

Development of an analytical method for the determination of pollutants in industrial water used for cooling of co-produced gases in the waste pyrolysis process

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Abstract—Pyrolysis dissolves waste and also produces useful by-products. In this case, gas, liquid and solid phases are formed. Gas mixture containing tar, among other components. Water scrubbing technology is used for pyrolytic gas purification. The disadvantage of this technology is that tar components gradually accumulate in the water. Most exposed to this process the readily soluble light heterocyclic aromatic compounds of tar, as well as heavy polyaromatic compounds of tar. Some light aromatic tar compounds, the content of which is usually very high in the pyrolytic gas, are present in small amounts in the cooling and cleaning water. In the pyrolytic gas purification process, not only does the total amount of tar in the cooling and cleaning water increase, but also the ratio of the individual tar compounds to each other changes, especially the heaviest polyaromatic tar compounds accumulate, which leads to problems. further purification and use of the cooling and rinsing water itself.

Keywords—gas chromatography, pyrolysis, pyrolytic gas, scrubber, tar.

1. Introduction

CONVERTING waste to energy is now gaining additional importance for solving economic and environmental problems [1]. In the process of global industrialization and urbanization, a variety of solid waste is generated, which puts enormous pressure on waste management. On the other hand, some hazardous waste is a potential pyrolysis feedstock. These materials include plastics, tire scraps, medical and household waste with tons of energy accumulated as waste.

Pyrolysis is a thermochemical recycling method in which organic polymers are converted to liquid oil at high temperatures (400–600°C) in the absence of oxygen (O₂). Pyrolysis dissolves waste and also produces useful by-products. In this case, gas, liquid and solid phases are formed [2].

The solid product of pyrolysis, known as biochar, consists mostly of carbon but also contains ash originating from biomass. Biochar, which represents 12–15 wt% of the products of pyrolysis, can be used as boiler fuel but more intriguing applications include soil amendment, carbon sequestration agent, and activated carbon. The pyrolysis oil from waste has characteristics similar to those of diesel fuel [3].

Pyrolysis of waste produces pyrolytic gas such as CO, H₂ and CH₄ of the desired composition. In addition to pyrolytic gas, contaminants such as particulate matter, tar and coal are generated [4]. During pyrolysis, a wide variety of aromatic hydrocarbons are formed, containing aromatic hydrocarbons with one or more rings, called tar. Tar can plug and contaminate downstream components [5] and corrode metal [4]. The typical dew point of tar is between 150°C and 350°C, which is usually well above the lowest process temperature (-30°C). The tar together with the pyrolytic gas condenses and

polymerizes inside the process pipelines, clogs the filters and forms harmful deposits inside the engine [6].

Tar and its compounds are not well defined. Milne et al., for example, think that tar is “the organic produced under thermal or partial-oxidation regimes (gasification) of any organic material and generally assumed to be largely aromatic” [7]. For example, in “Guideline for sampling and analysis of tar and particles in biomass producer gases” where the following definition of tar is given [8]: “Tar: Generic (unspecific) term for entity of all organic compounds present in the producer gas excluding gaseous hydrocarbons (C1 through C6). Benzene is not included in tar.” Although many authors exclude benzene from the definition of tar, it seems that more attention should be paid to the analysis of benzene in product gases. First, benzene plays a certain role in the formation of ozone [9] and thus may cause a variety of respiratory effects [10]. Second, benzene is ranked tenth in the list of hazardous air pollutants [11] producing both acute and chronic effects on human beings, including reproductive and developmental ones [12]. For example, risk assessors believe that benzene inhalation exposure of humans is potentially dangerous because benzene is known to cause leukaemia in occupational environments [13] and is associated with other non-cancer health effects [14].

Therefore, it is important to reduce the tar concentration and maintain the temperature above the dew point of the tar components. The main obstacle to the commercialization of small-scale combined heat and power technology for waste pyrolysis is the lack of a cost-effective technology for removing tar from pyrolytic gas. In many producer gas applications, the desired concentration of tar and particulates are <50 mg/m³ and <5 mg/m³, respectively (Table 1).

Table 1 Tar tolerance limit at different applications [15]–[16].

Application	Tar tolerance limit (mg/Nm ³)
Compressors	50-500
Internal combustion engines	50-100
Direct fired gas turbines	5
Methanol synthesis	0.1

Water scrubbing technology is used for pyrolytic gas purification. Water is chosen as the coolant because it is relatively easy to obtain. The disadvantage of this technology is that tar components gradually accumulate in the water used for pyrolytic gas purification. In the previous paper [17]–[21], an improved system of tar sampling and analysis in syngas and pyrolytic gas was suggested and described. The main objective of this study was the development of tar sampling from water used for pyrolytic gas purification.

2. Materials and Methods

2.1 Fixed-bed Pyrolysis Experiments

For research in a real life context was chosen technology, that is based on the principle of a quick heating of fine grained oil shale by the solid heat carrier (hot ash) in the rotary drum reactor followed by its thermal decomposition. The pyrolysis experiments were performed in a fixed-bed reactor situated in eastern Latvia (Daugavpils). The plant is based on the globally recognized horizontal rotating drum technology with a capacity of 9 t of shale per day. The stainless steel reactor has an inner diameter of 2.24 m with an 8 m tall. The main characteristics of the reactor are as follows: operating mode of the unit – cyclical; speed of rotation, ω/s – 0.15; oil shale feed, G_f (kg/s, dry basis) – 5.26; heat carrier feed, G_a (kg/s) – 10.46; working temperatures of pyrolysis – 350–480°C (depending on type of raw material); fuel oil performance, % for tyre/PP/ABS/PS/PE – 44/92/60/80/85; dry carbon residue capacity, % for tyre/PP/ABS/PS – 30/3/25/10; steel cord performance, % for tyre – 12; own fuel consumption for heating in pyrolysis mode and production of own gas, L/t of raw materials. This unit allow obtaining a high-calorific liquid fuel with a calorific value of 38–40 MJ/kg and gaseous fuel with a calorific value of 41–42 MJ/kg.

For cooling and cleaning pyrolytic gas was used wet scrubber. Scrubbers consist of three sections: a converging section, a throat, and a diverging section. The inlet pyrolytic gas stream enters the converging section and, as the area decreases, gas velocity increases. Water is introduced either at the throat or at the entrance to the converging section. The inlet pyrolytic gas, forced to move at extremely high velocities in the small throat section, shears the water from its walls, producing an enormous number of tiny droplets. Particle and tar removal occur in the throat section as the inlet pyrolytic gas stream mixes with the fog of tiny water droplets. The inlet stream then exits through the diverging section, where it is forced to slow down. The water circulates in a circle many

times, to replenish the evaporated water, a constant level is maintained by adding new water.

2.2 Extraction and Sample Preparation

Cooling water from the scrubber for analysis was sampled at the pyrolytic gas temperature of 250°C three times – after 5, 10, and 15 pyrolysis cycles. The analysed tar components were extracted from water using dichloromethane. To 100 mL of water was added 4 mL of dichloromethane and shake for 30 minutes. The procedure was repeated three times from the same sample to increase yield. The extracts were then combined and concentrated using a rotary evaporator, filtered through syringe filters and injected into GC-MS.

2.3 Analysis

A Shimadzu GCMS–QP2010 system (Shimadzu Corporation, KYOTO, Japan) was used for the analysis. The gas chromatograph was equipped with an electronically controlled split/splitless injection port. GC was carried out on a 5% diphenyl–95% dimethylpolysiloxane fused–silica capillary column (Rtx–5SIL–MS, 30 m·0.32 mm, 0.25 μ m film thickness; Restek). Helium (99.999%) was used as the carrier gas, at a constant flow of 1.6 mL/min. The injection (injection volume of 1 μ L) was performed at 250°C in the split mode, split ratio 1:10. The oven temperature program was as follows: the temperature was held at 30°C for 5 min, then 30–180°C at the rate of 10°C/min, 180–300°C at the rate of 15°C/min, and finally held at 300°C for 5 min. The mass spectrometer was operated in the electron ionization mode (ionization energy of 70 eV). The source and transfer line temperatures were 200°C and 310°C respectively. Detection was carried out in the SIM mode.

2.3 Calibration and Quantification

Quantified compounds are given in Table 2. Tert-butylcyclohexane and 4-ethoxyphenol were used as internal standards to quantify aromatics and phenolics, respectively. Calibration curves were performed with five points, each of them realised in triplicate. Five calibration mixtures were made using pure standards of the compounds to be quantified and a known amount of internal standards added to each calibration mixture and to the studied samples. All areas were measured and referenced to the area of the internal standards. To determine concentrations of the tar compounds that were not among the quantified ones, the response factor of the quantified compound with the retention times closest to the unquantified compound was used. The total tar concentration (mg/m³) was calculated as a sum of concentrations of all identified and quantified compounds. The instrumental limit of detections (LOD) was estimated from the chromatograms at the signal-to-noise ratio of 3. They ranged from 0.0023 ng for naphthalene to 0.0184 ng for phenanthrene (Table 2).

Table 2 Mass spectrometric data and LOD for quantified tar and internal standards

No.	Compound	Chemical formula	Molecular weight, g/mol	Mass spectrum (NIST 08), mass (abundance)	LOD, ng
1	Benzene	C ₆ H ₆	78	78 (999), 77 (283), 51 (221)	0.0026
2	Toluene	C ₇ H ₈	92	91 (999), 92 (776), 65 (121)	0.0042
3	m-p-Xylene	C ₈ H ₁₀	106		0.0045
4	o-Xylene	C ₈ H ₁₀	106	91 (999), 106 (501), 105 (206)	0.0061
5	Phenol	C ₆ H ₆ O	94	94 (999), 66 (387), 65 (266)	0.0127
6	tert-Butylcyclohexane	C ₁₀ H ₂₀	140	56 (999), 57 (674), 41 (236)	
7	4-Ethoxyphenol	C ₈ H ₁₀ O ₂	138	110 (999), 138 (333), 81 (299)	
8	Indane	C ₉ H ₁₀	118	117 (999), 118 (692), 115 (266)	0.0040
9	Indene	C ₉ H ₈	116	116 (999), 115 (792), 89 (100)	0.0069
10	o-Cresol	C ₇ H ₈ O	108	108 (999), 107 (673), 79 (253)	0.0093
11	m-p-Cresol	C ₇ H ₈ O	108		0.0087
12	Naphthalene	C ₁₀ H ₈	128	128 (999), 129 (109), 127 (107)	0.0023
13	Acenaphthylene	C ₁₂ H ₈	152	152 (999), 153 (152), 151 (137)	0.0099
14	Acenaphthene	C ₁₂ H ₁₀	154	153 (999), 154 (827), 152 (507)	0.0107
15	9H-Fluorene	C ₁₃ H ₁₀	166	166 (999), 165 (844), 167 (140)	0.0049
16	Phenanthrene	C ₁₄ H ₁₀	178	178 (999), 176 (202), 179 (150)	0.0184
17	Anthracene	C ₁₄ H ₁₀	178	178 (999), 179 (156), 176 (140)	0.0143
18	Fluoranthene	C ₁₆ H ₁₀	202	202 (999), 203 (173), 200 (153)	0.0062
19	Pyrene	C ₁₆ H ₁₀	202	202 (999), 203 (170), 200 (152)	0.0077
20	Chrysene	C ₁₈ H ₁₂	228	228 (999), 226 (271), 229 (203)	0.0051
21	Benzo(a)pyrene	C ₂₀ H ₁₂	252	252 (999), 253 (215), 250 (172)	0.0030

3. Results and Discussion

3.1 Tar Compounds Concentration Depending on the Number of Pyrolysis Cycles

Since the study used a pyrolysis reactor with a cyclical operating mode, cooling and cleaning water from scrubber was sampled for analysis three times – after 5, 10, and 15 pyrolysis cycles. The cooling and cleaning water was not renewed during these pyrolysis cycles, but was refilled to a constant volume to compensate for the evaporation loss of water. Theoretically, it could be assumed that the concentration of tar compounds in cooling and cleaning water after 10 pyrolysis cycles will be higher than after 5 pyrolysis cycles, and, accordingly, after 15 pyrolysis cycles it will be higher than after 5 and 10 pyrolysis cycles, since tar compounds accumulate in cooling and cleaning water.

Table 3 confirms these theoretical assumptions. But the concentrations of individual tar compounds in cooling and cleaning water increase in different ways with increasing

pyrolysis cycles. For example, for light aromatic tar compounds, poorly soluble in water, such as benzene and naphthalene, when pyrolysis cycles are tripled, their concentration in cooling and cleaning water increases only 1.69 and 1.57 times, respectively. But for light heterocyclic aromatics tar compounds readily soluble in water, such as phenol, m-cresol, p-cresol, and 2,3-xylene, with an increase in pyrolysis cycles by three times, their concentration in cooling and cleaning water increases by 2.54, 2.63, 2.48, and 2.74 times, respectively. Likewise, for heavy polyaromatic tar compounds poorly soluble in water, the increase in concentrations in cooling and cleaning water with an increase in pyrolysis cycles occurs significantly more than for light tar compounds. For example, for tar compounds such as pyrene, chrysene, and coronene, when pyrolysis cycles triple, their concentration in cooling and cleaning water increases 2.69, 1.91, and 2.52 times, respectively.

Table 3 Compound speciation in water with respect to the number of pyrolysis cycles

Retention time	Compound	Concentration, mg/m ³		
		5 pyrolysis cycles	10 pyrolysis cycles	15 pyrolysis cycles
2.222	Benzene	11.73	16.22	19.87
4.015	Toluene	4.96	8.17	10.03
8.667	Benzaldehyde	4.34	7.24	9.34
9.027	Phenol	46.72	81.96	118.84
10.048	m-Cresol	2.14	3.96	5.62
10.305	p-Cresol	6.62	11.42	16.44
11.371	2,3-Xylenol	2.11	3.91	5.79
11.660	Naphthalene	20.36	27.15	32.04
12.210	Quinoline	6.47	9.66	12.08
12.657	1-Indanone	12.06	22.75	33.90
14.999	2-Naphthaldehyde	7.62	11.04	14.35
15.724	1-Naphthalenemethanol	5.98	8.20	10.41
16.619	1-Acenaphthenone	45.17	83.65	117.11
17.456	Fluorenone	12.11	22.42	30.94
17.910	Phenanthrene	54.75	71.11	79.64
18.008	Anthracene	5.20	9.81	13.83
19.115	Benzo[c]cinnoline	84.66	145.97	198.52
19.767	2-Phenylnaphthalene	7.41	10.44	13.15
20.664	Fluoranthene	280.68	364.52	470.24
21.169	Pyrene	368.30	682.04	988.96
23.587	Cyclopenta[cd]pyrene	80.74	128.16	166.61
24.031	Benzo[ghi]fluoranthene	460.83	667.86	841.50
24.136	Chrysene	31.09	48.58	59.27
26.509	Benzo[b]fluoranthene	36.09	49.44	56.36
27.025	Perylene	45.43	65.84	77.69
27.118	Benzo[k]fluoranthene	90.47	137.08	165.87
29.649	Indeno[1,2,3-cd]pyrene	38.58	57.58	69.10
30.329	Benzo[ghi]perylene	104.3	196.79	273.54
30.703	Dibenzo[def.mno]chrysene	45.18	71.72	93.24
35.868	Coronene	70.60	126.07	177.76

3.2 Tar Compounds Concentration in Pyrolytic Gas and in Cooling and Cleaning Water

The study compared the mass part of the main individual tar compounds in percent of the total amount of tar in pyrolytic gas and in cooling and cleaning water. For this experiment, an analysis of pyrolytic gas for the content of individual tar compounds was made (this experiment will be described in detail in one of our next publications), as well as an analysis of cooling water from scrubber after 10 pyrolysis cycles. Fig. 1 shows a comparison of several tar compounds with the highest mass part in pyrolytic gas or in cooling and cleaning water. For example, benzene, the mass part of which of the total amount of tar in pyrolytic gas occupies more than 64 percent, in cooling and cleaning water in the total amount of tar occupies less than 1 percent. This can be explained by the poor solubility of benzene in water, as well as by the fact that it is a low-boiling substance, that is, it has a low dew point. For toluene, the mass part of the total amount of tar in pyrolytic gas is also greater than in cooling and cleaning water, but only

by about 19 times. For naphthalene, which has an even higher dew point, this value is just over ten. For heavy polyaromatic tar compounds, the solubility of which in water is poor, but the dew point is high, such as phenanthrene, pyrene, and chrysene, there is already more mass part of the total amount of tar in cooling and cleaning water than in pyrolytic gas, 3.5 times, 37 and almost 39 times. And the heaviest polyaromatic tar compound, coronene, whose mass part of the total amount of tar in cooling and cleaning water is more than 4 percent, was not found in pyrolytic gas at all - most likely, its amount was less than the LOD. And for light heterocyclic aromatics tar compounds, for example, phenol, although it has a low dew point, the mass part of the total amount of tar is still higher in cooling and cleaning water than in pyrolytic gas, by more than 2.5 times. since it is highly soluble in water.

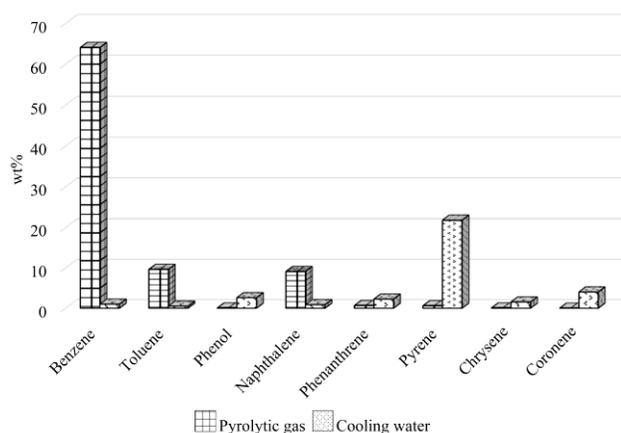


Fig. 1 Mass part of benzene, toluene, phenol, naphthalene, phenanthrene, pyrene, chrysene, and coronene in percent of the total amount of tar in pyrolytic gas and in cooling water

4. Conclusion

Cooling and cleaning water, in the process of contact with pyrolytic gas, gradually accumulates readily soluble light heterocyclic aromatic tar compounds, as well as heavy polyaromatic tar compounds. Some light aromatic tar compounds, the content of which is usually very high in pyrolytic gas, are present in small quantities in cooling and cleaning water. In the process of purification of pyrolytic gas, not only does the total amount of tar in the cooling and cleaning water increase, but also the ratio of individual tar compounds to each other changes, especially accumulating the heaviest polyaromatic tar compounds, which leads to problems of further purification and utilization of the cooling and cleaning water itself.

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