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Tar from pilot scale co-pyrolysis of biological dairy sludge and spruce wood chips

Alen Horvat^{a,*}, Marzena Kwapinska^{a,b}, James J. Leahy^a

^aDepartment of Chemical Sciences, Bernal Institute, University of Limerick, V94 T9PX, Ireland

^bDairy Processing Technology Centre, University of Limerick, Limerick, V94 T9PX, Ireland

Abstract

A pilot scale investigation of co-pyrolysis of biological dairy sludge and spruce wood chips and pyrolysis of spruce wood chips solely was carried out. Pyrolysis was tested as a waste treatment method aiming to reduce the volume of dairy sludge while producing a pyrolysis gas suitable for an internal combustion engine. Pyrolysis tests were carried out in a continuously fed, pilot scale rotating retort type of facility in the temperature range between 700 and 770 °C. Feedstock feeding rates were between 40.9 – 68.6 kg_{d.a.f.} h⁻¹. Tar yields and composition was measured by means of the solid phase adsorption method in order to assess gas quality with regard to the specified tar limits given for downstream applications. The yields of total gas chromatography detectable tar produced from the dairy sludge and spruce wood chips blend was in the range between 7.25 - 10.98 g_{total tar} Nm⁻³ dry raw gas, while spruce wood chips solely produced yields between 11.18 - 13.31 g_{total tar} Nm⁻³ dry raw gas. Composition wise, the main difference was a number of nitrogen-containing tar compounds reflecting the high nitrogen content in dairy sludge feedstock with 2-butenitrile, pyridine and 1H-pyrrole being the most abundant nitrogen-containing tar compounds. Raw pyrolysis gas from the two feedstocks tested did not meet the requirements regarding tar limits given in the manufacturer's specification for their internal combustion engine. The raw pyrolysis gas contained excessive amounts of 3 and 4+ aromatic ring tars. Therefore tar removal is required prior to combustion in the engine. The proposed tar removal strategy includes a thermal tar reformer using air as a reforming agent followed by adsorption using wood chips, or in-process generated bio-char, or torrefied biomass as a viable adsorbent.

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* Corresponding author. Tel.: +353 61 202 649;

E-mail address: alenhorvat@hotmail.com

1. Introduction

The dairy industry is one of the prime agriculture sectors in Ireland with 6.85 million tonnes of cows' milk collected by dairies in 2016. With respect to EU-28 milk production the Irish share accounts for 4.5 % [1]. A foreseen increase in primary milk production will inevitably lead to an increase in the generation of processing waste such as sludge from the treatment of waste water from milk processing plants. Principally, there are two main sludge types: (i) chemical sludge which is a mixture of fat, grease, oil and suspended solid particles removed from raw effluent in the waste water treatment plant together with some proteins and minerals by dissolved air flotation (DAF) and (ii) biological sludge which is an organic material, containing suspended solids, microbial biomass, and non-biodegradable pollutants such as heavy metals resulting from biological aerobic, anaerobic or anoxic waste water treatment processes [2,3].

Several approaches for dairy waste treatment have been presented in the relevant literature. Elvira et al. [4] introduced vermicomposting of dairy sludge mixed with cattle manure and achieved stabilized vermicompost appropriate for agricultural purposes. DAF sludge was tested as a feedstock for anaerobic digestion, but the milk fat is not easily bio-degraded and causes technological issues [5,6]. Rani et al. [7–9] investigated several pre-treatment methods of dairy sludge prior anaerobic digestion process. However, to date most research has focused on a dairy waste water treatment. Anaerobic digestion techniques [10–12] along with fewer anaerobic/aerobic digestions [13] were studied treatments aiming for biogas production. In Ireland the majority of the dairy sludge is land spread, in 2004 accounted for 120 000 tonnes [14]. The main issue of land spreading is local oversupply. Due to high transport costs, sludge is being spread on lands in the vicinity of the dairy factories which can lead to accumulation of certain substances in soil through annual application over many years.

In order to facilitate sustainable growth within dairy sector, the Irish government has investigated various strategies that offer framework for further expansion. Pyrolysis can reduce health risks and environmental impacts from problematic wastes [15,16] while providing an avenue for the recovery of energy and nutrients, accompanying by notable reduction of waste material volume [17]. In the endothermic pyrolysis process, conducted in an inert atmosphere, carbonaceous material is thermally decomposed into gaseous, liquid and solid products [18]. This study investigates the potential of pyrolysis as a waste treatment technology for air dried sludge from milk processing. The study offers a detailed evaluation of pyrolysis tar as an undesirable pyrolysis product. The objective of this study is to sample and chemically characterize the pyrolysis tar from two feedstocks; (i) dairy sludge blended with spruce wood chips (50/50) and (ii) spruce wood chips as a reference feedstock. Some data regarding tar yields were published by Kwapinska et al. [19], in a complementary publication to the present work. However, a detailed tar analysis is presented here, including the quality and quantity of tar in the raw pyrolysis gas with respect to the tar limits given for downstream applications and tar removal methods.

2. Materials and methods

2.1. Materials

Biological sludge from waste water treatment of an effluent from milk processing was supplied by a dairy company in Ireland. The sludge derived from biological treatment processes with cationic polyelectrolyte addition to aid coagulation. The sludge was air-dried outdoors in a simple drying bed decreasing moisture content from 93 to 20 wt. %. Spruce wood chips were sourced locally in Ireland. Fig. 1 shows the shape and the particle size of pyrolysis feedstocks used in the present work.



Fig. 1. (left) air-dried dairy sludge granules; (right) spruce wood chips.

Note that dairy sludge was mixed with 50 wt. % of spruce wood chips due the reasons presented in the section 3.1.

2.2. Experimental facility

Three separate experimental tests, conducted on different days, were carried out for each feedstock. The tests were carried out in the pilot scale facility at Premier Green Energy in Thurles, Ireland. The facility consisted of four main sections: feeding system, pyrolysis reactor, gas conditioning section (i.e. thermal tar cracking unit, ceramic filter, water scrubber and dehumidifier) and a gas engine or flare. The pyrolysis reactor is a stationary muffle furnace with a rotating retort. When char leaves the reactor it is separated from the raw pyrolysis gas. The muffle furnace enables pyrolysis temperatures of 750 ± 50 °C. High pyrolysis temperature was performed in order to maximize pyrolysis gas yield while keeping tar content at reasonably low level [20]. Residence time of the gas phase, the parameter which also promote tar reforming reactions [20], was set to seven seconds. The blend of dairy sludge and spruce wood chips was fed with the rates between $59.4 - 68.6$ kg_{d.a.f.} h⁻¹, whereas spruce wood chips achieved feeding rates between $40.9 - 45.5$ kg_{d.a.f.} h⁻¹.

2.3. Tar measurement method

Tar samples were taken from the duct connecting the pyrolysis reactor and thermal tar cracking unit. Thus, reported tar content refers to the raw gas prior gas conditioning. The tar sampling port was designed to enable so called solid phase adsorption (SPA) sampling. 100 mL of a raw pyrolysis gas was withdrawn by an SPA device assembled from a stainless-steel needle, a pre-packed Discovery[®] DSC-NH₂ SPE cartridge containing aminopropylsilane sorbent, and a 100 ml gas tight syringe. Tar compounds were extracted from the sorbent with 3×600 µl of dichloromethane. Tert-butylcyclohexane was added as an internal standard to each extracted tar solution. A gas chromatograph with flame ionization detection (GC-FID) was employed in order to quantify tar compounds eluting from the gas chromatography system between 2-methylpropanenitrile and benz[e]acephenanthrylene. A gas chromatograph coupled with a mass selective detector (GC-MSD) was used for the identification of the most abundant tar compounds. A simplified calibration of the GC-FID instrument was based on single quantitation curve prepared using known concentrations of naphthalene/tert-butylcyclohexane. Total tar yields refer to total gas chromatography detectable tar and are expressed on a volumetric basis as g_{total tar} Nm⁻³ dry raw gas.

3. Results

3.1. Properties of dairy sludge and spruce wood chips

In Table 1 the properties of the air-dried biological dairy sludge, spruce wood chips as well as the blend of both feedstocks (50/50) are presented. A relatively low volatile matter content of 60 wt. % and high ash content of 32 wt. % in dairy sludge compared to spruce wood chips (dry basis) is expected to result in lower total tar quantities. A fixed carbon of 17 wt. % in dairy sludge indicates the amount of unconverted carbon which will remain in the char after pyrolysis. A high nitrogen content of 5.8 wt. % is typical characteristic of dairy sludge [3], while measured sulphur and chlorine contents were below 1 wt. %. The bulk density of air-dried dairy sludge was 550 kg m⁻³, while this value was only 197 kg m⁻³ for spruce wood chips.

Table 1. Properties of biological dairy sludge, spruce wood chips, and the blend of biological dairy sludge + spruce wood chips (50/50).

| Proximate analysis (wt. %) | Dairy sludge | Spruce wood chips | (50/50) |
|----------------------------------|--------------|-------------------|---------|
| Moisture (after air drying) | 20.0 | 4.7 | 10.9 |
| Volatile Matter (d.b.) | 59.7 | 84.1 | - |
| Ash (d.b.) | 31.8 | 0.4 | 14.7 |
| Fixed Carbon ^a (d.b.) | 17.0 | 15.5 | - |
| Ultimate analysis (d.b.) (wt. %) | | | |
| N | 5.8 | 0.2 | 3.0 |
| C | 35.9 | 50.7 | 42.9 |
| H | 5.6 | 6.6 | 6.1 |
| S | 0.8 | 0.02 | 0.4 |
| Cl | 0.2 | 0.005 | 0.1 |
| O ^a | 19.9 | 41.9 | 32.7 |

^a Calculated by difference, d.b. – dry basis.

In order to draw additional information on chemical composition of both feedstock, thermo-gravimetric analysis (TGA) was carried out in a nitrogen flow at a constant heating rate of 20 °C/min. Fig. 2 shows the TGA and differential thermo-gravimetric (DTG) profiles for dried dairy sludge and spruce wood chips. The first peak, in the DTG curve of spruce wood, below 100 °C corresponds to the water loss. The second, large peak between 200 and 400 °C presents the decomposition of hemi-cellulose and cellulose. According to Yang et al. [21] hemi-cellulose decomposes at 220 -

315 °C, cellulose at 315 - 400 °C, while lignin decomposes over a wide temperature range from 160 to 900 °C. Spruce wood DTG shows that the peak of hemi-cellulose overlaps with that of cellulose suggesting the thermal decomposition of hemi-cellulose at about 316 °C, with the peak at 351 °C representing cellulose decomposition. The last peak appearing at 539 °C most likely corresponds to the lignin decomposition. The TGA curve of dairy sludge confirms its high ash content. It was reported that the thermal decomposition of milk protein casein, initiates at 176 °C and completes at 610 °C with the maximum degradation rate at 310 °C. The peak maximum temperature for decomposition of milk fat occurs at 413 °C [22,23]. The first peak, in the DTG curve for dairy sludge, extends beyond 100 °C. It originates from evaporation of moisture and probably light organic compounds such as aldehydes, ketones, and acids. The large peak at around 289 °C corresponds to degradation of protein, while a subtle shoulder at 450 °C perhaps conforms to a fat degradation. The biological dairy sludge feedstock contains high amounts of volatile inorganic elements, such as S, K and Na [24]. The last small peak observed between 600 and 700 °C may be induced by the release of these inorganic compounds [25].

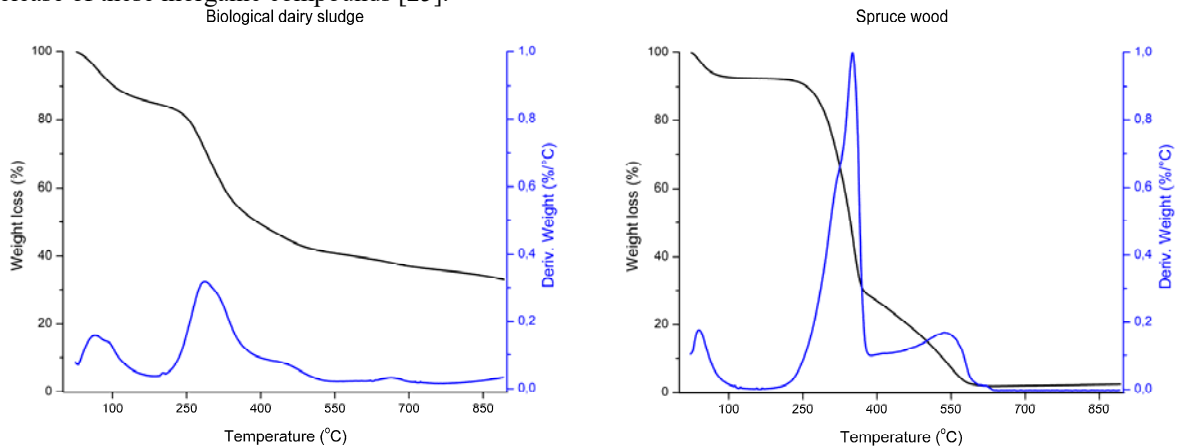


Fig. 2. Thermo-gravimetric analysis show TGA-percentage and DTG-rate for (left) air dry biological dairy sludge; (right) spruce wood chips.

Moreover, the presence of elements such as nitrogen, sulphur and chlorine in the sludge is also undesirable due to their corrosive potential on the process installation. The primary measure to reduce the amount of nitrogen, sulphur and chlorine as well as the ash content in the dairy sludge was to blend it with spruce wood chips at a 50/50 ratio by weight.

3.2. Pyrolysis tar yields and composition

Table 2 shows the identified tar compounds in the order in which they eluted. The left side of the Table 2 shows compounds from the co-pyrolysis of dairy sludge and spruce wood chips while at the right side the compounds from pyrolysis of spruce wood chips are listed. The experimental test number 3 (see Table 3) was chosen to present identified tar compounds. Note that minor variations with regard to identified tar compounds have been found among the tests of particular feedstock. The main differences in tar composition between two tested feedstocks are (1) a large number of nitrogen-containing tar compounds reflecting the high nitrogen content in dairy sludge, (2) higher lignin content in the spruce wood chips appears to result in larger number of polycyclic aromatic hydrocarbons (PAHs) with respect to blended dairy sludge and spruce wood chips. Nine nitrogen-containing tar compounds have been identified. In Table 2 they are denoted with *. Depending on a test run, the yields of nitrogen-containing tar compounds account for 8.0 – 16.8 % of total tar. 2-Butenenitrile, pyridine and 1*H*-pyrrole are found to be the most abundant nitrogen-containing tar compounds. Nitrogen-containing tar is considered problematic due to the carcinogenic and mutagenic character of their aromatic analogues [26]. Furthermore, HCN and NH₃ mainly originate from the secondary thermal cracking of nitrogen-containing tar. Upon combustion NO_x and N₂O get released. A single sulphur-containing compounds (i.e benzothiophene) has been found only in the test number 4.

Table 2. Identified pyrolysis tar compounds with the chromatographic retention times.

| Biological dairy sludge + spruce wood chips | | Spruce wood chips | | |
|---|--|-------------------|---|----------------|
| | Tar compound | Retention time | Tar compound | Retention time |
| 1 | 2-Methylpropanenitrile (Isobutyronitrile)* | 2.175 | / | |
| 2 | 5-Methylcyclopenta-1,3-diene | 2.268 | / | |
| 3 | 2-Butenenitrile* | 2.350 | / | |
| 4 | Benzene | 2.928 | Benzene | 2.978 |
| 5 | Pyrazine* | 4.332 | / | |
| 6 | Pyridine* | 4.707 | / | |
| 7 | 1 <i>H</i> -Pyrrole* | 5.280 | / | |
| 8 | Toluene | 5.340 | Toluene | 5.385 |
| 9 | 2-Methylpyridine* | 7.320 | / | |
| 10 | 4-Methylpyrimidine* | 7.507 | / | |
| 11 | 4-Methylpentanenitrile* | 8.260 | / | |
| 12 | Ethylbenzene | 8.758 | Ethylbenzene | 8.832 |
| 13 | 1,2/1,3/1,4-Dimethylbenzene | 9.067 | 1,2/1,3/1,4-Dimethylbenzene | 9.075 |
| 14 | / | | Ethynylbenzene | 9.543 |
| 15 | Ethenylbenzene (Styrene) | 9.883 | Ethenylbenzene (Styrene) | 9.888 |
| 16 | 2-Methyl-2-cyclopenten-1-one | 10.613 | / | |
| 17 | 1-Ethyl-3-methylbenzene (3-Ethyltoluene) | 12.445 | / | |
| 18 | Benzenecarbonitrile (Benzonitrile)* | 13.333 | / | |
| 19 | 1-Ethyl-2-methylbenzene (2-Ethyltoluene) | 13.597 | / | |
| 20 | Benzenol (Phenol) | 13.857 | Benzenol (Phenol) | 13.618 |
| 21 | / | | 1-Benzofuran | 13.675 |
| 22 | 1 <i>H</i> -Indene | 15.182 | 1 <i>H</i> -Indene | 15.203 |
| 23 | 2/3/4-Methylphenol (o/m/p Cresol) | 16.062 | 2/3/4-Methylphenol (o/m/p Cresol) | 16.168 |
| 24 | 2/3/4-Methylphenol (o/m/p Cresol) | 16.795 | 2/3/4-Methylphenol (o/m/p Cresol) | 16.965 |
| 25 | / | | 7-Methyl-1-benzofuran | 17.127 |
| 26 | 1,2-Dihydronaphthalene | 18.650 | 1,2-Dihydronaphthalene | 18.678 |
| 27 | 2,5-Dimethylphenol | 18.885 | / | |
| 28 | Naphthalene | 19.500 | Naphthalene | 19.543 |
| 29 | 2-Methylnaphthalene | 22.613 | 2-Methylnaphthalene | 22.625 |
| 30 | 1-Methylnaphthalene | 23.052 | 1-Methylnaphthalene | 23.068 |
| 31 | 1,1'-Biphenyl | 24.895 | 1,1'-Biphenyl | 24.920 |
| 32 | 2-Ethenylnaphthalene | 26.138 | 2-Ethenylnaphthalene | 26.167 |
| 33 | Acenaphthylene | 26.583 | Acenaphthylene | 26.610 |
| 34 | / | | Dibenzo[b,d]furan | 28.290 |
| 35 | 9 <i>H</i> -Fluorene | 29.778 | 9 <i>H</i> -Fluorene | 29.800 |
| 36 | / | | 4-Methyldibenzo[b,d]furan | 31.103 |
| 37 | Phenanthrene | 34.070 | Phenanthrene | 34.090 |
| 38 | Anthracene | 34.285 | Anthracene | 34.333 |
| 39 | / | | 4 <i>H</i> -Cyclopenta[def]phenanthrene | 36.825 |
| 40 | / | | 2-Phenylnaphthalene | 37.990 |
| 41 | Fluoranthene | 39.550 | Fluoranthene | 39.550 |
| 42 | Pyrene | 40.468 | Pyrene | 40.470 |
| 43 | / | | 11 <i>H</i> -Benzo[b]fluorene | 42.320 |
| 44 | / | | Cyclopenta[cd]pyrene | 46.133 |
| 45 | Tetraphene (Benz[a]anthracene) | 46.215 | Tetraphene (Benz[a]anthracene) | 46.270 |
| 46 | Benzo[k]fluoranthene | 52.013 | Benzo[k]fluoranthene | 52.008 |
| 47 | Benz[e]acephenanthrylene | 52.238 | Benz[e]acephenanthrylene | 52.235 |

To date no relevant work addressing the pyrolysis tar from dairy sludge fuels has been published, while information regarding tar when pyrolysis gas is a primary product is rather scarce. Several investigations have focused on maximizing bio-oil yields using various waste sludge materials as a feedstock. These waste sludges typically contain high nitrogen and ash content [26,27]. Pyrolysis bio-oil is typically produced at a temperature of 500 ± 50 °C under as short residence time as possible. It is a precursor material for pyrolysis tar whose formation is promoted by

increasing the pyrolysis temperature and extended the residence time. Fonts et al. [26] conducted tests in a laboratory scale fluidized bed reactor continuously feeding dry sewage sludge. Among well-known bio-oil constituents such as aliphatic/aromatic hydrocarbons and oxygen-containing aliphatic/aromatic compounds they also identified nitrogen-containing aliphatic/aromatic compounds, halogen-containing compounds as well as sulphur-containing compounds. The estimated proportions cover between 15 and 25 % of nitrogen-containing compounds and below 2 % represent sulphur-containing compounds. Among the nitrogen-containing aromatic compounds, benzonitrile, pyridine, indole were the most abundant [26]. Thangalazhy-Gopakumar et al. [27] carried out batch experiments in a fixed bed quartz reactor using palm oil sludge as a feedstock. The major compounds identified by GC–MS analysis of bio-oil included pyridine, pyrrole, phenol, indole and their ethyl, methyl derivatives, styrene, benzenitrile, benzenepropanenitrile, hexadecanitrile. On the other hand, Dominguez et al. [28] tested sewage sludge in a high temperature pyrolysis tests aiming to maximize hydrogen rich gas yield. They used an electrically heated quartz reactor reaching a pyrolysis of temperature 1040 °C. Although heterocyclic compounds with sulphur (benzothiophene) and nitrogen (quinoline, pyridine, benzonitriles and naphthalencarbonitrile) were found in the pyrolysis tar, the dominant compounds were polycyclic aromatic hydrocarbons (PAHs). The pyrolysis tar in the current study also contains long chain aliphatic compounds, such as fatty acid hexadecanoic acid and higher alkane dodecan. These type of compounds have also been reported by [26,27] but have not been found during high temperature pyrolysis [28].

Table 3 presents duplicates of total tar for each experiment conducted. The total tar yields from spruce wood chips pyrolysis are found to be on average 30 % higher than yields from dairy sludge and spruce wood chips co-pyrolysis. This observation is attributed to the higher lignin fraction in a spruce wood chips feedstock with respect to the blend of dairy sludge and spruce wood chips. Along with that, 14.7 wt. % of ash content in dairy sludge and spruce wood chips blend compared to 0.42 wt. % in spruce wood chips catalyze a decrease of total tar and char yields while the gas yield increased [26]. The calculations indicate that total tar yields comprise 0.5 wt. % of the initial weight of the dairy sludge and spruce wood chips feedstock. This proportion is slightly higher compared to spruce wood chips only. Dominguez et al. [28] sampled tar by the wet condensation method. A total tar yield less than 1 wt. % with respect to initial feedstock weight have been reported.

Table 3. Total gas chromatography detectable tar from three pyrolysis tests feeding a blend of biological dairy sludge + spruce wood chips and three tests feeding the spruce wood chips solely.

| Test nr. | Biological dairy sludge + spruce wood chips | | Spruce wood chips | |
|----------|--|----------------------------|--|----------------------------|
| | $g_{\text{total tar}} \text{ Nm}^{-3} \text{ dry raw gas}$ | Pyrolysis temperature (°C) | $g_{\text{total tar}} \text{ Nm}^{-3} \text{ dry raw gas}$ | Pyrolysis temperature (°C) |
| 2a | 10.01 | 700 | 11.18 | 700 |
| 2b | 10.67 | | 12.43 | |
| 3a | 7.25 | 700 | 12.17 | 735 |
| 3b | 7.63 | | 13.31 | |
| 4a | 10.32 | 770 | 11.54 | 740 |
| 4b | 10.51 | | 13.09 | |

Milne et al. [29] compiled acceptable tar limits in the gas with regard to the requirements of common downstream applications. Although, the values presented in Table 4 refer to biomass gasification tar, they should be equally valid for high temperature

Table 4. Upper limits of biomass gasification tar [29].

| Application | Tar ($\text{mg}_{\text{total tar}} \text{ Nm}^{-3}$) |
|----------------------------|--|
| Direct combustion | No limit specified |
| Syngas production | 0.1 |
| Industrial gas turbines | < 5 |
| Internal combustion engine | 50-100 |

pyrolysis tar. In direct-combustion systems (i.e. boilers, industrial kilns), hot raw gas is burnt directly. There is little chance of tar condensation and thus there is no need for prior tar removal. Internal combustion engines require cooled gas, but there is a probability of tar condensation inside the engine or in fuel-injection systems. Tar concentrations in the gas should therefore be well below 100 mg Nm^{-3} . The gas turbines impose even more rigorous restrictions because their blades are sensitive to tar deposits. The lowest tolerable tar limits refer to syngas applications since tar poisons/deactivates the catalyst. According to the internal combustion gas engine manufacturers specification issued by the Dresser-Rand Group gasification or pyrolysis tar limits are given for tar groups divided according to the aromatic ring number. 1 aromatic ring tar < 1.5 g MJ^{-1} , 2 aromatic rings tar < 0.2 g MJ^{-1} , 3 aromatic rings tar < 0.003 g MJ^{-1} , and no tar compounds with 4 aromatic rings or more are allowed to enter the gas engine. The manufacturer proposes the CEN/ BT/TF 143 standard technical specification, also known as tar protocol, as a methodology for determination of the tar content in the gas [30]. As an example, the average calorific value of raw and dry pyrolysis gas (excluding tar fraction) derived from three dairy sludge and spruce wood chips tests was 14.0 MJ Nm^{-3} . Thus, the upper tar limits for Dresser-Rand gas engine for dairy sludge and spruce wood mixture would have been < 21.0, < 2.8, and < 0.04 g Nm^{-3} referring to 1, 2, and 3 aromatic rings compounds, respectively. Average calorific value derived

from three spruce wood chips tests was 13.1 MJ Nm^{-3} setting upper tar limits close to those calculated for dairy sludge and spruce wood mixture.

According to the upper tar limits given by Milne et al. [29] the raw pyrolysis gas from none of the conducted test runs should be introduced in the gas engine prior to a tar removal step. On the other hand the manufacturer's specification allows for higher tar concentrations. In Table 5 the tar compounds are grouped and classified on the basis of aromatic ring number. The limits concerning 1 aromatic ring group are not exceeded in any of the pyrolysis tests conducted. Dairy sludge and spruce wood chips co-pyrolysis seems to satisfy the limits for the 2 aromatic rings group, whereas spruce wood chips feedstock indicates an overstep values. None of the fuels meet the requirements set for 3 aromatic rings group as the quantities exceed set limits by at least one order of magnitude. The most detrimental tar group 4+ aromatic rings is produced by both feedstocks, but spruce wood chips produce pyrolysis gas with a higher load of heavier PAH compounds. The group denominated as an unknown consist of identified non-aromatic tar and unidentified chromatographic peaks.

Table 5. The yields of tar groups classified according to the number of aromatic rings in the compound.

| Test nr. | Biological dairy sludge + spruce wood chips | | | | | Spruce wood chips | | | | |
|----------|---|--------|--------|---------|---------|---|--------|--------|---------|---------|
| | Sum ($\text{g}_{\text{tar}} \text{Nm}^{-3}$ dry raw gas) | | | | | Sum ($\text{g}_{\text{tar}} \text{Nm}^{-3}$ dry raw gas) | | | | |
| | 1 ring | 2 ring | 3 ring | 4+ ring | Unknown | 1 ring | 2 ring | 3 ring | 4+ ring | Unknown |
| 2a | 5.2 | 0.9 | 0.3 | 0.1 | 3.5 | 3.1 | 4.6 | 1.1 | 0.6 | 1.8 |
| 2b | 4.6 | 1.2 | 0.3 | 0.1 | 4.4 | 3.4 | 5.1 | 1.3 | 0.7 | 1.9 |
| 3a | 4.0 | 1.0 | 0.2 | 0.1 | 1.9 | 7.0 | 3.2 | 0.9 | 0.5 | 0.6 |
| 3b | 4.1 | 1.3 | 0.3 | 0.1 | 1.9 | 7.6 | 3.6 | 0.9 | 0.6 | 0.6 |
| 4a | 5.9 | 1.8 | 0.5 | 0.1 | 2.7 | 6.7 | 1.6 | 0.3 | 0.1 | 2.8 |
| 4b | 6.0 | 2.0 | 0.5 | 0.1 | 1.9 | 8.2 | 1.7 | 0.3 | 0.1 | 2.8 |

The results indicate that tar compounds consisting of 3 or more aromatic rings need to be significantly reduced or removed from the raw pyrolysis gas. Tar reduction methods were critically reviewed by [31,32]. Physical treatments such as commonly utilized water scrubber can efficiently reduce tar, but simultaneously reduce energy conversion efficiency and generate toxic waste water streams. Chemical (i.e. catalytic) treatments can reform tar at very low temperature, but shortcomings such as catalyst deactivation due to deposited carbon and H_2S still exists. Thermal tar cracking seems a viable approach for larger scale pyrolysis units, which may not however reduce tar yields sufficiently or even generate undesirable soot [33]. Phuphuakrat et al. [34] investigated pyrolysis tar removal, by the two-step function of thermal decomposition and physical adsorption. The reduction of the gravimetric tar mass was in the range of 77 – 92 % at thermal cracker temperature $800 \text{ }^\circ\text{C}$ and addition of reforming agents. During air reforming mode the authors observed increased yields of light PAH tar (i.e indene, naphthalene, fluorene, phenanthrene). These PAHs should be eliminated later by fixed-bed adsorption carried out at ambient temperature. Wood chips and activated charcoal were compared for their adsorption ability. Activated charcoal showed the best adsorption performance for light PAH tar but it also removed tolerable 1 aromatic ring compounds. In contrary, wood chips did not adsorb most of the 1 aromatic ring compounds, but the adsorption performance of light PAH tar was lower, exceeding the allowable light PAH limits for internal combustion engines.

Implementation of a thermal tar cracker using air as the reforming agent followed by adsorption seems an attractive and cost effective option for presented pyrolysis unit integrated with internal combustion unit. Wood chips or in-process generated bio-char can be utilized as a feedstock and an adsorbent. Adsorbent performance can be optimized by proper particle sizing or torrefaction treatment.

4. Conclusions

In the present study the tar from pyrolysis tests using solid phase adsorption method was measured. Pyrolysis tests were carried out in the temperature range between 700 and $770 \text{ }^\circ\text{C}$ with maximized gas yield and low tar yield being the main goal. Biological dairy sludge and spruce wood chips blend and spruce wood chips solely as a reference feedstock have been tested. The total gas chromatography detectable tar yields from spruce wood pyrolysis are found to be on average 30 % higher than yields from dairy sludge and spruce wood chips co-pyrolysis. This observation is attributed to higher lignin fraction along with lower ash content in a spruce wood feedstock with respect to dairy sludge and spruce wood chips blend. Main difference in tar composition is a number of nitrogen-containing tar compounds reflecting high nitrogen content in a dairy sludge feedstock. 2-Butenenitrile, pyridine and 1*H*-pyrrole are

found to be the most abundant nitrogen-containing tar compounds. According to given specification of internal combustion gas engine, both tested feedstocks produced excessive yields of 3 and 4+ aromatic rings tar calling for tar removal prior to combustion.

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