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Using green chemistry to progress a circular fashion industry

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Abstract
The fashion industry is strongly connected to consumer affluence and with more and more people worldwide, the demand for new and ever more sophisticated clothes seems inexhaustible. This translates into the production and consumption of very large quantities of natural and synthetic materials, and treatment chemicals. The lack of an established recycling industry to deal with the resulting waste streams coupled with the increasing complexity of the products means that we are losing most of the consumed resources as wastes. The presence of so many chemicals in these wastes can exaggerate the problem. Here, we look at the scale of the problem but also of the opportunity for waste valorisation. Particular attention is given to the different types of recycling that are possible and including the conversion of these wastes into valuable chemicals. Some methods to improve apparel lifecycles upstream are also considered.

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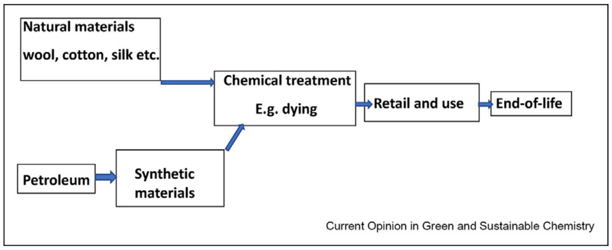
Green chemistry and circularity

The early days of green chemistry and the broader movement to make chemistry and in particular the chemical industry less environmentally harmful focussed on the chemical processes that converted raw materials, especially petrochemicals, into more valuable chemicals. This has led to many common processes such as oxidation reactions being reviewed especially if the process used hazardous reagents, was inefficient in use of resources including energy, or produced dangerous waste. More recently the focus has moved upstream and downstream with a switch to renewable resources such as biomass and the production of safer products becoming the targets of more and more research. The concept of circularity can be seen as overarching here [1]: if we can recycle the used products then the demand for fresh resources is reduced. Ideally, any virgin feedstocks that are needed (and there will always be some need: no recycling process can be 100% efficient) will be renewable so that overall we will be able to describe the products and processes that make them as *green and sustainable.* A critical part of this is *waste valorisation* whereby any wastes can be used through some form of recycling. Ultimately, we seek a *benign by design* approach that will make future products easy to recycle. However, this will take time and for the foreseeable future, we need to develop methods and associated value chains for wastes. Recycling a single chemical such as a volatile solvent is a well-established process (though not always the preferred option for example, when a large amount of energy is needed for the distillation) but almost all articles in today's society are complex. While many have discussed this in the context of modern electronics (with modern mobile phones for example, containing a plethora of chemicals and metals), clothing is also a good example of this with a typical item containing many different chemicals and materials including the fabrics (often more than one), protective coatings, dyes etc. The more complicated the article the more difficult it will be to get maximum recycle value from it — *complexity is the enemy of circularity.*

The apparel life cycle

The simplest form of life-cycle for apparel is shown in Figure 1. The raw materials can be natural or synthetic and are often a mixture of both. In all cases, some sort of chemical treatment is required and often more than one as the various additives are incorporated into the final product. Sale and use are inevitably followed by end-of-life which can in the worst case be landfill, incineration or some sort of recycling. Generally speaking, the more extensive the chemical treatment, the more difficult it is to recycle as these increasingly complex materials need to be separated before any meaningful recycling is possible. Reuse is the one exception although even here at least washing will be required. For the purpose of this article, we can consider reuse as being part of 'retail and use'. The overall environmental footprint of any item will be substantial. Green chemistry can reduce this by both improving the upstream chemical treatment stage(s) and in the critical end-of-life stage. Both of these stages will be considered here. The emphasis will be on end-of-life as waste/used apparel is currently

Figure 1



.A simple life-cycle for apparel.

largely disposed of and represents a huge lost resource opportunity as well as an environmental burden.

Waste in the apparel sector

The first task for any proposed program of circularity within a sector of industry is to understand the current waste streams and raw materials as well as any current recycling within or without the industry sector. The environmental impact of the apparel and footwear sectors has been the subject of much debate and discussion in the context of social and environmental impacts. Consumers have been bombarded with information about a multiplicity of issues including the pollution that arises from contract manufacturing in less regulated regions in Asia, the presence of microfibres in potable water supplies and the poor working conditions of many workers in the supply chain. The demands for fast fashion and for low-cost products add to these pressures.

The global apparel industry had an estimated market value of 1.5 trillion US dollars in 2021 and is growing with a CAGR of ca. 5% as consumers keep their clothing for less time and more people in the emerging economies expect more articles [2]. The volume of goods coming from China alone is ca. $150bn [3]. Over 70% of the material that is used in clothing ends up in landfill or an incinerator with only 12% recycled; the total waste from the industry is estimated at over 90 million tons [4]. More than 25% of textile fiber is wasted during garment production [5]. Those that are recycled are usually downgraded for example into insulation materials. Over 60% of the fiber used by the apparel industry is polyester and other synthetics. The polyester in clothes that is labelled as recycled mostly comes from recycled PET bottles and not from used fabrics. There is a growing movement to use more recycled fabrics in 'new' clothes although the day-to-day damage of fibres in clothes and the complexity of the finished products makes that difficult. This alone will not satisfy the growing demand for clothes with the increasing numbers of middle-class consumers in developing countries like India and China driving the 60% growth in demand over the last 20 years. The high environmental demands of new clothes add to the pressures for change – one polyester shirt for example, comes with a 5.5 Kg carbon cost. The estimated carbon cost for cotton clothes is less but the other environmental costs are high with one cotton short needing 2700 litres of water and large quantities of fertiliser.

The sources of waste can be broadly divided into two: pre- and post-consumer flows. Some of the primary sources of pre-consumer apparel textile waste are:

- Defective and other unsold garments
- Cut and sewn fabric scraps
- End-of-roll textile waste
- Fabric weaving waste
- Fabric dying waste
- Clothing sample waste

The logistics of utilising these wastes are much simpler than wastes from post-consumer flows although much of these wastes are unexploited. The best example of utilising post-consumer waste is the used clothing industry which has grown into a mature market via not-for-profit organisations such as the Salvation Army and for-profit enterprises like the Trans-America Trading Company. The greatest challenge for these organisations is sorting the wearable from the non-wearable with the latter still having value through sale back to the producers or recyclers. All stakeholders want solutions that ensure that the non-wearable fractions are recycled back into useful products be they used within the industry or elsewhere, and not landfilled or incinerated.

Commercial textile recycling

One of the most commercialised examples of textile recycling is chemical-based and involves the conversion of waste cotton into viscose. Companies including Birla Cellulose depolymerise the cotton into a pulp that is then turned into viscose in a process similar to that made from wood pulp [4]. Companies including Lenzing [6], divert waste textiles from landfill: when the quality of the waste textile is insufficient for reuse, this is overcome by blending with virgin cotton as well as wood-based or other renewable sources of cellulose (e.g., wastepaper).

New chemical recycling technologies for PET textiles are emerging and should eventually catch up with PET bottle recycling [7,8]. PET recycling is described in a case study below. Recycling is made more problematic by the complexity of many modern fabrics. The use of solvents to help get around the complexity problem seems logical and necessary but given the environmental drivers for recycling it is vital that all associated technologies are themselves 'green' or at least add little to the process environmental footprint. Many traditional solvents are being identified as environmentally unacceptable especially those that are now classified as toxic under REACH assessments [9]. Some but certainly not all ionic liquids have good green chemistry credentials although problems such as toxicity (for some), cost (for some) and separation/purification (for all) have restricted their commercial uptake. They should be considered alongside newer, often bio-based non-toxic solvents including Cyrene ™ and TMO [9,10]. One major advantage of chemical recycling is that it *may* enable direct recycling of contaminated wastes, but this is probably not true if sensitive catalysts are to be employed. Dissolution of waste fibres is the basis of several commercial processes especially those focussed on cellulosic materials including cotton and polycotton. Consistent with a green chemistry theme, new processes avoid the harmful carbon disulphide solvent associated with the original viscose process. This includes the work of company Infinited Fibre who work with global brands including H&M [11].

Challenges in waste textile recycling

While some 70% of global PET production is used for fibres, it is only the solid forms of the polymer that are widely recycled. This is largely due to the presence of chemical additives and other blended materials. As a result, much of the current PET-based fibres are downcycled to lower value products, incinerated or landfilled.

In all cases the first stage will be a ‘clean up’ with dirt, buttons, zippers, etc., removed for example, from cotton waste (Figure 2).

A significant challenge for textile recycling is sorting collected garments by fabric type. Separation is currently done by hand which is slow though automated systems are in development using infrared sensors or RFID tagging.

Some fabrics used in sportswear and some fashion contain polyurethane foams to enhance their performance. The polyurethane fabric is a composite material with one or more layers of polymer resins with a textile backing made of another material such as leather or nylon. The resulting material can have very similar properties to an all-leather product. Polycotton is a combination of cotton and polyester. The separate extraction of two polymeric materials can be achieved if they have different solubility characteristics. Initial swelling of the fibres enables removal of contaminants including dyes. The solvent-wet residues would then normally be heated to dissolve the polyester leaving solid cellulose as a useful product. Worn Again Technologies use the solvents DMSO or DMI [8] but other solvents may be used such as propyl benzoate. Adding an anti-solvent like ethanol precipitates the polyester while keeping the environmental footprint low. Solvent-based recycling is very attractive if the solvents used are safe and ideally renewable [13].

Textile waste conversion technologies

Chemical recycling such as of PET-based products requires several steps including separations, so it is economically challenging. Despite this, several companies have begun operations in this area including Poseidon Plastics [14]. Fermentation is at an early stage of development for polymer waste and while it has some benefits such as mild conditions, it also some drawbacks such as long reaction times. Thermochemical processes including gasification and including the use of microwaves can also be used although the products (pyrolysis oils, syngas, etc.) will have much lower value than the feedstocks used to make the original materials.

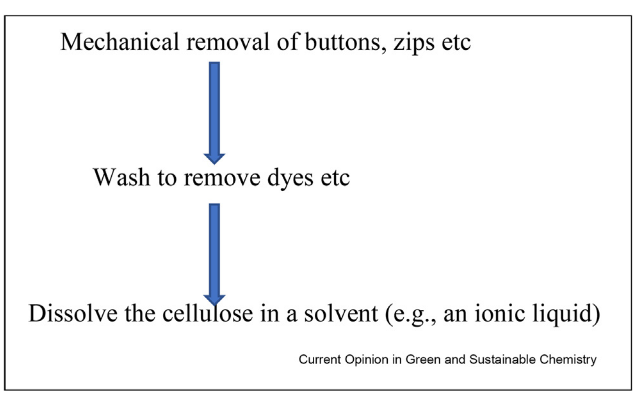
Chemicals from waste textiles

The problems associated with reusing old clothes because of worn and damaged fibres can be overcome by chemical recycling that converts the materials into (usually small) molecules including the monomers that were used to make any synthetic materials present (e.g., polyesters). The best example of this is for PET-based fabrics.

Case study: Depolymerising PET

In most cases depolymerisation of PET yields monomers suitable for repolymerisation. In practice this is achieved by reacting the PET waste with a reactive small molecule including water and ammonia to produce useful compounds via hydrolysis and aminolysis, respectively. Companies active in this area include WornAgain [8]. Alcoholysis is also popular whereby alcohols such as methanol produce dimethyl terephthalate and ethylene glycol, which can subsequently

Figure 2



.Pre-treatment steps for recycling waste cotton.

Figure 3

(1) Hydrolysis	$nPET + (2n\text{-}1)H_2O$	$\rightarrow$	$nC_8H_6O_4 + nC_2H_6O_2$
(2) Electro reforming.	$C_2H_6O_2 + 2OH^-$	$\rightarrow$	$2HCOO^- + 3H_2$
(3) Anode.	$C_2H_6O_2 + 8OH^-$	$\rightarrow$	$2HCOO^- + 6H_2O + 6e^-$
(4) Cathode.	$6H_2O + 6e^-$	$\rightarrow$	$3H_2 + 6OH^-$

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.The most important reactions in the electrocatalytic upcycling of PET.

be polymerised to make PET. The greatest challenge with such processes is the separation and clean-up of the monomer before it can be used in a new polymerisation process. This is a common challenge with waste valorisation projects – the number of unit operations must be kept to a minimum as each one of these will inevitably consume energy and usually other resources, as well as generate waste streams.

Pyrolysis of polyesters including PET is another processing option yielding a gaseous fraction, a liquid oil fraction, and a solid char fraction. The use of a catalyst such as a zeolite can promote the cracking of the product streams into smaller molecules and generate useful oxygenated products, such as syngas (CO, H_2, CO_2 and H_2O) which can be used as a chemical feedstock, and phenols. The liquid content from PET pyrolysis is usually low while the gas content is high [15].

In a clever application of electrocatalysis to PET waste valorisation, Zhou has reported the upcycling of PET to commodity chemicals and hydrogen using a nickel-modified cobalt phosphide ($CoNi_{0.25}$ P) electrocatalyst [16]. The most important reactions are shown in Figure 3.

Case study: Recycling cotton waste

Cotton is a natural fibre and is mostly made of cellulose. Cellulose is one of the most promising starting points for the ‘biomass to chemicals’ revolution that is slowly starting to replace traditional petrochemical-based chemicals with renewable alternatives or drop-ins. Cellulose is nature’s largest volume material and can be found in almost all types of biomass including trees, grasses and cereal (straws) and is produced at a rate of at least 10^{11}tonnes per annum. Thus, its overall volume is not an issue, but its actual availability is more relevant with the amount of cellulose processed each year being about three orders of magnitude lower and the associated waste much lower again. The emerging cellulose-to-chemicals processes tend to rely on paper mill waste streams and excess cereal straws; waste cotton could nicely add to this especially as it contains some 90% cellulose, a much higher percentage than most other plants (wood is 40%–50% cellulose).

Upstream of any cotton waste valorisation project, the clean-up of the waste will require effort. Nowadays many clothes contain both cotton and other materials such as polyesters. This fundamental separation challenge is probably best met with modern green solvent technology typically involving the preferential dissolution of the polyester using for example, an ester solvent [12] although the cotton can also be preferentially dissolved though perhaps in a less green solvent such as an alkali/urea mixture [17]. The subsequent valorisation of the (cleaned up) cotton waste to individual valuable chemicals is yet to mature although some less valuable routes have been proposed such as pyrolysis to make mixtures of chemicals including phenols, syngas, ketones, furans and aldehydes [18]. One advantage of this approach is that the process may be more forgiving of the presence of impurities. This is also the case for the conversion of cotton and other fabric wastes into porous carbonaceous solids, typically using an acidic catalyst like phosphoric acid, zinc chloride, or ferric chloride (Figure 4). The real breakthrough will come with successful waste-to-platform-chemicals projects such as the production of levoglucosenone that is attracting increasing interest both as a platform chemical and as a precursor of making green solvents [19]. Some valuable chemicals may be accessed indirectly by first converting the cotton into glucose and then using fermentation technology to convert the glucose to specific chemicals including ethanol.

Greening the production of textiles

The processes to make chemicals provide many environmental challenges – in the reagents used, the conditions employed, and the wastes generated. It is the greening of these processes where the bulk of green

Figure 4

$$\text{Cotton waste} + FeCl3 \xrightarrow{130C} \text{Glucose} \xrightarrow{190+C} \text{Porous carbon-}FeCl_3$$

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Conversion of cotton waste into porous carbon encapsulated salts.

chemistry research continues to be focussed. For clothing, the relevant processes can be broadly divided into two areas: the textiles and the additives.

Synthetic textiles are made in one or more reaction steps. PET is the most important of these and is made by the condensation reaction of terephthalic acid (benzene-1,4-dicarboxylic acid) and ethylene glycol (1,2-ethanediol). The most important issue with the reagents is the terephthalic acid which is made by the oxidation of para-xylene (1,4-dihydroxybenzene) itself derived from petroleum. The oxidation process requires harsh conditions that are highly energy demanding, hazardous and generate waste. We need greener methods for such important reactions and ideally, we need alternative renewable chemical starting materials. The condensation reaction is not difficult but metallic catalysts can be used to help push the polymerisation reaction to higher molecular weight polymers, and these catalysts are likely to stay in the final polymeric material which even if it does not present a toxicity issue in use, can be a problem in end-of-life processes. Where polymerisation catalysts are used, then they should be non-toxic.

Natural fabric treatments may not have changed over many years and can be a source of environmental problems including the use of dangerous chemicals and the production of hazardous waste. A famous example of this is leather tanning which is used to enhance the physicochemical properties of the material before use. This tanning process involves several crosslinking reactions between the tanning agent and the active groups ($-NH_2$ and $-COOH$) in the collagen matrix, aimed at improving the dispersion and fixation of the collagen fibers. This procedure not only endows the leather with a high resistance against putrefaction, chemicals and heat but also with high mechanical strength. Mineral salts, such as chromium, aluminium, titanium, iron and zirconium salts, are widely used as tanning agents due to their favourable tanning effect, low cost and availability. Of these chromium salts are the most popular but their human health and environmental risks (especially when oxidised to the carcinogenic chromium (VI)) makes their use increasingly problematic. In a breakthrough article, novel aluminium-oligosaccharide complexes are reported as safer tanning agents. Using a so-called Trojan horse strategy, aluminium chloride is used both to depolymerise cellulose and complex the resulting oligosaccharides in situ [20].

The various additives employed in fabrics are mostly synthetic and include dyes, flame retardants, and surface treatments. It is beyond the scope of this article to look at the very many chemical processes involved in the syntheses of the various chemical additives, but they include halogenations and oxidations both of which are notorious for their green chemistry challenges including harsh, energy demanding and corrosive conditions, and atom inefficient reactions that lead to large volumes of often hazardous wastes. There is considerable scope in finding greener routes for these processes including the greater use of catalysts rather than stoichiometric reagents. More substantial improvements would involve replacing synthetic additives with natural ones and indeed, avoiding additives all together where possible. Some additives such as polybrominated compounds (flame retardants but with high persistence in the environment) should be avoided. Two important points to be recognised in this context: (i) using virgin materials will need the various additive treatments so as to achieve the desired appearance and properties; at least some of this can be avoided if the complete fabrics are reused; and (ii) additives will always make recycling by depolymerisation more problematic (by contaminating the product streams and possibly by poisoning any catalysts used in the depolymerisation process).

Concluding remarks

While the demand for new clothes may be reduced somewhat by increased consumer awareness of the need to make greater use of the articles of society including clothes, there is little sign of this stopping an inexorable growth in the consumer desire for new fashion. We must combine educational pressure on consumers especially about the true cost of waste, with a new vibrant recycling industry that treats used clothes as a valuable resource. Reuse of largely untreated fabric waste to make 'new' clothes is a vital part of this but the limited recyclability of most materials means we have to have available more fundamental recycling technologies. In particular, we need efficient methods for recycling the wastes into valuable chemicals including monomers that can be used to make new synthetic materials. The complexity of modern fabrics including the use or multiple materials and many chemical treatments makes their conversion into the more valuable chemicals more difficult and the simplification of upstream processing will really help their valorisation at end-of-life. This can be combined with lower environmental footprint chemical treatments such as the use of greener solvents and the avoidance of hazardous chemicals.

The subject is gaining in popularity especially in the context of socio-economic factors and on establishing methods of assessing true sustainability. Recent articles of particular note include those reporting the development of the second-hand clothes market [21], on how we can use the popularity of sustainability to enhance circularity in clothes [22,23] and on the use of sound methods of assessment [24].

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

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