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Characterization of Tar from the Pyrolysis/Gasification of Refuse Derived Fuel: Influence of Process Parameters and Catalysis

Paula H. Blanco, Chunfei Wu, Jude A. Onwudili, and Paul T. Williams*

Energy Research Institute, University of Leeds, Leeds LS2 9JT, U.K.

ABSTRACT: Two nickel-based catalysts were prepared and investigated in relation to their influence over aromatic compounds contained in tar from the pyrolysis–gasification of refuse derived fuel (RDF), using a two-stage reaction system. The results were compared with those obtained in experiments carried out using a bed of sand, both with steam and without steam. The condensed tar was analyzed for its polycyclic aromatic hydrocarbon (PAH) content using gas chromatography–mass spectrometry (GC-MS), size exclusion chromatography (SEC), and Fourier transform infrared spectroscopy (FTIR) techniques. It was found that, in the presence of Ni/ α -Al₂O₃ catalysts, some of the PAHs from three to four rings were eliminated; however, some single-ring and two-ring compounds such as styrene and indene were identified. This was also inferred from the molecular mass data (SEC). The identified PAHs consisted mainly of naphthalene, biphenyl, acenaphthylene, fluorene, and phenanthrene, but other PAHs also were identified for example: methylnaphthalenes. The influence of catalyst type on the gas composition showed that, using a 10 wt % Ni/ α -Al₂O₃ catalyst, ~45 vol % of hydrogen was achieved, while the CH₄ and C₂–C₄ concentrations were markedly reduced, compared with the 5 wt % Ni/ α -Al₂O₃ catalyst, which gave similar results to those obtained with the sand bed under the same conditions. The presence of oxygenated compounds in the tar samples was compared at different gasification temperatures. The results showed the presence of oxygenated compounds such as catechols and alcohols at 600 °C, these compounds were reduced as the gasification temperature increased, while the concentration of aromatic compounds increased.

1. INTRODUCTION

Large amounts of municipal solid waste (MSW) are generated through the world every year; for example, the United States produced 243 million tonnes of MSW in 2009,¹ and the U.K. generated about 33 million tonnes in 2008.² The most common components found in a MSW stream are kitchen and garden waste, paper and card, plastics, and ferrous metals, among others.³ Refuse derived fuel (RDF) is a combustible fraction obtained from municipal solid waste stream by means of a presorting process consisting of several steps aimed to separate the noncombustible fractions such as glass and metals, resulting in a higher calorific value derived fuel consisting of mainly paper, cardboard, and plastics.⁴

Currently, there is an excessive global demand for energy that has promoted the search for alternate energy supplies other than fossil fuels. The pyrolysis–gasification of RDF is a promising technology and a viable source to obtain high-energy value synthesis gas (syngas). However, one of the major issues associated with the process is tar formation, which reduces the quality of the gas produced.^{5,6} Tar is a mixture of aromatic hydrocarbons contained in the product gas, mainly consisting of aromatic compounds together with oxygenated compounds.^{7–9} Due to its chemical composition, tar tends to condense in the gasifier or in the postgasification process, causing problems such as blockages in engines, turbines, and pipelines, and as a result, there is a reduction in the overall yield of the gasification process.¹⁰ The formation pathway for the different types of tar as a function of temperature is depicted in Figure 1.^{9,11}

Catalytic steam reforming is a widely employed technique that seeks both the reduction of tar formation and the increase of the calorific value of the syngas. Nickel-based catalysts have

been extensively studied to reduce tar formation, mainly in the biomass gasification process,^{11–15} and are preferred over other catalysts such as Rh, Ru, or Pt because of their comparative lower cost, availability, and efficiency of tar removal.^{16–18} Different catalyst preparation methods, such as sol–gel and impregnation, have been reported to be effective to improve both catalyst characteristics and their performance during the gasification process.^{19–21}

Many tars derived from biomass and wastes gasification are known to contain polycyclic aromatic hydrocarbons (PAHs) and some oxygenated compounds, depending on the operational process conditions. For example, Elliott and Baker²² analyzed tars produced from noncatalytic and catalytic biomass gasification at 750 °C. The major PAH compounds found for biomass gasification were phenol, cresol, indene, naphthalene, and methylnaphthalenes; however, the PAHs found by using catalytic gasification were benzene, toluene, naphthalene, xylene, and styrene. Later, Baker et al.²³ reported that the tar composition from biomass gasification at 750 °C was primarily aromatic single-ring phenolic compounds. Miccio¹⁴ tested a nickel-based catalyst during biomass gasification at 780 °C, finding benzene and naphthalene as the major PAH compounds. Dufour²⁴ characterized the tars derived from biomass pyrolysis–gasification at different temperatures, finding benzene, toluene, *o*- and *m*-xylenes, phenol, indene, and phenanthrene, among other PAH compounds. Williams et al.²⁵ reported that the PAHs contained in pyrolysis oils from

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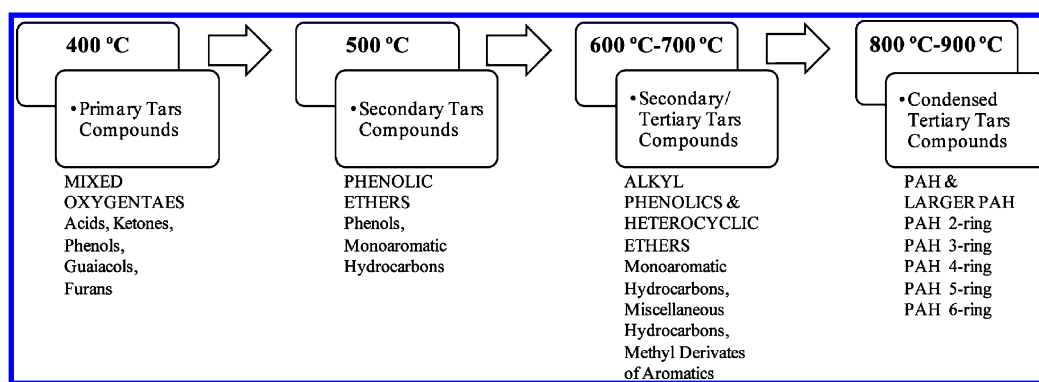


Figure 1. Pathway tar formation as a function of temperature.^{9,48}

biomass and RDF pyrolysis included naphthalenes, methyl-naphthalenes, dimethylnaphthalenes, methylbiphenyl, fluorene, methylfluorene, phenanthrene, methylphenanthrene, benzo-fluorene, pyrene, chrysene, and methylchrysene.

In this paper, the product gas yield and composition and the derived tar composition from the pyrolysis–gasification of RDF were investigated in the absence (using sand) and presence of two Ni-based catalysts at different gasification temperatures. The tar was characterized using gas chromatography–mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), and size exclusion chromatography (SEC) techniques.

2. MATERIALS AND METHODS

2.1. Materials. The refuse derived fuel used in this research was selected to be representative of municipal solid waste, with the removal of recyclable glass and metals. The RDF was in the form of 16 mm diameter by 80 mm long pellets. To increase the homogeneity of the material for this test work, a reasonably large quantity of the RDF was taken and mixed and coned and quartered repeatedly. The sample was then shredded and ground to produce a large quantity of RDF sample of particle size ~1.00 mm diameter, which was then further coned and quartered to produce the feedstock for the pyrolysis–gasification experiments. The elemental analysis of the RDF sample, as received, is presented in Table 1.

Table 1. Properties of RDF

proximate analysis (wt %)	
moisture content	7.3
ash content	15.0
volatile matter	67.5
fixed carbon	10.2
ultimate analysis DAF (wt %)	
C	42.7
H	6.1
O	32.0
N	0.5

Nickel-based catalysts with two different weight percentages (5 wt % and 10 wt %) were prepared by an impregnation method, using α - Al_2O_3 support (Aldrich, 99%) and a prepared aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (from Aldrich). After drying at 105 °C, the catalysts were calcined at 750 °C, with a heating rate of 20 °C min^{-1} for 3 h and under an air atmosphere. Both catalysts were sieved to obtain granules with a size range between 80 and 200 μm . The activation of the catalysts was performed inside the gasification reaction system before the experiment by preheating at 800 °C under nitrogen atmosphere. Sand with

similar particle size was used for comparison with the catalytic gasification.

2.2. Reaction System. The pyrolysis–gasification process of RDF was performed in a two-stage fixed-bed reactor (Figure 2). The

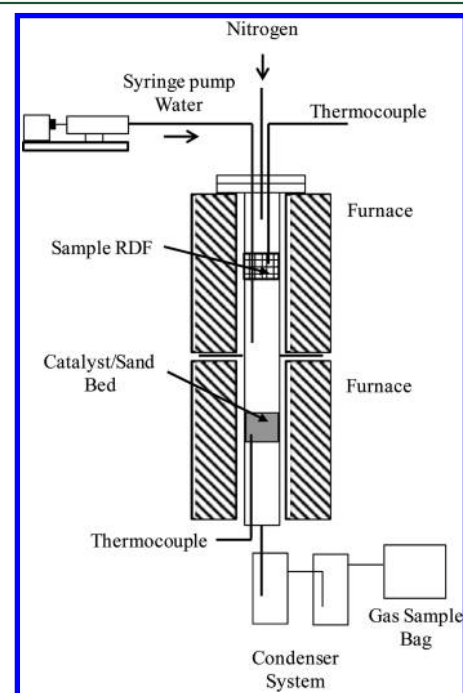


Figure 2. Schematic diagram of the two-stage fixed-bed catalytic reactor.

pyrolysis reactor was constructed of stainless steel with a length of 26 cm and diameter of 5 cm; the gasification reactor was 35 cm in length and 2.5 cm in diameter and was also constructed of stainless steel. The reactors were mounted vertically with the pyrolysis in the upper reactor and catalytic gasification in the lower reactor and were separately heated by two electrical furnaces to the desired temperature. There was negligible heat transfer between the reactors. The reactors were continually purged with nitrogen. The RDF sample (1.0 g) was placed in the first stage of the reactor where the pyrolysis process takes place. The sample container was weighed before and after the experiment to calculate the conversion rate of the RDF to gas and liquids, with the balance being char. The evolved pyrolysis gases and vapors from the first stage are directly passed to the second stage reactor where the catalyst is held and steam is introduced; thereby, gasification of the evolved pyrolysis products occurs. The furnaces of each stage were thermally controlled independently. About 0.5 g of sand or catalyst was placed in the second stage that was initially heated up to 800 °C; a nitrogen flow rate was passed through the reactor, and

Table 2. Results of Pyrolysis–Gasification of RDF with Different Bed Materials

	sand bed				Ni/ α -Al ₂ O ₃	
	no steam	steam			5 wt %	10 wt %
temp.	800 °C	600 °C	700 °C	800 °C	800 °C	800 °C
water flow rate (g h ⁻¹)	0.00	5.00	5.00	5.00	5.00	5.00
gas composition (vol %)						
CO	27.09	20.90	21.00	18.15	16.70	17.00
H ₂	18.70	21.70	20.10	31.61	39.42	45.54
CO ₂	20.58	27.20	19.50	20.04	21.06	23.81
CH ₄	20.58	12.60	15.80	18.23	12.19	7.52
C ₂ –C ₄	11.01	17.50	23.50	11.98	10.64	6.13
H ₂ /CO ratio	0.69	1.04	0.96	1.74	2.36	2.68
gas yield (wt %)	30.85	25.40	31.50	34.71	37.08	45.89
conversion to gas/oil (wt %)	69.81	70.20	71.50	69.26	67.51	69.11
mass balance (%)	84.85	92.10	91.37	92.54	101.14	102.30

then, the first pyrolysis stage was heated up to 600 °C with a heating rate of 30 °C min⁻¹. Once the temperature in the pyrolysis stage reached around 230 °C, at which temperature the RDF started to decompose,²⁶ the water was introduced by using a syringe pump in the case of the steam gasification experiment. The experiment was completed after 30 min, when the first reactor reached 600 °C. The gaseous products after leaving the gasification reactor were condensed by an air-cooled condenser followed by a dry ice cooled condenser. The noncondensed gases were collected in a 10 L Tedlar gas bag for an additional 20 min after the experiment to ensure all of the produced gases were collected. Experiments were repeated three times to ensure the reliability of the results. For example, the experiment with 5 wt % Ni/Al₂O₃ at 600 °C pyrolysis temperature and 800 °C gasification temperature gave mass balance data with an average of 100.62 wt % and standard deviation of 0.59 wt %.

2.2.1. Gas Chromatography (GC). Hydrocarbons (C₁–C₄) in the gases collected in the gas sample bag were analyzed by a Varian CP-3380 gas chromatograph with a flame ionization detector (FID) and a column packed with an 80–100 mesh Hysep and using nitrogen as carrier gas. Permanent gases (H₂, CO, N₂, O₂, CO₂) were analyzed in a second Varian CP-3380 chromatograph comprised of two columns with two thermal conductivity detectors (TCD). One column, packed with a 60–80 mesh molecular sieve, was used to separate hydrogen, carbon monoxide, nitrogen, and oxygen, and the other column, packed with 80–100 mesh Hysep, was used to analyze carbon dioxide. The carrier gas used was argon.

2.3. Characterization of Tar. The tar trapped in the condensers was carefully collected using dichloromethane (DCM, analytical reagent grade, Fischer Scientific) as solvent. Where water was present with the tar, the water was separated by passing the tar sample through a bed of sodium sulfate (Na₂SO₄), which was initially dried for 2 h at 140 °C to eliminate any traces of moisture. The composition of the tar samples was determined by GC-MS using a PerkinElmer Clarus 580 gas chromatograph coupled with a PerkinElmer Clarus 560S mass spectrometer. The gas chromatograph was equipped with a split/splitless injection port. The analysis was carried out on a DB-5 capillary column (30 m × 0.25 mm i.d., 0.25 μm; Perkin-Elmer). Helium was used as carrier gas with a constant flow of 1.0 mL/min. The injection volume was 1.0 μL; the column was temperature programmed from 40 to 300 at 5 °C min⁻¹ heating rate and was directly coupled to a 560S mass spectrometer operating in the electron ionization mode. The source and transfer line temperatures were 180 and 220 °C, respectively. Detection was carried out in the scan mode: *m/z* 50–500. The detector was switched off in the initial 5 min to avoid solvent overloading of the column.

The tar samples were also analyzed by Fourier transform infrared spectroscopy (FTIR) to determine the functional group chemical composition and by size exclusion chromatography (SEC) to determine the molecular mass of the samples. The FTIR analysis was performed

using a Thermo Nicolet Corporation iS10 (Thermo Scientific) spectrometer. The FTIR spectra were recorded within the region from 4000 to 650 cm⁻¹. The FTIR sample plate was carefully cleaned *in situ* with acetone by scrubbing twice and dried with a tissue before loading each sample. Before this analysis, the samples were centrifuged under vacuum at around 35 °C to eliminate the DCM contained in the samples, and a parallel FTIR analysis was carried out for a DCM sample in order to compare both spectra (DCM and tar sample).

Size exclusion chromatography (SEC) is a nondestructive technique in which the largest molecules are eluted first. The equipment used to obtain information on the molecular mass distribution was a Perkin-Elmer Modular, Series 225. A solution of tetrahydrofuran (THF) was used as mobile phase during the analysis. The samples were prepared by dissolving a small amount of oil (tar) in THF in an approximate concentration of 0.2%. The column used was a Polymer Laboratories 5 μm SEC column and was calibrated using polystyrene samples of low polydispersity in the MW range of 800–860 000, and also included single ring and PAH standard samples for low molecular mass calibration. The detector used was a Perkin-Elmer Series 200a refractive index detector.

3. RESULTS AND DISCUSSION

In this paper, experiments were carried out in a two-stage fixed-bed reactor with two Ni-based catalysts in relation to catalyst temperature to determine the influence on tar composition produced from the pyrolysis–gasification of RDF. The influence of Ni concentration in the catalyst was also investigated in relation to tar composition and gas yield.

3.1. Mass Balance and Gas Composition. The product yield and mass balance of the experiments are shown in Table 2. The mass balance was calculated according to the flow and concentration of N₂; the general equation used for this calculation was as follows:

$$\text{mass balance} = \frac{\text{gas} + \text{oil} + \text{char (residue)} + \text{lost water}}{\text{sample} + \text{water (\% wt)}}$$

The conversion rate of the RDF sample was calculated by weight difference between the initial and final weight of the sample as follows:

$$\text{conversion rate} = 100 - \text{residue (\% wt)}$$

The conversion rate of RDF to gas and liquid was stabilized at about 69 wt % for each experiment, as expected, with a consequent char yield of ~30 wt %. As shown in Table 2, the gas production was increased from 25.40 to 34.71 wt % as the

gasification temperature was increased from 600 to 800 °C. In addition, the total gas production was increased from 30.85 to 45.89 wt % in the presence of the 10 wt % Ni/Al₂O₃ catalyst. Higher gas yield was obtained when the Ni content of the catalyst was increased from 5 wt % Ni/Al₂O₃ to 10 wt % Ni/Al₂O₃ catalyst.

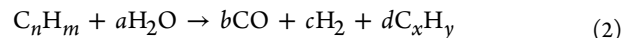
The volumetric concentration of gas products was calculated for each experiment (nitrogen free), these results are also shown in Table 2. For the experiments carried out with a sand bed in place of any catalyst, the H₂ molar fraction significantly increased from 18.70 vol % to 31.61 vol %, and CO concentration decreased from 27.09 vol % to 18.15 vol % when steam was injected into the reaction system at 800 °C. This is most probably due to the promotion of the water–gas shift reaction by adding steam. By using a bed of Ni/Al₂O₃ catalyst, the hydrogen content in the product gas was higher than 32 vol %, and it attains about 45 vol % when the 10 wt % Ni/Al₂O₃ catalyst was used (Table 2). The addition of a bed of nickel-based catalyst increased the hydrogen content, and the CO₂ concentration was slightly increased, whereas methane and C₂–C₄ concentrations were decreased, and the CO concentration remained somewhat constant. This trend was also observed in the reported work of Li, et al.²⁷ The addition of nickel-based catalyst in the second reactor increases the cracking of the gaseous products derived from the pyrolysis of RDF in the first reactor. The general increase of both H₂ and CO₂, and the decreasing of CO concentration in the product gas can be due to the promotion of water–gas shift reaction (reaction 1) carried out in the presence of NiO contained in the Ni–Al catalyst.



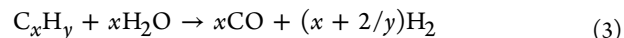
The syngas composition from RDF gasification under different process conditions has been reported previously. Galvagno et al.,⁶ worked with the gasification of RDF at different temperatures, the resulting syngas composition at 850 °C, by adding steam and using nitrogen as carrier gas was almost 43 vol % of H₂, around 18 vol % CO, 17.63 vol % of CO₂, and around 16 vol % of CH₄; these results are similar to those reported in this work (sand bed, steam at 800 °C). Dalai and collaborators,²⁸ analyzed gases from the gasification of RDF at 725 °C without using a catalyst, reporting a composition of about 18 mol % of H₂, around 50 mol % CO, and almost 20 mol % of CO₂, while methane and other hydrocarbons concentrations were lower than 8 mol %.

Much work has been carried out by using different nickel-based catalysts in order to increase the yield of the syngas produced and to reduce tar formation during the biomass gasification process. Miccio and collaborators¹⁴ reached a maximum H₂ content of about 30 vol % in the producer gas from biomass gasification by using two different nickel-based catalysts. Liu, et al.,²⁹ demonstrated that a specific nano-nickel-based catalyst has the capability to increase the gas quality in catalytic steam reforming of MSW with about 50% H content at 800 °C, 21.4 vol % CO, and 20.5 vol % CO₂. In the present work, the maximum hydrogen content (45 vol %) was attained by using 10 wt % Ni/Al₂O₃, which is in accordance to those values reported in the literature. The gas yield in relation to the type of bed increased at least 2% by modifying the bed from sand to catalyst under the same conditions and also increased about 8% when the nickel concentration was increased from 5 wt % to 10 wt %.

The use of nickel-based catalysts has an effect on the tar formation process. A global mechanism for tar steam reforming was proposed by Zhang,³⁰ which focused on the formation of light hydrocarbons as follows (reaction 2):



Where, C_nH_m represents tar and C_xH_y the light hydrocarbons. Furthermore, the reforming of light hydrocarbons enhances the hydrogen yield by means of reaction 3:



The promotion of dehydrogenation reactions leads to an improvement of the calorific value of syngas through the increase in the hydrogen content from 18 vol % to 45 vol %, as shown in Table 2.³¹

3.2. Tar Analysis. The characterization of tar samples collected from the pyrolysis/gasification of RDF was carried out by using GC-MS, SEC, and FTIR.

3.2.1. GC-MS Analysis of Collected Tar. The tars collected from the experiments with sand bed, at 600, 700, and 800 °C were analyzed by GC-MS. The chromatograms obtained are presented in Figure 3, and the identified compounds are shown in Tables 3 and 4. It can be seen that, at lower gasification temperatures (Figure 3a), the amount of oxygenated compounds identified in the chromatogram was higher, and it decreases as the gasification temperature increases. At 600 °C, the oxygenated compounds identified were benzenediols and alcohols, while at 700 °C some methylphenols and naphthols were detected. In the Figure 3a, it can also be noted a typical pattern of triplets consisted of alkadienes, alkenes, and alkanes at the later stages of the chromatogram. Williams et al.³² have reported similar GC-MS results from the pyrolysis of low density polyethylene. Predel and Kaminsky³³ also reported similar GC-MS analysis of a light wax from the pyrolysis of high density polyethylene at 500 °C. Therefore, it can be suggested that there are some plastics contained in the RDF sample used in this work.

At 800 °C, the tar composition is dominated by polycyclic aromatic compounds, as shown in Figure 3d and Table 3. According to Elliot,³⁴ the tar composition is directly related to the operating temperature. Comparing the chromatograms obtained at different temperatures, there was a large decrease in the number of compounds at 800 °C (Figure 3d) compared to those at 600 and 700 °C (Figure 3a and b); this was also observed by Gilbert and collaborators³⁵ during the analysis of vapors from biomass pyrolysis.

Figure 3c–f shows the chromatograms obtained by GC-MS analyses for the experiments carried out with different second stage reactor bed materials at 800 °C. Some aromatic and polyaromatic hydrocarbons such as naphthalene and phenanthrene were identified in the four chromatograms. The increase of aromatic species can be noticed in the experiments carried out with the sand bed (Figure 3c and d), where 3-ring and 4-ring compounds such as anthracene, fluoranthene, and pyrene are present in the chromatograms. It is important to mention that the small peak that elutes between biphenyl and acenaphthylene (Figure 3d–f) could be from acenaphthene, based on the *m/z* spectrum shown. The peak that elutes after acenaphthylene, labeled as unidentified, could be dibenzofuran, based on the *m/z* spectrum. In Table 4 are presented the tar compounds identified using different bed materials. A relative yield is shown by using different asterisks; for the experiments

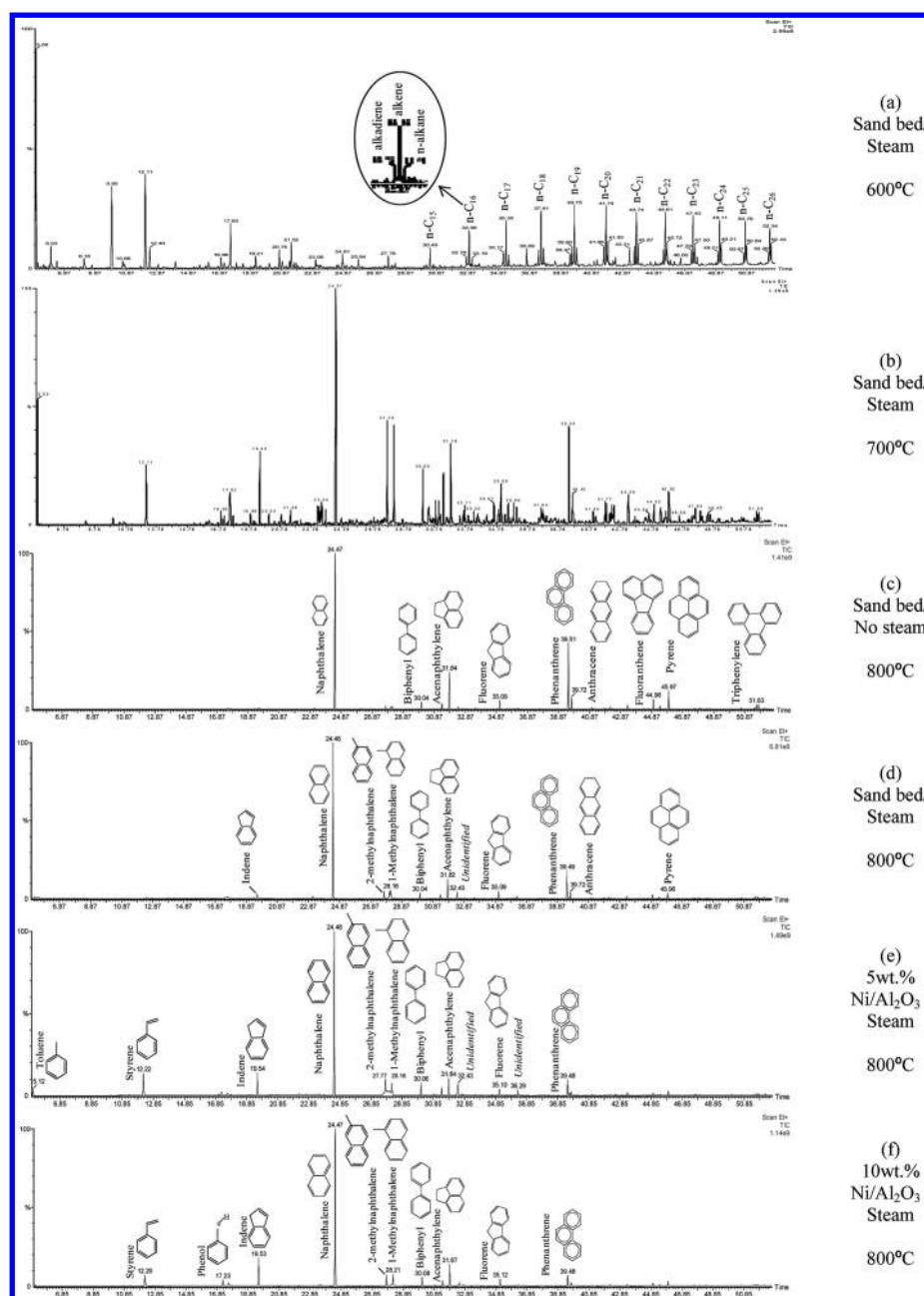
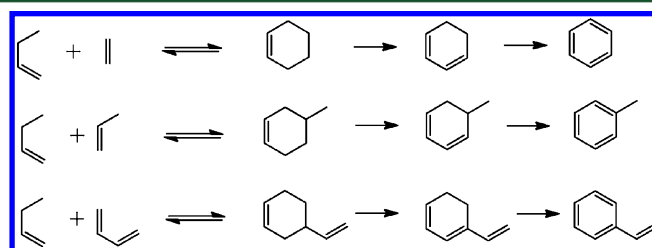


Figure 3. Effect of the gasification temperature (a,b) and bed type (c,d,e,f) over tar composition.

carried out with sand, there are no signals from single ring compounds, but the presence of higher aromatic compounds such as fluoranthene, pyrene, and triphenylene is clear. By using a catalyst bed instead of sand, this trend changes, reducing the signals of 3 and 4-ring compounds such as phenanthrene; however, single ring compounds such as styrene are detected in the chromatograms (Figure 3e and f). This reduction in the intensity of the signals could be due to higher molecular weight hydrocarbons being thermally degraded into lighter hydrocarbons. The lighter hydrocarbons can be subsequently aromatized via Diels–Alder type reactions due to the thermal degradation of alkanes into alkenes resulting in the formation of single ring compounds such as toluene and styrene.^{31,36} The following reactions show the formation mechanism for toluene and alkylaromatics produced by thermal degradation of alkanes via Diels–Alder reaction.³⁶



Regarding the oxygenated compounds the primary cracking reaction for phenol includes the formation of CO and cyclopentadiene as follows:

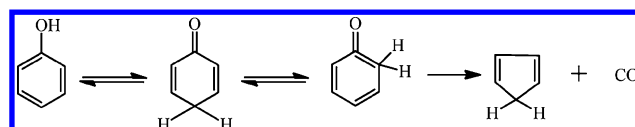


Table 3. Identified Compounds in Tars from the Gasification of RDF at 600, 700, and 800 °C

retention time (min)	gasification 600 °C	gasification 700 °C	gasification 800 °C
5.08–5.09	toluene	toluene	—
6.03	1,2,3-trimethylcyclopentane	—	—
8.16	2,5-dimethylfuran	2,5-dimethylfuran	—
9.95	ethylbenzene	ethylbenzene	—
10.66	<i>o</i> -xylene	<i>o</i> -xylene	—
12.11	styrene	styrene	—
12.40	benzene, (1-methylethyl)-	—	—
16.95–16.98	α -methylstyrene	α -methylstyrene	—
17.52–17.60	benzene-propyl	benzene-propyl	—
18.86	—	benzene-2-propenyl	—
19.21	5-butyl,1,3-cyclohexadiene	—	—
19.44	—	indene	indene
20.04	—	2-methylphenol	—
20.75	benzene, 1-ethyl-2-methyl	—	—
21.46	—	4-methylphenol	—
21.52	2-furancarboxaldehyde, 5-methyl	—	—
23.08	1,3,5-trimethylbenzene	—	—
23.44	—	naphthalene, 2-dihydro	—
24.37	—	naphthalene	naphthalene
24.81	1,2-benzenediol	—	—
25.84	2-furancarboxaldehyde	—	—
27.70	—	2-methylnaphthalene	2-methylnaphthalene
27.76	benzyl alcohol	—	—
28.16	—	1-methylnaphthalene	1-methylnaphthalene
30.00	—	biphenyl	biphenyl
30.30	—	naphthalene, 1-ethyl	—
30.45	<i>n</i> -C ₁₅	—	—
31.33	—	acenaphthene	—
31.78	acenaphthylene	acenaphthylene	acenaphthylene
32.71	—	2-methyl-1,1'-biphenyl	—
32.98	<i>n</i> -C ₁₆	—	—
33.30	—	1-naphthol	—
34.61	—	2-naphthol	—
35.06	—	naphthalene, 1-(2-propenyl)	—
35.35	<i>n</i> -C ₁₇	—	—
35.88	—	fluorene	fluorene
36.69	unidentified	—	—
37.61	<i>n</i> -C ₁₈	—	—
37.64	—	9H-fluorene, 1-methyl	—
39.44	—	phenanthrene	phenanthrene
39.67	—	anthracene	anthracene
39.75	<i>n</i> -C ₁₉	—	—
41.00	—	2-methylanthracene	—
41.77	—	1-methylanthracene	—
41.79	<i>n</i> -C ₂₀	—	—
43.29	—	2-phenylnaphthalene	—
43.74	<i>n</i> -C ₂₁	—	—
44.64	—	4,5,9,10-tetrahydropyrene	—
44.95	—	fluoranthene	—
45.61	<i>n</i> -C ₂₂	—	—
45.92	—	pyrene	pyrene
46.60	—	<i>m</i> -terphenyl	—
47.40	<i>n</i> -C ₂₃	—	—
47.63	—	benzanthrene	—
48.45	—	benzo[<i>c</i>]fluorene	—
49.11	<i>n</i> -C ₂₄	—	—
50.76	<i>n</i> -C ₂₅	—	—
51.59	—	triphenylene	—
52.34	<i>n</i> -C ₂₆	—	—

Table 4. Influence of the Bed Type over the Tar Composition, Gasification at 800 °C^a

retention time (min)	M_w (g mol ⁻¹)	identified component	boiling point (°C)	sand/no steam	sand/steam	5 wt % Ni/Al ₂ O ₃	10 wt % Ni/Al ₂ O ₃
5.1	92	toluene	110.6			*	
12.2	104	styrene	145			**	*
17.2	94	phenol	181				*
19.5	116	indene	183		*	**	**
24.4	128	naphthalene	218	***	***	***	***
27.7	142	2-methylnaphthalene	241–243		*	*	*
28.2	142	1-methylnaphthalene			*	*	*
30.0	154	biphenyl	256	*	*	*	*
31.8	152	acenaphthylene	279–280	**	**	**	**
32.4	—	unidentified	—		*	*	
35.1	166	fluorene	295	*	*	*	*
36.3	—	unidentified	—			*	
39.5	178	phenanthrene	340	**	**	**	*
39.7	178	anthracene	340	*	*		
44.9	202	fluoranthene	375	*			
45.9	202	pyrene	404	*	*		
51.6	228	triphenylene	425	*			

^aMore asterisks means higher concentration.

The major tar compounds identified were indene, naphthalene, methylnaphthalenes, biphenyl, acenaphthylene, fluorene, and phenanthrene. These aromatic species have been reported as tar compounds in different thermal processes such as pyrolysis and gasification of both biomass and wastes.^{14,23–25,37–41} Williams and Besler²⁵ reported naphthalene, fluorene, and phenanthrene as major compounds in tars produced from the pyrolysis of RDF as also shown in this work (Figure 3c and d). In some of the reported work on biomass gasification,^{14,23,24,41} benzene has been also reported as a tar compound; however, toluene and benzene are volatile enough to be lost during the collection and analyzing process in our work. Hence, the resulting samples were deficient in lighter compounds such as benzene. Oxygenated compounds such as alcohols were found in tar samples obtained at lower gasification temperatures (600 and 700 °C), together with other benzene derivatives.

Some of the PAHs presented in Figure 3 represent concern due to their carcinogenic characteristics, and some of them have been shown to be mutagenic; for example acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, and fluoranthene, together with other PAH compounds, have been classified by the Environmental Protection Agency (EPA) as priority pollutants.⁴²

3.2.2. SEC Analysis. The samples derived from the non-catalytic and catalytic pyrolysis–gasification of RDF at 800 °C were analyzed using size exclusion chromatography (SEC) to determine the molecular mass of the tars. The SEC chromatograms are shown as a linear function of the molecular weight (Figure 4), in the region between 88 and 240 Da. The molecular mass distributions of these fractions are similar and three major regions were identified. The first region appears at ~95 Da; this peak could be due to the presence of toluene or phenol. The second region is between 126 and 135 Da; according to the GC-MS results, compounds such as naphthalene appear in all the analyzed fractions and its molecular weight belongs to this region. Finally, the third region is around 219 Da; the highest intensity of the large-molecular mass compounds was obtained for the oil derived in the absence of the catalyst and steam; this is probably due to the presence of higher molecular weight compounds such as pyrene and

triphenylene. The SEC curve for the experiment without steam shows that higher MW species are produced; it is suggested that the presence of three- and four-ring aromatic compounds are formed, and this was also confirmed by the GC-MS chromatogram. The addition of Ni catalyst into the gasification stage promoted the formation of single- and two-ring aromatic compounds of lower molecular weight, as shown by the first region of the chromatogram (Figure 4); however, there is a minor signal for higher compounds at the end of the chromatogram. This confirms the effect of the catalyst and the cracking of higher compounds.

3.2.3. FTIR Analysis. FTIR was conducted for the tar samples with the aim to determine the chemical functional groups present in the samples derived from different Ni catalyst. The results (Figure 5) show a very similar pattern in the four spectra obtained, indicating that the main chemical groups are similar for all the samples. The peaks observed between 3000 and 2850 cm⁻¹ (a) correspond to C–H stretching vibrations, and those between 1450 and 1350 cm⁻¹ (d) represent C–H deformation vibrations that verify the presence of –CH₃, CH₂, and C–H groups.⁴³ The signal around 1700 cm⁻¹ (b) probably corresponds to some oxygen-containing compounds such as phenol, which can be barely identified in the GC-MS analysis. The absorption peaks detected from 1625 and 1575 cm⁻¹ (c) as well as those between 950 and 800 cm⁻¹ (g) indicate the presence of mono- and polycyclic aromatic compounds. The peak between 1675 and 1352 cm⁻¹ (b) represents double bonds (C=C) from the alkene functional group. The presence of alkenes in pyrolytic oil from municipal solid wastes has been previously reported.^{44–46} The spectra observed around 1100 and 1050 cm⁻¹ (f) shows single bonds (C–H) and long linear aromatic hydrocarbons; it is, however, difficult to assign this spectrum, as corresponds to the fingerprint region. According to the literature, the patterns of ring frequencies for most aromatic materials are usually observed near to 1600, 1590, 1490, and 1450 cm⁻¹;⁴⁷ those signals can be seen in (c), and (d). The functional groups identified in the FTIR spectra supports the GC-MS results, where most of the identified compounds, confirm the aromatic character of the samples.

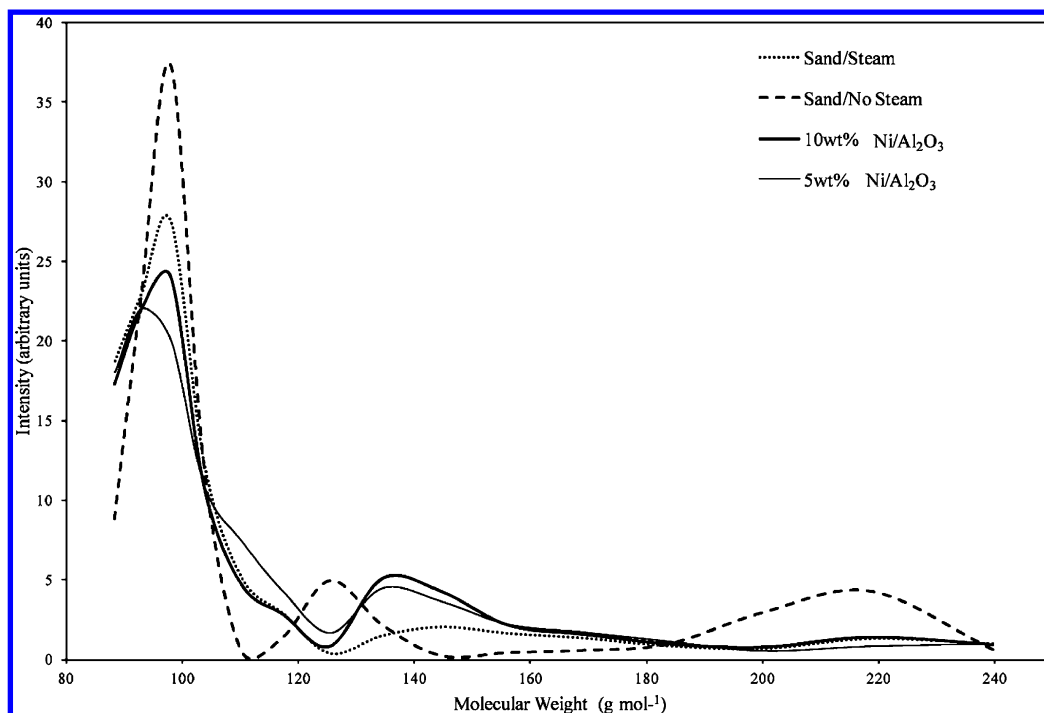


Figure 4. Size exclusion chromatogram of the tar.

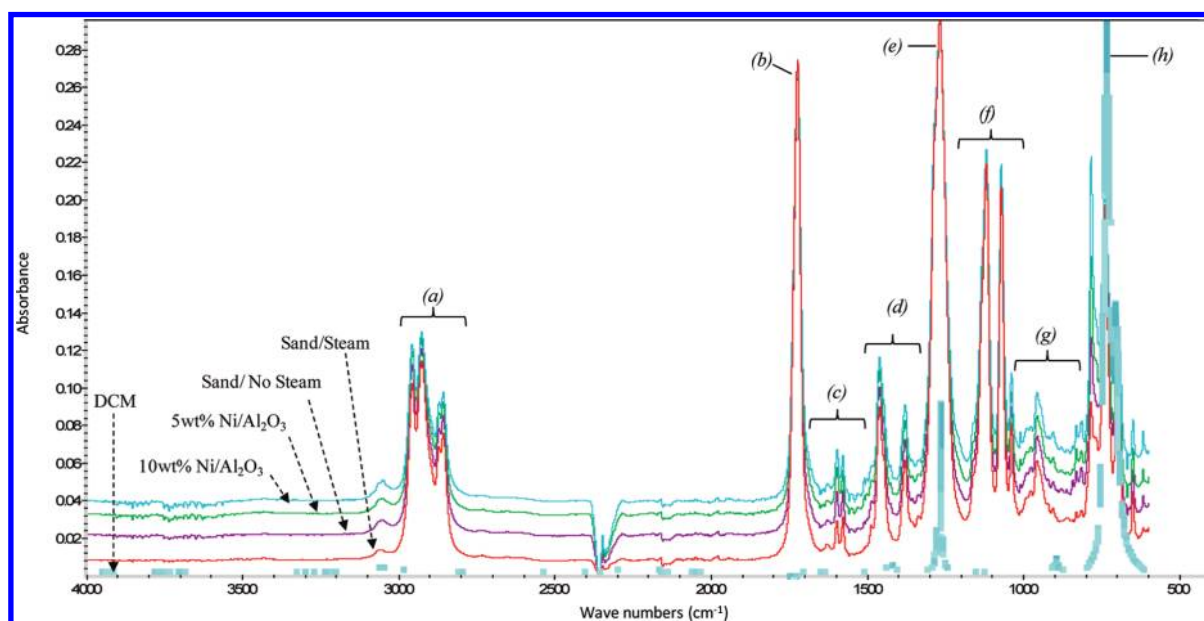


Figure 5. Fourier transform infrared (FTIR) spectra of tar from pyrolysis–gasification of RDF at frequency of 4000–650 cm^{-1} .

4. CONCLUSIONS

The pyrolysis–gasification of RDF was investigated in relation to the yield and the composition of both the gas fraction and a tar byproduct. The gas composition of the produced gases was strongly influenced by the introduction of steam to the system. By using a catalyst bed of 10 wt % $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$, the hydrogen production was significantly improved, increasing by almost 14%, compared with the sand bed under the same conditions, while the methane and $\text{C}_2\text{--C}_4$ gas concentrations were reduced by about 10% and 5% respectively. The tar obtained at high temperature (800 $^\circ\text{C}$) was found to contain PAHs, consisting mainly of naphthalene, biphenyl, acenaphthylene, fluorene, and

phenanthrene. The PAHs were assumed to be formed via Diels–Alder reactions and deoxygenation reactions. Using the $\text{Ni}/\alpha\text{-Al}_2\text{O}_3$ catalyst promoted the reduction of three- and four-ring aromatic compounds and the increase of hydrogen yield in the syngas. It was found that lower gasification temperatures of 600 $^\circ\text{C}$ promote the formation of oxygenated compounds; at higher temperatures the formation of aromatic compounds is preferred.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: #44 1133432504. E-mail: P.T.Williams@leeds.ac.uk.

Notes

The authors declare no competing financial interest.

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