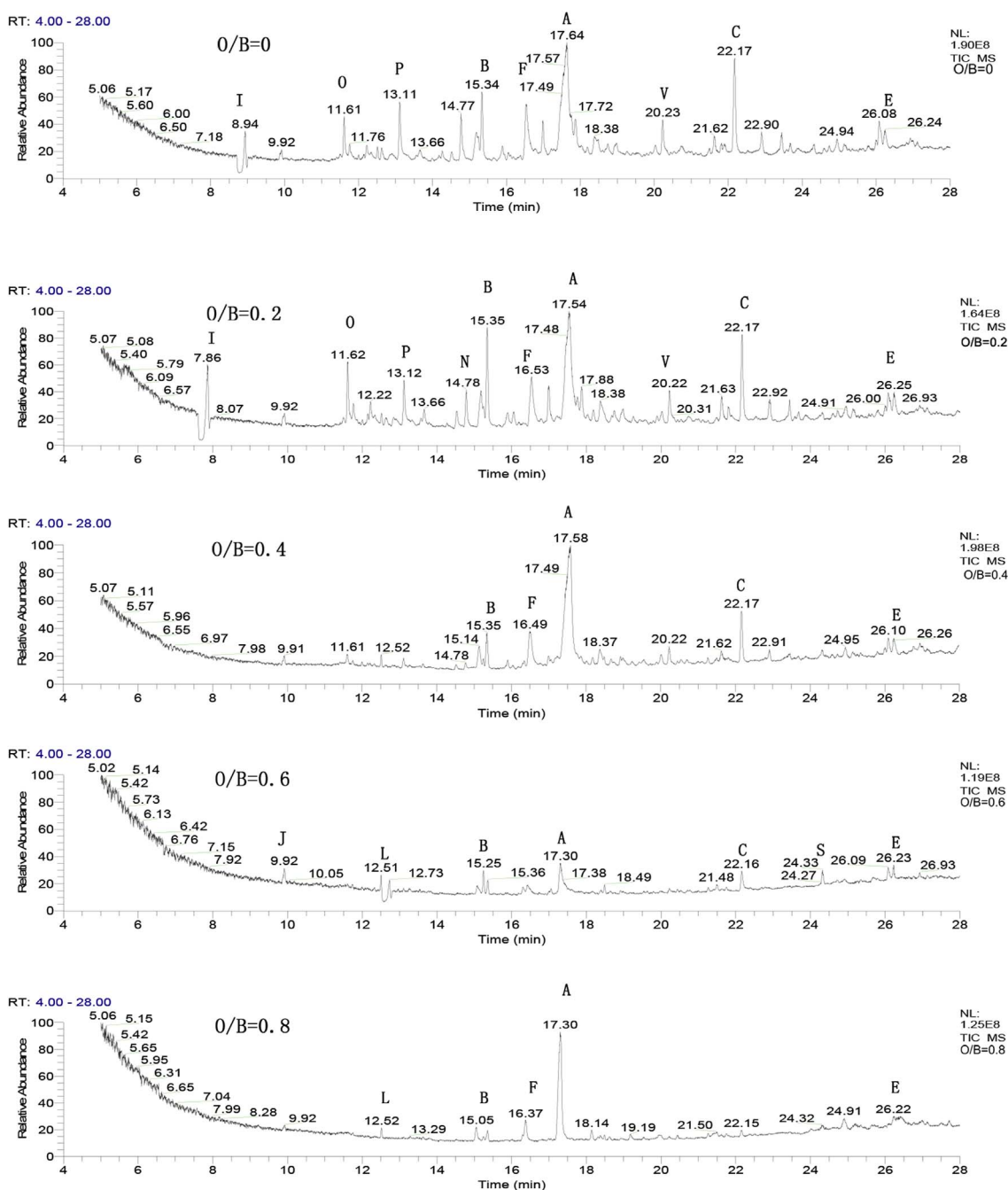
little change. As the temperature kept increasing, the content of each compound was basically unchanged again. Fig. 7b shows the mass concentration of the three kinds of compounds in tar. It was observed that the total mass concentration of tar presented a downward trend with the increase of temperature. Among the three compounds, both the yield of class A and B decreased, while the change of class C was not so significant due to its naturally typical low concentration. And the change of class B was especially significant when the temperature increased to 800 °C. More specifically, the mass concentration of class B decreased from 5.18 g/kg at 700 °C to 2.27 g/kg at 800 °C, and it was 7.09 g/kg at 500 °C.

As can be concluded from the results shown above, the increase of temperature was beneficial to the decomposition and conversion of the large molecular compounds into small ones. In addition, the increase of temperature can also promote the conversion of small molecular compounds into syngas [37,38]. On the one hand, higher temperature can improve the reactivity of OC and promote the reaction between OC and organic macromolecular. On the other hand, higher temperature can also provide enough energy for the fracture of the internal chemical bond of organic molecules. In this sense, a higher temperature is necessary for the primary reduction of tar during the biomass-derived CLG process.

3.2.3. Effect of O/B

In this section, the influence of O/B on the reforming of tar was investigated, also using Cu5Fe5 as OC. The values of S/B and temperature during reaction were maintained at 0.75 and 800 °C, respectively. Fig. 8 shows the total ion chromatogram of tar under different O/B conditions. It can be found that with the addition of OC, there were less response peaks detected. And when O/B was 0.2 and 0.4, the numbers of sample detection response peaks were larger than those under the conditions of 0.6 and 0.8, indicating more complicated sample compositions in the tar generated.

The variation of tar contents in each sample under different O/B values is shown in Fig. 9a. With the increase of O/B, the mass fraction of class A increased first and then decreased, while the mass fraction of class B and C decreased first and then increased. As shown in Fig. 9b, when Cu5Fe5 OC was not introduced, the mass concentration of class A, B and C compounds were 8.03 g/kg, 4.57 g/kg and 1.95 g/kg, respectively. And when O/B was 0.2, the mass concentration of the three kinds of compounds decreased significantly, especially for class B and C, which decreased to 1.60 g/kg and



V: Ethanone, 1-(1-hydroxy-2,6,6-trimethyl-2,4-cyclohexadien-1-yl)

Fig. 8. Total ion chromatogram of tar under different O/B conditions.

0.57 g/kg, respectively. When the value of O/B continued to increase to 0.4 and 0.6, the mass concentration of B and C changed little, while the mass concentration of the class A decreased to 4.74 g/kg at O/B = 0.4 and 2.4 g/kg at O/B = 0.6, respectively. However, further increase of O/B showed no significant change in the fractions of tar. Moreover, the increase of O/B would consume a large amount of syngas, which led to the decrease of gas production quality [10]. And this was not a desirable outcome.

According to the results obtained above, it can be inferred that

the presence of OC will promote the transformation of macromolecular compounds (Class C) into small molecules. Additionally, the OC will react with small molecules to generate syngas and other products. But with the increase of OC feeding amount, the improvement of the catalytic reactivity was not so significant, which may be explained by the limited catalytic performance of Cu5Fe5 OC. And the increase of OC amount may reduce the reduction degree of the OC, which will eventually affect the cracking and transformation of tar.

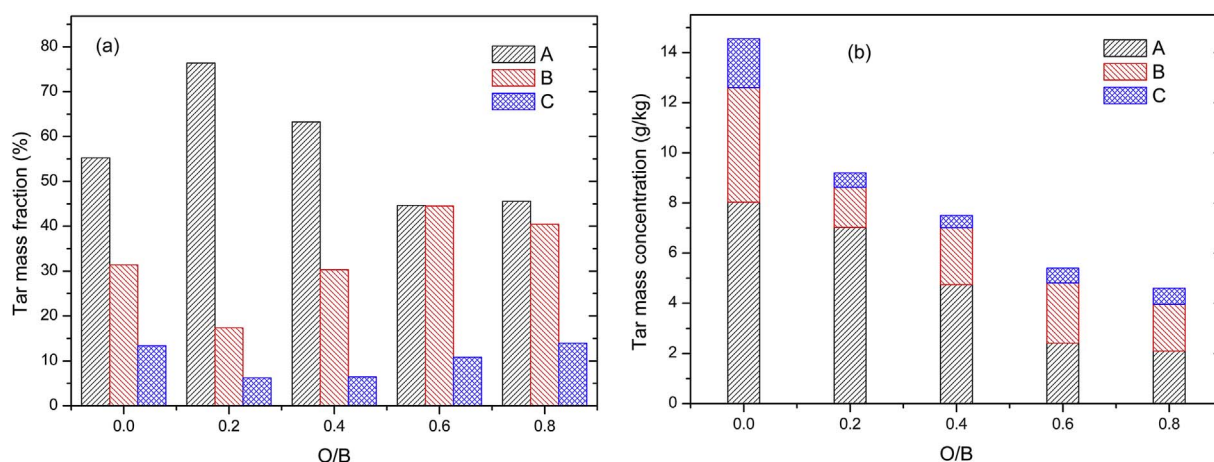


Fig. 9. The effect of O/B on the mass fraction (a) and concentration (b) of three tar components.

3.2.4. Effect of CuO/Fe₂O₃ molar ratio in the OC

To explore the effect of Cu and Fe components in the OC on tar yield, the performance of other four kinds of Cu-Fe OCs (obtained by changing the molar ratio of CuO/Fe₂O₃) in biomass-derived CLG process was also investigated. In this section, the effects of CuO/Fe₂O₃ molar ratio in the Cu-Fe OCs on tar yield were explored under the condition of 800 °C, O/B = 0.4 and S/B = 0.75. Fig. 10 shows the total ion chromatogram of tar with different OCs, and quartz sand was chosen as the blank material. As it can be seen, with the decrease of Cu content in the OC, more detection response peaks were observed, which indicated that more complicated compositions of the tar were generated during the biomass gasification process.

The variations of the mass fraction in tar when using different OCs are shown in Fig. 11a. It can be found that with the decrease of Cu content in the OC, the mass fraction of class A increased first and then decreased, while the mass fraction of class B decreased first and then increased. And the mass fraction of class C decreased gradually. As can be detected from Fig. 11b, the total mass concentration of tar decreased significantly with the increase of Cu content in the OC, which was in accordance with the ion chromatogram analysis results presented above. As for the variation of the three classes of compounds, it can be found that the mass concentration of class A, B and C were the highest for the blank test. In this sense, the addition of OC can effectively reduce the yield of the three kinds of compounds to a certain extent.

With the decrease of Cu content in the OC, the mass concentration of class A increased gradually, while the mass concentration of class C showed a decreasing trend. The mass concentration of the class B was essentially unchanged till when there was less than 50 mol% of CuO content in the OC sample, and then the mass concentration of class B increased gradually. When pure CuO was used as OC, the mass concentration of class A was the minimum, which was only 1.33 g/kg, while the mass concentration of class C got the maximum value of 1.63 g/kg when compared with the other four kinds of OCs. However, when pure Fe₂O₃ was used as OC, the mass concentration of class C reached the minimum, and both the mass concentration of class A and B came to the maximum, which were 6.81 g/kg and 5.35 g/kg, respectively.

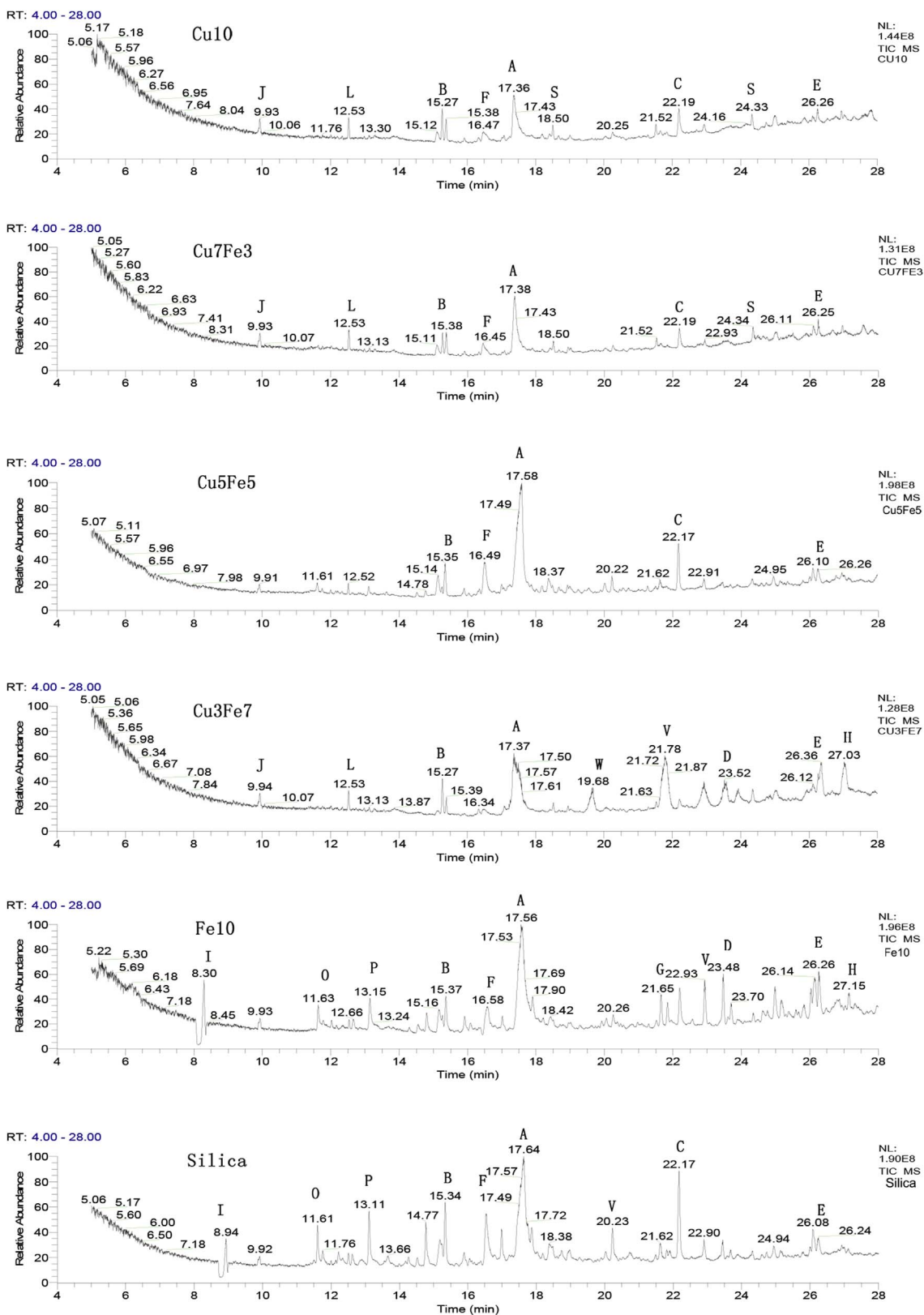
It can be inferred that the Cu component in Cu-Fe OC was conducive to reducing the yield of these small molecular compounds in tar, such as class A and B compounds. This may be mainly attributed to the higher

reactivity of Cu components, which is beneficial to the reaction of OC with smaller molecular weight tar components. In addition, it was found that Cu content has no obvious promotion effect on the transformation of large molecules in tar. However, the increase of Fe content in OC was beneficial to decrease the yield of large molecular weight compounds. From this perspective, the Fe component can be used as a catalyst for the cleavage of large molecular compounds into small ones. The results indicate that Cu-Fe bimetallic OCs demonstrated a synergistic effect in the treatment of tar.

4. Conclusion

The tar evolution characteristic in the biomass-derived chemical looping gasification process was investigated under different conditions with synthetic Cu-Fe metal oxides as OC. The tar collected when using Cu₅Fe₅ as OC was first qualitatively analyzed. The results showed that the molecular weight of the compounds in tar was mostly concentrated at about 200 and the mass content D-Allose was the highest, as 29.61%.

According to the quantitative analysis of tar collected under different experimental conditions, it was found that the increase of steam concentration can effectively promote the decomposition of macromolecular compounds in tar into small ones, which were further converted into syngas. However, typical high steam content had no obvious effect on the reduction of large molecules in tar. The increase of temperature was beneficial to the decomposition and transformation of tar molecules. A higher temperature condition was favorable for the decomposition and conversion of class B compound (with larger molecular weights) into class A compound (with smaller molecular weights). The relatively low O/B value (< 0.6) posed a significant influence on the tar yield, while the variation of tar yield was not obvious when the O/B was higher than 0.6. The effect of CuO/Fe₂O₃ molar ratios in the Cu-Fe OCs on the tar yield was also investigated. It was found the Cu component can reduce the tar yield by reacting with small molecular weight compounds, while its catalytic reactivity towards macromolecular compounds was not so obvious. As for the Fe component, it exhibited relatively low reactivity on the catalysis of small molecule compounds in tar, while it was beneficial to decrease the yield of high molecular weight compounds. To sum up, Cu-Fe metal oxides OC can achieve synergistic effect in the treatment of tar.



W: Benzene, 1,1'-(1,3-butadiyne-1,4-diyl)bis-

Fig. 10. Total ion chromatogram of tar with different bed materials.

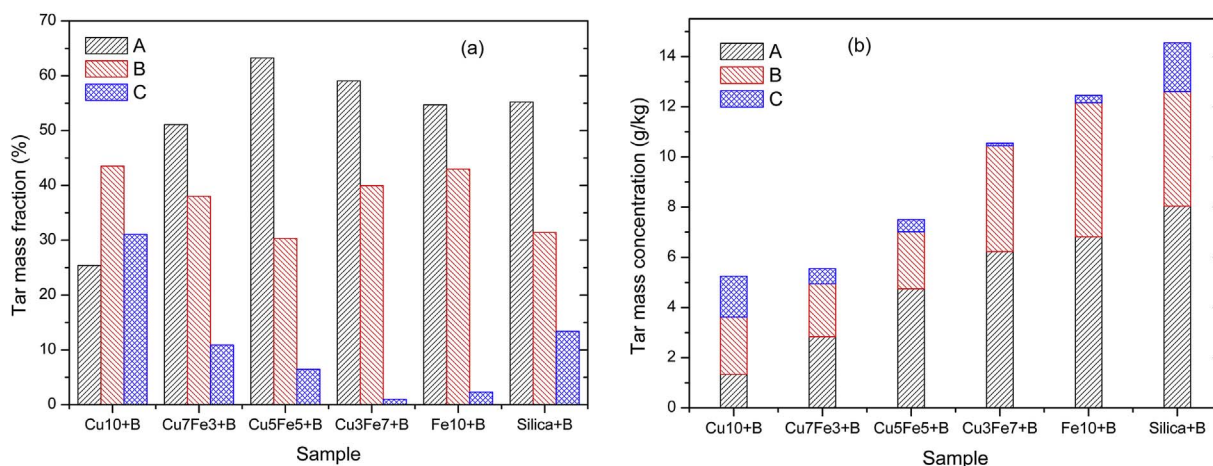


Fig. 11. The variation of the mass fraction (a) and concentration (b) of three tar components with different samples.

Acknowledgements

These authors were supported by “National Natural Science Foundation of China (No. 51522603)”. Mr. Lei Guo is appreciated for preliminary sample analytical work.

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