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Research article

Analysis of tar compounds and quantification of naphthalene from thermal treatment of household biowaste

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A B S T R A C T

Household biowaste represent the organic fraction of municipal solid waste and are an underutilized resource. Although previous studies have performed pyrolysis of organic waste, the vast majority has been on specific presorted feedstock or conventional lignocellulosic streams. Therefore, there is a lack of pyrolysis applications on representative food waste as retrieved from households and this can be attributed primarily to their high water content and their degradability. But via the intermediate step of drying, long-term storage and thermal treatment have become possible. In the framework of this study, household biowaste were pyrolyzed for the production of carbonaceous materials with a main focus on the analysis of produced tar compounds. Tars can be corrosive or cause clogging and disrupt the operation of pyrolysis and gasification plants. Their analysis has faced several difficulties due to inconsistency in the methodologies that have been applied by various groups. The tar protocol has provided a solid framework for consistent analysis of tars but until now has been solely used for the case of gasification. This study aimed to apply the tar protocol for pyrolysis and to enhance the detectability of the method for a wider range of tars by means of elemental analysis, attenuated total reflectance (ATR) and gas chromatography-mass spectrometry (GC-MS). GC- MS was performed by means of a specific column for PAHs identification and calibration methods were developed for the proper quantification of naphthalene which is the dominant tar compound. The results of the analysis showed that naphthalene concentration increased from torrefaction to carbonization but then decreased significantly for high temperature pyrolysis at 860 °C.

1. Introduction

Products from thermochemical conversion of biomass can be very diverse and are distributed among the solid, the liquid and the gas phases (Bridgwater, 2012). Pyrolysis takes place in an oxygen-deprived atmosphere and favors the production of tar compounds in comparison to combustion and gasification where a significant fraction of heavier hydrocarbons/tars combust or convert to syngas. Heavier hydrocarbons are primarily defined as “tar” and this term officially includes all the condensable organic hydrocarbons that have higher dew points (or alternatively higher molecular weight) than benzene (Neeft et al., 1999). The formation of tar compounds in thermochemical processes with low presence of oxygen like pyrolysis and gasification can be a major issue. For treatment temperatures below 1300 °C the presence of heavy hydrocarbons within the gaseous fraction of the products is significant (Rabou et al., 2009). In most cases the gases from high temperature pyrolysis or gasification are combusted as fuel in internal combustion engines or gas microturbines. The direct use of gases with high contents of tar is not possible because it would cause clogging and corrosion in the energy conversion units. In addition, the overall handling of the gas becomes more challenging because tars tend to condense on the walls of the pipelines and cause congestion. Thus, tar removal methods like condensation or filtering become necessary for the undisrupted and efficient operation of pyrolysis and gasification facilities (Devi et al., 2003). Specifically the gaseous products from biomass pyrolysis tend to contain such high amounts of tar that, unless proper treatment measures are applied, the downstream operations get

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compromised (Phuphuakrat et al., 2010).

There are hundreds of tar compounds that have significant differences between them. But a main categorization can be performed according to their principle characteristics, their detectability and the number of the aromatic rings in their molecules. Bergman et al. (2010) identified six major classes of tar compounds. The first class contains the compounds that cannot be detected by means of gas chromatography. The second class includes the heterocyclic tar compounds which also share the common property of being water soluble, while the third class includes the aromatic components. Classes four and five include the polyaromatic hydrocarbons (PAHs) in accordance to the number of their rings. The former class includes PAHs with two or three rings and the latter includes the PAHs with four or more rings. Finally, the sixth class contains the tars that can be detected by means of gas chromatography, i.e. a detectable peak for a specific retention time in the column, but are not identified.

Specific operating conditions within the pyrolysis or gasification reactor favor the formation of different tar compounds. Heavy tars have in principle high dew points and condense as the temperature drops. On one hand this enhances the separation of the tar compounds from the gas but on the other hand this is a major cause for fouling of the pipes (Anis and Zainal, 2011). In addition, the removal of tars comes along with an energy penalty since tar compounds have significant heating value and - by filtering them out – the heating value of the products decreases (Vakalis et al., 2015). Although the high concentration of tars in pyrolysis (and gasification) gases is generally perceived as problematic, it is the case that "not all tars are created equal". As Prando et al. (2014) pointed out, there are several tar compounds, like toluene and octane, which not only combust efficiently in the engine but they also increase the heating value of the input gaseous fuels. Therefore the focus should not be on lighter and combustible tars but on heavier and sticky tars that cause the clogging. Tumuluru et al. (2012) acknowledged the importance of the composition of volatile compounds also during mild pyrolysis which is commonly known as torrefaction. As a result of these arguments, several researchers are focusing primarily on the heavier hydrocarbons and their management. Di Gregorio et al. (2016) emphasized the technical challenges that arise from the presence of polynuclear hydrocarbons with high molecular weight and dew points over 300 °C, and focused specifically on naphthalene. Similarly, Patuzzi et al. (2016) monitored four small scale gasification plants and concluded that naphthalene is the tar compound with the highest concentration. In addition, for the three out of four cases naphthalene represented more that 50% of the total tars by weight. Thus, the analysis of naphthalene is crucial for extracting meaningful results about the quantity of the total tars.

Pyrolysis of organic waste for the production of fuels and materials has been applied in previous studies as well, but the feedstock was in principle presorted and conventional, i.e. lignocellulosic. Characteristically, Opatokun et al. (2017) pyrolyzed food waste digestate and assessed its agronomic benefits. From the application of pyrolyzed food waste digestate as fertilizer/soil-enhancer the authors observed positive effects on the germination index and in the enrichment of the plants with nutrients. In another study the pyrolysis of short rotation coppice was assessed as a viable economic and an environmentally-friendly alternative in comparison to combustion and gasification (Kuppens et al., 2010). Flash pyrolysis of short rotation coppice biomass produced bio-oil with reduced heavy metals content. For the construction of wetlands, the sustainable management of biomass is very important for the success of the operation. Pyrolysis of wetland biomass waste showed significant potential on sequestrating the carbon (Cui et al., 2016). Finally, Randolph et al. (2017) produced biochars from municipal organic waste but the waste mixtures were created as well from conventional biomass feedstock like woodchips, cardboard and newspapers.

In respect to sampling and analyzing, tars present several difficulties and many research groups develop their own methodologies in order to cope with these issues (Romar et al., 2010). This creates several drawbacks like the inability to compare the results between different studies or the application of methods that are not optimal. A recent solution, in respect to consistency, has been the introduction of the tar protocol (Van de Kamp et al., 2005). The tar protocol includes standardized methods for sampling and analyzing tars from gasification plants, but no similar effort has been developed for the case of pyrolysis. For the purpose of compound identification, the tar protocol guidelines provide the alternatives of gravimetric methods and gas chromatography with the former being the one that is widely applied for the case of gasification tars. Gravimetric determination of tars is done by distillation of the solvent, i.e. isopropanol, and gradual evaporation of the tar compounds usually by means of a rotary evaporator. Although this is a widely applied method, it has several drawbacks that directly compromise the integrity of the results, especially for the case of pyrolysis which produces bigger volumes of tar in comparison to gasification. Gravimetric methods are subjected to the control of temperature which is a key factor to the identification of tar compounds and it is the case that several compounds have neighboring evaporation temperatures. In addition, evaporation does not take place under ideal conditions since the heavier tars tend to stick on the surface of the rotary vessel of the evaporator. Also the continuous application of heat in the tar solution results to thermal cracking of the tars. For the latter issue there has been an effort for assessing the cracking as part of the identification process (Namioka et al., 2009) but the number of the numerous tar compounds along with the numerous cracking pathways, make this task very challenging.

This manuscript is a continuation of the work performed by Vakalis et al. (2016). Household biowaste were converted into char by means of pyrolysis under different temperatures. This work introduced an alternative thermochemical pathway for the valorization of organic waste which, although are produced in significant amounts, end up mainly in landfills (EUROSTAT, 2012). Moreover, converting disposable streams into valuable materials is in accordance with the Waste Framework Directive which encourages recovery and reuse prior to disposal of municipal waste (Council Directive, 2008). The present study has the scope to analyze the tar compounds in the product gases from pyrolysis of household biowaste in different temperatures. The novelty of this work arises on one hand from the uniqueness of the pyrolyzed material and on the other hand from the novel combination of the sampling and analysis methods. The main two novelty aspects are the following:

- The present study treats unsorted food waste from households which were sampled during an 8-month monitoring campaign. This is a clear step forward in respect to feedstock representativity and diversity in comparison to most studies that create their own waste mixtures which usually consist from conventional materials, e.g. woody biomass.
- This manuscript presents a unique experimental setup that was designed in order to sample, analyze and identify the tars in the pyrolysis gases. Moreover, additional calibration has been applied in order to optimize the quantification of naphthalene which is the tar compound with the highest concentration by far.

The details of the food waste sampling campaign and the tar identification methods are analytically described in Section 2 of this manuscript.