Reduction of water content in sewage sludge pyrolysis liquid by selective on-line condensation of the vapors

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Abstract

A selective on-line condensation system, including a scrubber and an electrostatic precipitator, has been tested in a lab-scale fluidized bed pyrolysis plant with the aim of reducing the water content of the pyrolysis liquid obtained from sewage sludge. Water and triethylene glycol at different temperatures were tested as washing liquids in the scrubber. The pyrolysis liquids collected with this liquid recovery system showed lower water contents (13 - 30 wt-%) than those collected with a previous system (48 wt-%) consisting of two condensers and an electrostatic precipitator. In spite of these significant reductions in the water contents, the liquids obtained still separated into three phases (light organic phase, heavy organic phase and aqueous phase). The properties and yields to these phases were also affected by the operational conditions used in the scrubber. The aqueous phase was the most affected since the compounds present in this phase are those with greater affinity for the polar washing liquid used in the scrubber. The properties of the organic phases were less affected by the condensation system, although it is of interest that when using triethylene glycol at 80 ºC as washing liquid, the yield to the light organic phase was increased by about 41% compared to the previous system without affecting its good properties as fuel.

Keywords

Water content reduction, pyrolysis liquid, on-line condensation system.

1. Introduction

Pyrolysis liquids can be used directly or after some upgrading treatment as fuel in electricity and heat generation processes, and also in transport applications.[1-4] The diverse applications of pyrolysis liquids require different values of their physicochemical properties. One of the main issues for these applications is the high water content of certain pyrolysis liquids. A high water content has a negative influence on some properties of the liquid such as the heating value,[5] the homogeneity or the solubility in petroleum-based fuels,[6-8] whereas a moderate water content could be beneficial for the viscosity,[5, 9] the atomization,[10] the ignition delay [9] and the NO_x emissions generated in the liquid combustion.[3]

Given the influence of the water content on the aforementioned physicochemical properties of the liquids, different applications will tolerate different levels of water content in the pyrolysis liquid. For example, water contents lower than 25 - 27 wt-% are desirable when using pyrolysis liquids as fuel in boilers and engines.[11] On the other hand, in order to utilize pyrolysis liquids as feed in refineries, almost all the water and most organically bound oxygen compounds should be removed.[6]

Pyrolysis liquids contain a variable quantity of water (15 - 50 wt-%),[12] coming from the moisture of the feedstock and formed during the pyrolysis process itself. Even if the pyrolysis conditions are optimized, the pyrolysis liquids obtained from some raw materials may have water contents over 30 wt-% or even circa 50 wt-%. This is the case of lignocellulosic materials with a high moisture content (10-20 wt-%) [13] or of sewage sludge samples with an elevated amount of OH groups.[14]

Pyrolysis oils differ in their ability to dissolve water, depending on the hydrophilicity of their organic compounds. Usually, the higher the oxygen content the greater the water

solubility. The water is dissolved or mixed in the form of drops with the other pyrolysis liquid compounds.[10] This water cannot be separated from the rest of the pyrolysis liquid compounds by centrifugation,[15] since this procedure also separates a high proportion of other compounds, with the subsequent loss of liquid yield.

Nowadays, new methods related to liquid recovery systems are under study with the aim of improving the water content and other physicochemical properties of the pyrolysis liquids obtained from different types of lignocellulosic biomass.[13, 16] Oasmaa et al.[16] investigated the effect of light volatiles in the storage stability of pyrolysis liquids. They found that when light volatiles and some water was removed by evaporation and substituted by a short-chain alcohol, the quality of liquid product (homogeneity, viscosity, stability, odor, acidity and heating value) improved significantly. According to the authors the elimination of these undesirable compounds (light volatiles and some water) from the rest of the liquid compounds could be achieved using a condenser temperature of around 50 ºC. Within these conditions, up to 23 wt-% of the feed and the pyrolysis water is not condensed with the rest of the pyrolysis liquid compounds in the condensers. Westerhof et al.[13] tried to collect the organics without condensing most of the moisture present in the vapor stream. In order to achieve this objective, they studied a liquid recovery system equipped with a spray column in which the pyrolysis vapors are washed with oil at different temperatures (20 - 70 ºC). The authors achieved significant reductions in the pyrolysis liquid water contents, although these decreases always resulted in a loss of organic vapors leading to a lower liquid yield. Recently, other authors have also focused on the study of the liquid recovery system, especially on reactive condensation systems in which the vapors obtained from the pyrolysis reactions are collected and reacted at the same time. For example, Hilten et al.[17] have investigated the on-line esterification of pyrolysis vapors

with ethanol with the aim of improving the heating value and the storage stability of the pyrolysis liquids. Other authors have studied the production of triacetonamine by using acetone as washing liquid in the scrubbers of the condensation system.[18]

The main objective of this work was to reduce the water content of pyrolysis liquids obtained from sewage sludge samples with a large amount of OH groups by changing the condensation system used in the experimental plant, in order to favor a selective condensation of the vapors. Since the reduction in the water content could have a positive affect on some physicochemical properties of the pyrolysis liquid, the influence of the liquid recovery system on the properties of the collected liquids has been studied. Different configurations of an on-line selective condensation system were tested in the experimental plant. This condensation system consists of a scrubber, which substituted the two condensers used previously, and an electrostatic precipitator, where the final liquid product is collected. The different configurations of this new condensation system are related to the different operational conditions studied in the scrubber, where it is desired to retain the water from the rest of the vapors obtained in the pyrolysis process. In addition, the results obtained with this on-line selective condensation system are compared with those obtained with the previous system (consisting of two condensers and an electrostatic precipitator and denoted in this paper as the "conventional system"), in which almost the entire vapors are collected.

2. Materials and methods

2.1. Raw material

Anaerobically digested and thermally dried sewage sludge (SS) was supplied by an urban waste water treatment plant. Feedstock analyses were carried out employing standard methods: moisture according to ISO-589-1981, ash according to ISO-1171-1976, volatiles according to ISO-5623-1974, ultimate analysis CHNS using a Carlo Erba 1108, and heating value according to ISO-1928-89 (see Table 1). FTIR and X-ray diffraction analyses were also carried out in order to characterize the sewage sludge sample. FTIR spectra showed different bands which corresponded to stretching and bending vibrations of groups such as O-H (present in water, alcohols, phenols and carboxylic acids), N-H bends (amines and amides), C-H, C-C and C=C (aliphatic and aromatic structures) and C=O (aldehydes and ketones). A more detailed description of these spectra is reported elsewhere.[14] The main minerals identified in the sample by X-ray diffraction were ilite, caolinite, magnetite, albite, quartz, calcite, microline and dolomite, the most abundant being quartz and calcite. Moreover, the composition of the inorganic material of the sewage sludge was analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES). This analysis showed the important presence of Si, most likely from sand and soil. The ash also contained Fe, Ca, Na, K and Mg; some of these could catalyze some pyrolysis reactions.[19]

The amount of extractives was determined by Soxhlet extraction with dichloromethane, followed by acetone extraction. The content of the extractives (as raw material basis) was 5.04 wt-%. Qualitative analyses of the extractives were carried out by GC-MS. The main extractives determined were aliphatic hydrocarbons from C_{10} to C_{30} (mainly linear alkanes and alkenes with some cyclic and branched), fatty acids (for example, tetradecanoic, hexadecanoic acid and 9-ocatadecenoic acid), steroids and sterols (C_{27}-

C_{29}, mainly derived from cholestene, cholesterol, and ergosterol) and benzenes with side chains from C_1 to C_9. Small amounts of naphthalene methyl derivatives, ketones, aldehydes, fatty alcohols, phenols, amines, and fatty acids with side fatty ester chains were also present.

2.2. Experimental plant

In this section the laboratory scale plant used for the pyrolysis experiments and the different systems used for the liquid collection are described.

2.2.1. Liquid production. The sewage sludge pyrolysis experiments were carried out in a laboratory scale fluidized bed unit (< 1 kg/h) operating at atmospheric pressure. The unit was equipped with continuous feed of solids and nitrogen as fluidizing gas. The solid bed was constituted by char of the sewage sludge itself. The bed height was maintained at 150 mm by means of an internal pipe, which works by an overflow mode and enables ash to be continuously removed. Smashed and sieved sewage sludge (250 - 500 μm) was fed to the reactor at a solid feed rate of 3.4 g/min. The average solid residence time was around 8 min, since most of the solid is removed by overflow. The inlet nitrogen flow rate was 4.5 dm^3(NTP)/min ($u/u_{mf} = 8$) and the residence time for pyrolysis vapors inside the bed was around 1 s. The pyrolysis temperature was 530 ºC. The vapors produced exited the reactor and passed through a cyclone and a hot filter, both at 450 ºC. The liquid recovery system was placed after the hot filter. A more detailed explanation of the experimental system can be found elsewhere.[20]

The operational conditions used in the pyrolysis reaction were the same in all the experiments in order to analyze exclusively the influence of the configuration of the liquid condensation and recovery system. To prove the reproducibility of the pyrolysis reaction, the char yields obtained from the different experiments were examined. It can

be assumed that the pyrolysis reaction took place in the same way in all the experiments, since the one-way variance analysis (ANOVA) did not show significant differences on the char yields, with a 95% confidence level (p-value = 0.8452). The mean value ± standard deviation of the char yields obtained in the different experiments was 51.59 ± 0.451.

2.2.2. Liquid recovery system. Many different configurations of the condensation system were used in this work. First, the system usually employed in previous experiments carried out in the same plant was tested. This system (conventional system) was composed of two ice-cooled condensers (C1 and C2) and one electrostatic precipitator (EP) (see Figure 1). The pyrolysis liquid product was collected in the three devices (C1, C2 and EP). Some previous experiments carried out with this condensation system, in which a micro GC was used to analyze the gas product, showed that mass balance closed above 95% [14, 20] so it can be assumed that almost the entire condensable vapors are recovered with this condensation system. Some properties (yield and water content) of these condensed fractions were characterized separately in order to find out the best design for the new liquid recovery system. Furthermore, the three liquid fractions were mixed and the physicochemical properties of the whole condensed liquid product were determined and compared with those of the liquids obtained with the new liquid recovery system.

Secondly, a new condensation system for the experimental plant was implemented during this work. In this system, both condensers were substituted by a scrubber (spray column) with the aim of removing part of the water vapor prior to the condensation of the rest of the vapors in the electrostatic precipitator. Only the vapors collected in the electrostatic precipitator composed the pyrolysis liquid product.

The washing liquid was fed into the scrubber as very fine drops through a spray shower. Inside the scrubber, the washing liquid was in countercurrent contact with the pyrolysis vapors and some compounds were retained in it. The temperature of the vapors was measured at the entry and at the exit of the scrubber. The washing liquid worked in closed circuit during the 120 minutes that the pyrolysis experiments lasted. By means of a pump, the washing liquid was continuously introduced into the scrubber from a vessel located inside a thermostatic bath, which enabled the washing liquid temperature to remain constant. After exiting the scrubber, the washing liquid returned to the aforementioned vessel. A schematic representation of the new liquid recovery system is shown in Figure 2.

Different configurations of this liquid recovery system can be studied by changing some of its main operational parameters.

2.3. Experimental planning

First, three replicas of the experiment using the conventional liquid recovery system were carried out. The results of these experiments enabled the new condensation system to be designed and the subsequent comparison of the liquids to be made.

The pyrolysis experiments with the new liquid recovery system were carried out using two polar washing liquids, water and triethylen glycol (TEG), with the main aim of removing moisture from the gases and vapors. Working with water is usually easy and cheap. TEG was chosen due to its high boiling point (285 ºC), which enables a high temperature to be used in the scrubber, and to its use for drying natural gas.[21-24] The flow rate of both washing liquids was 22 dm^3/h. The residence time of the gases and vapors in the scrubber was approximately 11 seconds (the volume of the scrubber being 800 cm^3, with a diameter of 5.5 cm and a height of 34 cm). Several temperatures for the

washing liquids were set in the thermostatic bath: 6, 15, 35 and 55 ºC for water (water vapor pressure increases rapidly above 50 ºC) and 50 and 80 ºC for TEG. Moreover, another experiment was carried out using a scrubber of 400 cm^3 volume (3.5 cm diameter and 45 cm height) and, consequently, half the gas residence time.

One more experiment was performed heating the scrubber in order to set the temperature of the gases at the exit of the scrubber at 80 ºC. As can be seen in Table 2, a total of 13 experiments were carried out.

2.4. Liquid product characterization

The pyrolysis liquid yield was determined by weight difference of the devices before and after the experiment. In the case of the conventional liquid recovery system, these vessels were the two condensers and the electrostatic precipitator, while in the new liquid recovery system the liquid was only collected in the electrostatic precipitator.

All the pyrolysis liquids obtained in each experiment were separated into three different phases (light organic phase, heavy organic phase and aqueous phase) by centrifugation during 30 minutes at 4500 rpm. After centrifugation, the graduated tubes used enabled the volumetric proportions of each phase to be determined. Next, several physicochemical properties of the three phases were analyzed separately. Densities of the heavy organic phase and of the aqueous phase were determined using a densimeter model Densito 30 PX Mettler Toledo. Due to the lack of sample, density of the light organic phase was calculated by weight difference using a microsyringe of 100 µl. Water contents (WC) of the three phases were determined by Karl-Fisher titration (Mettler Toledo V-20). The higher heating values (HHV) of the organic phases were analyzed using a C2000 IKA Bomb Calorimeter. The dynamic viscosity of the heavy organic phase was determined at 20 and 40 ºC by means of a rotational viscometer

(Visco Basic Plus). The pH of the aqueous phase was measured directly using a pH/ISE meter (Sension 4).

Other variables such as the total water content of the liquid and the yield to each phase were calculated using the values of the whole liquid yield and the volumetric proportion, the density and the water content of each phase. Moreover, the water yield was calculated as the product of the liquid yield by the water content of the liquid. This variable enabled a comparison to be made of the amount of water collected as liquid product in the different systems. The organic yield is the difference between the liquid yield and the water yield (both calculated over fed sewage sludge) and this enabled the loss of organic compounds in the scrubber to be evaluated in relation to those collected with the conventional system.

Other analyses were carried out on the three phases of the liquids in order to compare their chemical composition. These analyses included ultimate analyses of the liquid phases using a Carlo Erba 1108, chemical composition of the heavy organic phase using a solvent fractionation scheme developed for biomass pyrolysis liquids according to Oasmaa et al.[25] and qualitative analyses of the composition of the organic phases by GC-MS using a HP-5 capillary column of 30 m x 0.32 mm and coated with a 0.52 μm thick 5% phenilmethilsiloxane (HP-5) film.

2.5. Data analysis

One-way analysis of variance (one-way ANOVA) was used to evaluate the influence of the condensation system configuration (see Table 2) on the studied variables relating to the whole liquid (yield, water content, water yield and loss of organic compounds in the scrubber) and to the separated phases (yield, water content and density of all the phases, HHV of the organic phases and pH of the aqueous phase). When the ANOVA analysis

detected significant differences, the least significant difference (LSD) test (significance level of 0.05) was employed to determine differences between pairs of experimental data. The LSD intervals have been included in the bar diagrams where the results are shown.

3. Results and discussion

3.1. Liquid fractions collected in each device of the conventional liquid recovery system

Almost all the condensable vapors constituting the liquid product were collected in these items of equipment, obtaining a total liquid yield of 33.1 wt-% over fed sewage sludge. However, a small fraction of the condensable vapors was not collected in liquid form. Due to the high temperature of the nozzle that joined the hot filter and the first condenser, the vapors that condensed in this nozzle (0.3 wt-% over fed sewage sludge) suffered polymerization and appeared as a laminated solid, which could block the path of the vapors coming from the pyrolysis reactor during the continuous operation in a plant. This solid has a high content of carbon as shown by its elemental analysis: C = 76.42%; H = 6.88%; N = 12.11%; S = 0.27%. A similar condensed product has also been found at the entry of the condensation system by other authors studying the pyrolysis of sewage sludge.[26] Besides, another small fraction of the condensable vapors (0.1 wt-% over fed sewage sludge) passed through the condensation equipment without being collected and was caught in a cotton filter situated after the electrostatic precipitator. Therefore, if these two fractions of vapors are considered, the yield to condensable vapors becomes 33.5 wt-%. That is to say, with this conventional system of condensation, 98.8% of the total condensable vapors were recovered as liquid product.

The fractions of the liquid product collected in the different devices of the conventional

liquid recovery system were characterized separately in order to know where the organics and the water preferably condensed. Most of the liquid (68.1 wt-%) condensed in the first condenser, while only 5.2 wt-% of the liquid was collected in the second condenser and 26.7 wt-% in the electrostatic precipitator. The liquid collected in both condensers showed phase separation into an organic and an aqueous phase. The fraction of liquid collected in the electrostatic precipitator was very sticky and viscous and apparently did not show evidence of phase separation. As can be observed in Table 3, similar quantities of organic compounds were recovered in the electrostatic precipitator and in the first condenser. However, most of the water was collected in the first condenser (C1). For this reason, in the new liquid recovery system the two condensers were substituted by a scrubber, in which a polar washing liquid, water or TEG, was used with the aim of removing moisture from the gases and vapors prior to the condensation of the rest of the vapors in the electrostatic precipitator. Other authors have proposed collecting first the organics without condensing the water using a non-polar washing liquid.[13] However, this procedure would not be of interest for pyrolysis liquids from sewage sludge since these liquids contain a high amount of hydrocarbons, steroids and other non-polar compounds (5 wt-% over fed sewage sludge) which could be difficult to recover from a non-polar washing liquid due to their high solubility.[27]

3.2. Effect of the liquid recovery system on the liquid yield, total water content, water yield and loss of organic compounds

As can be observed in Figure 3a, the liquid yield was significantly lower in all the experiments carried out with the systems that included the scrubber in their configuration than in the conventional condensation system. This fact was mainly due to the removal of water in the scrubber, but the possible loss of organic compounds has also been taken into account. Although these compounds are described as organic, other

non-organic compounds, such as ammonia, could also be removed.

Water contents of the pyrolysis liquids collected in the systems with the scrubber were significantly lower than those obtained with the conventional system, except for the liquid collected in the system with the heated scrubber (see Figure 3b). The lowest water content (13 - 14 wt-%) was obtained when TEG was used as washing liquid, and this represents a reduction of more than 70% compared to the value obtained with the conventional system (48 wt-%).

To make a reliable comparison of the amount of water collected as liquid product in the different systems, the water yield has to be taken into account. As can be seen in Figure 3c, the amount of water collected as liquid product was smaller in all the configurations that included the scrubber, except for the system that worked with the heated scrubber. This means that when the heated scrubber was used, the decrease in yield compared to the conventional system was due to a high loss of organic compounds and not to a removal of water, so that this system is not of interest for the aim of this study. However, with all the other systems that included the scrubber in their configuration, important decreases in water yield were achieved.

When all the vapors are collected as liquid product in a pyrolysis process with a typical liquid condensation system, the water yield would be always higher than the moisture content of the raw material. However, with a selective condensation of the vapors the water yield could be reduced. In this work (see Figure 3c), the use of the scrubber allowed water yields below the moisture content of the sewage sludge (6.6 wt-%). Therefore, this kind of condensation system could be appropriate to reduce the water yield in the pyrolysis process of raw materials with high moisture content.

On the other hand, in the condensation system which includes the scrubber, the

retention of compounds in the scrubber is due mainly to the polarity of the compounds (solubility in the two solvents used) and in a lesser extent to heat transfer. If the only mechanism were heat transfer, water removal would be similar when different liquids were used at the same temperature. For example, when using water at 55 ºC and TEG at 50 ºC as washing liquids, water yields were significantly different (4.8 wt-% and 1.7 wt-% respectively). Moreover, according to the ANOVA analysis, there were not significant differences in water yield when using TEG at 80 ºC (1.6 wt-%) or water at 6ºC (2 wt-%). However, water vapor pressure is quite different at 6 ºC (almost null) and at 80 ºC (around 350 torr), so it is thought that polarity (solubility) had a greater effect than heat transfer.

Apart from the reduction in the water yield, the loss of organic compounds in the scrubber is an important parameter that has to be considered. As can be seen in Figure 3d, the loss of organic compounds was quite similar in all cases (34 - 42% with respect to the conventional system) except for the heated scrubber, in which it was higher, maybe because the heating of the vapors made their collection in the electrostatic precipitator difficult.

Concerning the water content reduction, one of the properties which was expected to improve was the liquid homogeneity. When the conventional system was used, the whole liquid separated into three phases after mixing and centrifuging the different fractions collected in the three devices. However, the liquids collected in the electrostatic precipitator with the new system still separated into three phases in spite of the important reductions achieved in the water content. This could mean that in pyrolysis liquid from sewage sludge, phase separation is not only due to the high water content, but also to the important presence of extractives (around 20.4 wt-%).[27] The percentage of extractives in the liquids obtained in these experiments will depend on the

liquid yield, since the 5.04 wt-% of extractives contained in the sewage sludge will become part of the liquid product after the pyrolysis process. It is known that the extractives are responsible for phase separation in pyrolysis liquids obtained from forest residue.[8] Pyrolysis liquids obtained from forest residue contain around 12 wt-% of extractives and 21 wt-% of water and separate into two phases. However, pyrolysis liquids from stem pine, which have similar water content (23 wt-%), are homogeneous because they have a lower extractive content (4 wt-%).[25] In fact, pyrolysis liquids obtained from lignocellulosic materials with low extractives content do not show phase separation for water contents lower than 30 wt-%.[28] For this reason, a liquid recovery system similar to that proposed in this work could be appropriate to avoid phase separation in liquid when the only cause of the appearance of phases is the high water content.

The three phases that appeared in all the liquids after centrifugation are designated in this paper as aqueous phase, heavy organic phase and light organic phase. Their aspect and localization in the liquid were the same in all the experiments: the aqueous phase was located at the bottom, the heavy organic phase in the middle and the light organic at the top. A representative ultimate analysis of each phase is shown in Table 4.

Unlike the appearance and the order of the phases in the liquid, the volumetric proportions of the different phases changed with the condensation system configuration (see Figure 4) due to the removal of water and other compounds in the scrubber. When the conventional system was used, the majority phase in the liquid was the aqueous, but when the scrubber was included in the system, the contribution of this phase in the whole liquid was lower due to the removal of water and polar organic compounds that came from this phase.[27, 29, 30]

On the other hand, the reduction achieved in the water content could positively affect other physicochemical properties of the liquid product. This aspect is analyzed in the next section.

3.3. Effect of the liquid recovery system on the physicochemical properties of the liquid

As the phase separation in the pyrolysis liquid was not avoided, it is interesting to study how the condensation system influences the yield and properties of these phases in relation to their possible applications.[27]

3.3.1. Aqueous phase. The properties of the aqueous phase were the most influenced by the condensation system. The yield to this phase (see Figure 5a) decreased considerably when the systems with scrubber were used, from approximately 20 wt-% to around 2-3 wt-% over fed sewage sludge (except when water at 55 ºC was used as washing liquid, in which the aqueous phase yield was a little higher, 6.4 wt-%). Similarly, the water content in this phase was reduced using the scrubber in the condensation system. The lowest values were achieved when TEG was used as washing liquid; in this case the water content of the aqueous phase was reduced from 74 wt-% in the liquid collected with the conventional system to around 40 wt-% (see Figure 5b). According to the results of the ANOVA test, the density of this phase also showed significant differences when the liquid collected with the conventional system was compared with the one collected using TEG in the scrubber (see Figure 5c). However, in practice, these differences are almost negligible since they do not exceed 5%.On the other hand, as can be seen in Figure 5d, the highest pH of the aqueous phase (9.76) was measured in the liquid collected with the conventional system.

Lastly, significant differences have been detected in the compounds determined by GC-

MS in the aqueous phase obtained with the conventional system and in the aqueous phases obtained in the experiments carried out with the scrubber. In general, the compounds determined in the aqueous phases are organic compounds highly oxygenated and nitrogenated. Many of these compounds contain more than one functional group for example an alcohol and an amine group or a ketone and an amine group, what gives them a high polarity. The most abundant functional group of these compounds is the amine group. This fact would point to their formation from the proteic fraction of the sewage sludge. Examples of compounds found in the aqueous phases are carboxylic acids of short chain, some sulfur-containing compounds, some compounds with ketone groups and alcohol groups, some phenolic compounds, and numerous nitrogen-containing compounds, which sometimes contain other functional groups like compounds derived from pyridinol, pyrazole, piperidine, pyrrol or parabanic acid.[27,29, 30]

With the selective on-line condensation system set up in this work, this phase was almost eliminated from the final liquid product by its collection with the washing liquid. In this way, a new by-product is produced and therefore it would be essential to find an appropriate application for it. For that purpose it is necessary to characterize the composition of the washing liquid. The organic compounds retained in the washing liquids were analyzed by GC-MS. The results of these analyses showed that the compounds that were preferably condensed in the scrubber were highly polar, had a lot of amine groups and came mainly from the aqueous phase of the liquid. For this reason, the pH of the washing liquids at the end of the experiments had a markedly basic character (9.78 to 10.12) and the pH of the aqueous phases had taken a more neutral value. For further information of the organic compounds that appeared in the aqueous phases or in the washing liquids, GC-MS results have been enclosed to this paper as Supporting Information (see Tables S.I.3, S.I.4 and S.I.5). Nowadays, one of the most

promising applications for the compounds collected in the scrubber is their use as fertilizers.[29]

3.3.2. Heavy organic phase. Unlike the aqueous phase, the ANOVA analysis did not show significant differences in the yield to the heavy organic phase nor in the HHV (see Table 5). However, other physicochemical properties of the heavy organic phase were affected by the configuration of the condensation system. The only significant difference in the water content of this phase was detected when TEG was used in the scrubber, in which cases higher water contents (9.9 and 12.4 wt-%) were obtained (see Figure 6a). Regarding the density of this phase, the highest values belonged to the liquids collected in the systems that worked with TEG while the lowest was found in the liquid collected with the conventional system (see Figure 6b). The viscosity analyses of this phase showed a wide range of values, between 450-1550 cP at 20 ºC (see Table 6). This variability may be caused by a change in its chemical compositions, but the GC-MS analyses did not reveal significant differences in the qualitative composition. The organic compounds that appeared on the heavy organic phases were triglycerides, aminosugars, phenolic compounds, nitrogen-containing compounds, fatty nitriles, fatty alcohols and fatty acids (see Table S.I.2 in the Supporting Information).[27] In fact, the variations in the viscosity of this phase could be due to heavy compounds undetectable by gas chromatography.[31] In order to determine which compounds were responsible for the important differences in the viscosities of the heavy organic phases, the composition of this phase was studied by the solvent fractionation scheme developed by Oasmaa et al.[25] This method characterizes the whole sample separating its compounds into four fractions according to their polarity. These fractions are water, water soluble-ether insoluble, water soluble- ether soluble and water insoluble compounds. The results of this method showed that there were differences in the distribution of the four fractions

depending on the configuration of the condensation system (see Figure 7). Comparing these results with the viscosity values, it was detected that the more viscous the phase, the higher proportion of water insoluble compounds and the smaller fraction of ether soluble compounds it contained, a result consistent with the results found by other authors for pyrolysis liquids from lignocellulosic biomass.[32] Lastly, the pH of the water soluble fractions separated from the heavy organic phases was measured (see Table 6) and the higher value was obtained in the liquid collected in the conventional system. This again supports the view that some of the compounds that were removed in the scrubber contributed to the basic character of the pyrolysis liquid.

3.3.3. Light organic phase. Concerning this phase, only the yield showed significant differences between some of the configurations of the liquid recovery system (see Figure 8). The highest yield to the light organic phase (3.1 wt-% over fed sewage sludge) was obtained in the system that used TEG at 80ºC as washing liquid in the scrubber. This yield was 41% higher than the yield to the same phase obtained with the conventional system (2.2 wt-% over fed sewage sludge). As commented before, the highest water contents of the heavy organic phase corresponded to the liquids collected in the systems that worked with TEG in the scrubber. This fact could cause a decrease in the affinity of some non-polar organic compounds which were present in the heavy organic phase when its water content was lower and, therefore, they tend to dissolve in the light organic phase, thus increasing its yield. The rest of the physicochemical properties of this phase hardly changed with the different configurations of the liquid recovery system (see Table 7). The light organic phase did not have water in any of the liquids. Neither was the HHV affected by the configuration of the liquid recovery system, being around 43 MJ/kg in all cases. Furthermore, the chromatographic analyses of these phases did not show differences in their qualitative composition and all the

light organic phases contain aliphatic hydrocarbons, steroids and triglycerides (see Table S.I.1 in the Supporting Information). On the other hand, the viscosity of this phase could only be measured in the most abundant sample (light organic phase of the liquid collected in the system with TEG at 80 ºC in the scrubber) and the values obtained were 21.9 cP at 20 ºC and 9.2 cP at 40 ºC.

In all cases this phase seems to keep its good combustible properties, so for the aim of maximizing its yield, the use of TEG at high temperature (in this study 80 ºC) in the scrubber could be of interest.

However, the yield to this phase is still very low and therefore it would be of even greater interest to obtain one single organic phase formed by the light and the heavy organic phases. The catalytic pyrolysis of sewage sludge could help to modify the organic composition of the liquid by means of the transformation of the fatty acids of the heavy organic phase into hydrocarbons, which are one of the main constituents of the light organic phase.[33, 34]

4. Conclusions

Significant reductions in the water content of pyrolysis liquid were achieved with the on-line selective condensation of the pyrolysis vapors set up in this work. In the best operational conditions studied (TEG at 80 ºC as washing liquid in the scrubber), the water content was reduced from 48% obtained with the conventional liquid recovery system to 13%. In spite of this significant reduction in the water content, the pyrolysis liquid still separated into three phases due probably to its high extractive content.

The yield and properties of the aqueous phase were the most affected by the utilization of the scrubber in the condensation system, because this phase consists of water and polar compounds susceptible to be retained in the scrubber. Using TEG at 80 ºC, the

yield to this phase was reduced by 90%; therefore, it is thought that in more severe conditions the compounds of this phase could be completely removed in the scrubber.

The organic phases were less affected by the utilization of the scrubber. The most important result for these phases was that, when TEG at 80 ºC was used as washing liquid, the yield to the light organic phase was almost doubled without modifying its good properties as a fuel. This phase does not contain water and has a heating value of around 43 MJ/kg. The increase in the yield to this light organic phase is caused by the increase in the water content of the heavy organic phase which promotes the migration of its apolar compounds to the light organic phase. Apart from the water content in the heavy organic phase, other properties such as the pH, that was lower using the scrubber, or the viscosity, that was higher, were also influenced by the utilization of the scrubber. When the scrubber is used, it is thought that some compounds such as fatty acids tend to be concentrated in this heavy organic phase, since these are the kinds of compounds that increase the viscosity of pyrolysis liquids.

Although the selective condensation of the vapors in the scrubber enables the yield to the light organic phase to be nearly doubled, it is still very low. In this way, the application of this selective on-line condensation in a sewage sludge catalytic pyrolysis process would make it possible to obtain separately in different items of equipment the aqueous phase, with a possible application as a fertilizer, and the organic phase, which would then be formed by the light organic phase and also by the aliphatic hydrocarbons coming from the catalytic pyrolysis of the fatty acids. Lastly, this condensation system could be of even greater interest for decreasing the water content in pyrolysis liquids obtained from raw materials with high moisture content.

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Supporting Information Available

Chromatograms and lists of compounds detected by GC-MS in the three phases of pyrolysis liquids obtained with different configurations of the condensation system and in one sample of the washing liquid. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Brammer, J. G.; Lauer, M.; Bridgwater, A. *Energy Policy* **2006,** *34*, 2871-2880.

(2) Briens, C.; Piskorz, J.; Berruti, F. *Int. J. Chem. Reactor Eng* **2008,** *6*, R2.

(3) Chiaramonti, D.; Oasmaa, A.; Solantausta, Y. *Renewable Sustainable Energy Rev* **2007,** *11*, 1056-1086.

(4) Czernik, S.; Bridgwater, A. V. *Energy Fuels* **2004,** *18*, 590-598.

(5) Westerhof, R. J. M.; Brilman, D. W. F.; van Swaaij, W. P. M.; Kersten, S. R. A. *Ind. Eng. Chem. Res.* **2010,** 49, 1160-1168.

(6) Baldauf, W.; Balfanz, U.; Rupp, M. *Biomass Bioenergy* **1994,** *7*, 237-244.

(7) García-Pérez, M.; Adams, T. T.; Goodrum, J. W.; Geller, D. P.; Das, K. C. *Energy Fuels* **2007,** *21*, 2363-2372.

(8) Oasmaa, A.; Kuoppala, E.; Gust, S.; Solantausta, Y. *Energy Fuels* **2003,** *17*, 1-12.

(9) Solantausta, Y.; Nylund, N.-O.; Gust, S. *Biomass Bioenergy* **1994,** *7*, 297-306.

(10) Boucher, M. E.; Chaala, A.; Roy, C. *Biomass Bioenergy* **2000,** *19*, 337-350.

(11) Oasmaa, A.; Peacocke, C.; Gust, S.; Meier, D.; McLellan, R. *Energy Fuels* **2005,** *19*, 2155-2163.

(12) Mohan, D.; Shi, J.; Nicholas, D. D.; Pittman, C. U.; Steele, P. H.; Cooper, J. E. *Chemosphere* **2008,** *71*, 456-465.

(13) Westerhof, R. J. M.; Kuipers, N. J. M.; Kersten, S. R. A.; van Swaaij, W. P. M. *Ind. Eng. Chem. Res.* **2007,** *46*, 9238-9247.

(14) Fonts, I.; Azuara, M.; Gea, G.; Murillo, M. B. *J. Anal. Appl. Pyrolysis* **2009,** *85*, 184-191.

(15) Elliott, D. C. *Biomass Bioenergy* **1994,** *7*, 179-185.

(16) Oasmaa, A.; Sipila, K.; Solantausta, Y.; Kuoppala, E. *Energy Fuels* **2005,** *19*, 2556-2561.

(17) Hilten, R. N.; Bibens, B. P.; Kastner, J. R.; Das, K. C. *Energy Fuels* **2009,** *24*, 673-682.

(18) Cao, J.-P.; Zhao, X.-Y.; Morishita, K.; Li, L.-Y.; Xiao, X.-B.; Obara, R.; Wei, X.-Y.; Takarada, T. *Bioresour. Technol.* **2010,** *101*, 4242-4245.

(19) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K. *Energy Fuels* **2010,** 24, 1380-1388

(20) Fonts, I.; Juan, A.; Gea, G.; Murillo, M. B.; Sanchez, J. L. *Ind. Eng. Chem. Res.* **2008,** *47*, 5376-5385.

(21) Gandhidasan, P. *Energy Sources* **2003,** *25*, 189-201.

(22) Twu, C. H.; Tassone, V.; Sim, W. D.; Watanasiri, S. *Fluid Phase Equilib.* **2005,** *228*, 213-221.

(23) Darwish, N. A.; Hilal, N. *Chem. Eng. J.* **2008,** *137*, 189-197.

(24) Mostafazadeh, A. K.; Rahimpour, M. R.; Shariati, A. *J. Chem. Eng. Data* **2009,** *54*, 876-881.

(25) Oasmaa, A.; Kuoppala, E.; Solantausta, Y. *Energy Fuels* **2003,** *17*, 433-443.

(26) Pokorna, E.; Postelmans, N.; Jenicek, P.; Schreurs, S.; Carleer, R.; Yperman, J. *Fuel* **2009,** 88, 1344-1350

(27) Fonts, I.; Kuoppala, E.; Oasmaa, A. *Energy Fuels* **2009,** *23*, 4121-4128.

(28) Mohan, D.; Pittman, C. U.; Steele, P. H. *Energy Fuels* **2006,** *20*, 848-889.

(29) Azuara, M.; Ábrego, J.; Fonts, I.; Gea, G.; Murillo, M. B. In *Ammonia content of bottom phase liquid from pyrolysis of sewage sludge in a fluidized bed*, 18th European Biomass Conference & Exhibition, 2010; ETA-Renewable Energies and WIP-Renewable Energies: 2010.

(30) Kaminsky, W.; Kummer, A. B. *J. Anal. Appl. Pyrolysis* **1989,** *16*, 27-35.

(31) Fratini, E.; Bonini, M.; Oasmaa, A.; Solantausta, Y.; Teixeira, J.; Baglioni, P. *Langmuir* **2006,** *22*, 306-312.

(32) Oasmaa, A.; Kuoppala, E. *Energy Fuels* **2003,** *17*, 1075-1084.

(33) Boocock, D. G. B.; Konar, S. K.; Mackay, A.; Cheung, P. T. C.; Liu, J. *Fuel* **1992,** *71*, 1291-1297.

(34) Maher, K. D.; Bressler, D. C. *Bioresour. Technol.***2007,** *98*, 2351-2368.

Table 1. Proximate analysis, ultimate analysis and heating value of sewage sludge (in moisture ash basis)

Proximate analysis (wt-%, ad)	
Moisture	6.6
Ash	41.3
Volatiles	46.1
Fixed carbon	6.0
Ultimate analysis (wt-%, ad)	
C	27.7
H [a]	4.4
N	3.9
S	0.8
O [b]	21.9
HHV ($MJ \cdot kg^{-1}$)	11.9
LHV ($MJ \cdot kg^{-1}$)	10.8

[a] including hydrogen in the moisture; [b] by difference

Table 2. Operational conditions used in the scrubber.

Experiment		Washing liquid	Temperature of washing liquid (ºC)	Volume of the scrubber (dm^3)	Control of exit gas temperature
1	Conv				
2	Conv	Conventional system (without scrubber)			
3	Conv				
4	W55ºC	Water	55	0.8	No
5	W35ºC	Water	35	0.8	No
6	W35ºC	Water	35	0.8	No
7	W15ºC	Water	15	0.8	No
8	W6ºC	Water	6	0.8	No
9	LowVol	Water	15	0.4	No
10	Q80ºC	Water	35	0.8	Yes, exit of gases at 80 ºC
11	TEG50ºC	TEG	50	0.8	No
12	TEG80ºC	TEG	80	0.8	No
13	TEG80ºC	TEG	80	0.8	No

Table 3. Characterization of the liquid product collected in each equipment of the conventional condensation system.

	C1		C2		EP
Liquid yield (wt-% over fed sewage sludge)	22.5		1.7		8.8
Volumetric proportion of phases (vol-%)	Top 27	Bottom 73	Aqueous phase with some drops of organic phase		Non phase-separated
Water content (wt-%)	Top 8.03	Bottom 77.38	Top n.an.[a]	Bottom 76.95	7.58
Percentage of total water collected in each device (wt-%)	87		9		4
Percentage of total organic compounds collected in each device (wt-%)	52		2		46

[a] non analyzed.

Table 4. Representative ultimate analyses of each phase of the pyrolysis liquid.

Ultimate analysis (wt-%, ad)	Aqueous phase	Heavy organic phase	Light organic phase
C	11.17	69.54	85.92
H	10.45	8.97	11.83
N	6.52	9.44	1.80
S	0.37	1.24	0.18
O [a]	71.49	10.81	0.27

[a] by difference

Table 5. Heavy organic phase properties non-significantly influenced with a 95% of confidence level by the configuration of the condensation system.

Condensation system configuration	Yield (wt-%)	HHV ($MJ \cdot kg^{-1}$)
Conv	9.4 ± 0.5	31.66 ± 1.94
W55ºC	7.1	32.93
W35ºC	7.8 ± 0.3	32.10 ± 0.40
W15ºC	7.8	32.21
W6ºC	7.0	30.41
LowVol	6.5	31.61
TEG80ºC	7.7	30.19
TEG50ºC	7.3	29.75
p-value	0.1275	0.7109

Table 6. Heavy organic phase viscosity and pH of its water soluble fraction obtained with the different configurations of the condensation system.

Condensation system configuration	Viscosity (cP) at 20ºC	Viscosity (cP) at 40ºC	pH
Conv	448	84	8.76
W55ºC	977	168	8.28
W35ºC	1023	174	8.05
W15ºC	1406	201	7.94
W6 ºC	1572	221	7.88
LowVol	1516	226	7.77
TEG80ºC	1390	21	8.47
TEG50ºC	625	119	8.27

Table 7. Properties of the light organic phase non-significantly influenced with a 95% of confidence level by the configuration of the condensation system.

Condensation system configuration	Density ($kg \cdot dm^{-3}$)	Water content (wt-%)	HHV ($MJ \cdot kg^{-1}$)
Conv	0.94 ± 0.00	0	43.14 ± 0.06
W55ºC	0.94	0	43.43
W35ºC	0.92 ± 0.01	0	43.18 ± 0.18
W15ºC	0.92	0	43.11
W6ºC	0.95	0	43.28
LowVol	0.94	0	43.10
TEG80ºC	0.91	0	43.31
TEG50ºC	0.89	0	43.20
p-value	0.0530	n. an.[a]	0.6148

[a] non analyzed.

Figure caption

Figure 1. Conventional liquid condensation system.

Figure 2. New liquid condensation system.

Figure 3. (a) Liquid yield (wt-% as raw basis); (b) water content of the liquid products (wt-%); (c) water yield (wt-% as raw basis) and (d) lost of organic compounds referred to the conventional system obtained with the different configurations of the condensation system (■ conventional, ■ water, □ TEG).

Figure 4. Volumetric proportions of the three phases (■ aqueous, ■ heavy organic, □ light organic) obtained with the different configurations of the condensation system.

Figure 5. Aqueous phase (a) yield (wt-% as raw basis), (b) water content (wt-%), (c) density ($kg \cdot dm^{-3}$) and (d) pH obtained with the different configurations of the condensation system (■ conventional, ■ water, □ TEG).

Figure 6. Heavy organic phase (a) water content (wt-%) and (b) density ($kg \cdot dm^{-3}$) obtained with the different configurations of the condensation system (■ conventional, ■ water, □ TEG).

Figure 7. Fractions (■ water, □ water soluble-ether insoluble, □ water soluble-ether soluble, ■ water insoluble) of heavy organic phase depending on the configuration of the condensation system.

Figure 8. Light organic phase yield (wt-% as raw basis) obtained with the different configurations of the condensation system (■ conventional, ■ water, □ TEG).

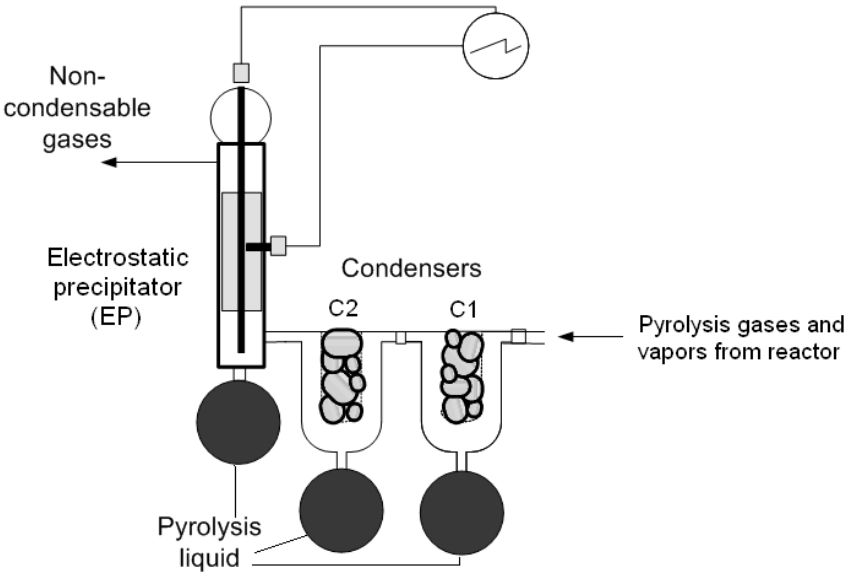
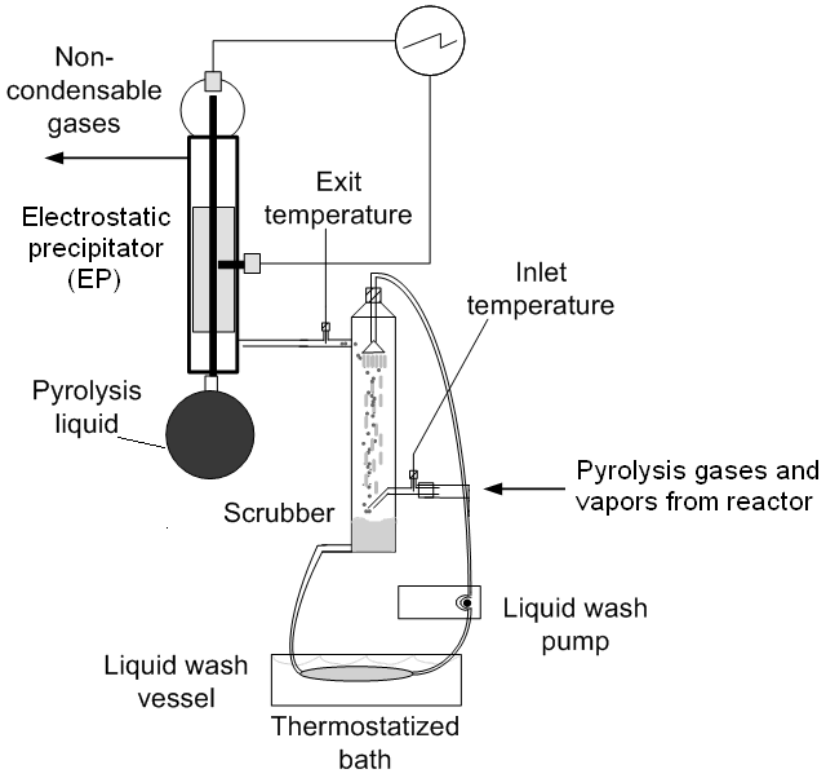

Non-
condensable
gases
Electrostatic
precipitator
(EP)
Condensers
C2
C1
Pyrolysis gases and
vapors from reactor
Pyrolysis
liquid

Figure 1

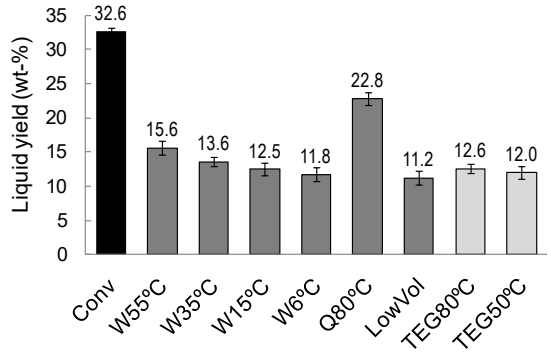
1

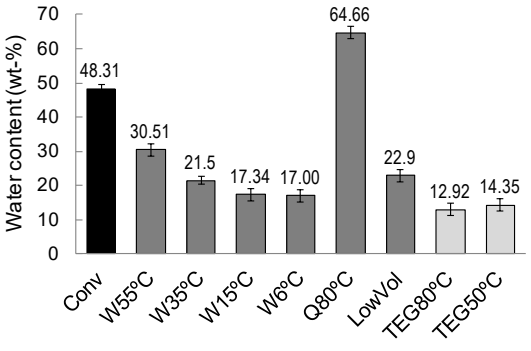


2

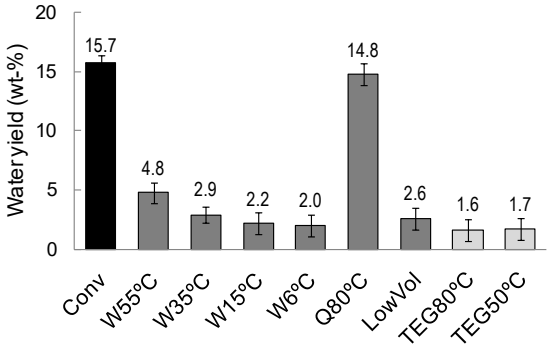
3 **Figure 2**

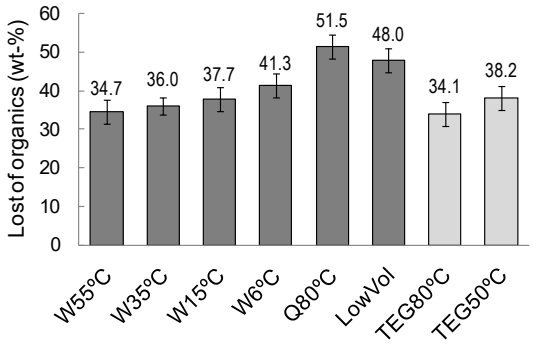
4





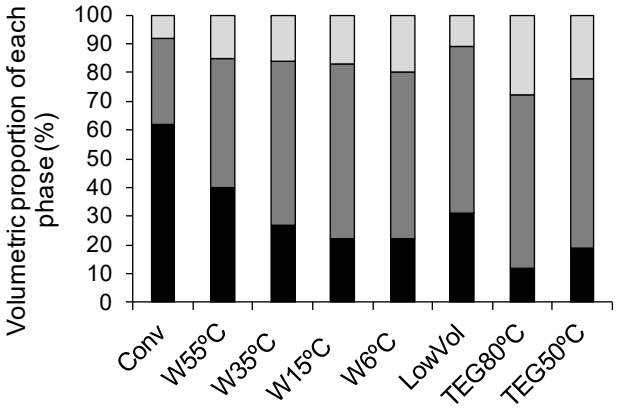
(a) **(b)**





(c) **(d)**

Figure 3


Volumetric proportion of each phase (%)
100
90
80
70
60
50
40
30
20
10
0
Conv
W55°C
W35°C
W15°C
W6°C
LowVol
TEG80°C
TEG50°C

1

2 **Figure 4**

3

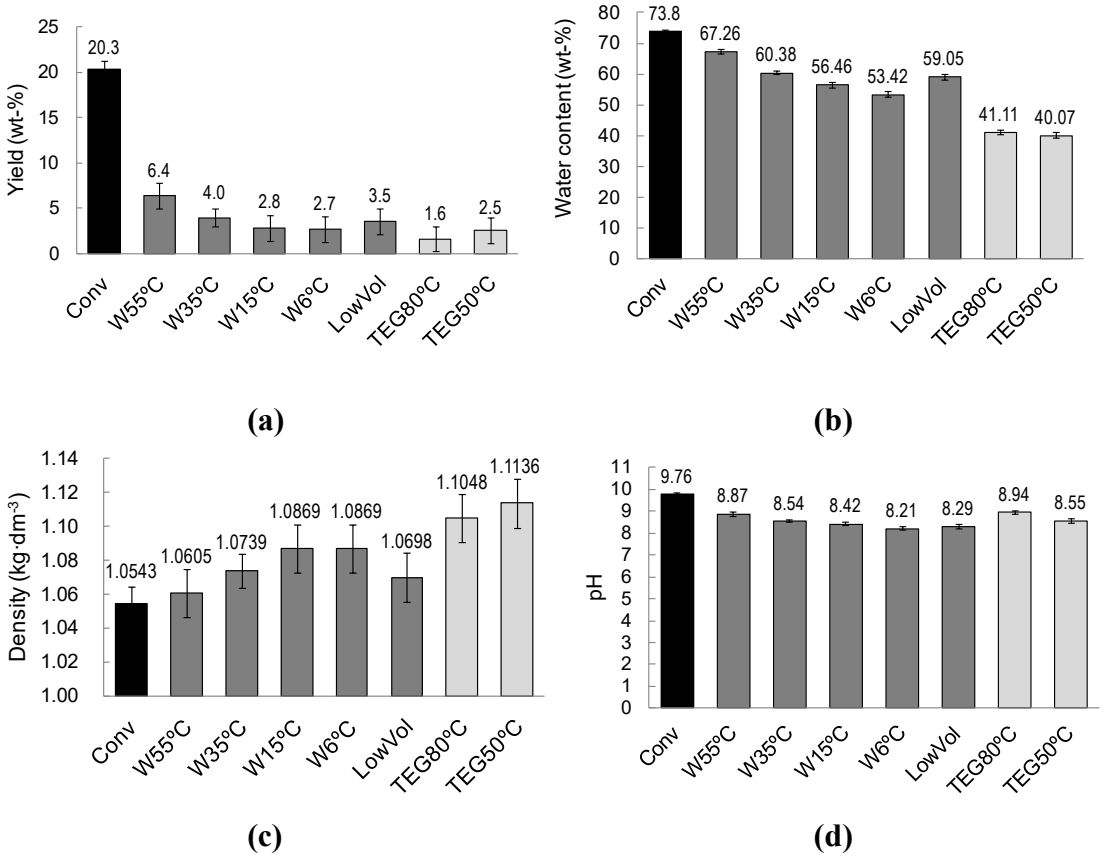
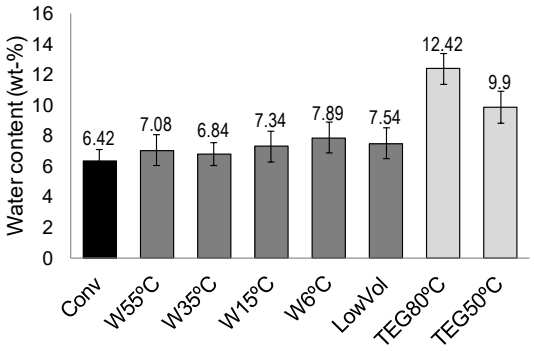
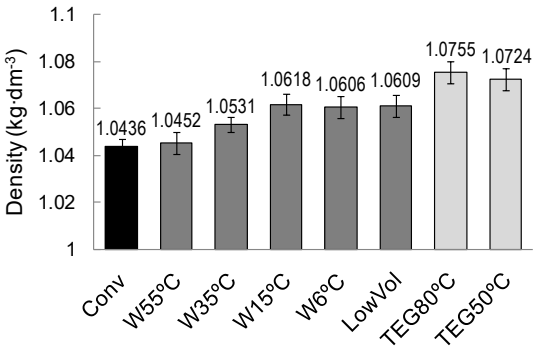

Yield (wt-%)
20.3
6.4
4.0
2.8
2.7
3.5
1.6
2.5
Conv
W55°C
W35°C
W15°C
W6°C
LowVol
TEG80°C
TEG50°C
(a)
Water content (wt-%)
73.8
67.26
60.38
56.46
53.42
59.05
41.11
40.07
(b)
Density (kg·dm-3)
1.0543
1.0605
1.0739
1.0869
1.0869
1.0698
1.1048
1.1136
(c)
pH
9.76
8.87
8.54
8.42
8.21
8.29
8.94
8.55
(d)

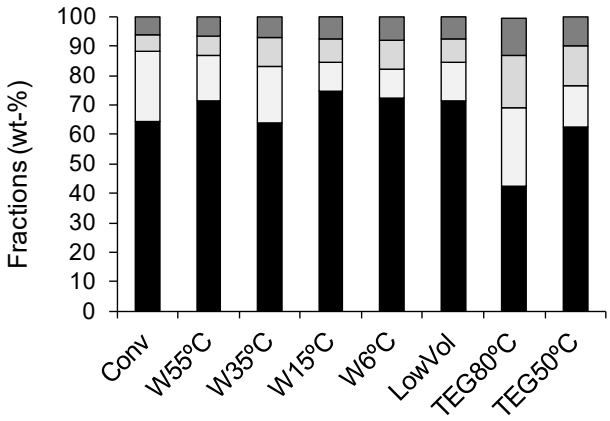
Figure 5


Water content (wt-%)
16
14
12
10
8
6
4
2
0
6.42
7.08
6.84
7.34
7.89
7.54
12.42
9.9
Conv
W55°C
W35°C
W15°C
W6°C
LowVol
TEG80°C
TEG50°C


Density (kg·dm-3)
1.1
1.08
1.06
1.04
1.02
1
1.0436
1.0452
1.0531
1.0618
1.0606
1.0609
1.0755
1.0724
Conv
W55°C
W35°C
W15°C
W6°C
LowVol
TEG80°C
TEG50°C

(a) **(b)**

Figure 6



1

2 **Figure 7**

3

4

5

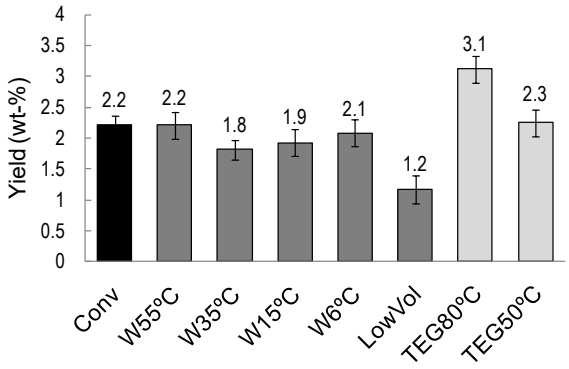

Yield (wt-%)
4
3.5
3
2.5
2
1.5
1
0.5
0
2.2
2.2
1.8
1.9
2.1
1.2
3.1
2.3
Conv
W55°C
W35°C
W15°C
W6°C
LowVol
TEG80°C
TEG50°C

Figure 8