

THE EFFECT OF TEMPERATURE AND STEAM CONCENTRATION ON THE YIELDS OF TAR COMPOUNDS IN FLUIDIZED BED PYROLYSIS

D. Fuentes-Cano*, A. Gómez-Barea, S. Nilsson, M. Campoy, P. Ollero

Chemical and Environmental Engineering Department. Escuela Superior de Ingenieros (University of Seville) Camino de los Descubrimientos s/n. 41092 - Seville. Spain

*corresponding author: Tel.: +34 95 4486045; Fax: +34 95 4461775; e-mail address: dfcano@esi.us.es

ABSTRACT: The effect of temperature and steam concentration on the yields of different tar compounds was investigated. Wood pellets and dried sewage sludge spheres (DSS) were pyrolyzed in a fluidized bed reactor in the temperature range of 500-800°C. The reactor has two independent electrically heated zones, enabling independent adjustment of the temperature of generation of volatiles (release of volatiles during thermal decomposition of the fuel particle) and secondary conversion of the volatiles on homogeneous phase. The temperatures of the bed and the freeboard were varied independently keeping constant the residence time of volatiles in each zone. This work is one of the tasks within a project whose overall objective is the development of a three stage gasification process to generate a gas with low tar content. The specific aim of this task is to identify the conditions minimizing the heavy tar formation. Parameters such as the air injection points or the steam addition could be adjusted on the gasifier design and they are of capital significance on temperatures distribution and hence on tar formation and conversion. Therefore this works try to clarify the effects of temperature stratification and steam addition on tar formation and conversion in order to be an useful tool during the gasifier design.

Keywords: tar, steam, fluidized bed, pyrolysis

1 INTRODUCTION

The increasing energy demand and the environmental problems caused by the use of fossil fuels motivate the search of new renewable energy sources. The use of biomass and wastes in thermochemical applications have been deeply investigated in the last two decades. The most promising techniques are the pyrolysis and the gasification. The first tries to maximize the recovery of the biomass energy in a liquid-oil phase useful for chemicals production or fuel applications. The objective of gasification is to recover a fuel gas with most of the energy of the parent fuel (biomass or wastes). At high heating rates and temperatures between 400 and 550°C the liquids production is maximum^{1,2} so this is the usual range of temperatures in flash pyrolysis reactors.

Autothermal fluidized-bed gasifiers usually work at temperatures between 750 and 900°C which enhance the production of low-weight combustible gases, however the presence of tars in the gas limits the utilization of the gas in other application than direct firing of the gas.

For the end use of gas it is important to reduce the gas dew point as much as possible to avoid tar condensation in the downstream processes. In gasifier design the temperature of different zones can be adjusted to some extent (by adjusting the air injection points) so it is interesting to know the effects of temperature on tar formation during fuel devolatilization and secondary reactions such as cracking, reforming and ring grow reactions.

The nature of tars varies widely with the temperature of generation and the residence time at high temperatures (severity conditions). Pyrolysis tar is a mixture chemically very complex, it is mainly composed of aliphatic and oxygenated chains (alcohols, esters and acids)³ or aromatic structures such as guaiacols or syringols derived from the parent fuel. Fairly less abundant are the unsubstituted polyaromatics hydrocarbons (PAH) such as naphthalene or pyrene at temperatures below 700°C^{1,4}. However in fluidized bed gasifiers the proportion of PAH is substantially increased at the expense of the structural rearrangement of primary compounds. Furthermore the ring-grow reactions leads to

important soot yields when the temperature is increased above 850°C^{5,6}. The two main mechanisms involved in the ring-grow reactions is supposed to be the direct interaction between two aromatic molecules or the HACA mechanism where C2 units are added to the aromatic structure^{7,8}.

The main objective of the present work is to characterize the tars generated at two different temperatures and determine the structural changes that they undergo in a thermal and (or) steam treatment.

2 EXPERIMENTAL

2.1 Fuels

The two fuels used were commercial wood pellets and dried sewage sludge (DSS) granulates. Both fuels were dried for 16 hours at 105°C and stored in a dry ambient before the test. The wood pellets had 6 mm diameter and between 8 and 12 mm of length. The DSS was sieved between 2 and 2,8 mm in most experiences, however the effect of the particle size was also studied for the particle ranges of 1-1,4 mm and 4-5 mm DSS in some tests.

The ultimate and proximate analyses of the two biomasses tested are presented in table 1.

Table I : ultimate and proximate analysis of the biomasses tested.

	Wood pellets		DSS	
	Wet basis	Dry basis	Wet basis	Dry basis
C (wt%)	-	49,47	-	30,88
H (wt%)	-	5,79	-	4,36
N (wt%)	-	2,03	-	4,76
S (wt%)	-	0,06	-	1,24
O (wt%)	-	41,94	-	15,61
Moisture (wt%)	1,03	-	0,65	-
Ash (wt%)	0,70	0,71	42,87	43,15
Volatiles (wt%)	80,15	80,98	51,41	51,75
Fixed C (wt%)	18,12	18,31	5,07	5,10

2.2 Reactor

The reactor (figure 1) was constructed from steel AISI 310 and had two separately controlled heated zones.

The lower zone was a cylindrical fluidized bed with 53 mm of internal diameter and 192 mm of height. The upper zone, freeboard, had 81 mm of internal diameter and 240 mm of height with a transition zone of 50 mm of height. The inert bed material was bauxite (aluminosilicate) sieved between 250 and 500 μm with a static bed height of 80 mm. The biomass is introduced discontinuously through the freeboard to the bed. On every addition 3 g of wood pellets or 5 g of DSS were fed to the reactor. The fluidizing agent (N_2) was introduced, preheated, through the distributor in the base of the bed and through the transition zone. The N_2 and the steam were introduced in two points in order to control the residence time of volatiles in the fluidized bed and in the freeboard. The residence time in the bed and freeboard was fixed, respectively, at 0,6 and 1 second for every tests. In the experiences where the addition of 30% of steam to the fluidizing agent was tested the water was fed with a peristaltic pump to the bottom of the reactor (primary feeding) and with a syringe pump to the secondary feeding port located in the transition zone between the bed and freeboard.



Figure 1: Fluidized bed reactor

The product gas passes through an impinger train (7 impingers) filled with isopropanol at -20°C . In order to improve the contact between liquid and gas, four of these impingers had glass frits. After each sampling the solvent was recovered and the impinger's train was washed with acetone. The acetone used to wash the train was mixed with the isopropanol and stored at -20°C . The char yield was calculated by analyzing the gases produced during burning with air the remaining carbonaceous material in the reactor after the pyrolysis.

2.3 Reactor temperatures

Four different temperature configurations, given in Table 2, were programmed for the experiences. In configurations 1 and 2 the freeboard was kept at 600°C to minimize the secondary conversion of tar so the tars measured was assumed to be similar to that generated in bed at 500°C and 800°C . In configurations 3 and 4 the tar generated at 500°C and 800°C passed through the high temperature freeboard at 800°C . Then, the tars measured in these tests are expected to inform about the extent of conversion of the reactions between 500°C and 800°C tars.

Table II : Temperatures configuration in pyrolysis reactor

	Config. 1	Config. 2	Config. 3	Config. 4
Bed temperature ($^\circ\text{C}$)	500	800	500	800
Freeboard temperature ($^\circ\text{C}$)	600	600	800	800

2.4 Gas analysis

Permanent gases (CO_2 , CO , H_2 and CH_4) were monitored using an on-line gas analyzer (IR for C containing gases and TCD for H_2).

2.5 Tar analysis

In order to characterize the tars captured after each test the samples will be analyzed using 2 analytical procedures.

- 1- The total tar amount was determined by a gravimetric method using a rotary evaporator. The solvent was evaporated at 55°C and 1,5 KPa to constant weight.
- 2- The yields of aromatics (from benzene to perylene) were quantified by gas chromatography-mass spectrometry. Aromatic tars represent only a small fraction of the total tar mixture in pyrolysis^{1,9}, however these compounds are by far the most stable at high temperatures. That is why most tars found in gasifiers belongs to this group of molecules and why is so important to determine the effects of operative variables on its composition. The analysis system used a capillary column model TRB-Meta X5 (60mx0.25mmx0.25 μm) with polysiloxane packing. More than 30 aromatic compounds are quantified using analytical standards to calibrate the system. Some PAH with 4 and 5 rings and with no analytical standards were quantified using the calibration curves of their isomers. Some experiences were conducted to check if it was possible to analyze primary tars (highly oxygenated), however due to its high polarity it was not feasible. In order to simplify the analysis all the tars were classified according to¹⁰ in tar classes from 2 to 5, see Table 3.

Table III : Tar classification

Classes	Representative compounds
Tar class 1. GC-undetectable	Acids, poly-alcohols, ... Determined by subtracting the GC-detectable fraction from the total gravimetric tar
Tar class 2. Heterocyclic	Phenol, cresol, thiophene
Tar class 3. 1 aromatic ring	Toluene, indene. Benzene is here considered a tar class 3.
Tar class 4. 2-3 aromatic rings	Naphthalene, Phenanthrene
Tar class 5. 4-7 aromatic rings	Pyrene

3 RESULTS

The yields of the pyrolysis products and gravimetric tar are presented in Tables 4 and 5. The values presented are the average of two or more experiences. The gas and char yields were calculated by balances with the gas on-line measures. The “other compounds” yield (tars, non quantified hydrocarbons and pyrolytic water) was calculated by difference.

Table IV : DSS product yields in pyrolysis

DSS Product yields (wt% daf)	Config. 1	Config. 2	Config. 3	Config. 4
Gas	16,7	39,1	33,2	52,0
Char	18,8	14,4	21,3	14,7
Other compounds (tar, light hydrocarbons, H ₂ O) by difference	64,5	46,5	45,5	33,3
Gravimetric tar	32,9	25,0	11,7	15,4
Light hydrocarbons, H ₂ O (Others – Gravimetric tar)	31,6	21,5	33,8	17,9

Table V: Wood pellets product yields in pyrolysis

Wood pellets product yields (wt% daf)	Config. 1	Config. 2	Config. 3	Config. 4
Gas	21,4	46,0	44,8	57,3
Char	20,1	18,9	21,5	17,5
Others compounds (tar, light hydrocarbons, H ₂ O) by difference	58,5	35,1	33,7	25,2
Gravimetric tar	23,2	12,7	9,3	7,1
Light hydrocarbons, H ₂ O (Others – Gravimetric tar)	35,3	22,4	24,4	18,1

The light hydrocarbon yield (and pyrolytic water) is here estimated subtracting the gravimetric tar yield to the yield of tars and hydrocarbons calculated by balances (“other compounds”). The char yields varied slightly with temperature. DSS produces higher gravimetric tar yields and lower gas yields than wood pellets in all tests.

Variation of char yields with temperature is more pronounced in DSS (from 20% aprox. to 14,5%) than in wood.

3.1 Tar analyses

Tables 6 and 7 show the aromatic tar yields of DSS and wood pellets divided in families according with¹⁰.

Experiences with different DSS particle size are included in the average results presented in table 6 due to the small differences found. Unfortunately in wood tests only one chromatographic analysis was completed for each configuration, therefore these results must be analyzed with caution.

Table VI : DSS aromatic tar yields divided in families

DSS tar yields (ppmw daf)	Config. 1	Config. 2	Config. 3	Config. 4
Tar class 2 yield	2944	4846	6198	6449
Tar class 3 yield	4452	16363	33121	33039
Tar class 4 yield	992	2802	8380	10353
Tar class 5 yield	228	289	1290	1962
Total yield	8615	24300	48989	51802
Gravimetric yield	329000	250000	117000	154000

Table VII : Wood pellets aromatic tar yields divided in families

Wood pellets tar yields (ppmw daf)	Config. 1	Config. 2	Config. 3	Config. 4
Tar class 2 yield	1204	5908	4286	4426
Tar class 3 yield	2164	25535	18577	28216
Tar class 4 yield	620	4370	3133	5753
Tar class 5 yield	1065	598	587	911
Total yield	5053	36410	26583	39306
Gravimetric yield	232000	127000	93000	71000

In tables 6 and 7 the total aromatic yield is compared with the gravimetric yield. It is observed that the yield of aromatic tars is low at the lowest temperature, increasing with temperature being 1/3 of total tars in Configuration 4 with DSS. With wood pellets the aromatics proportion is even higher. Another important fact is the similarity in aromatic tar yields between Configuration 3 and 4 with DSS. This reveals that, the temperature at which the tar is generated has little effect on the final aromatics composition. Comparing Configurations 1 and 2 it is seen that the gas yield increases with temperature but the yield of heavy families (the most problematic ones) does not increase significantly. However in Configuration 2 the yield of tar class 3 are several times higher than that in Configuration 1. These increases highlights the sequential ring grow reactions of aromatic tars.

Different results were obtained by testing wood pellets. Gravimetric tar decreases from configuration 1 to 4 (approximately as in DSS tests), however aromatic tars seem to “mature” faster than those produced in DSS tests.

Small differences in aromatic tars were found between configurations 2, 3 and 4. In Configuration 2 (0.6 s at 800°C) the aromatic yield increases markedly.

However tests providing longer residence times at 800°C do not significantly change the tar composition.

The extremely high yield of tar class 5 in Configuration 1 must be due to a contamination of the tar sample.

3.2 Steam experiences

The effect of steam addition on tar composition was studied adding steam to the fluidizing agent (N₂) in a proportion 30/70 (steam/N₂). In Table 8 the gravimetric tar yields of experiences without steam are compared with the results obtained in the experiences with steam.

Table VIII : Gravimetric tar yields in tests with and without steam addition

Gravimetric tar (wt% daf)	Config. 1	Config. 2	Config. 3	Config. 4
DSS (no steam)	32,9	25,0	11,7	15,4
DSS (30% steam)	23,3	13,5	Not finished	5,8
Wood (no steam)	23,2	12,7	9,3	7,1
Wood (30% steam)	17,7	8,2	5,0	0,1

The gravimetric tar obtained with steam shows a significant influence of steam in the four configurations studied. The reductions of gravimetric tars are in the range between 26% (wood, Configuration 1) and 98% (wood, Configuration 4). Tars from both wood and DSS seem to be reduced in similar proportions.

4 FUTURE WORKS

Quantification of ethane, ethylene, acetylene, propane, propene and pyrolytic water is necessary to characterize the gases formed during the experiences.

Furthermore if gas yields are measured properly it could be achieved a more accurate estimation of primary tar yields by balance.

In future experiences five gas samples will be taken, during the devolatilization, using gas-tight syringes.

These gas samples will be taken after the impingers train and will be analyzed with a micro-GC model 3000A with 2 channels. The channel A with a plot U/MS capillary column measures the concentration of H₂, O₂, N₂, CO and CH₄, and the channel B with Plot U/U capillary column measures the concentration of CO₂, C₂H₆, C₂H₄, C₂H₂, C₃H₈ and C₃H₆. Both channels have a micro-TCD detector and use argon as carrier gas.

Pyrolytic water yield will be measured by analyzing with a Karl-Fischer device the water content in the tar-capture liquid.

In order to complete the structural information of tars formed in the tests described three additional analysis will be done to tar samples.

- 1- The elemental analyses of evaporated tar samples will be performed with a LECO CHNS-932. In these analyses the content of C, H, N and S will be measured and the content of oxygen will be calculated by difference.
- 2- RMNs analyses will be performed to determine the structural changes of tars with the reactor temperature. ¹H NMR will be obtained with a Bruker advance 300 (13 MHz, 2 hours) and ¹³C NMR with the same spectrometer (75.48 MHz, 48 hours). The sample will be prepared by dissolving the tar in Acetone-D₆ using TMS as an internal reference.
- 3- The range of molecular masses is expected to be determined by HPLC-mass spectrometry analyses. The analyses will be performed using H₂O and MeOH as eluents, a Zorbax eclipse XDB-C18 (2.1x150mm, 3.5µm) column and EMS (enhanced mass spectrum) EPI (enhanced product ion), XIC (extracted ion chromatogram), spectra will be performed to obtain the mass distribution.

5 CONCLUSIONS

- DSS produces more tar and more heavy aromatics than wood, making the utilization of DSS gas more difficult than that generated with wood.
- For DSS the bed temperature has little influence on tar composition if a thermal treatment is applied later to the gas.

- Changing the DSS particle in the range of 1-5 mm has only a slight effect on tar composition.
- Steam addition strongly enhances tar conversion, especially at higher temperatures.
- Further tar analyses are needed to understand the results properly.

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