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Valorisation of textile waste via steam gasification in a fluidized bed reactor

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Abstract

Demand for textile production is constantly increasing together with population expansion and economic development of the society. Reaching the end-of-life, textile products are becoming waste, which is nowadays mostly incinerated and landfilled. Pathways of fibre recycling are known for single-material garments i.e. cotton, despite this, several textile products contain a blend of both synthetic and natural fibres which are hard to sort and recycle. Those abundant textile waste fractions can, via feedstock recycling, be converted to high-value chemicals. The principle of the process is to break polymer chains from the textile to its constituents, which can be used as chemicals, replacing fossil fuels as feedstock. This paper analyses the potential of feedstock production from steam gasification of textile waste through experimental work in a fluidized bed bench-scale reactor. Additionally, the monomer recovery was studied for textiles with diverse chemical structure: natural polymer type-cellulose, synthetic polymer and blends. Results showed that both syngas and aromatics (BTXS) could be recovered from gasification. While cotton is more suitable for syngas production, polyester and blends could produce both syngas and aromatic compounds.

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1. Introduction

The textile production is constantly increasing together with population expansion and economic development of the society. Fabrics are largely made of synthetic fibres, which places the 3rd largest end-use market of plastic production, while it is the 2nd largest plastic waste generator, after the packaging sector (IEA, 2019). Textile products are mostly incinerated and landfilled at the end-of-life, operating almost in a linear path. For the case of clothing, only 1% are closed-loop recycled, and barely 12% is reused in lower-quality applications such as wiping, stuffing or insulation materials (MacArthur, 2017). Resembling packaging, textile presents a waste-handling problem, therefore, the recycling share needs to increase to go towards a circular economy.

Understanding the composition of the textile stream is essential to assess potential recycling methods. Textiles can be divided into 3 groups: animal-based, plant-based, and synthetic fibres. Animal-based fibres, such as wool, down or silk, comprehended only 1,5% of the total textile production in 2017, followed by plant-based fibres with a total of 36,3%, including cotton (24,5%) and Man-Made Cellulosic fibres (6,3%). Synthetic textiles made most of the production, 62,2%, which comprise of Polyester (51%), nylon (5,4%) and others (5,6%) such as Polypropylene, acrylic or elastane. Synthetic fibres have dominated the textile market since the mid-1990s when they overtook cotton. In 2017, 65 million tons of synthetic fibres, mainly polyester with 54 Mt while cotton had had a stable production 25 Mt per year in the last decade (Textile exchange, 2018).

There are two big challenges for textile recycling: (i) it consists of a variety of polymers which complicate sorting and (ii) many textiles produced today are fibre blends (Textile exchange, 2018, MacArthur, 2017). Recycling pathways of single-material garments i.e. 100% cotton are known. However, fibre blends recycling is particularly challenging due to the mix of natural and synthetic fibres. One common example is polycotton, a blend of polyester and cotton, which reduce cost and increase durability. Another example is adding small amounts of elastane to cotton improve stretch to a garment (MacArthur, 2017). Blends make more demanding material recovery, they can be mechanically processed, but the material composition of the recycled yarn is difficult to control. That leads to using those materials in downgraded applications such as wiping, stuffing or insulation. Hence, recycling alternatives should be examined for blended textiles.

Although incineration allows the recovery of energy from this blended and mixed fraction, from the point of view of circular use of materials, a technology that enables producing new materials with the same quality is needed. Thermo-chemical recycling of textiles could constitute an important alternative to recycle hydrocarbons from synthetic textiles, thus enabling a more sustainable life cycle. For instance, plastic gasification can produce a gas that can be further synthesized into energy-rich gas, e.g. H₂, to different kinds of biofuels, e.g. methanol, or to base chemicals e.g. olefins and Benzene, Toluene, Xylene, Styrene (BTXS), for the generation of new products. A large benefit of gasification-based recycling of plastics compared to other options, such as pyrolysis, is the possibility of utilizing mixtures of different types of plastics, or plastics mixed with other types of feedstock, e.g. biomass (Lopez, 2018).

Thermal conversion of textiles, pyrolysis and gasification, has been investigated to the relatively low extent and in reactor systems (Gholamzad, 2014; Miranda, 2007; Nahil, 2010). Chemical recycling by steam cracking, which is the focus here, refers to the recovery of monomer molecules from textile and their reuse for production of valuable chemicals. High-temperature causes that synthetic polymer fraction degrades into smaller fragments of original polymer, aromatics and oligomers. In this paper, an overview on the valorisation of textile wastes via steam gasification in a fluidized bed is shown aiming to the production of chemicals. As stated beforehand, it is important that the process can handle diverse types of textile mixtures. Dual Fluidized Bed (DFB) gasification system has shown to be suitable for nonhomogeneous fuels, such as waste fractions, and for low heat transfer fuel and high polymerization materials such as plastics (Maric, 2018). DFB system is composed of two connected reactors, combustor and a gasifier, where sand-like bed material loop is used as a heat carrier in the process. The bed material is heated in the combusting part of the unit and circulated to the gasifier where the heat is delivered for endothermic gasification reaction. The non-gasified char is then carried by the bed material to the boiler

where char is combusted, and the bed is heated again. The principle of the system considers that the process is providing enough char for the heat balance to be satisfied.

The yields of specific hydrocarbons highly depend on the molecular structures of the waste stream and the positions at which chemical bonds are likely to break under the applied conditions. In this work, the most common textiles types were investigated, polyester and cotton as pure materials, as well as a blended garment. Additionally, since the temperature is a key parameter for thermochemical processes, a variation of this operational parameter was studied to gain an understanding of the textile gasification and eventually have insight on possible optimization of the process.

2. Experimental section

2.1 Materials

In the experiment, three garments were used with the following composition: (i) 100% polyester, (ii) 100% cotton and (iii) a cloth containing 50% of cotton and 50% of polyester, which were pelletized for feeding purposes. The garments ultimate analysis was obtained through Thermogravimetric analysis (TGA 701) and the results are shown in Table 1.

The bed material used was fresh olivine, with composition MgO (49,6%), SiO₂ (41,7%), Fe₂O₃ (7,4%) and others. 700 g of olivine was used with a bulk density of 2.4 kg/m³ and an average particle diameter of 250 μm.

Table 1. Fuels TGA

Fuel (% wt)	H ₂ O	Ash	Vol	FC
Polyester (PES)	0,27	0,19	91,06	8,47
Cotton (Cot)	5,41	0,38	85,87	8,33
50PES/50Cot	2,40	0,42	83,49	13,69

2.2 Equipment

The experiments were performed in a bubbling bed bench-scale reactor, with dimensions: 77,9 mm inner diameter and 1,27 m high, as depicted in Figure 1.

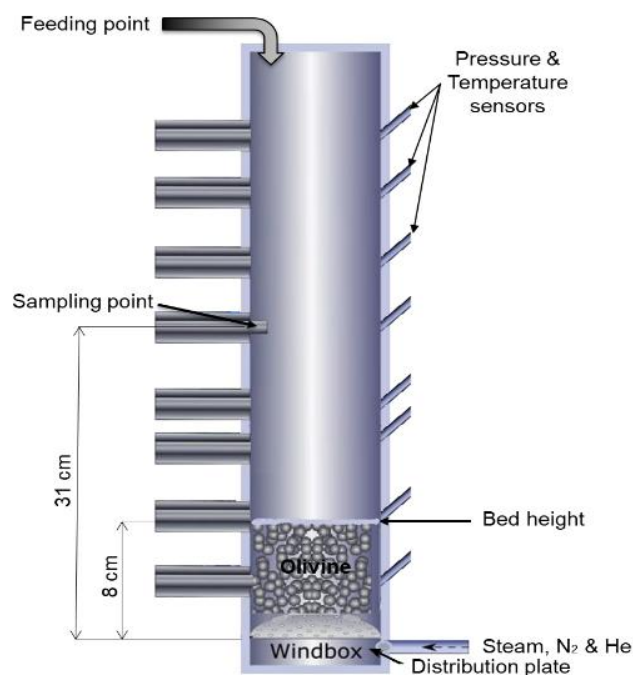


Figure 1. Bench-reactor used for the gasification tests

The reactor setup enables continuous measurements of pressure and temperature along with the height, including the wind box, as well as measurement positions for gas sampling. The temperature can be precisely controlled by means of an oven divided into 3 sections, measured and controlled by temperature sensors, which allows an even distribution along the full reactor. The fluidization media was fluidized steam, produced at 190°C by a steam generator. Additionally, nitrogen was introduced to achieve the desired fluidization conditions. Fluidization gases were pre-mixed in the wind-box, heated up and fed through a distribution plate with 0,6 mm holes to the bed.

2.3 Measurements

The process was evaluated through the characterisation of the gas produced in the gasifier. The samples were taken at a port located 32 cm from the distributor plate, as shown in Figure 1. The concentration of the main constituent of the products gas, H₂, CO, CO₂, CH₄ and light hydrocarbons (C₂-C₃ species) were collected in the gas bags Tedlar© which were directly after analysed with µGC. A flow of high purity helium (0.05 l/min) was added into the reactor as a tracer gas, to quantify the total dry gas flow and calculate the gas product distribution related to the fuel conversion. Helium was introduced into the fluidized bed together with the fluidization gases and regulated by a mass flow controller. The aromatic fraction was sampled at the same point using the Solid Phase Adsorption (SPA) method and determined by gas chromatography with flame ionization detection (GC-FID). The species identified in this work are aromatic compounds with boiling points lying between those of benzene and coronene (Table 2).

Table 2. Species Analysed and Sorted by Groups

Permanent gas	H ₂ , CO, CO ₂ , CH ₄ and C ₂ -C ₃ : C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C ₃ H ₆ , C ₃ H ₈
SPA-measurable tars	
Group 1	benzene
Group 2	1-ring: toluene, o/p-xylene, styrene, methyl-styrene
Group 3	naphthalene
Group 4	2-rings: indene, 1,2-dihydronaphthalene, 1-methylnaphthalene, 2-methylnaphthalene, biphenyl, benzofuran
Group 5	≥3-rings: acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, xanthene, fluoranthene, pyrene, chrysene, dibenzofuran
Group 6	phenols: phenol, o/p-cresol, 1-naphthol, 2-naphthol
SPA-unknowns	Species for which the instrument was not calibrated but for which corresponding peaks are observed in the chromatograms

2.4 Experimental conditions

As temperature is one of the key parameters in thermochemical processes, each of the three above mentioned textile materials :100% polyester, 100% cotton and 50% cotton/ 50% polyester were tested at 650, 750 and 850°C, with an aim to investigate the most suitable operational point for steam gasification of textile, which results in highest obtained product yields.

The experiments were performed in batch operation composed of two steps (see Figure 2). Firstly, the gasification step, where 2g of fuel was fed from the top of the reactor. Steam was fed as a main fluidizing agent, keeping Steam to Fuel Ratio (SFR) equal to 1. Nitrogen was also added to obtain a bubbling regime as well as maintain the gas residence time (RT_g) at 3s. The residence time of the fuel in gasification step was 2 min and products sampling was performed during this same time. Secondly, the combustion step, where the unconverted fuel was combusted using air. The idea behind the 2-step process was to simulate a Dual Fluidized Bed Gasification system, which is composed of two reactors: one gasifier where the useful products are generated, and one char combustor where the circulating bed material is heated up.

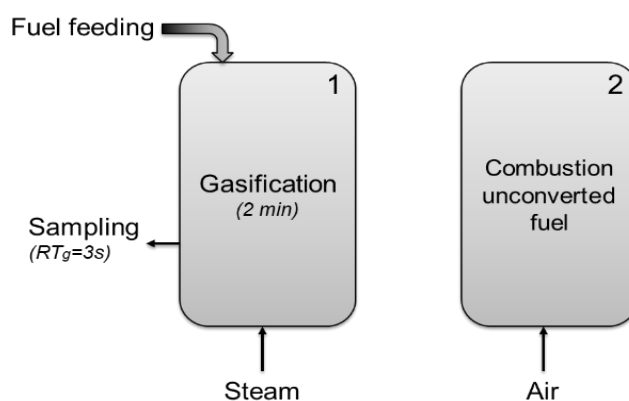


Figure 2. Representation of the batch experiments composed of 2 steps
(Textile gasification and combustion of unconverted fuel)

3. Results and Discussion

3.1 Polyester - Temperature influence

Figure 3 displays the permanent gas and aromatics produced during gasification of polyester for the 3 different temperatures. The left panel shows the gas yields in mol/kg of dry ash free fuel (kg_{daff}). Higher temperatures gave higher gas yield, going from 20 mol/ kg_{daff} at 650°C to 32 mol/ kg_{daff} at 850°C. Additionally, it can be observed that the main gas products were carbon oxides, which yields increased with the temperature increase. The same trend can be seen for the hydrogen yields which greatly increased, almost 10 times higher when rising for 200 degrees. Methane also increases but in a minor degree. The low levels of light hydrocarbons measured on 650°C ($\text{C}_2\text{-C}_3$ species) almost diminished with temperature increase.

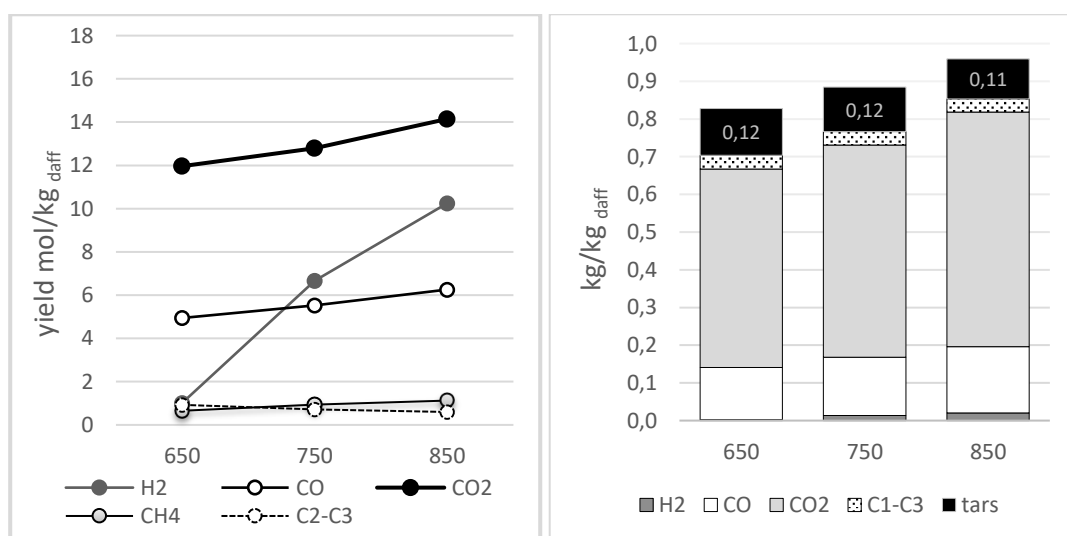


Figure 3. *Left*: Product yields of permanent gas as a function of the temperature for polyester gasification; *Right*: Mass distribution of the products in the gas, incl. aromatic fraction ($\text{kg}/\text{kg}_{\text{daff}}$)

The influence of the fuel chemical structure can be seen in the distribution of the products. This polyester fibre is poly(ethylene terephthalate), PET, which is composed by a benzene ring, two carboxylic groups and ethylene. Therefore, benzene derivatives and oxygenated compounds are expected from thermal degradation. The right panel of Figure 3 illustrates the mass distribution of all measured products, expressed in $\text{kg}/\text{kg}_{\text{daff}}$, confirming that aromatics are a considerable share of the products, 12% at 650 and 750°C and 11% at 850°C, as well as, a higher portion of carbon oxides which range from 66% to 80%. Another aspect to consider is the total conversion, which increases with temperature, probably due to char gasification (C_o and

H₂ increases). Additionally, the conversion do not achieve 1 kg/kg_{daff}, probably due to unmeasured compounds that may fly away and/or soot.

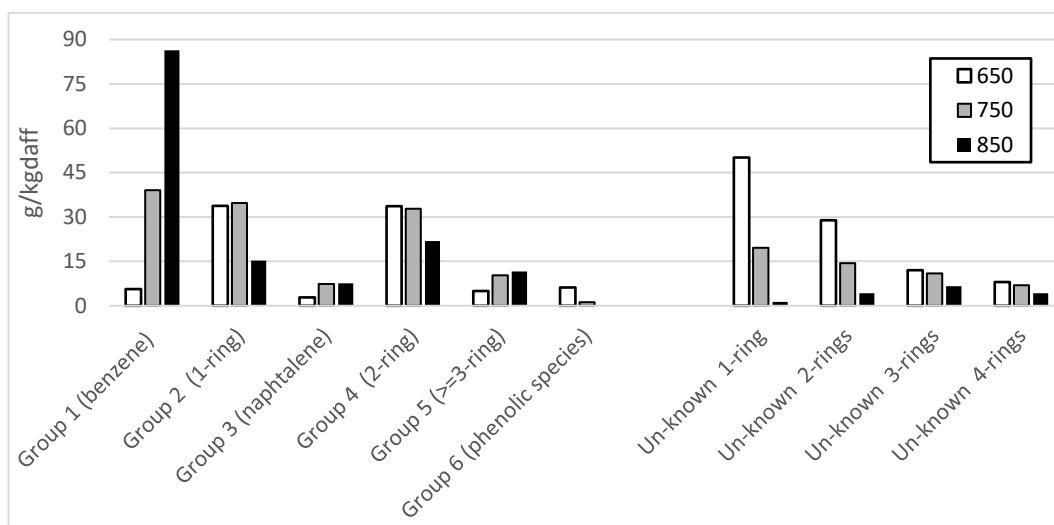


Figure 4. Aromatic composition as a function of the temperature for polyester gasification (SPA-measurable tars and SPA-unknown)

Figure 4 shows the tar grouping for the performed test with polyester. As expected, temperature highly influences the distribution of aromatics. At low temperature, 650°C, there is a greater fraction of 1-ring, 2-ring and phenolic species, while at high temperature, 850°C, those species decrease, and naphthalene and 3-ring aromatics increase due to polymerization, as they are not present in the fuel. Additionally, if BTXS are of interest, it can be observed that benzene increases with temperature increase owed to branch chopping. Toluene and Styrene are the main components of 1-ring aromatics, where the higher production happened at 750°C. Another important aspect is the unknown species, where at low temperatures there is a high portion of the unknown, $\approx 50\%$ of the tars at 650°C and $\approx 30\%$ at 750°C, which are mainly found at low boiling points. At 850°C, only 10% is unknown, which is mainly consisting of tars with high boiling points. In other words, the growth of high aromatic components and the formation of more stable ones, such as benzene and naphthalene, can be explained by a higher severity and a better conversion, while if the production of BTXS is desired, a temperature close to 750°C should be aimed.

3.2 Cotton - Temperature influence

The cotton gas yields are observed in Figure 5 at different temperatures. Higher temperatures produced higher gas yields, going from 21 mol/kg_{daff} at 650°C to 41 mol/kg_{daff} at 850°C, which can be explained by the increase of the fuel conversion. Both hydrogen and carbon dioxide spiked when the temperature rises as well as methane to a somewhat lower degree. Carbon monoxide started growing and then diminished, however, the total Carbon mols in the permanent gases remain the same, 26.3 mol/kg_{daff} at 750°C and 850°C, probably due to influence of the water gas shift (WGS) reaction which, goes towards more products (H₂, CO₂) when temperature rises. Furthermore, oligomers (C₂-C₃) have a yield peak at 750°C, which decreases at 850°C, perhaps converting to methane and carbon oxides.

Cotton is a cellulosic material, which can be assimilated to biomass, thus, lesser condensable species were produced compared to the synthetic polymer, being only 0.02 kg/kg_{daff} that did not largely change with temperature, as shown in the right panel of Figure 5. In the same picture, it can be observed that the permanent gas mass fraction is lower at low temperature, just 0.53 kg/kg_{daff} at 650°C, while vastly increases at 750 and 850°C, 0.81 and 0.9 kg/kg_{daff} respectively. Yet, as stated before, the C mols remained constant, the mass increase can be explained due to the high fraction of CO₂. In addition, if both the recovery C₂-C₃ and syngas are of interest, the gasification at 750°C may be a suitable choice because it produced the highest fraction of C₂-C₃ as well as a decent amount and composition of the syngas, yet, if only syngas is preferable, a higher temperature may be advantageous.

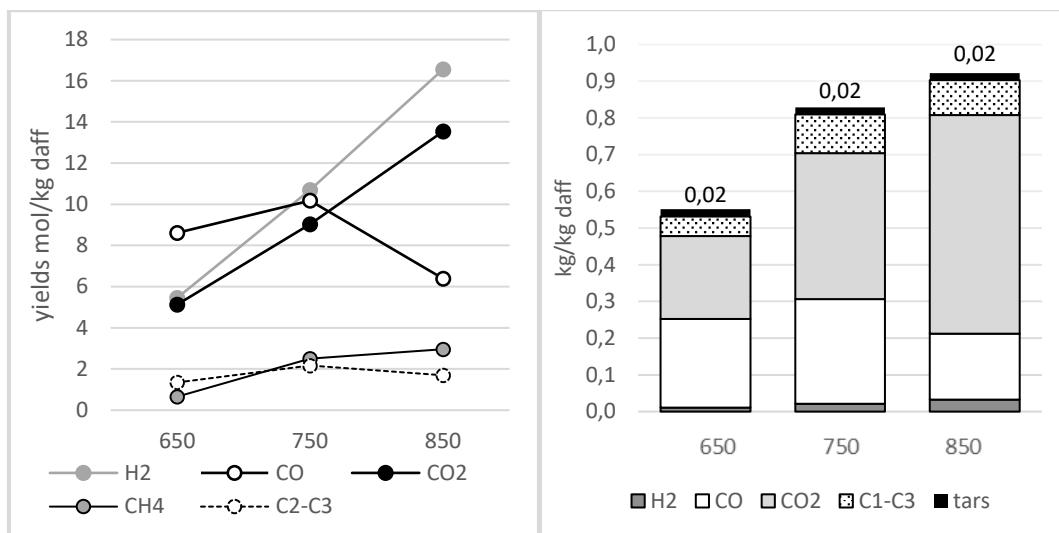


Figure 5. *Left*: Product yields of permanent gas as a function of the temperature for cotton gasification; *Right*: Mass distribution of the products in the gas, incl. aromatic fraction (kg/kg_{daff})

Although the total yield of tars did not largely change, there is a small decrease with temperature as well as a big variation in composition (see Figure 6). Comparable polyester gasification, a high fraction of unknown species is founded at low temperatures, $\approx 45\%$ of the tars at 650°C , almost exclusively found at low boiling points. While the un-known fraction was lesser at 750°C ($\approx 14\%$) and 850°C ($\approx 8\%$) which is mainly consisting of tars with low boiling points. At 650°C , there is low content of naphthalene, 2-ring and 3-ring, while when temperature increases, those species increase, and phenolic species decreases. In this case, although benzene increases with temperature, due to the general low quantity of aromatics, the recovery of BTXS is probably not suitable. Again, the growth of high aromatic components and the formation of more stable ones, such as benzene and naphthalene, can be explained by a higher severity and a better conversion.

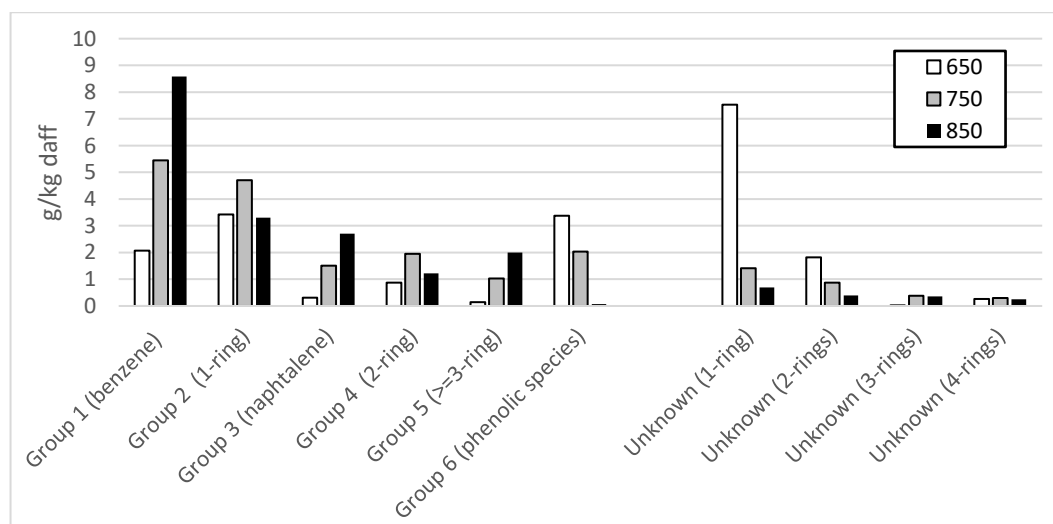


Figure 6. The aromatic composition as a function of the temperature for cotton gasification (SPA-measurable tars and SPA-unknown)

3.3 Blend - Temperature influence

Figure 7 displays the permanent gas and aromatics produced during gasification of the textile composed by a blend of 50% polyester and 50% cotton, for the 3 different temperatures. The left panel shows the gas yields in mol/kg of dry ash free fuel (kg_{daff}). It can be observed that permanent gas yield produced is lower than both the cotton or polyester textile, as well as a synergy effect of polyester/cotton in the product distribution. But likewise, higher temperatures gave higher gas yield, going from 17 mol/kg_{daff} at 650°C to

27.5 mol/kg_{daff} at 850°C. On the one hand, it can be noticed that the main gas products produced were both hydrogen and carbon dioxide, increasing along with the temperature, whereas methane also increases but in a minor proportion. On the other hand, oligomers (C₂-C₃) have a yield pick at 750°C, which decreases at 750°C, perhaps converting to methane and carbon oxides. As well, CO started growing and then diminished, probably due to WGS reaction.

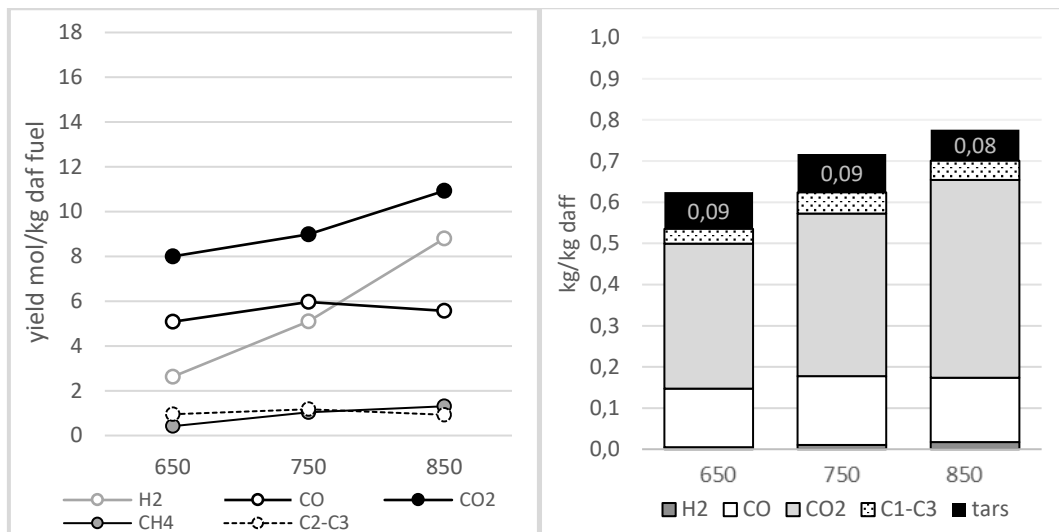


Figure 7: *Left*: Product yields of permanent gas as a function of the temperature for the textile blend gasification; *Right*: Mass distribution of the products in the gas, incl. aromatic fraction (kg/kg_{daff})

The blend shows the influence of fuels with a considerably different chemical structure. Figure 8 presents the dry-ash-free-fuel converted into permanent gases and tars. The total conversion is lower than for Cotton and polyester, which can be partially explained due to a higher Fixed Carbon (see table 1) and the fact that the experiments were performed during 2 min, which will limit the slow char gasification reaction. Possibly originated from PET, aromatics are a considerable portion of the products, 8-9%wt. Once more, a high portion of carbon oxides is generated, from 0.49 to 0.64 kg/kg_{daff}.

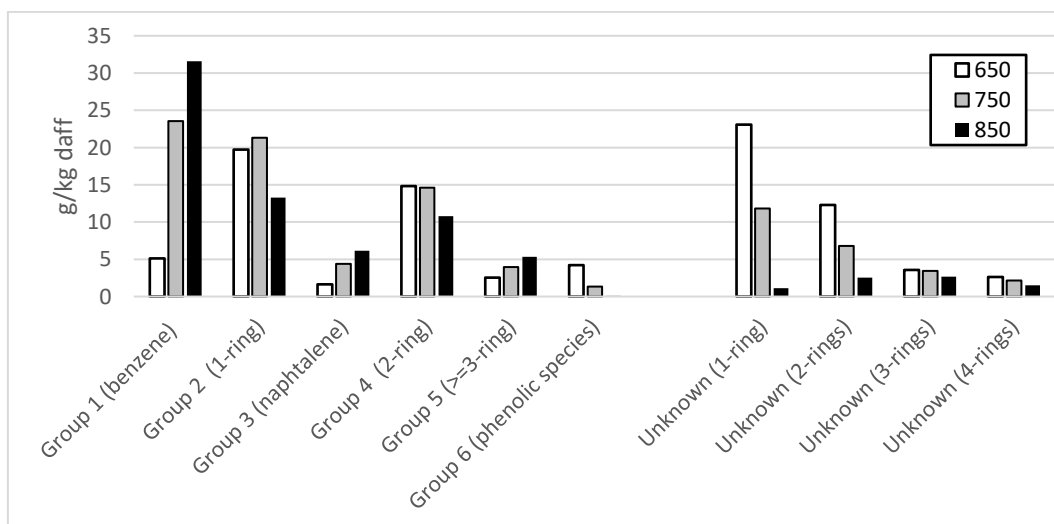


Figure 8. The aromatic composition as a function of the temperature for blend gasification (SPA-measurable tars and SPA-unknown)

With regards to aromatics production, as presented in Figure 8, there is a big variation in composition with temperature. Like the previous cases, a high fraction of unknown species is founded at low temperatures, ≈45% of the tars at 650°C and ≈25% at 750°C, which are mainly found at low boiling points. While the unknown fraction was lesser at 850°C (≈10%) with a mix of low and high boiling points tars. At 650°C, there is

low content of naphthalene, 2-ring and 3-ring, while when temperature increases, those species increase, and phenolic species decreases. the growth of high aromatic components and the formation of more stable ones, such as benzene and naphthalene, can be explained by a higher severity and a better conversion. Additionally, if BTXS are of interest, it can be observed that benzene increases with temperature, nevertheless, Toluene and Styrene are the main components of 1-ring aromatics, where the higher production happened at 750°C. Like for polyester, if the production of BTXS is desired, a temperature close to 750°C should be aimed.

4. Conclusion

An outline of textile gasification in a fluidized bed has been presented in this work and has shown to be a feasible option to convert this fraction into valuable feedstocks. The fuel conversion was good in all cases, while better at higher temperatures. Both syngas and BTXS could be recovered from the process. First, a tar condensation step will be needed. Then, the gas could be synthesized into methanol, DME or in a Fischer Tropsch synthesis, after previously adjusting the H/CO-CO₂ ratio in a WGS reactor.

On the one hand, 100% cotton produced high yields of permanent gas at high temperatures, 0.8-0.9 kg/kg_{daff}, with low aromatic content, suitable for synthesis processes. On the other hand, 100% polyester generated high yields of permanent gas, 0.7-0.8 kg/kg_{daff}, as well as aromatics, compounds ≈0.1 kg/kg_{daff} which makes valorisation of Benzene, Toluene, Xylene, Styrene (BTXS) a suitable option. However, the main component in the permanent gases was CO₂, which may not be beneficial for gas synthesis processes.

Even so, the textile blend represents a closer reality case, and, although the total yield was lower than the pure cases, 0.5-0.7 kg/kg_{daff} could be recovered in a synthesis process. Additionally, ≈0.1 kg/kg_{daff} can be recovered as BTXS and the unconverted could be used to produce the energy necessary for the gasification. In other words, the valorisation of mixed and blended textiles via gasification could be useful to produce both syngas and aromatics.

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