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Effect of interactions of biomass constituents on polycyclic aromatic hydrocarbons (PAH) formation during fast pyrolysis

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Abstract

The interactions of biomass constituents (hemicellulose, cellulose and lignin) were investigated during fast pyrolysis at 800 °C in a fixed bed reactor. The formation of polycyclic aromatic hydrocarbons (PAH) as well as mass distribution and gas products is presented. The possible interactions of biomass constituents were compared with the results of the expected results based on the pyrolysis of single components. For the interaction of xylan and cellulose, the mass distribution was similar to that expected from calculation of single component addition, however, PAH were increased. The interaction of xylan and lignin produced a decrease in PAH concentration compared to that expected from single component data. There was evidence of strong interaction between cellulose and lignin, where gas and solid residue yield was decreased and tar/oil yield was increased. In addition, naphthalene, acenaphthylene, and chrysene/benzo[a]anthracene were decreased compared with the concentrations expected from the single component pyrolysis. However, the amounts of 1-methynaphthalene, 2-methynaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, and pyrene were increased.

KEYWORDS: Polycyclic aromatic hydrocarbons (PAH); Biomass; Cellulose; Hemicellulose; Lignin

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1. Introduction

The world's reliance on the use of fossil fuels and the consequent concerns around climate change has stimulated interest in renewable fuels such as biomass [1]. Thermal conversion of biomass, including combustion, pyrolysis and gasification are important technologies for biomass utilization [2]. Pyrolysis is operated in the absence of oxygen at elevated temperatures, which is regarded as a fundamental process of thermal conversion [3]. In addition, pyrolysis presents an alternative process to enhance both the energy and economic value of biomass utilization compared with combustion, due to the option for the production of syngas and bio-oil that have potential to be further utilized [4].

Extensive work on biomass pyrolysis has been carried out recently [2,5]. However, the formation of polycyclic aromatic hydrocarbons (PAH) is one of the challenges of biomass pyrolysis [6]. PAH are group of semi-volatile compounds which have been linked to a range of health concerns, including cancer, mutations or malformations of the human body [7]. The US Environmental Protection Agency (US EPA) has listed 16 PAH which are regarded as priority pollutants, i.e. naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenzo[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3-cd]pyrene [8]. It has estimated that the global total annual atmospheric emission of these priority pollutant PAH in 2007 was 504 Gg (331-818 Gg, as the interquartile range), with residential/commercial biomass burning

(60.5% of the total), open-field biomass burning (agricultural waste burning, deforestation, and wildfire, 13.6% of the total) as the major sources [9].

Biomass has three main constituents, hemicellulose, cellulose, and lignin [10]. Hemicellulose is a complex, branched and heterogeneous polymeric network, based on pentoses such as xylose and arabinose, hexoses such as glucose, mannose and galactose, and sugar acids. Cellulose is a long chain polysaccharide formed by D-glucose units, linked by β -1,4 glycosidic bonds. Lignin is a racemic, heteropolymer consisting of three hydroxycinnamyl alcohol monomers differing in their degree of methoxylation: p-coumaryl, coniferyl and sinapyl alcohols [11]. Generally, biomass has hemicellulose contents ranging from 16 to 23%, cellulose contents from 42 to 49%, and total lignin contents from 21 to 39% [12].

It is reported that during the pyrolysis/gasification process, the three biomass constituents may act with a synergistic effect [11,13]. Giudicianni et al. [11] have studied the steam pyrolysis of three the single biomass constituents (hemicellulose, cellulose and lignin) and of three binary mixtures in order to evaluate possible interactions between the biomass constituents. The results obtained highlight the importance of the interactions between constituents, mainly cellulose and lignin, on the yield and characteristics of solid and gaseous products [11]. Wang et al. [14] investigated the interactions of biomass constituents using thermogravimetric (TG) analysis and showed that the thermal decomposition of levoglucosan was extended over a wider temperature range according to the interaction of hemicellulose or lignin with cellulose; and the amount of phenol,

2,6-dimethoxy was enhanced by the interaction of cellulose and hemicellulose [14]. A considerable influence of the interaction between cellulose and lignin on the pyrolysis behavior, including gas, tar/oil, and char formation as well as product composition has also been reported by Hosoya et al. [15] at a gasification temperature of 800 °C. Lignin inhibited the formation of levoglucosan formed from cellulose and enhanced the formation of the low molecular weight products from cellulose resulting in reduced yield of char fractions; cellulose reduced the secondary char formation from lignin and enhanced the formation of some lignin-derived products including guaiacols, 4-methyl-guaiacol and 4-vinyl-guaiacol [15].

The interactions of biomass constituents during fast pyrolysis may be different from those in slow pyrolysis. During the process of slow pyrolysis, different constituents decompose at different temperatures. If the pyrolysis of one constituent begins, while the pyrolysis of the other constituent has finished, few interactions would be expected. In particular, of relevance to the work reported here, there are few studies in relation to the interaction of biomass constituents on PAH formation during fast pyrolysis.

In this paper, the thermal behavior of the single biomass constituents, hemicelluloses, cellulose and lignin, of binary mixtures of the components has been investigated with the aim to evidence and quantify possible interactions between the three components during fast pyrolysis. The influence of component interaction on the yield and composition of products, including PAH have been investigated.

2. Materials and methods

2.1. Materials

Xylan has been commonly used as a representative of hemicellulose, and xylan produced from beech wood was used here and obtained from Sigma-Aldrich. Cellulose (microcrystalline) was provided from Research Chemicals Ltd. Lignin (dealkaline) used in this research was obtained from a dealkalization process of alkaline lignin provided by Tokyo Chemical Industry Co., Ltd. The sample was in granular form with a size of less than 150 μm . Before the experiments, all the samples were dried at 105 °C to obtain the sample on a dry basis. The results of the proximate and ultimate analysis of the samples are shown in Table 1, which shows that; xylan has a notable amount of nitrogen (2.70 wt.%); cellulose shows the highest volatile content (97.94 wt.%); lignin has considerable ash (16.15 wt. %) and fixed carbon content (29.25 wt. %); the sulphur content of lignin was also quite high (5.67 wt.%). The high volatile content of cellulose and high sulphur content of lignin have been reported by other researchers [16,17].

2.2. Fast pyrolysis process

Fast pyrolysis of the samples was carried out using a fixed bed reactor system (Figure 1). The reaction system was composed of a pyrolysis reactor, tar/oil collection system and

gas collection. During the experiment, N₂ (100 ml min⁻¹) was used as carrier gas, and the residence time of volatiles was approximately 2.6 s. During the experiment, the reactor was initially heated to the set point (800 °C). Once the temperature had stabilized, the sample (1 g) was inserted into the hot zone of the reactor and rapidly pyrolysed. The average heating rate was approximately 350 °C min⁻¹, which was a rough evaluation of how fast the sample was heated. The reactor was kept at the reaction temperature for a further 30 minutes. The products from the pyrolysis were cooled using air and dry ice cooled condensers, thereby collecting the condensed tar/oil. The non-condensed gases were collected using a Tedlar™ gas sample bag, and further analysed off-line using packed column gas chromatography (GC). An additional 20 minutes was allowed to collect the non-condensed gases to ensure complete collection of gas products. All experiments were repeated to ensure the reliability of the results.

2.3. Products analysis and characterization

2.3.1. Gas chromatography

Non-condensed gases collected in the Tedlar™ gas sample bag were analysed off-line by packed column gas chromatography. H₂, CO and N₂ were analysed with a Varian 3380 GC on a 60–80 mesh molecular sieve column with argon carrier gas, whilst CO₂ was analysed by another Varian 3380 GC on a Hysep 80–100 mesh column with argon carrier gas. C₁–C₄ hydrocarbons were analysed using a third Varian 3380 gas chromatograph with a flame ionisation detector, with an 80–100 mesh Hysep column and nitrogen carrier

gas. From the known input of nitrogen flow rate and collection time, the volume and mass of other gases could be calculated.

2.3.2. Characterization of PAH

After each experiment, the condenser and the tar/oil connecting sections were weighed to obtain the mass of tar/oil by weight difference. The tar/oil products from the condensers were washed by ethyl acetate. The water content in the liquid mixture was removed by filtering through a column of anhydrous sodium sulphate.

Finally, the liquid fractions, which contained PAH, were analysed using a Varian CP-3800 gas chromatograph coupled with a Varian Saturn 2200 mass spectrometer (GC/MS) fitted with a 30m × 0.25µm DB-5 equivalent column. 2 µl of the extracted tar/oil sample was injected into the GC injector port at a temperature of 290 °C; the oven programme temperature was at 50 °C for 6 min, then ramped to 210 °C at 5 °C min⁻¹, held for 1 min and ramped at 8°C min⁻¹ to 300 °C (total analysis time of 61 min). The transfer line was at 280 °C, manifold at 120 °C and the ion trap temperature was held at 220 °C. The ion trap was initially switched off for 7 min to allow the elution of the solvent prior to data acquisition to safeguard the life of the trap. The PAH compounds were quantified by internal standard method with 2-hydroxyacetophenone as internal standard (IS). The GC/MS was calibrated using standard PAH supplied by Sigma-Aldrich Ltd., thus PAH could be quantitatively determined. The analysis reported 10 of the 2-4-ring PAH from US EPA priority list and also 2 naphthalene derivatives (1-methylnaphthalene and 2-methylnaphthalene). The GC peaks of benzo[a]anthracene and chrysene could not be

separated clearly by the GC system used; therefore the concentration of these two compounds was reported together.

3. Results and discussion

3.1. Fast pyrolysis of single biomass constituents

3.1.1. Product mass distribution

The product mass distribution for the fast pyrolysis of, xylan, cellulose, and lignin is shown in Figure 2. Xylan generated the highest tar yield (43.2 wt.%). Cellulose produced the highest gas yield (69.5 wt.%), with no solid residue yield, which was consistent with the proximate analysis results reported in Table 1. The higher tar yield and lower gas yield from cellulose pyrolysis have been reported by other researchers [18]. The relatively long gas residence time of this research of ~2.6 s may have produced secondary reactions and thermal degradation of the tar/oil compounds to produce gas. Lignin had the highest solid residue content (41.3 wt.%), due to the high fixed carbon and ash content of the lignin, as shown in Table 1. The high solid residue yield of lignin pyrolysis has also been reported by others [18].

3.1.2. Gas composition

The gas products from the pyrolysis of xylan, cellulose, and lignin are shown in Figure 3. The yield of hydrogen from the different biomass constituents were similar (~100 ml g⁻¹ sample). Cellulose produced the highest CO yield (342 ml g⁻¹ sample), from

decarbonylation and decarboxylation reactions [19]. Xylan produced the highest CO₂ yield (100 ml g⁻¹ sample), mainly due to the cleavage of acetyl groups linked to the xylan unit [19]. Lignin produced the lowest yield of hydrocarbons.

3.1.3. PAH analysis

The main PAH found in the product tar/oil from the fast pyrolysis of the single biomass constituents, xylan, cellulose, and lignin are shown in Table 2. The fast pyrolysis of xylan and lignin generated a tar/oil containing a range of 2-4 ring PAH, whereas the PAH found in the tar/oil from cellulose pyrolysis was low. Stefanidis et al. have reported similar results [20]. The pyrolysis of lignin produced more PAH than that of xylan and cellulose. Naphthalene was the most abundant PAH in the tar of lignin. The large amounts of PAH from lignin pyrolysis were consistent with our previous research in a two-stage reactor system [21]. The high PAH yields might be due to the unique phenyl-propane units of the lignin structure which are not found to any extent in the other biomass constituents [14].

3.2. Interactions of biomass constituents during fast pyrolysis

In this section the possible interactions between the biomass constituents during fast pyrolysis are discussed comparing the results obtained via the processing of binary mixtures of hemicellulose, cellulose and lignin. The data obtained were compared with calculations obtained from the expected results produced from the fast pyrolysis of the single biomass constituents, a method widely used in other research of interactions of

biomass constituents [11,14,15]. The ratio of two biomass constituents was 1:1 (50%:50%). As shown in Figures 4-6, the experimental results (exp) were from the co-pyrolysis of biomass constituents; calculated results (cal) were from the simple addition of the results obtained from the fast pyrolysis of the single biomass constituent in the same weight percentage of real mixtures (Eq. (1)).

$$X(\text{cal}) = 50\% X_1 + 50\% X_2 \quad (1)$$

Where $X(\text{cal})$ is the calculated result from the single component data; X_1 and X_2 represent the product yield from the pyrolysis of xylan, cellulose or lignin.

3.2.1. Mass distribution

As shown in Figure 4(a), there was no significant interaction between xylan and cellulose (less than 5 wt.%), which has also been reported by other researchers [11,15]. The interactions between xylan and lignin were very weak, as shown in Figure 4(b), which was consistent with the results reported by thermogravimetric studies of biomass constituents [22,23]. However, the interaction between cellulose and lignin in terms of product mass distribution was significant. Due to interactions, gas yield was decreased by 7 wt.%, tar/oil yield was increased by 15 wt.% and solid residue yield was decreased by 6 wt.%. The results of these interaction effects between cellulose and lignin were consistent with the data reported by Hosoya et al. during the fast pyrolysis of biomass constituents at 800 °C [15]. It was postulated that lignin inhibits the formation of levoglucosan from cellulose and enhances the formation of the low molecular weight products from cellulose with changes in the secondary degradation mechanism of volatiles species and a

reduction in the yield of char [11,14]. However, Worasuwannarak et al. [23] has reported that the interactions between cellulose and lignin during thermogravimetric pyrolysis (heating rate $10\text{ }^{\circ}\text{C min}^{-1}$) contributed to a decrease in tar yields but an increase in char yield. However, the work reported by Worasuwannarak et al. [23] was undertaken at slow pyrolysis conditions, whereas the work reported here was fast pyrolysis, indicating that the interactions for fast pyrolysis are different from the interactions for slow pyrolysis.

3.2.2. Gas analysis

The comparison of gas products from biomass constituent mixtures and the calculated expected results based on the single component data are shown in Figure 5. For the fast pyrolysis of the xylan and cellulose mixture, experiments generated less CO yield, which has also been reported by Giudicianni et al. during the gasification of biomass constituents in steam [11]. Figure 5 shows that the interaction between xylan and lignin on the gas composition was not significant. However, for the interaction of cellulose and lignin, there was less hydrogen and carbon monoxide generated from the experimental mixture of the two components compared to that expected from calculation.

3.2.3. PAH analysis

Figure 6(a) shows that during the fast pyrolysis of the mixture of xylan and cellulose, the yield of all the PAH was increased compared with the calculated results expected from the single component data. For example, the yield of naphthalene increased from 11.9 to $44.0\text{ }\mu\text{g g}^{-1}$ sample, and the yield of acenaphthylene increased from 13.2 to $48.8\text{ }\mu\text{g g}^{-1}$

sample.

Currently, there are few reported data in relation to PAH generation from the interaction of biomass constituents during pyrolysis. Wang et al. [14] reported that 2,5-hiethoxytetrahydrofuran concentration increased with increasing hemicellulose content in mixtures of biomass constituents when the cellulose content was kept constant. In addition, the presence of cellulose enhanced the formation of hemicellulose-derived acetic acid and 2-furfural [14]. Stefanidis et al. [20] has reported that the interactions of xylan and cellulose during pyrolysis of the mixture of the two components increased yields of phenols, which were regarded as PAH precursors.

During the pyrolysis of the xylan and lignin mixture, several PAH were decreased in terms of yield compared with the calculated results. Particularly, the yield of naphthalene decreased from 79.9 to 44.5 $\mu\text{g g}^{-1}$ sample; the yield of acenaphthylene decreased from 54.2 to 28.9 $\mu\text{g g}^{-1}$ sample; and the yield of phenanthrene decreased from 36.3 to 16.9 $\mu\text{g g}^{-1}$ sample. This finding was different compared with the PAH formation from the fast pyrolysis of the xylan and cellulose mixture, where PAH yields obtained experimentally were increased compared to the calculated expected results from the single component fast pyrolysis data. In addition, a different trend of PAH formation resulted from the pyrolysis of the cellulose and lignin mixture (shown in Figure 6 (c)). For example, the amounts of naphthalene, acenaphthylene, and chrysene plus benzo[a]anthracene were decreased, while the amounts of 1-methynaphthalene, 2-methynaphthalene, acenaphthene, fluorene, phenanthrene, anthracene, and pyrene were increased.

Currently, the PAH formation mechanisms from pyrolysis of biomass single constituent are not clear. For example, Hosoya et al. [24] reported on the phenol derivatives produced from interactions of lignin and cellulose. Some compounds (such as catechols) were increased compared to the expected results based on the single component, whereas some compounds (such as o-cresols) were decreased compared to the expected calculated results [24]. Asmadi et al. reported that catechols and pyrogallols from the pyrolysis of lignin could decompose to form PAH [25,26]. Meanwhile, benzenes or phenols from the pyrolysis of xylan or cellulose might be intermediates for PAH formation [20]. In addition, there might be another route of PAH formation linked with the generation of char [27]. The interaction of biomass constituents is clearly a complex process and in particular, the influence of the formation of PAH, therefore, further work should be performed to investigate the influence and mechanisms of biomass interaction.

4. Conclusions

The interactions of biomass constituents (hemicellulose, cellulose and lignin) were investigated during the fast pyrolysis of the individual components and simple mixtures in a fixed bed reactor at 800 °C. The process was investigated in terms of product yield and gas composition and the content of polycyclic aromatic hydrocarbons (PAH) in the product tar/oil. The possible interactions of the biomass constituents were compared using the experimental data from the mixtures of the components and the calculated

expected data from the single component experiments. For the interactions of xylan and cellulose, the product mass distribution was similar to that of the calculated expected results; however, several PAH in the product tar/oil were increased. The interaction effect of xylan with lignin was not significant but several PAH in the product tar/oil were decreased. Fast pyrolysis of the cellulose and lignin mixture showed the highest influence of interaction, with decreased product gas and solid residue yield and a consequent increase in tar/oil yield. Analysis of the tar/oil showed that some PAH were decreased while some were increased, indicating the interactions between cellulose and lignin were complex.

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Table 1

Proximate and ultimate analysis of the biomass constituents.

Samples	Proximate Analysis ^d (%)			Ultimate Analysis ^{daf} (%)				
	Ash	Volatile	Fixed carbon	C	H	O	N	S
Xylan	3.83	82.60	13.57	40.26	5.49	51.55	2.70	0.00
Cellulose	0.07	97.94	1.98	41.66	5.71	52.20	0.41	0.02
Lignin	16.15	54.61	29.25	63.86	4.45	25.83	0.18	5.67

^d: dry basis; ^{daf}: dry ash free basis.

Table 2

PAH concentrations in the tar/oil produced from the fast pyrolysis of biomass constituents ($\mu\text{g g}^{-1}$ sample).

PAH	Xylan	Cellulose	Lignin
Naphthalene	16.1	7.7	143.8
1-methylnaphthalene	32.8	0.0	79.0
2-methylnaphthalene	33.6	0.0	103.9
Acenaphthylene	19.9	6.4	102.0
Acenaphthene	2.9	0.0	3.1
Fluorene	19.6	6.7	33.0
Phenanthrene	21.6	34.5	50.9
Anthracene	4.1	3.7	7.9
Fluoranthene	0.0	0.0	0.0
Pyrene	5.5	0.0	6.7
Chrysene/benzo(a)anthracene	0.0	0.0	10.7
Total	156.2	59.1	541.0

Figure Captions

Fig. 1. Schematic diagram of the fast pyrolysis reaction system.

Fig. 2. Product mass distribution from the fast pyrolysis of biomass constituents.

Fig. 3. Gas concentration produced from fast pyrolysis of single biomass constituents

Fig. 4. Product mass distribution in relation to the interactions of biomass constituents.

Fig. 5. Gas composition in relation to the interactions of biomass constituents.

Fig. 6. PAH formation in tars/oil in relation to the interactions of biomass constituents.

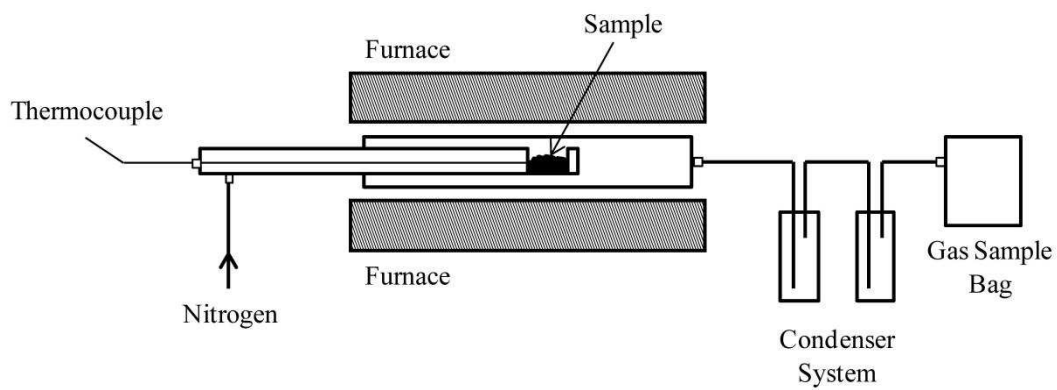


Fig. 1. Schematic diagram of the fast pyrolysis reaction system.

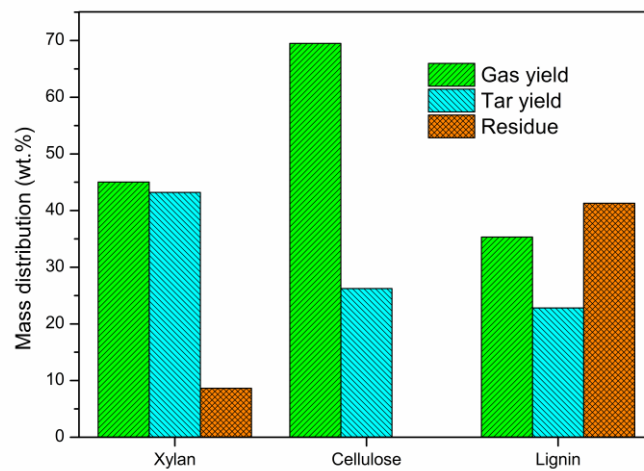


Fig. 2. Product mass distribution from the fast pyrolysis of biomass constituents.

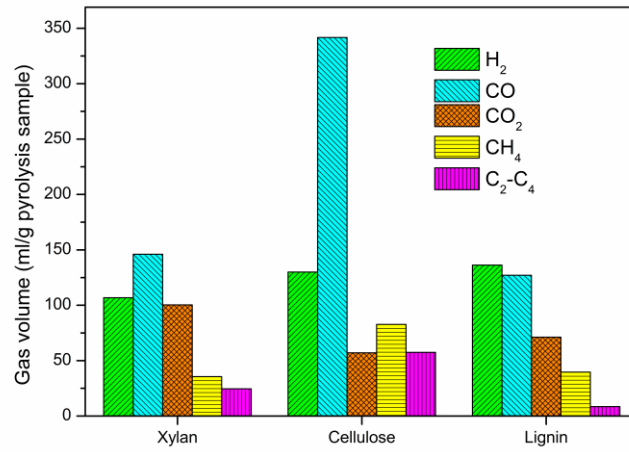


Fig. 3. Gas concentration produced from fast pyrolysis of single biomass constituents.

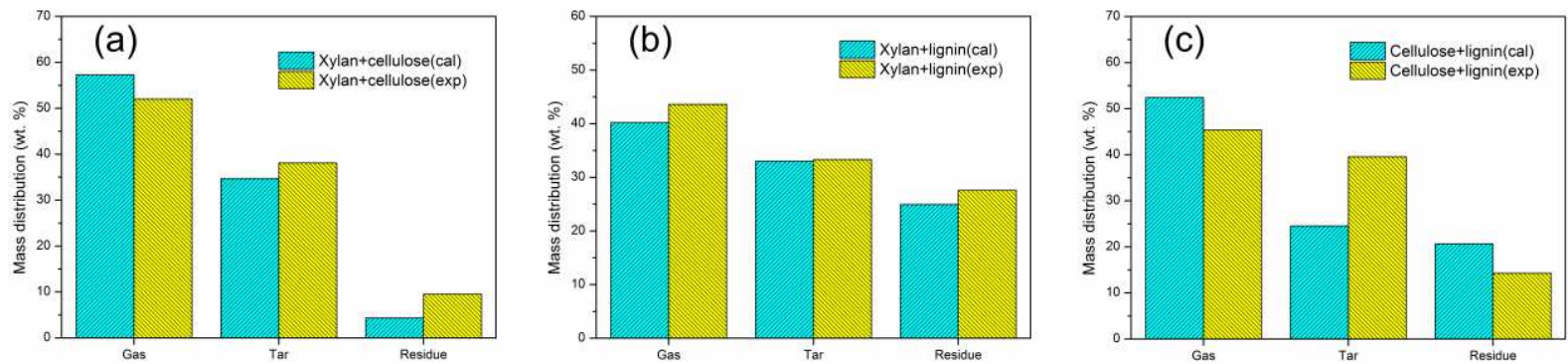


Fig. 4. Product mass distribution in relation to the interactions of biomass constituents.

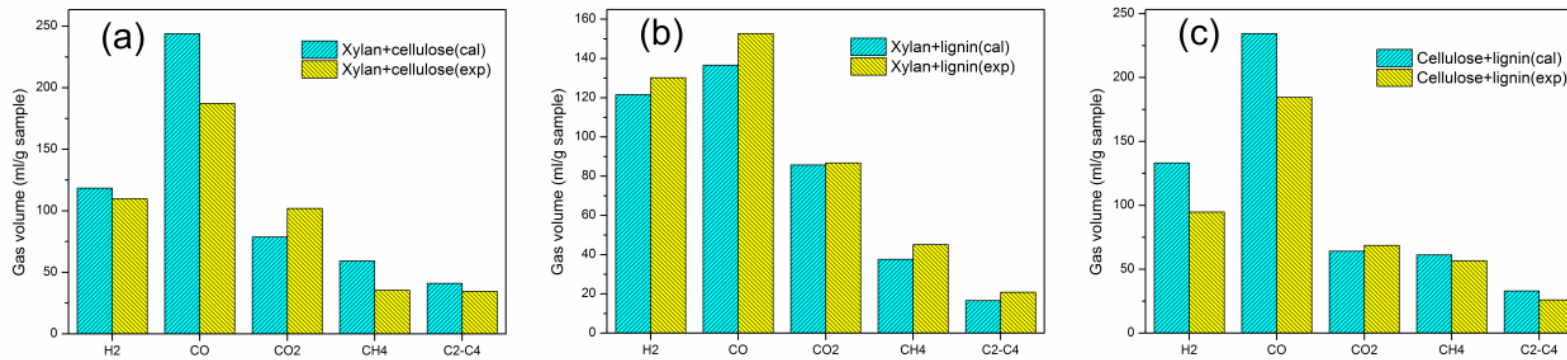


Fig. 5. Gas composition in relation to the interactions of biomass constituents.

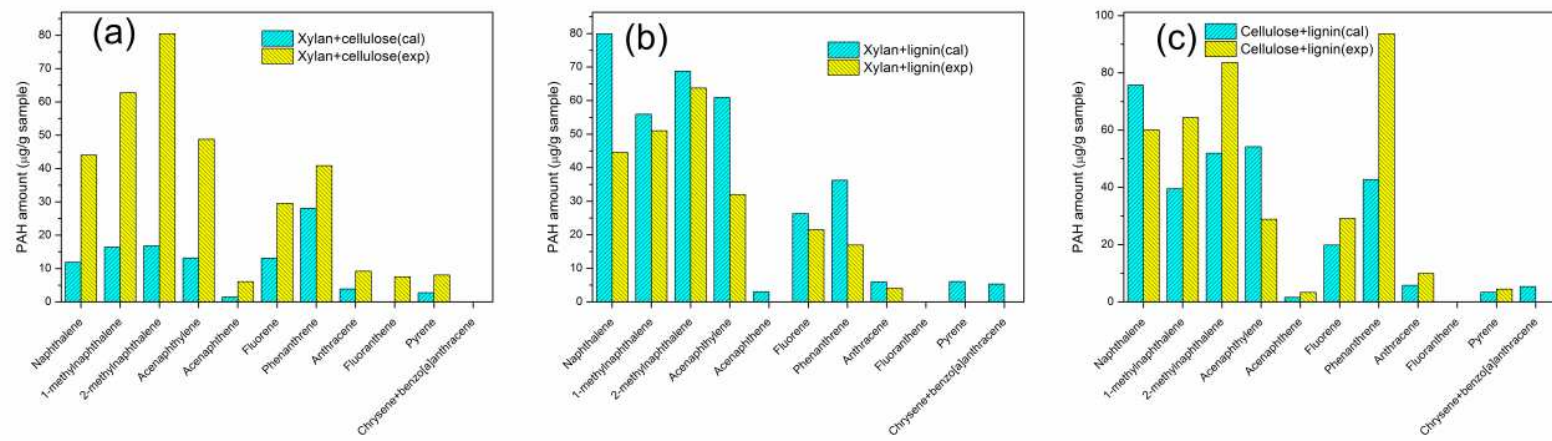


Fig. 6. PAH formation in tars/oil in relation to the interactions of biomass constituents.