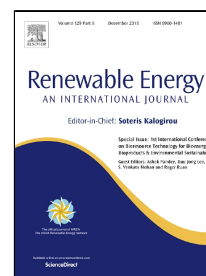


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Experimental Investigation of Tar Formation and Producer Gas Composition in Biomass Steam Gasification in a 100kW Dual Fluidised Bed Gasifier

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Abstract

In this study, three types of biomass including corn stover, radiata pine wood and rice husk in the form of pellets were gasified with steam as gasification agent in a 100kW dual fluidised bed gasifier. Tar formation in initial devolatilization stage and its correlation to the final tar concentration in the producer gas were investigated. In addition, the yields and composition of the producer gas for each type of biomass were also examined. In the gasification experiments, operating temperature was controlled, respectively, at 700°C and 800°C. Silica sand was used as the bed material with an inventory of 30kg. For simulation of the initial devolatilization stage in the steam gasification, N₂ was used as fluidisation agent.

From this study, it is found that there was a positive correlation between tar contents in the devolatilization product gas and those in the final producer gas from gasification. In the devolatilization stage, radiata pine biomass yielded more phenols, while corn stover generated more toluene. Based on the results of this study, tar formation mechanism was proposed which is verified by the observation that more naphthalene was present in the producer gas from gasification of radiata pine while gasification of corn stover produced more biphenyl. The experimental results also show that at gasification temperature of 700°C, the producer gas yield was the highest for corn stover followed by rice husk and then radiata pine wood. However, for gasification at

800°C, the trend was reversed with radiata pine having the highest yield followed by risk husk and the corn stover. At both 700 and 800°C, the radiata pine biomass produced a producer gas with higher contents of H₂ and CH₄ while the producer gas from rice husk had a higher content of CO and that from corn stover had a higher content of CO₂, C₂H₄ and C₂H₆. These differences are closely related to the chemical composition of the biomass which was also analysed in this study. Radiata pine had a higher content of lignin (31.96wt%), rice husk had a higher content of hemicellulose (25.30wt%) while corn stover was rich in cellulose (69.85 wt%).

Keywords: biomass steam gasification, devolatilization, producer gas composition and yield, tar formation and transformation, biomass chemical composition.

1. Introduction

Recently, extensive research has been conducted to optimise and commercialize biomass gasification technology for production of hydrogen-rich syngas [1-3]. The biomass is widely available [4] and can be used as one of the key renewable resources for the future energy production [5]. The key advantage of gasification technology is the high efficiency (70-80%) of converting a solid fuel into a gas which provides flexibility for it to be used for various energy products [6]. However, during the gasification process, part of the fuel is transformed into condensable tar compounds [7-9] which is one of most problematic by-product in biomass gasification processes. The tar compounds exist in the vapour phase in the gasifier but condense into liquid droplets while being cooled in gas transportation and ion downstream processing. Once condensed, the tar may block the pipes and valves, and contaminates the processing equipment, therefore, tar is one of the technical issues that hinder the commercialization of biomass gasification technology [10].

In previous studies, tar removal technologies have been developed [11-14] which can be characterized into two approaches: (i) primary method in which tar is reduced within the gasifiers, and (ii) secondary method in which tar is removed through post-gasifier processes [15]. Although tar removal after gasification is necessary to achieve the gas purity required by the downstream processing, it increases operating costs and reduces the overall efficiency of the gasification process [16]. The objectives of this project

were to understand and reduce the tar formation during biomass gasification, and to investigate the effect of chemical composition of biomass on tar yield and producer gas composition.

Tar formation is the result of a series of complex chemical reactions and molecular structure change. Tar concentration and composition in the gas product are dependent on the operational conditions, gasifier type, bed material used and biomass type. It has been reported that tar-cracking reactions are endothermic [16-21], therefore, increasing operation temperature is expected to promote the cracking reactions thus decreasing tar concentration in the producer gas. Meanwhile, using steam as gasification agent has been observed to favour the tar reforming reactions [20]. Feedstock properties have noticeable effects on the tar formation. Different biomass materials can have different chemical proportions of cellulose, hemicellulose and lignin. The difference in chemical composition and nature of these three components can also significantly affect tar characteristics. A better understanding of the tar formation mechanism would be helpful to hinder the tar formation and thus to reduce the tar concentration in the gas product.

Biomass gasification is known to proceed as a two-stage process, which includes the initial devolatilization in which primary tar and char are formed, and the subsequent gasification process in which the final gas product and tars are formed through the secondary reactions. However, there is a knowledge gap on the correlation of products between devolatilization and final gasification. Our previous studies [22-24] has indicated that gasification temperature, residence time and steam to biomass (S/B) ratio had varying impacts on the gas and tar products during steam gasification. From these results, it can be found that the total tar concentration in the syngas was reduced by increasing the temperature, residence time and S/B ratio, respectively. However, the effects of major biomass components, such as cellulose, hemicellulose and lignin on the correlation between the devolatilization and the final steam gasification are still unknown.

At present, most studies assume that the initial devolatilization in biomass gasification is the same as independent biomass pyrolysis, and the reaction models for the pyrolysis are proposed based on assumption that the decomposition of cellulose, hemicellulose and lignin takes place independently without interaction among the three components

[25-29]. It is known that cellulose contains more OH and C-O chemical groups, hemicellulose has a higher proportion of C=O compounds [30, 31], while lignin is rich in methoxyl-O-CH₃, C-O-C and C=C chemical groups [32]. The chemical composition of feedstock will affect the products from pyrolysis and consequently the final producer gas from gasification. From experimental study on a bench-scale entrained gasifier, Yu et al. [33] reported that in lignin gasification, PAHs as the key compounds of tar were mainly derived from phenols whereas in gasification of cellulose and hemicellulose, PAHs were mainly derived from benzene, toluene and hydrocarbons.

In contrast, Qin et al [34] reported that the PAHs were mainly from phenol as a precursor in the gasification of cornstalks (rich in cellulose) due to oxygen-containing compounds in cellulose. The conflicting results reported in literature may be due to the interaction among the biomass components during the initial devolatilization and subsequent gasification. In addition, most of the reported studies were based on bench-scale experiments.

The present study was designed to investigate the effects of biomass chemical composition on tar formation in the initial devolatilization and its transformation in the subsequent gasification. The biomass species, corn stover, rice husk and pine wood, were selected based on their compositions with different contents of cellulose, hemicellulose and lignin. Experiments were conducted on a pilot scaled (100kW) dual fluidised bed steam gasifier.

2. Experimental and materials

2.1. Materials and chemical analysis

In the present study, three types of biomass were chosen to represent feedstocks with different compositions: corn stover for its high cellulose content, rice husk for its high hemicellulose content and pine wood pellets for its high lignin content. The selected biomass was in the form of pellets of 10-15 mm long and 6 mm in diameter. Using pellet ensured that the variability for a given biomass species can be minimised thus other variables can be identified and investigated. In addition, the feeding of the biomass to the gasifier was problem-free in the experiments. However, the results from

this study are applicable to large gasification systems where biomass in its original forms can be consistently fed.

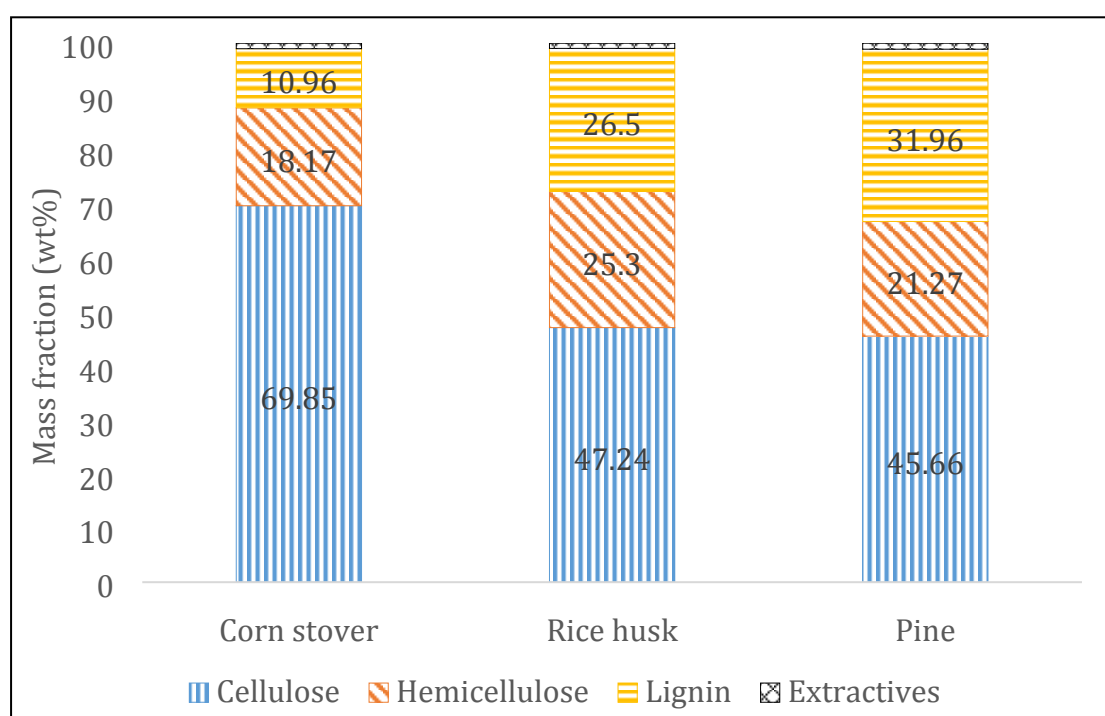
Corn stover was supplied by a local farm in New Zealand which was processed to pellets in our laboratory. Pellets of rice husk were provided by a company in Indonesia. Pellets of radiata pine were purchased from a local retailer in Christchurch, New Zealand.

Before the gasification experiments, samples of each type of biomass were sent to a commercial lab for proximate analysis and ultimate analysis, and the results are presented in Table 1. In addition, the chemical composition of each biomass was also determined in this study. The lignin content was measured based on TAPPI Standard methods, and the holocellulose (cellulose and hemicellulose) was tested by the modified method from Pettersen [35]. The results on the composition of these three feedstocks are shown in Fig. 1. By comparing these three types of biomass, it is found that corn stover is rich in cellulose (69.85wt%), pine has the highest content of lignin (31.96wt%), and rice husk has the highest content of hemicellulose (25.30wt%).

Table 1. Results of proximate and ultimate analysis of the three types of biomass species.

		Corn stover	Rice husk	Pine
Proximate (%) (received basis)	Method			
Total moisture	ISO5068	10.4	8.9	8
Volatile matter	ISO 562	73.3	52.5	77.4
Fixed carbon	By difference	12.2	20.6	14.2
Ash	ASTM D1102	4.1	18	0.4
Ultimate (%) (Dry Basis)				
Carbon	Microanalytical	48.5	38.5	51.3
Hydrogen	Microanalytical	6.2	5.2	5.8
Nitrogen	Microanalytical	1.1	0.5	<0.2
Sulphur	ASTM D4239	0.03	<0.1	<0.1
Oxygen	By difference	44	34.7	42.6
LHV (MJ/kg) (dry basis)	ISO1928	18.2	13.2	14.4

150



151

152 Fig. 1. Cellulose, hemicellulose and lignin contents in three types of biomass.

153

154 **2.2. Equipment and procedures**

155 Experiments were conducted on a 100kWth dual fluidised bed (DFB) gasifier system
 156 which schematic diagram is shown in Fig. 2. There are two columns in this gasifier
 157 system, one is the bubbling fluidised bed (BFB) column, that has an internal diameter
 158 of 0.2 m with a height of 2 m; the other is the fast-fluidised bed (FFB) column, which
 159 has an internal diameter of 0.1 m and length of 3.7 m.

160

161 In the biomass gasification, the reactions occur in the BFB column, in which the gas
 162 products (syngas) flows out from the top of BFB. At the same time, solid char generated
 163 from the gasification process and the bed material flow out from the bottom of BFB,
 164 by gravity, to the FFB column where the char is combusted and the bed material is
 165 heated. Supplementary liquefied petroleum gas (LPG) is added into FFB, if required,
 166 to provide enough heat. Then the hot bed material is carried up by the flue gas into a
 167 cyclone where the bed material is separated from flue gas and flows into the BFB
 168 column through a siphon to provide heat for the endothermic gasification process. The
 169 siphon acts as a seal to prevent by-pass flow of flue gas into the BFB column and to
 170 prevent the producer gas flow into the cyclone. In this way, there is no mixing between
 171 the flue gas from the FFB and the product gas from BFB.

In order to investigate the correlation between tar yields in the early devolatilization stage and the tar concentration in the producer gas from gasification, both devolatilization and gasification experiments were performed at the gasifier. In the experiment of devolatilization, N_2 was used as a fluidization agent, while in the gasification experiments, steam was used as the gasification and fluidization agent. More detailed descriptions of the DFB gasifier are given elsewhere [24].

In each of the experiments, 10 kg of silica sand with an average particle size of $245\mu m$ was initially introduced to the DFB gasifier as bed material. Then the two columns were heated up by combustion of LPG ($35 \sim 40$ L/min) with air in which period air was also introduced into the chute and the siphon to assist the bed material circulation. Once the target temperature in the BFB column was achieved, additional 20 kg of the same bed material was gradually introduced to the gasifier through the bed material charger. After this, the air supply to the BFB, chute and siphon was gradually changed over to steam for the gasification tests or N_2 for the devolatilization tests. LPG supply to the FFB was controlled to maintain the BFB temperature at the required point.

When the system was stable for 20 minutes, biomass was fed into the BFB bed through a screw feeder. The biomass feeding rate was varied according to biomass type and preset steam to biomass (S/B) ratio. The S/B ratio was defined as total water mass (the supplied and the water in the biomass) divided by the weight of dry and ash free (daf) feedstock, and it was controlled as 0.89 for all of the gasification experiments. Once the gasification tests were completed, the steam supply was replaced by N_2 gas for the devolatilization tests. The operation conditions of the gasification experiments in the present study are given in Table 2.

204 **Table 2.** The operating conditions of the present study on the DFB gasifier.

Test		Devolatilization	Gasification
Bed Material	(kg)		30
Gasifier temperature	(°C)		700, 800
Combustor temperature	(°C)		750-850
Nitrogen to BFB	(Nm ³ /h)	6.19	-
Nitrogen to Chute	(Nm ³ /h)	1.57	-
Nitrogen to Siphon	(Nm ³ /h)	2.02	-
Steam to BFB	(kg/h)	-	7
Steam to Chute	(kg/h)	-	2
Steam to Siphon	(kg/h)	-	1.5
S/B ratio		-	0.89
Corn stover	(kg/h)		15.8
Rice husk	(kg/h)		18.5
Pine	(kg/h)		14.2

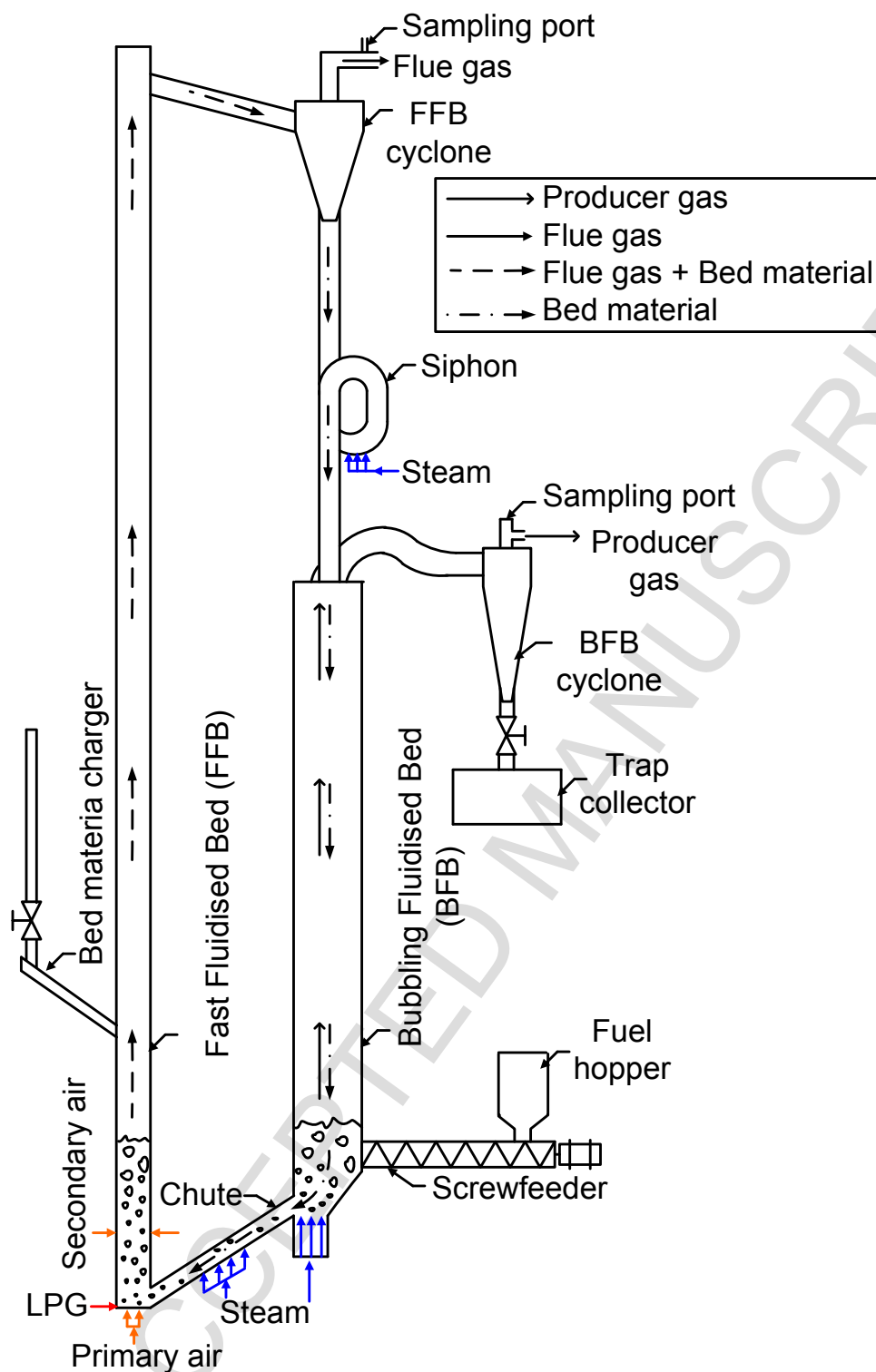


Fig. 2. Schematic diagram of dual fluidised bed steam gasifier [36].

2.3. Products analysis and characterization

The methods for sampling and analysis of the producer gas and tar were developed in previous studies [23, 24, 36, 37]. Producer gas was analysed off-line by an Agilent 3000 micro gas chromatography (GC). H_2 , CO , CH_4 and N_2 were analysed with a 10 m ×

0.32 mm molecular sieve 5A Polt column with argon as carrier gas while CO₂, C₂H₄ and C₂H₆ were analysed by an 8m × 0.32 mm Plot Q column with helium as carrier gas.

In the tar sampling, a controlled volume of producer gas was extracted from the gasifier sampling line using a specially designed syringe in which the tar was absorbed by a filter. Detailed descriptions of the methods of tar extraction and analysis are given elsewhere [7, 30-32]. The classification of tar compounds detected in the present study was listed in Table 3. Class 1 tar was characterized as very heavy compounds which are undetectable using GC and its content was very low thus it is ignored in this study. The remaining tars (Class 2 to Class 5) were analysed using a Varian CP-3800 GC with a flame ionisation detector (FID).

Table 3. The classification of tar compounds detected in the present study according to Kiel et al. [38].

Tar class	Class name	Compounds
Class1 (C1)	GC-undetectable	Very heavy tars, cannot be detected by GC
Class2 (C2)	Heterocyclic	Pyridine, Phenol, Cresol
Class3 (C3)	Light aromatic (single rings)	Toluene, Xylene
Class4 (C4)	Light polyaromatic hydrocarbon (PAH) compounds (2-3 rings)	Naphthalene, Biphenyl, Phenanthrene
Class5 (C5)	Heavy PAH compounds (4-7 rings)	Fluoranthene, Pyrene, Chrysene

3. Results and discussion

3.1. Gas products

In the following discussion, the producer gas yield was determined as the mass yield of the producer gas per kg of dry and ash-free biomass, which was the total volumetric yields of all gas species (H₂, CO₂, CO and CH₄) times their corresponding standard densities in the producer gas. The results for the three types of biomass at the gasification temperatures of 700°C and 800°C are shown in Fig. 3. From this figure, it can be seen that at 700°C, the producer gas yield was 0.58 kg/kg_{daf} for corn stover, 0.55

kg/kg_{daf} for rice husk and 0.54 kg/kg_{daf} for pine. However, at 800°C, the producer gas yields were increased for all of the biomass species and the pine had the highest gas yield (0.81 kg/kg_{daf}) followed by rice husk (0.78 kg/kg_{daf}) while the gas yield for corn stover was the lowest at 0.63 kg/kg_{daf}. It is known that high temperature favours the producer gas generation, however, effects of the gasification temperature varied with biomass species which can be attributed to differences in biomass chemical composition (cellulose, hemicellulose and lignin) as measured in this study.

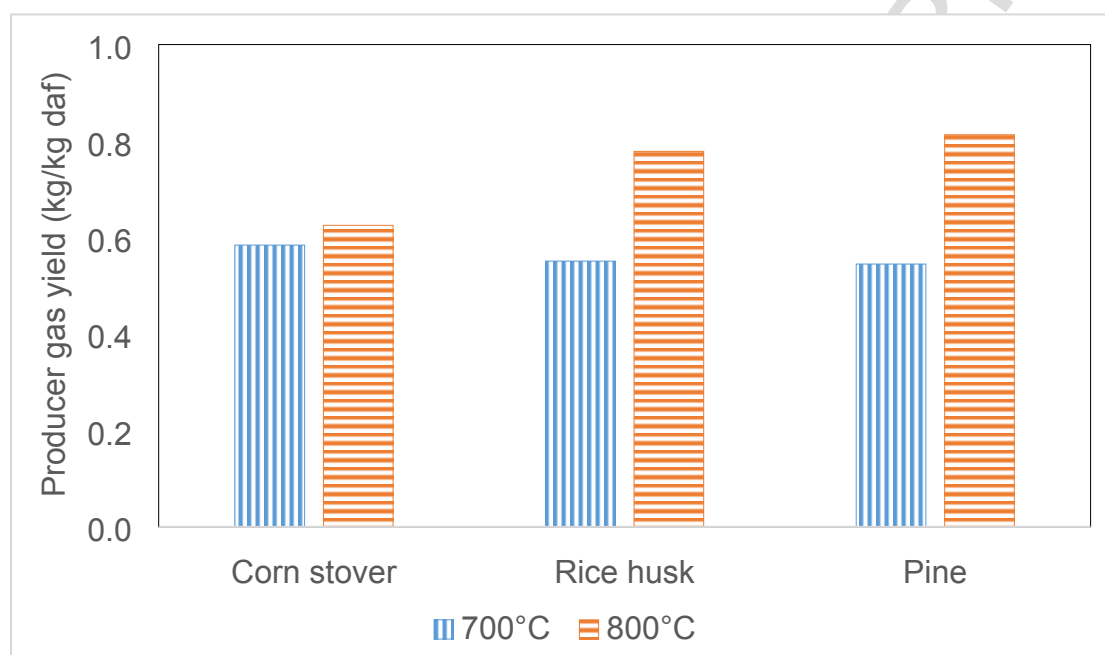


Fig. 3. Yields of producer gas in the gasification of corn stover, rice husk and pine at 700 and 800°C.

From these findings, it is believed that the cellulose, hemicellulose and lignin in the biomass play a different role for gasification process, since their thermal stability and cracking characteristics are different. Cellulose and hemicellulose start to decompose at the temperature of 250-400°C [39], therefore, the corn stover, which contained 88% of combined cellulose and hemicellulose, would have released most of the volatiles at 700°C, thus further increasing the gasification temperature had only marginal impact on the gas yield. On the other hand, lignin is more difficult to decompose and needs much higher temperature for complete decomposition. Therefore, the gasification temperature had a significant effect of the lignin-rich pine (31.96% lignin) and rice husk (26.5% lignin). It was also reported that the lignin-rich biomass would generate more char in the gasification [40].

Table 4 presents results of composition and lower heating value (LHV) of the producer gas from gasification of the three biomass species at the temperature of 700 and 800°C. From Table 4, it is seen that the CO₂, C₂H₄ and C₂H₆ contents in the producer gas in the gasification of corn stover were significantly higher than those from gasification of both pine and rice husk. In contrast, the contents of H₂ and CH₄ from pine gasification were higher than those from gasification of corn stover and rice husk. Meanwhile, in the rice husk gasification, CO content in producer gas was the highest.

The results of gas composition in this study are consistent with those reported in literature. Yang et al. [41] have reported that cellulose and hemicellulose with higher carboxyl content had higher yields of CO and CO₂ as well as the higher presence of aromatic ring and methoxyl in the volatile gas during pyrolysis which is similar to process of initial devolatilization stage during gasification. Decomposition and cracking of lignin at high temperatures released volatiles with high contents of H₂ and CH₄. A separate report also found that in the gasification process, the derivatives from cellulose decomposition were readily cracked into gases of light hydrocarbons such as C₂H₄ and C₂H₆ [32].

Table 4. Composition of producer gas from the gasification of three types of biomass at gasification temperatures of 700 and 800°C.

	700°C			800°C		
	Corn stover	Rice husk	Pine	Corn stover	Rice husk	Pine
Gas composition (mol%)						
H ₂	22.7	22.4	25.0	25.9	28.1	30.7
CO	28.1	36.8	35.2	28.9	37.1	36.3
CO ₂	29.8	23.9	22.3	26.3	18.3	16.2
CH ₄	11.1	12.0	12.8	10.1	11.3	12.1
C ₂ H ₄	6.9	3.8	3.7	8.1	4.6	4.2
C ₂ H ₆	1.4	1.0	1.0	0.7	0.5	0.6
Lower Heating value (MJ/Nm³)						
	13.4	12.9	13.2	13.7	13.4	13.6
Supplementary LPG (L/min)						
	9.3	7.2	6.5	16.8	20.2	15.1
Cold gas efficiency (%)						
	64	61	62	65	67	69

Table 4 also gives results of the cold gas efficiency (CGE) of the gasifier system and the lower heating values (LHV) of the producer gas which are important parameters to assess the gasifier performance and producer gas quality. The CGE was the chemical energy content in the producer gas divided by the total input energy, including the energy in the biomass feedstock, the supplied steam and supplementary liquefied petroleum gas (LPG) to the FFB column. The supplementary LPG was used to maintain the gasification temperature in BFB at pre-set value when the char generated from the gasification was not sufficient during the gasification stage, although the LPG use was much less than that in the start-up stage (Table 4). However, in the full commercial gasification plant, LPG may only be needed in start-up stage as the relative heat loss in a large-scale plant is much less than in the pilot scale plant.

At 700°C, the gasification of corn stover presents a higher CGE (64%) because the producer gas had a high content of C_2H_4 and C_2H_6 and, consequently, a higher LHV. However, for gasification at 800°C, the LHVs of the producer gas from the three types of biomass were similar (13.4 to 13.7 MJ/Nm³), and the pine biomass showed the highest CGE (69%) whereas the corn stover had the lowest (65%). The change of CGE is related to the producer gas yield and composition as well as the consumption of supplementary LPG during the gasification. At operation temperature of 800°C, the producer gas yield in pine gasification was the highest (shown in Fig.3), and the producer gas had the highest H_2 content and the lowest CO_2 content as given in Table 4. In addition, gasification of pine used less LPG than gasification of other biomass species which is believed to be due to the high content of lignin in pine biomass, which resulted in more char than other biomass in the gasification [26].

3.2. Tar products from devolatilization to final steam gasification

Fig.4 shows the tar yields and tar classes in producer gas from gasification of three types of biomass at two temperatures (700 and 800°C). The tar yield (g/kg_{daf}) was defined as the total tar concentration in the producer gas (g/Nm³) divided by the total gas yield per unit mass of dry and ash free fuel (Nm³/kg_{daf}). The tar classification has been described in Section 2.3 of this paper. From Fig. 4, it can be found that at gasification temperature of 700°C the total tar yield was 7.77 g/kg_{daf} for corn stover, 7.32 g/kg_{daf} for rice husk and 7.56 g/kg_{daf} for pine. With increase of gasification temperature from 700 to 800°C, the total tar yield for all of the biomass species was

decreased by 16% to 6.40 g/kg_{daf} for corn stover, by 10% to 6.61 g/kg_{daf} for rice husk, and by 12% to 6.67 g/kg_{daf} for pine. These results confirm that tar decomposition reactions (cracking and reforming) are endothermic and, therefore, favoured by increasing the temperature. However, the change of each class tar compounds with increase in gasification temperature was different for each type of biomass due to the differences in molecular structure and proportion of the cellulose, hemicellulose and lignin in the biomass.

At gasification temperature of 700°C, the yields of Class 2 tar compounds were the highest for all biomass species, 4.09 g/kg_{daf} for corn stover, 2.95 g/kg_{daf} for rice husk and 3.04 g/kg_{daf} for pine. However, in corn stover gasification, the yield of Class 4 compounds was the second highest (2.09 g/kg_{daf}) followed by Class 3 (1.4 g/kg_{daf}) while the yield of Class 5 tar compounds was the least at 0.19 g/kg_{daf}. Interestingly rice husk and pine had a similar order of yields of tar class compounds with Class 3 being the second highest (2.35 g/kg_{daf} for rice husk, 2.19 g/kg_{daf} for pine) followed by Class 4 tar compounds (1.66 g/kg_{daf} for rice husk, 1.87 g/kg_{daf} for pine). The yields of Class 5 tar compounds were again the least for these two biomass species (0.36 g/kg_{daf} for rice husk and 0.46 g/kg_{daf} for pine). At 800°C, the yields of Class 4 tar compounds became the highest for all of the three biomass species, followed by Class 2 tar compounds. In this case, the yields of Class 3 tar compounds were at the same level as those of Class 5 tar compounds.

Tar formation in gasification is a complex process. In the initial devolatilization stage with temperature ranging from 300 to 500°C, the so-called “primary tar” is produced which is a complex mix of heteroatoms. When the temperature is further increased to 600°C or higher, the primary tar compounds decompose into lighter vapours of lower molecular weight hydrocarbons and substitution aromatic compounds that are more stable at the high temperatures than aliphatic chains. At the same time, the secondary tar compounds are formed which consist of various molecules from mono-aromatic to poly-aromatic hydrocarbons (PAH) through polymerisation reactions [42].

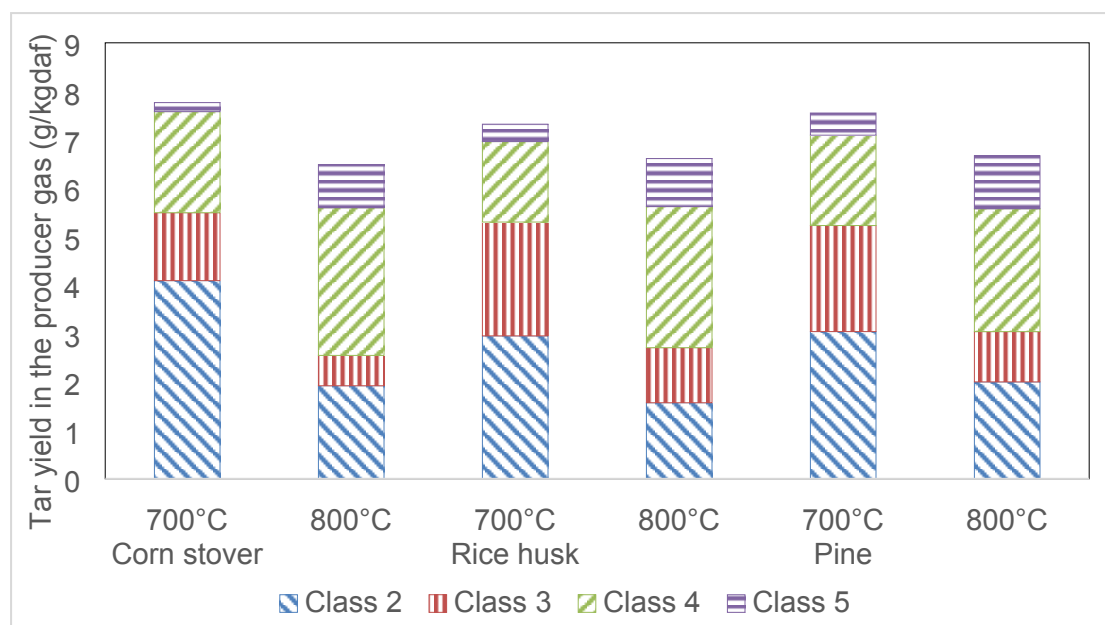
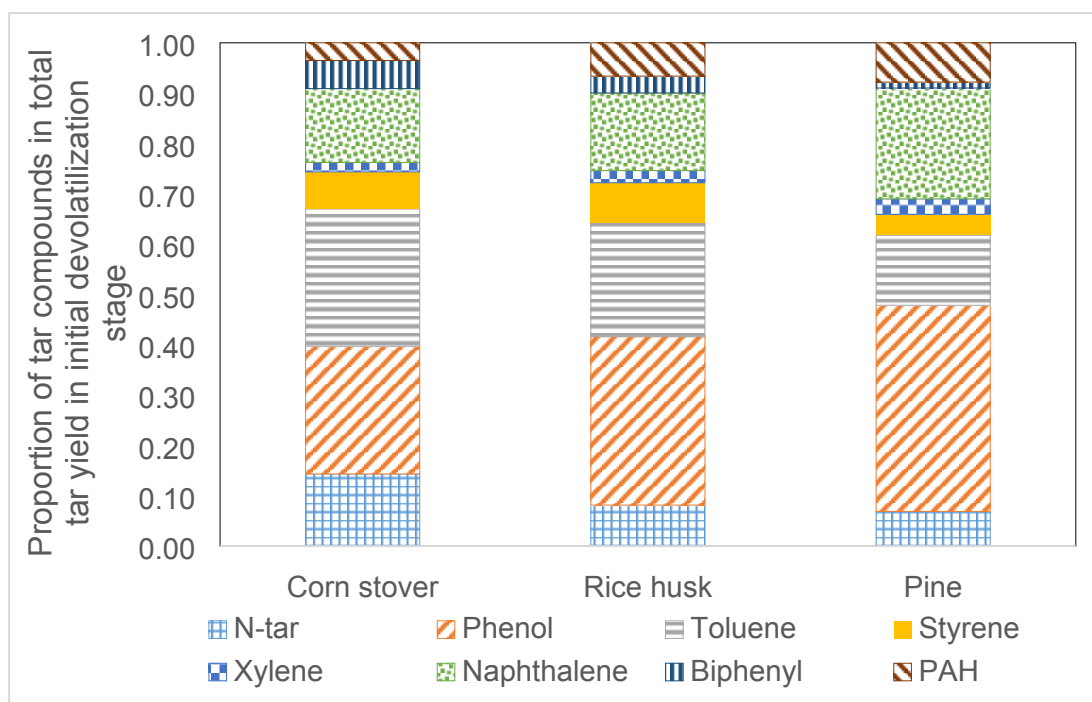
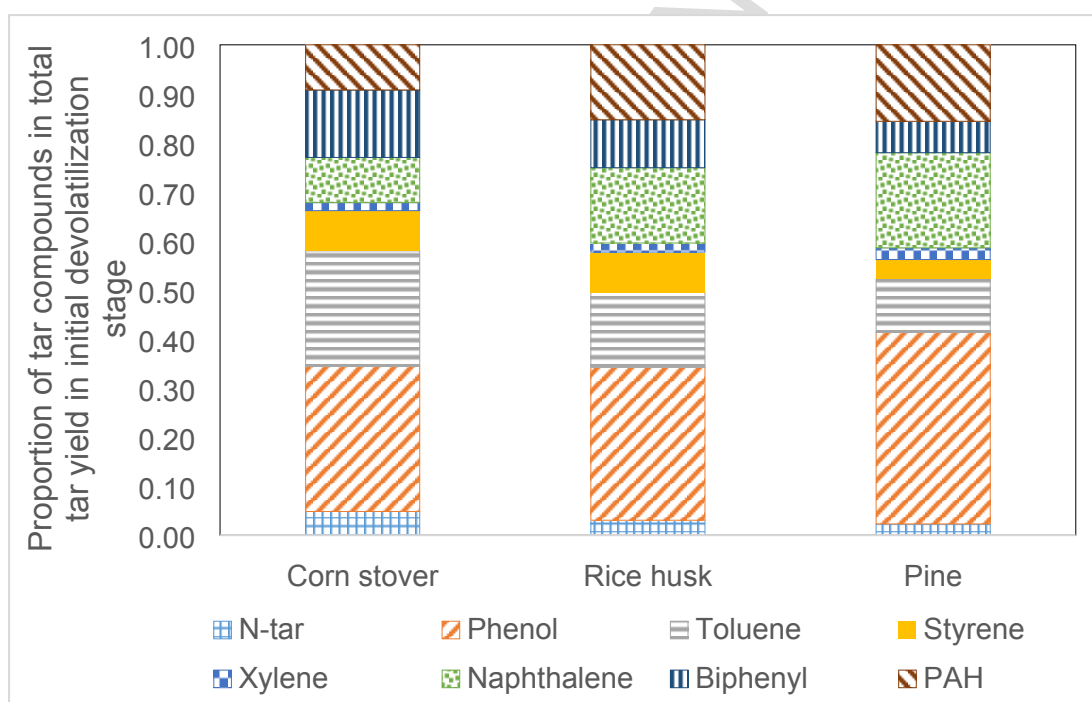


Fig. 4. The effect of temperature on the total tar yields and yields of each class tar compounds in gasification of three biomass species.

Based on the above analysis and chemical composition of the biomass, tar formation can be considered to consist of three stages. The first stage is the formation of primary tar compounds in which cellulose, hemicellulose and lignin are decomposed into heterocyclic tar compounds and aromatic tar compounds, such as phenol, benzene and toluene [23]. The second stage of tar formation is the purification and conversion of aromatics products formed from the first stage to intact aromatic rings by cleavage of heterocyclic groups through dehydrogenation and dealkylation and decarboxylation [43]. The final stage is the growth of large PAHs in which the combination of intact aromatic rings activates the mono-aromatic molecules to successively form the PAH tar compounds with more ring numbers, such as the reaction of H_2 -abstraction- C_2H_2 addition [44].



(a)



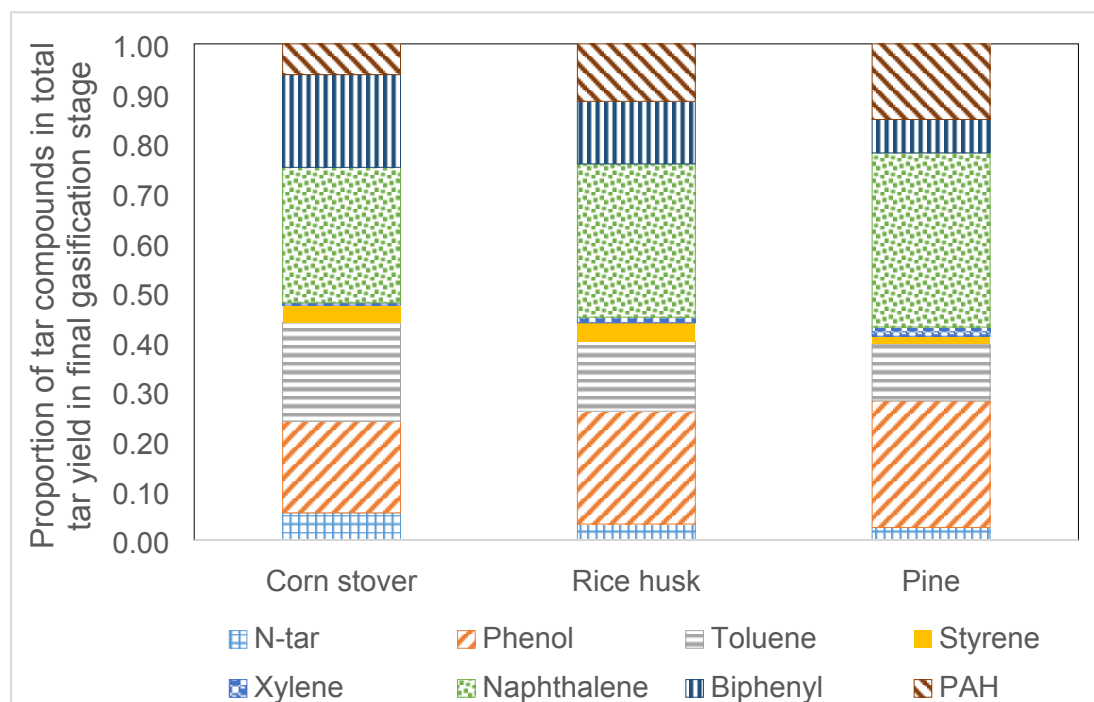
(b)

Fig. 5. Proportions of various tar compound yield to total tar yield in the initial devolatilization at 700°C (a) and 800°C (b).

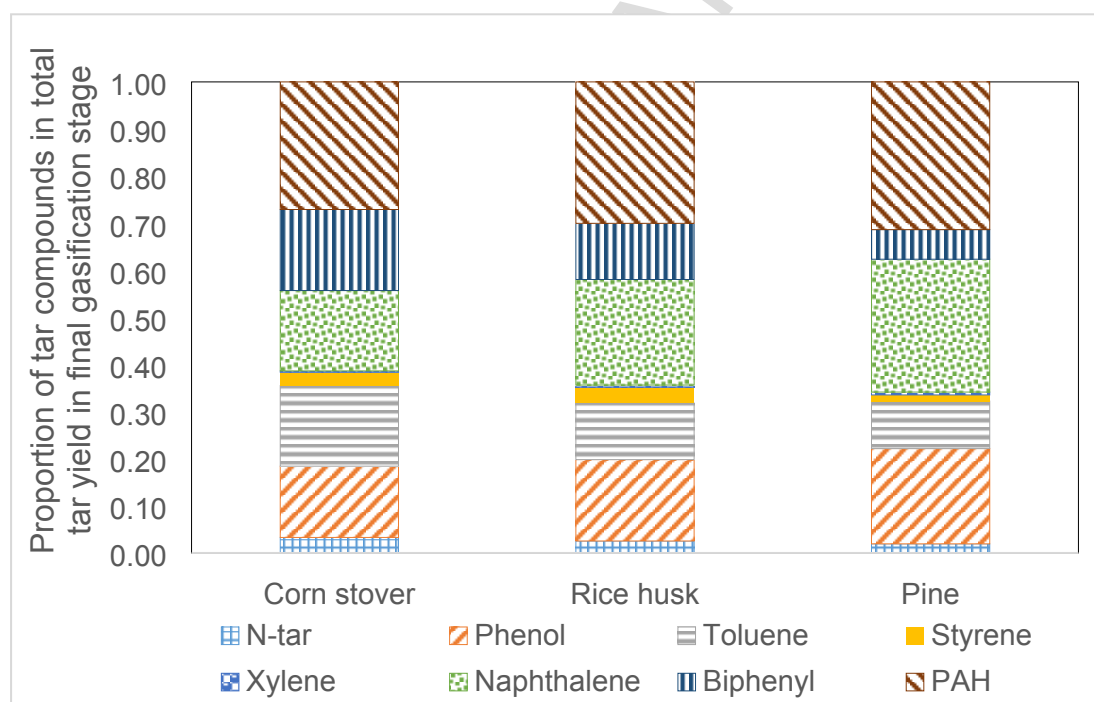
In order to quantify tar formation in the first stage, tar samples were collected from the devolatilization experiments and analysed using GC-FID, and the results are shown in Fig.5(a) for 700°C and in Fig.5(b) for 800°C. From the tar analysis, eight types of tar

compounds were detected including N-based compounds (pyridine and quinoline), phenol, toluene, styrene, xylene, naphthalene, biphenyl and PAH (3 and more aromatic rings). The total yields of tar compounds from the biomass devolatilization at 700°C were, respectively, 9.22 g/kg_{daf} for corn stover, 9.85 g/kg_{daf} for rice husk and 12.19 g/kg_{daf} for pine. As shown in Fig.5(a), the yields of N-tar compounds were 1.15, 0.68 and 0.63 g/kg_{daf}, respectively, for corn stover, rice husk and pine. These results confirm that high yield of N-tar compounds from devolatilization of biomass is directly related to the N content in the biomass. Corn stover had higher nitrogen content than pine as presented in Table 1. In Fig.5(a), the phenols yield in the devolatilization of corn stover, rice husk and pine were 2.03, 2.80 and 3.72 g/kg_{daf}, respectively. This was the major contributor to tar compounds for rice husk and pine wood. However, toluene was the major tar components from the devolatilization of corn stover, whose yield was 2.20 g/kg_{daf}. The corresponding yields for rice husk and pine wood were 1.89 and 1.26 g/kg_{daf}. The other key contributor to the tar compounds was naphthalene which yield was 1.18 g/kg_{daf} for corn stover, 1.29 g/kg_{daf} for rice husk and 2.00 g/kg_{daf} for pine. The yields of other tar compounds were variable from 0.11 to 0.71 g/kg_{daf} depending on the type of biomass.

The effect of temperature on the tar composition in the pine wood gasification had been discussed in our previous study [22] and the tar yields at 800°C from this study are shown in Fig.5(b) from which similar trends have been found. In a general trend, the PAHs yields increased with temperature. The relative percentages of PAHs for corn stover increased from approximately 24% at 700°C to 35% at 800°C, from 26% to 37% for rice husk and from 30% to 42% for pine wood. At the same time, the light tar compounds such as N-containing tar, toluene and phenols was reduced for all three tested biomass species with increase in temperature from 700 to 800°C. It is believed that the deoxidisation and aromatisation reactions of primary and secondary tar, generated at a lower temperature, were strengthened with increasing temperature.



(a)



(b)

Fig. 6. Proportions of various tar compound yield to total tar yield in the final gasification stage at 700°C (a) and 800°C (b).

The intermediate tar compounds generated from the initial devolatilization remained or were logically transformed to the new tar compounds in the subsequent gasification

process. The changes in relative yield of each type of tar compounds through the final gasification process following the initial devolatilization at the same temperature is present in Fig. 6(a) for 700°C and in Fig. 6(b) for 800°C, respectively. Similarly to the initial devolatilization stage, the yields of light tar compounds such as N-based tar compounds, phenols and toluene were reduced while the yields of PAH tar compounds were increased. For example, the N-based tar compounds were reduced from 0.36 to 0.19 g/kg_{daf} for corn stover, from 0.24 to 0.16 g/kg_{daf} for rice husk and from 0.21 to 0.13 g/kg_{daf} for pine wood. Meanwhile, the PAH compounds were increased from 0.41 to 1.50 g/kg_{daf} for corn stover, from 0.85 to 1.89 g/kg_{daf} for rice husk and from 1.26 to 2.03 g/kg_{daf} for pine wood. It can be concluded that the tar substance groups shifted from light tar compounds (phenols, toluene and N-based tar) to PAH tar compounds with increasing temperature.

3.3. Mechanism of tar conversion from devolatilization to final gasification

The biomass gasification yields a complex mixture of products from gasification of three components, cellulose, hemicellulose and lignin. In literature, it has been reported that lignin contains a high proportion of aromatic and methyl functional groups, therefore, more PAH compounds were formed in gasification of lignin-rich pine biomass. On the other hand, the monomer of cellulose and hemicellulose contains a larger number of hydroxyl and carboxyl groups, therefore, more oxygen-containing tar compounds were generated in the gasification of biomass with rich cellulose and hemicellulose.

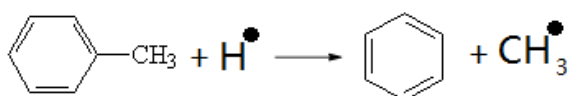
As shown in Fig. 5(a), phenol, which represented approximately 41% of the tar, as well as naphthalene (22%) were found to be major components of tar derived from the devolatilization of pine wood at 700°C. In contrast, the major tar components derived from corn stover and rice husk devolatilization were toluene and phenols. Phenols and their derivatives are major components for lignin-rich biomass, whereas toluene and xylenes are major components for cellulose and hemicellulose rich biomass.

The tar transformation from devolatilization to final gasification stage is related to PAHs formation. The observed change in Fig.5(a) and in Fig.6(a) indicated that the

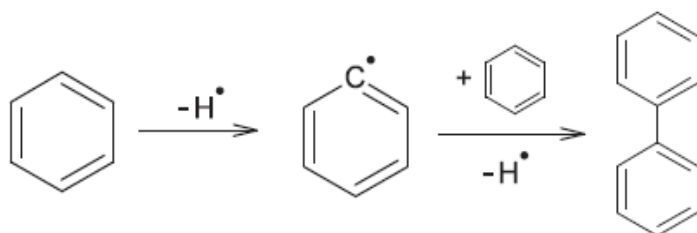
pure PAH tar compounds including naphthalene and biphenyl in the total tar yields increased from 25% to 52% for corn stove, from 24% to 54% for rice husk and from 32% to 57% for pine wood at 700°C. The similar trends at 800°C have been found as well. Therefore, it is important to better understand the PAHs formation mechanism.

It is believed that during the gasification stage, the light tar compounds (such as N-tar, phenols and toluene) were consumed as the precursor for the formation of PAHs (biphenyl and naphthalene). This is supported by the experimental results that in the final gasification stage at 700°C, the major PAH tar components for pine wood was naphthalene, which was 35% of the total tar yields. At the same time, phenols, which was significantly reduced due to the precursor consumption to form naphthalene. On the other hand, biphenyl was increased in the final gasification process of corn stover and rice husk, which represented 19% and 13%, respectively, of the tar compounds. Meanwhile, the toluene yield was reduced in the gasification which had acted as precursor for biphenyl formation. This pathway may be incorporated with the PAHs formation as described in previous paragraph. Therefore, there could be two possible pathways for PAHs generation. The PAH tar compounds formed either by H₂-abstraction-C₂H₂ addition (HACA) sequence successive growth of small radicals to larger PAHs, or directly combination of aromatic rings.

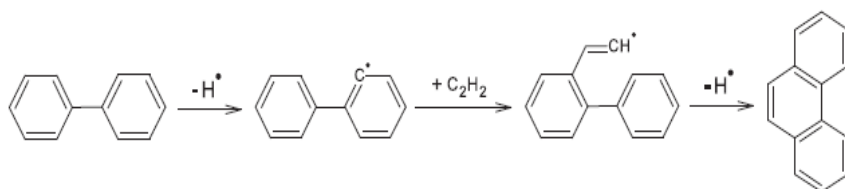
The first pathway with a precursor of toluene is listed in Reactions (1) to (3). In Reaction (1), benzene (C₆H₆) is formed by the cleavage of alkyl groups (CH₃[•]) attached on toluene (C₇H₈) via dealkylation reaction. Then, phenyl (C₆H₅) is generated by losing the H⁺ radical from the benzene as shown in Reaction (2). After this, a combination of two phenyls ring leads to biphenyl (C₁₂H₁₀). Finally, phenanthrene grows by the HACA sequence from biphenyl, in which H-abstraction activates the aromatic molecules, and acetylene addition propagates molecular growth by cyclisation via Reaction (3) [43].



Reaction (1)

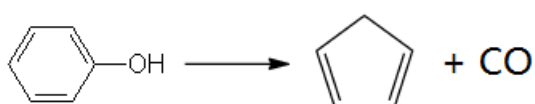


Reaction (2)

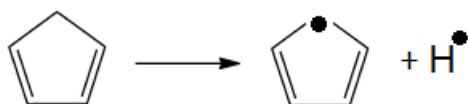


Reaction (3)

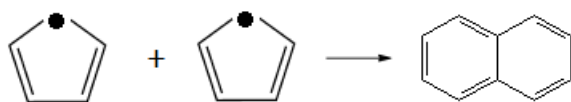
The formation of PAH tar compounds with phenols as a precursor is elucidated via Reactions (4) to (8). In the pathway, phenol is cracking by losing CO to form cyclopentadiene (C_5H_6) as shown in Reaction (4). Then, in Reaction (5), cyclopentadienyl (C_5H_5) produces through losing H radicals from cyclopentadiene. After this, naphthalene ($C_{10}H_{10}$) is formed by the combinations of two cyclopentadienyls via Reaction (6), Naphthalene loses H radical and carbon into indenyl (C_9H_8) under the reaction ($C + H_2O \rightarrow CO + H_2$) as described by Reaction (7). Finally, phenanthrene ($C_{14}H_{10}$) is formed when indenyl reacts with cyclopentadiene as shown in Reaction (8) [45].



Reaction (4)

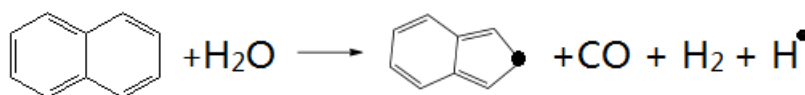


Reaction (5)



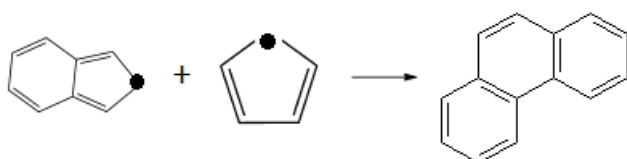
488

Reaction (6)



489

Reaction (7)



490

Reaction (8)

491 4. Conclusions

492 In this study, gasification experiments were conducted for three biomass species of corn
 493 stove, rice husk and pine on a 100 kWth dual fluidised bed gasifier with steam as
 494 gasification agent. Effects of biomass species on producer gas yields, gas composition
 495 and tar yields have been investigated. Chemical composition of each biomass has been
 496 analysed and the results are used for analysis of the tar formation process. It is found
 497 that corn stove is rich in cellulose, rice husk contains a high content of hemicellulose
 498 and pine has a high content of lignin. These differences are the key contributors to the
 499 differences in producer gas yield, gas composition and the yields of tar compounds.

500

501 Tar formation is a complex process and can be divided into three stages: (1). Formation
 502 of primary tar compounds, (2). Tar reforming, and (3). Tar polymerization. Eight tar
 503 compounds have been detected in the gas products both from the devolatilization and
 504 the final gasification, which are N-based compounds (pyridine and quinoline), phenols,
 505 toluene, styrene, xylene, naphthalene, biphenyl and PAHs (3 and more aromatic rings).
 506 Changes of tar compounds from initial devolatilization to the final gasification have
 507 been examined and mechanisms of tar formation are proposed.

508

509 Key findings from the present studies are:

- 510 • As reaction temperature increased, the producer gas yields were increased for all
511 three biomass species. At 700°C, the yields of producer gas are the highest for corn
512 stover followed by rice husk and pine has the lowest gas yield. In contrast, at 800°C,
513 the gas yield for pine is the highest followed by rice husk and then corn stover. At
514 both 700 and 800°C, the contents of H₂ and CH₄ are higher from gasification of
515 pine, the content of CO is higher from gasification of rice husk while contents of
516 CO₂, C₂H₄ and C₂H₆ are higher from gasification of corn stover.
517
- 518 • During the initial devolatilization stage of gasification, the light tar compounds are
519 dominant, in which pine biomass generates more phenols while both corn stover
520 and rice husk produce more toluene. Through the sequent steam gasification, the
521 total tar yields for all of the biomass species are significantly reduced while light
522 tar compounds, such as N-based tar compounds, phenols and toluene are
523 transformed to PAHs.
524
- 525 • It is proposed that the PAHs are formed either by H₂-abstraction-C₂H₂ addition
526 sequence successive growth of small radicals to larger PAHs, or directly
527 combination of aromatic rings. Naphthalene is the major PAH tar compound in
528 gasification of pine wood gasification whereas biphenyl is major PAH compound
529 in gasification of corn stover and rice husk. The above tar formation process can
530 be described by two reaction pathways.
531
- 532 • Tar yields are reduced with an increase in gasification temperature for all of the
533 biomass species tested. In a general trend, with increasing gasification temperature,
534 light tar compounds (phenols, toluene and N-based tar) are transformed to PAH tar
535 compounds.
536
- 537 • This study provides inside understanding of linkage between the initial
538 devolatilization and the final gasification, and the results can be used in further
539 studies on kinetics of tar formation in biomass gasification and gasification
540 modelling.

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- 678

Highlight

- Three types of biomass feedstocks were tested for steam gasification in a pilot scale DFB gasifier.
- Tar formation and tar composition have been investigated.
- Tar formation mechanisms have been analysed.
- Producer gas yield and gas composition have been analysed.
- Gasification performance of the biomass are related to biomass chemical composition.