

Yield and Characteristics of Tar Formed during Biomass Fluidised-Bed Gasification

Kaweewong Wongayara^{1,2} and Suneerat Fukuda^{1,2,*}

¹The Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi, Bangkok, Thailand

²Center for Energy Technology and Environment, Ministry of Education, Thailand

*Corresponding Author: suneerat@jgsee.kmutt.ac.th

Abstract: In this study, the behavior of gasification tar formed was investigated in a 100 kW_{th} bubbling fluidized-bed gasifier using rubber woodchip as fuel. Tar yield and characteristics as well as the composition of product gas were monitored and correlated with respective gas residence time, which were varied by means of gas sampling at different positions, i.e. four along the height of the gasifier and one after the cyclone. At selected experimental condition (ER=0.33), the significant concentrations of CO and H₂ were formed at 4.8 s, after which the increased concentrations of CO and H₂ at longer residence times may be attributed to the tar reforming reactions and thermal cracking. The total gravimetric tar increased from 4.5 to 10.5 g/Nm³, when the residence time was increased from 2.5 to 9.8 s. The increasing gravimetric tar yield as the residence time increased inside the gasifier suggests that more tar was formed as it was exposed to high temperature. The concentrations of all tar major species also increased following the trend of gravimetric tar yield, but the ratio of smaller molecular weight materials increased at extended residence time. This therefore suggests that longer residence time would be preferable as it would allow more time for the reaction of tar vapor to crack into smaller molecular weights and to form more product gases.

Keywords: Tar, Biomass gasification, Bubbling fluidised-bed gasifier, Residence time.

1. Introduction

Gasification process converts solid fuel into fuel gas. Generally, it takes place at around 800-1000°C and under a restriction of oxygen level less than the air required for a complete combustion process [1]. The major components of fuel gas produced from gasification are carbon monoxide (CO) and hydrogen (H₂) [2]. Although the fuel gas has relatively low calorific value, i.e. 4-6 MJ/Nm³, it can be used as fuel in most thermal applications including boilers, internal combustion engines or gas turbines. However, the raw fuel gas produced often cannot be used readily due to contamination of unwanted matters, such as tar, dust, etc. In particular, tar, the product from decomposition of organic materials during gasification containing a wide range of molecular weights, most of which are larger than that of benzene [3], is difficult to remove. In zones where temperature is below the tar dew point, e.g. exit pipes, particulate filters, engine gas lines and injectors, tar will condense and cause blockages. This leads to a decrease in performance and an increase in the need of maintenance.

The composition of tar from biomass pyrolysis and gasifier units can be divided into four major classes as proposed by Milne et al. [3]. These classes include: (1) primary tars, which are characterized by the derivative products of oxygenated compounds, (2) secondary tars are products from the conversion of primary tars, (3) tertiary tars or alkyl tertiary tars are characterized by methyl derivatives of aromatics, and (4) condensed tertiary tars are poly-aromatic hydrocarbons (PAHs) without substituent. The amount and chemical structure of gasification tar depend on the fuel types (biomass properties) and the gasification conditions [1] such as the fuel-to-air ratio, the amount of steam addition, the ratio between H and C of feedstock, pressure and temperature, etc.

Previous investigations have shown that by high-temperature exposure the primary tars can be converted into secondary and subsequently tertiary tar [4-6]. The scheme of tar conversion from primary tars to tertiary tars is shown in Figure 1 [7]. Li and Suzuki [2] proposed that soot can also be formed as intermediate, which may not further react and can eventually survive in the product gas, as shown in Figure 2. Van der Hoeven [8] described that, during the high temperature exposure and long of the gas residence time, the mechanism of tar thermal

conversion includes both cracking and polymerization reactions, as shown in Figure 3.

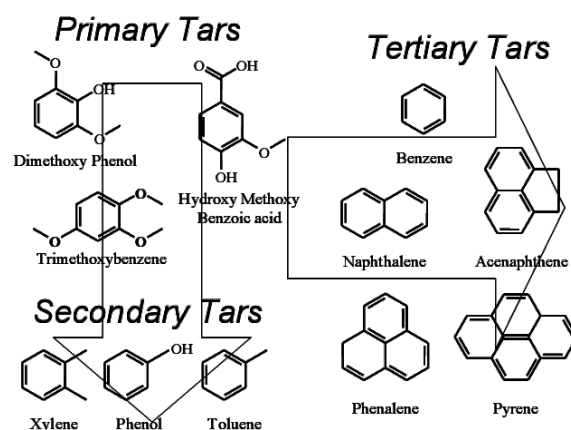


Figure 1. The scheme of tar conversion from primary to tertiary tars [7].

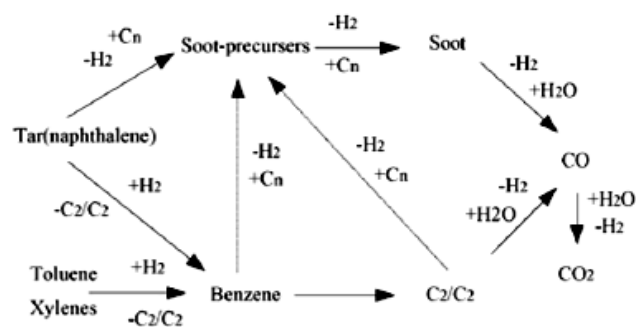


Figure 2. The scheme of tar thermal cracking [2].

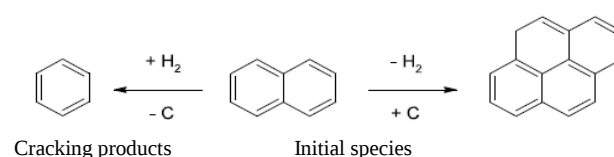


Figure 3. Cracking and polymerization products of gasification tar [8].

Although there have been a number of research studies focusing on the reduction of tar formed, e.g. catalytic cracking [9-10], thermal cracking [4,11-12], etc, the tar related problems are still the major barrier in implementing biomass gasification system for both technical and economic aspects. Better understanding of the tar formation mechanism on a molecular basis would be very helpful for developing suitable tar reduction for gasification processes and therefore became the main objective of this study.

This study investigated the behaviour of tar formed during biomass gasification in an atmospheric-pressure bubbling fluidized-bed gasifier. The total yield and structural characteristics of tar as well as composition of the product gas at various sampling points along the height of the gasifier were monitored and correlated with the gas (hence tar vapour) residence time inside the gasifier.

2. Experimental

2.1 Raw Material and Property Analysis

In this study, rubber wood was used as the raw material for the gasification experiment. The wood was supplied in chip form and reduced to less than 30 mm (approximately) in length, which was the maximum limit acceptable for the screw feeding system. The moisture content of the chips was also controlled at about 10%. The basic properties of the rubber woodchip were determined by ultimate and proximate analysis and the results are shown in Table 1.

Table 1. Property analysis of rubber woodchip.

Proximate analysis	wt. % dry basis
Volatile matter	84.3
Fixed carbon	14.9
Ash	0.8
Ultimate analysis	wt. % dry ash free
Carbon	46.4
Hydrogen	5.7
Nitrogen	0.2
Sulfur	0.0
Oxygen	47.7

2.2 Bubbling Fluidised-Bed Gasification System

A bubbling fluidised-bed gasification system was designed and constructed at the Joint Graduate School of Energy and Environment (JGSEE), King Mongkut's University of Technology Thonburi, for gasification studies on various solid fuels including biomass, wastes, coal or those in combination. The bubbling fluidised-bed gasifier was designed for an atmospheric-pressure operation and having 100 kW_{th} rated capacity. The system components are illustrated in Figure 4. As for the bed material for bubbling fluidized-bed, 25 kg of silica sand was used. The average particle size of silica sand was 250 µm. Details of the gasification system and experimental procedure have been published elsewhere [13]. Only the detailed description of the tar collection unit, of which the improvement was also made in the current study, will be given in the next section.

2.3 Tar Collection Unit

The previous version of tar collection unit developed in this laboratory [13] was modified from the technical guideline developed by Neeft et al. [14]. The guideline specification applies for sampling and analysis of tars in a wide concentration range (1-300 mg/Nm³) at all relevant sampling point conditions (0-900°C and 0.6-60 bar). In this study, the tar collection unit was further modified to improve the tar recovery. The "improved" version, as schematically shown in Figure 5, consists of (1) a shut-off valve (ball valve) and a filter section (a glass micro-fiber filter; Whatman 934-AH), (2) impinger bottles, (3) a flow

adjustor, (4) a flow meter, and (5) a suction pump or a vacuum pump. This tar collection unit could be connected in any gas sampling ports provided. In both versions, six 250-ml impinger bottles were connected in series by silicone bends. Each bottle was filled with approximately 120 ml of isopropanol, which was used as the tar capturing solvent. Isopropanol is considered to be the most suitable solvent to capture fluidised-bed generated biomass gasification tar due to its solubility. Neeft et al. [14] reported the high tar capture efficiency when using isopropanol in combination with suitable sampling temperature.

Compared to the first version, the gas sampling line in the improved version was shortened to 0.38 m to avoid pre-condensation and allow a more constant and even temperature control. The sampling line was heated at 200°C by electrical heating tape in order to prevent the condensation of water vapour and condensable tar before being captured in the impinger bottles. The temperature of tar capturing solvent was also lowered to ensure that the tar and moisture would be completely removed from the gas stream. The first three bottles were still kept in a salted ice bath at about 5°C, while the other three were cooled down by dry ice to lower the temperature to around -20°C.

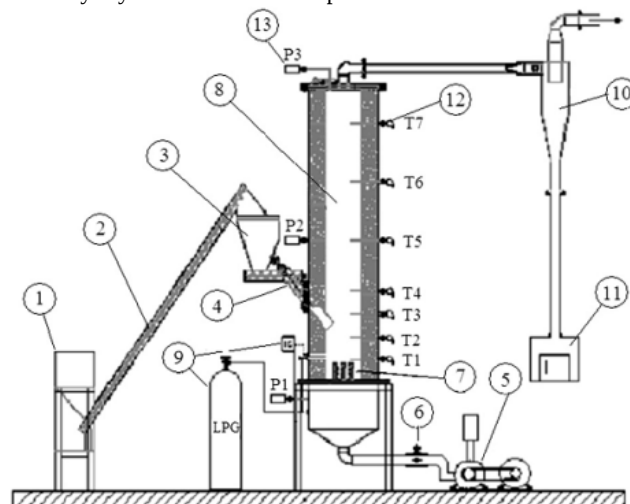


Figure 4. Schematic diagram of bubbling fluidised bed gasification system: (1) ground hopper; (2) screw conveyor; (3) upper hopper; (4) injections crew; (5) force draft fan; (6) air flow meter; (7) air distributor plate; (8) fluidised bed reactor; (9) preheating system; (10) dust cyclone; (11) ash container; (12) thermocouples (T1-T7); and (13) pressure transducers (P1-P3).

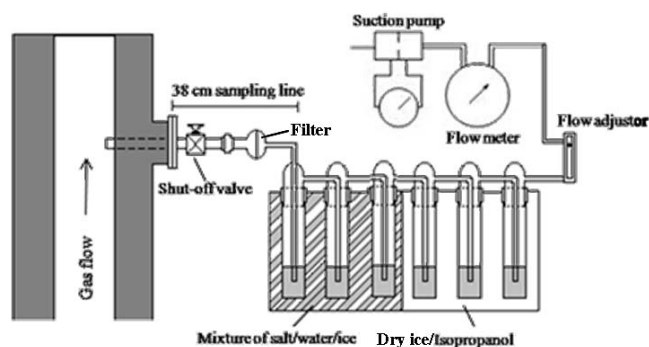


Figure 5. Schematic diagram of the tar collection unit developed in the current study.

2.4 Operating conditions and tar analyses

2.4.1 Investigation of tar recovery using the improved tar collection unit

A set of experiments were performed using the previous and the improved version of tar collection unit under otherwise similar conditions to compare the efficiency of tar recovery. The

conditions used were the biomass feed rate and the air flow rate at 38.7 kg/h and 57.1 Nm³/h (73.5 kg/h), respectively. This corresponded to the equivalent ratio or ER of 0.36. Here, ER is defined as the weight ratio of air to biomass used divided by the weight ratio of air to dry biomass at the stoichiometric proportion. The location of samplings for gas composition analysis was after the dust cyclone. Then, the tar solutions were subjected to analyses for the gravimetric tar yield and concentration of major tar species for comparison.

2.4.2 Investigation of the effect of residence time on tar yield and characteristics

In this experiment, the residence time of tar vapor was varied by sampling the tar containing gas at different positions along the gasifier. There were five different positions, four of which were installed along the gasifier height (SP1-4) and one after the cyclone (SP5), as shown in Figure 6. The conditions used were the biomass feeding rate at 38.72 kg/h and the air flow rate at 51.37 Nm³/h (or 66.15 kg/h), which corresponded to the ER of 0.33. The gas residence time at each sampling position depends on the height of the sampling position from air distributor and the average temperature within that zone height and the corresponding gas residence times are shown in Table 2.

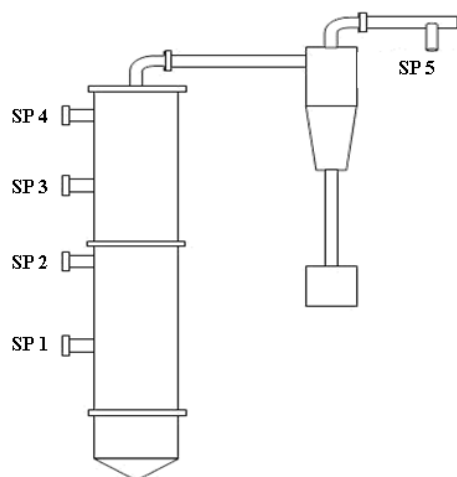


Figure 6. Positions of sampling port along the gasifier height and after cyclone.

Table 2. The corresponding parameters at different sampling positions (SP).

Sampling position	SP1	SP2	SP3	SP4	SP5
Distances from air distributor plate (m)	0.5	0.96	1.46	1.96	3.12
Gas residence time (s)	2.5	4.8	7.3	9.8	15.6
Temperature (°C)	803	620	502	418	250

For gas and tar collection for further analyses, the sampled gas with the controlled volume flow rate of 3.0 l/min was passed through the filter and then the series of impinger bottles for a determined period of time. After the sampling, the gas sampling line and filter were rinsed with iso-propanol to collect any pre-condensed tar deposit and the solution was added into that from the impinger bottles. The mixture was then filtered through a glass micro-fiber filter (Whatman 934-AH) before dividing into three fractions. The first fraction was used to determine the gravimetric tar. The second fraction was for tar composition analysis and the third fraction was used to analyze the molecular mass distribution. The non-condensable gas after the tar collection unit was analyzed online by micro-gas chromatography with thermal conductivity detector (Micro GC-

TCD; Varian CP-4900 model) The analyzed gas components included O₂, N₂, H₂, CO, CO₂, CH₄, C₂H₄ and C₄H₆.

2.4.3 Tar analyses

The gravimetric tar can be defined as a residue from the evaporation process. In order to determine the gravimetric tar, a rotary evaporator (BUSHI R-205 + V-800 model) was used to evaporate iso-propanol from the tar solution under reduced pressure. The residue from the evaporation process is defined as the gravimetric tar.

The individual tar species were quantified using Gas Chromatography with Flame Ionization Detector (GC-FID). The gas chromatography (GC; Clarus 500 Perkin-Elmer) equipped with RTX-1701 capillary column with a 60 m × 0.25 mm, 0.25 μm film thickness was used in this study. A set of chemicals that were considered as the likely species in gasification tars [15]; including benzene, toluene, p-xylene, styrene, phenol, indene, naphthalene, phenanthrene, anthracene and pyrene were used as external standard reagents.

By a different analysis mechanism, gel permeation chromatography (GPC) can detect a wider range of tar molecular weights which include both GC-detectable and GC-undetectable fractions. In this study, the tar molecular weight distribution was analysed by GPC (Shimadzu LC-10A) with UV detector. The column used was Shodex GPC KF-801 (8 mm × 300 mm). The range of molecular weight covered from 126 to 2,970 amu. Tetrahydrofuran was used as an eluent with a flow rate of 1 ml/min and polystyrene was used as a standard compound. The column was operated at 1.4 MPa and 25°C. The UV spectrum was extracted at 254 nm (at 40°C of cell temperature) which responded primarily to compounds with aromatic structure.

3. Results and Discussion

3.1 Performance comparison of existing and improved tar collection unit

The resulting gasification temperature, product gas composition, total gravimetric tar and concentration of major tar species from two experiments using existing and improved tar collection unit under identical conditions are given in Table 3. The gasification temperature and product gas composition were monitored to ensure that the resulting total gravimetric tar and concentration of major tar species were not influenced by the experimental conditions.

Table 3. Performance comparison between the two tar collection units.

	Tar collection unit	
	Previous version	Improved version
Temperature (°C)	806	803
Gas compositions (%mol, N ₂ free basis)		
Hydrogen	8.5	7.6
Carbon monoxide	37.2	38.7
Carbon dioxide	43.8	42.4
Methane	8.6	8.6
C ₂ H ₄	2.0	2.1
Total gravimetric tar (g/Nm³)	3.58	12.20
Tar concentration (mg/Nm ³)		
Toluene	-	99.92
Xylene	15.21	55.33
Styrene	28.53	72.59
Phenol	36.60	70.80
Indene	-	135.42
Naphthalene	21.59	23.34

The results from Table 3 show no significant difference of the gasification temperature and product gas composition between the two experiments, which confirms that any differences in the tar yield obtained would have been due solely to the different collectability of the employed tar collection units. Considering tar yield and tar characteristics, it is very clear that using the improved unit significantly improved the tar collection. The tar yield increased from 3.58 to 12.2 g/Nm³ when replacing the previous version with the improved one. It is likely that the leakage and condensation inside the sampling line of tar could be largely reduced by the shortened length of the sampling line. In addition, using the improved tar unit not only increased the ability of tar capture but also affected some tar compositions such as toluene and indene. From Table 3, the toluene and indene were not detected when using the previous version of the tar collection unit; while they appeared at high concentration when using the improved version. This was likely due to the low temperature (-20°C) that improved the rate of tar condensation.

The comparison of the tar yield from the bubbling fluidized bed gasification system obtained from the current measurement in this study with those reported in other studies shows that the value was agreeable. According to the review of Han and Kim [16], the mean tar content in the bubbling fluidized-bed gasifier was about 12 g/m³, while Mile et al. [3] reported that a fluidised-bed biomass gasifier produced the synthesis gas with a tar content of 10 g/m³. This concludes that the improved version provided more realistic tar yield results than did the previous version and was therefore employed in this study.

3.2 Effect of gas residence time on product gas compositions

The product gas (containing tar) was collected along the gasifier height in order to vary the gas (and hence tar) residence time or the exposure of tar in the gasifier. At the ER=0.33, the average temperature of the bed zone was found at 810°C (±10°C).

The compositions of gas sampled at different residence times are shown in Figure 7. The major gas compositions were CO and CO₂, with smaller but significant amounts of CH₄, H₂ and light hydrocarbon gases (C₂H_n). The significant concentrations of CO and H₂ formed were found at the position SP2, after which the increased concentrations of CO and H₂ at longer residence times may be attributed to the tar reforming reactions and thermal cracking. H₂ is also a good indicator when converting the primary and/or secondary tar into PAH compounds [3]. C₂H_n initially increased but later decreased at extended residence times. C₂H₂ and C₂H₄ are unsaturated compounds, which are an important precursor in explaining in the tar reaction mechanism. Li et al. [17] indicated that C₂H₂ can be produced from decomposition of benzene. It is an important precursor for the growth of PAH formation and that is important also to the reactivity of hydrogen for tar transformation.

3.3 Effect of gas residence time on tar yield and characteristics

The gravimetric tar yields determined from different positions of sampling are plotted against the gas residence time as shown in Figure 8. The tar yield increased from 4.5 to 10.5 g/Nm³ when increasing the residence time from 2.5 to 9.8 s. This suggests the formation of tar (probably both primary and secondary tar) due to a longer exposure at high temperatures inside the gasifier. At the position after the cyclone (i.e. at 15.6 s), the tar concentration slightly decreased, likely due to the partial capture by cyclone. Although the gas residence time has little effect on tar yield, it has a significant effect on composition of major tar species and molecular weight distribution.

Figure 9 shows the concentration of major tar species, including toluene, xylene, styrene, phenol, indene and naphthalene in the range of gas residence time 2.5-9.8 s. The trend follows

that of the total gravimetric tar yield, especially between 7.3 to 9.8 s. At the position after the cyclone, the concentrations of all tar species (except indene) moderately decreased as compared to the position SP4 inside the gasifier. Since the gas temperature leaving the gasifier is sufficiently low, the long travelling time of the product gas would have little effect on the tar concentrations. The observed reduction of tar concentration is likely due to the partial capture by the cyclone.

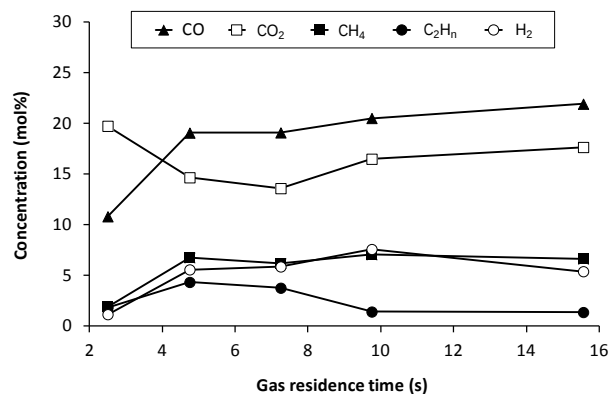


Figure 7. Effect of gas residence time on gas compositions (N₂-free basis).

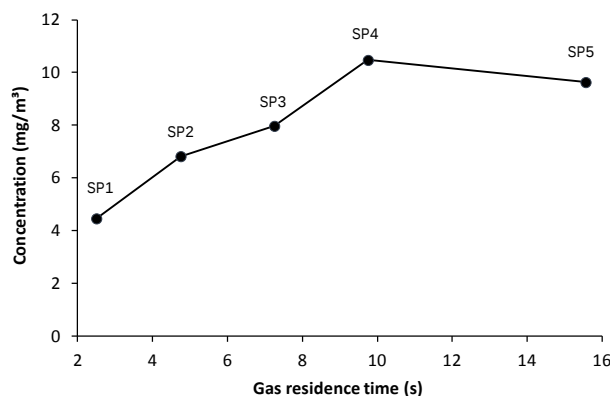


Figure 8. Effect of gas residence time on gravimetric tar yield.

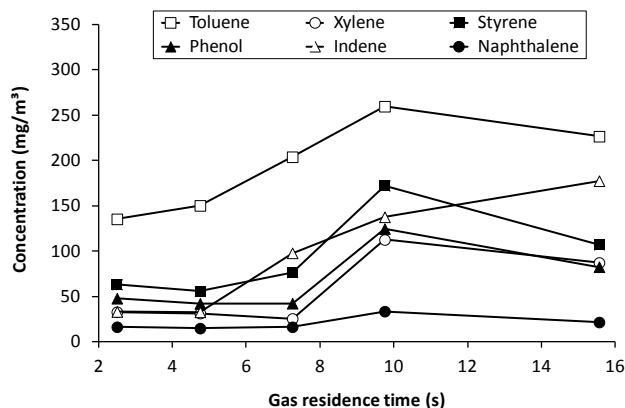


Figure 9. Effect of gas residence time on concentrations of major tar species.

The molecular weight distributions of tar analyzed by gel permeation chromatography (GPC) are as shown in Figure 10. Three resolved peaks centered at 100-150 amu, 240-280 amu and 350-380 amu could be observed for the four samples collected along the gasifier (SP1-4), while the middle peak disappeared for the sample collected after the cyclone (SP5). From the relative intensities, the first peak representing smaller molecular mass materials increased as the gas residence time

was extended, while the other two peaks representing larger molecular mass materials decreased. The relative ratio between small-to-large molecular mass materials generally increased, which was an indication of tar decomposition due to cracking, steam and dry reforming reactions to form smaller compounds. However, the increased ratio between the third and the second peak as the residence time was extended to 9.8 s, which indicated the growth of the aromatic ring (PAH) in the tar structure.

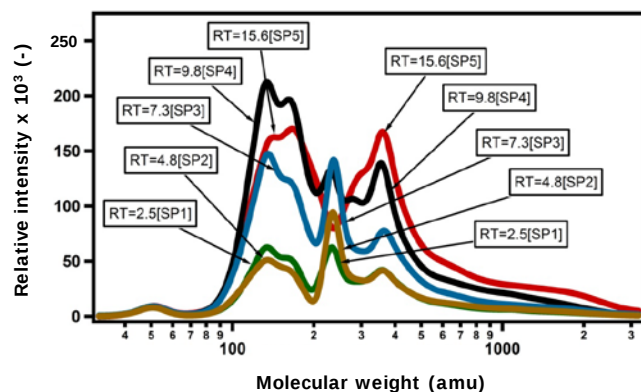


Figure 10. The effect of gas residence time on tar molecular weight distribution.

4. Conclusions

This study investigated the behaviour of tar formed during fluidized-bed gasification. Experiments were carried out in a 100 kW_{th} bubbling fluidized bed gasifier using rubber woodchip as fuel. The total yield and structural characteristics of tar as well as the composition of product gas were monitored and correlated with respective gas (and hence tar vapour) residence time. Gas sampling at different positions, i.e. four along the height of the gasifier (SP1-4) and one after the cyclone (SP5), was carried out, which gave the range of residence time from 2.5 to 15.6 s. The improved version of tar collection unit, which was also proved to provide more realistic tar yield, was employed in this study.

The experiment was carried out at ER=0.33. The major gas compositions were CO and CO₂. The significant concentrations of CO and H₂ formed were found at the position SP2 or 4.8 s, after which the increased concentrations of CO and H₂ at longer residence times may be attributed to the tar reforming reactions and thermal cracking. The total gravimetric tar increased from 4.5 to 10.5 g/Nm³ when the residence time increased from 2.5 to 9.8 s. The increasing gravimetric tar yield as the residence time increased inside the gasifier suggests that more tar (probably both primary and secondary tar) was formed as it was exposed to high temperature. The concentrations of all tar major species (i.e. toluene, xylene, styrene, phenol, indene, naphthalene) also increased following the trend of gravimetric tar yield. However, considering the molecular weight distribution of tar, the GPC analysis showed that the ratio of large to small molecular weight materials decreased at extended residence time. The results have shown that the longer residence time would be preferable as it would allow more time for the reaction of tar vapor to crack into smaller molecular weights and to form more product gases.

Acknowledgements

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