Green hydrolysis conversion of wool wastes into organic nitrogen fertilisers

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Abstract

Management of waste wool is a problem related to sheep farming and butchery in Europe. Since the primary role of European flock is meat production, sheep are crossbreds not graded for fine wool production. Their wool is very coarse and contains a lot of kemps (dead fibres), so that it is practically unserviceable for textile uses, and represents a by-product which is mostly disposed of. The Life+GreenWoolF project aims to demonstrate that waste wool can be recycled into amendment-fertilisers for the management of grasslands and other cultivation purposes, with a green and economically sustainable process, based on the hydrolysis of wool with superheated water.

In this way wool keratin (the wool protein) is degraded into simpler compounds, tailoring the release speed of nutrients to plants. Wool, when added to the soil, increases the yield of grass grown, absorbs and retains moisture very effectively and reduces run off of contaminants such as pesticides. Moreover, the closed-loop cycle grass-wool-grass is an efficient form of recycling, because the wool-grass step is solar powered and grazing sheep increases soil carbon sequestration on grasslands and fertilisation, if not over-used, can enhance the carbon sequestration rate.

Economical results are expected from the increase of the management yield and the extension of the pasture lands that may contribute to employment and profit of sheep farming, increase European sheep population, and reduce European dependency of imported meat which is forecast to rise in the next years.

Keywords: wool waste, management, hydrolysis, fertilisers.

1. Sheep rearing and wool production in Europe (EU)

EU-27 has the second world sheep population, numbered about 100 million sheep in December 2011, the majority of which were based in the United Kingdom (25%), Spain (20%), Romania (10%), Greece (10%), Italy (9%), France (9%) and Ireland (4%). As regard the Italian situation, more than 70% of the total Italian flock is located in Sardinia, Sicily, Lazio and Tuscany (Source EU-Eurostat 2012).

The primary role of EU sheep flock rearing is meat production; the sheep milk market is relatively small, being confined to Mediterranean regions [1]. European wool, which is coarse and generally heavily contaminated by dead fibres (kemps), has historically been a valuable commodity, used for mattresses or manufacturing articles of clothing or home textiles. In spite of such a low quality of the EU wool clip, wool price has been able in the past to cover costs such as grassland fertilizer or land rental. Today, with the exception of small wool lots locally exploited for handicraft or felting products, EU wool price is not able to cover cost for shearing, and wool is essentially perceived as a by-product on sheep farms. Even if there is a certain demand of poor quality wools from Asian countries (Pakistan, India, China) to be used for furnishing production, there is no profit in selling the EU crossbred coarse wool. Synthetic fibres have outclassed it in most of the traditional applications. Moreover, the EU wool textile industry, in particular the Italian wool industry, which is the world leader of the high quality wool garment manufacturing, is entirely supplied with fine Merino wool from the Southern Hemisphere, in particular from Australia and New Zealand.

Nevertheless, the annual EU coarse wool clip amounts to more than 200 thousands tons (18-20 thousand tons are produced in Italy) and its management is a problem that is specific for the EU livestock sector. Annual shearing of EU sheep produces 1.5 – 3 kg head of coarse wool perceived as a by-product which is mostly disposed of, or illegally thrown over. Indeed, management costs and early processing costs (scouring and carbonising) are economically unsustainable for such a poor quality wool.

2. Different project for coarse wool valorisation

The valorisation of coarse and crossbred wool from EU sheep farming and butchery industry has been the aim of a number of efforts financially supported from local and EU Development Plans.

Nevertheless, only niche applications have been proposed till now, whilst the exploitation of the bulk of the low quality coarse wool clip still remains an unsolved problem.

For instance, the Project “Medlaine: à la recherche des coleurs et des tissues de la Méditerranée” was aimed to valorise the wools from Tuscany, Sardinia and Corsica native sheep, within the 3rd Objective "Territorial Cooperation" of the EU Regional Development Fund (ERDF) Operat. Progr. 2007-2013 [2].

The Italian Ministry of Employment and Social Policy supported the Project “Percorsi di Orientamento 2008-2011” including the valorisation of native wools from Tuscany, Emilia-Romagna, Campania and Sardinia in the context of the rural development and women’s employment in the handicraft sector and Piedmont is currently supporting the Project “Cartonlana”, aimed to exploit coarse wools for thermal and acoustic insulation for bio-building applications.

However, in spite of these attempts, coarse raw wool from landscaping sheep still remains perceived as a by-product and is mostly disposed of, or illegally thrown over. Indeed, management costs and early processing costs (scouring and carbonising) are economically unsustainable without public financial support.

3. Problems related to the disposal of waste wool

Unserviceable raw (greasy) wools are a special waste subjected to restrictions provided by the Commission Regulation (EU) Nº 142/2011 for Class 3 Materials.

EU Control Regulation and EU Implementing Regulation come into force on 4 March 2011 on animal by-product controls, lay many restrictions to collection, storage, transport, treatment, use and disposal of unprocessed wool, being a potential source of risks to public and animal health.

Improper use of animal by-products has resulted in outbreaks of serious diseases such as foot and mouth disease, classical swine fever, avian flu and the spread of bovine spongiform encephalopathy. Legislation has been in place for many years to control these risks by setting out the rules for collection, storage, transport, treatment, use and disposal of animal by-products.

However, in spite of these attempts, coarse raw wool from landscaping sheep is mostly disposed in landfill, or illegally thrown over with serious ambient threats.

Each tonne of raw wool contains approximately 150 kg of lanolin, 40 kg of suint (soluble contaminants such as potassium salts from sweat and faeces), 150 kg of dirt (soil), 20 kg of vegetable matter, and residues of insecticides, leaving 640 kg of wool fibre.

Insecticides or insect growth regulators are used to protect sheep from ectoparasites (lice, mites, blowfly, tikes, etc.); their presence on wool is variable and depends on the permitted legal use pattern in each country. Under the new regulations, raw wool has to be washed or treated with a method that ensures that no unacceptable risks for health remain.

The recommended procedures of world Organisation for Animal Health (OIE) include: factory or industrial scouring consisting of the immersion of the greasy wool in a series of baths of warm water (about 50 °C), depilation by means of slaked lime or sodium sulphide; fumigation in formaldehyde in a sealed chamber for at least 24 hours; industrial scouring; storage at 18 °C for 4 weeks, or 4 °C for 4 months, or 37 °C for 8 days (OIE, World Organisation for Animal Health – (2011), Terrestrial Animal Health Code) (animalhealth.defra.gov.uk).

Sheep farmers can carry out these processes themselves or to delegate to a technical plant. But scouring of grease wool is costly (about 1 €/kg) and gives rise to severe environmental problems of safe treatment of scouring effluents wastes and resulting sludge. For every kg of clean wool produced by aqueous scouring, some 20 litres of effluent is generated

(Eco-Efficient Dry Wool Scouring with total by-products recovery, LIFE+ project, 01-SEP-2012 to 31-AUG-2015) which is extremely polluting to the environment, containing high levels of organic wastes, mineral dirt and insecticides. The effluent contains high concentration of soil particles picked up during grazing; wool wax (lanolin) and sweat (source of potassium); additives from scouring and related processes such as detergent residues (anionic or alkylphenolethoxylate non-ionic detergents); pesticide residues. COD reaches 100, 000 mg/l, BOD ranges from 20, 000 to 40, 000 mg/l and the disposal of the sludge generated by the effluent treatment is very difficult to manage [3].

Moreover, the Directive 75/442/EEC establishes a waste management hierarchy. The most desirable is waste prevention and minimization of waste generation. This is followed (in descending order of priority) by: re-use of waste, recycling of waste, recovery of waste, use of waste as source of energy, incineration without energy recovery, landfilling. In addition burning wool for fuel is inefficient because it is self-extinguishing (LOI > 21%), and cofiring is polluting because of its high sulphur content (3-4% by weight.). Landfilling is considered the least desirable waste management option and wool in landfill not readily degrade.

4. Wool as a fertiliser

Grease (unclean) raw wool is rich in plant nutrients that are released in the soil over a long time fluently. Wool contains elements such as carbon (50 %), nitrogen (16-17 %) and sulphur (3-4 %) which play an essential role in plant nutrition [4]. Wool fibres absorb and retain moisture very effectively; this property can be a benefit when applied to soils where it can reduce runoff of contaminants such as pesticides, and can aid in water conservation. Wool when added to the soil, greatly increases the yield (wet and dry matter) of grass grown. The suitability of wool wastes as fertiliser is confirmed by elevated levels of essential elements such as nitrogen (19%), sulphur (19%) and magnesium (7%) in the grass grown on wool fertilised plots as compared to the control grass [5]. The known disadvantages to using wool fibrous wastes in direct grassland application are the inherent handling problems, lack of ready availability of nutrients, weed problems and low bulk density [6]. The slow release of nitrogen from wool indicates that the soil micro-organisms could not easily digest the chemical fibre structure, which is made of keratin, one of the most abundant non-food, animal proteins, being the major component of hair, feathers, nails and horns. Keratin is a structural protein characterised by a large amount of the amino acid cysteine, a sulphur-containing amino acid that forms sulphur–sulphur cystine bonds with other intra- or inter-molecular cysteine moieties.

Intermolecular cystine bonds, plus peptide and hydrogen bond, are responsible for the high stability of keratin, giving it strength and stiffness, but also insolubility, thus limiting nature recycling [7].

5. Hydrolysis of wool in superheated water

The modification of keratin structure can be achieved by chemical, physical and enzymatic treatments, with cleavage of disulfide bridges (sulphur–sulphur cystine bonds) and peptide bonds.

Hydrolysis can be carried out in different process conditions with different chemical agents. Boiling in alkali media represents the most common way to carry out a strong hydrolysis of keratin. The effect of adding alkaline hydrolysate of sheep's wool waste on grassland soil is that the organic material positively influenced microbial soil populations and ryegrass growth [8]. However, hydrolysis with superheated water under controlled process conditions, with the aim of tailoring the extent of the peptide length, is very interesting since the processes produce a considerable amount of unhydrolysed solid residue that should act as a slow release fertilizer thus feeding plants additionally.

Steam explosion and treatment with superheated water have shown to be effective to carry out partial hydrolysis of wool. Investigation on the steam explosion of wool with water vapour has shown the nature and extent of the conversion of wool fibre keratin by effect of the strong physical conditions of the process [9]. The resulting products, when compared with the original wool, showed disruption of the histological structure, reduction of the molecular weight leading to water-soluble peptides and free amino acids and change of the structure of the remainder of the protein, associated with breaking of disulfide bonds and decomposition of the high-sulphur-content protein fraction. The hydrolysis of the wool biomass with superheated water has been studied in depth. The hydrolysis of wool was performed by a microwave-assisted laboratory-scale reactor, at different temperature (150 - 170 e 180 °C), with the aim of tailoring scission of the protein chains into oligopeptides and amino acids, leaving a certain amount of fragments of wool fibers and other insoluble protein aggregates [10]. As regard the behaviour of wool hydrolysates in soil, if the rupture of chemical bonds modifies keratin structure, the rate of mineralization increases [11].

6. The GreenWoolF project

Life+GreenWoolF is a project co-funded by the European Community under the LIFE financial instrument with the Grant Agreement LIFE+12 ENV/IT000439.

The project aims to demonstrate the viability of converting waste wool into amendment fertilisers using small-scale, local hydrolysis with superheated water plant, thus reducing transportation costs of both fertilisers and wool wastes, and eliminating scouring and disposal of coarse wools.

The hydrolysis of raw wool can be modulated as a function of time and temperature treatment, using superheated water only in order to tailor the release of fertilizers and their absorption from grasslands.

The proposed approach for green hydrolysis of wool wastes is a complementary step towards the establishment of environmental friendly and less expensive technology for treatment of wastes from sheep farming and butchery. The process is designed to be cheap and chemical-free, since neither alkalis or acids nor toxic sulphides or expensive enzymes are used.

The energy consumption will be minimised by restricting the liquor ratio, namely the amount of water per mass of waste wool processed. Finally, also the economic and environmental sustainability of the process (which only uses water and heat) with respect to scouring and selling wool for low price applications, will be demonstrated.

Unserviceable grease wool will be converted into an effective soil conditioner fertiliser, with a demonstration unit able to manage 1/3 of the Piedmont (a region in the north west of Italy) annual wool clip (1 ton/day), specifically designed and built. Tuning of the process will tailor the release speed of nutrients and bio-stimulants and the water storage capacity, which will be specifically tested.

The project combines competencies of the Public University (Faculty of Engineering of the Polytecnic of Turin- Italy), a private Company (OBEM S.p.A.- Biella - Italy) and a Public Research Institution (Institute for Macromolecular Studies- Biella- Italy) of the Italian National Research Council (CNR).

7. Expected results

The project will demonstrate that unserviceable coarse wools, which represent in Europe a by-product estimated in more than 150.000 tons per year (about 75% of the annual EU wool clip), may be totally recycled, without any preliminary scouring treatment, into a value added green material, with benefits for the ambient and profit for the EU livestock sector.

Recycling unserviceable wool into amendment-fertilisers is a way of exploiting natural renewable resources, reducing organic wastes disposed in landfills (thus promoting waste prevention); moreover the closed-loop cycle grass-wool-grass is an efficient form of recycling, because the wool-grass step is solar powered and reduces the use of synthetic fertilisers.

7.1. Environmental results – pasture to maintain marginal lands

Amendment-fertilisation of grassland contributes to the reduction of soil degradation, including erosion and decline of organic matter.

Soil organic matter or soil ‘humus’ is a major determinant of carbon and nutrient cycling in the biosphere: it is the main nutrient source for plant growth (after microbial decomposition) and contributes to the soil quality (soil structure, resistance to erosion). One method for recovering exhausted soils is to add organic matter in order to improve soil characteristics, thereby enhancing biogeochemical nutrient cycles [8].

Hydrolysed wool absorbs and retains moisture very effectively; this property can be a benefit when applied to soils where it can reduce runoff of contaminants such as pesticides, and can aid in water conservation. Superheated water will also hydrolyse wool wax and inactivate pesticide residues.

Grasslands are an important land use in Europe covering more than a third of the European agricultural area (FAO, 2006). Grasslands have a basic role in feeding herbivores and ruminants and provide important regulating ecosystem services (e.g. reducing erosion by supporting slope stability; regulating water regimes; purifying water from fertilizers and pesticides). Grasslands also support biodiversity and cultural services, e.g. by contributing to a region's cultural heritage and to recreational values [12]. The proportion of agricultural land used as grassland differs between European regions [13]. Permanent grasslands have been in constant decline since 1975, but the extent differes between regions (Eurostat, 2006) [14].

Grazing is also critical for maintaining many of Europe's cultural landscapes and sustaining rural communities [15]. For example, in the Mediterranean region, sheep grazing is essential for the prevention of shrub encroachment and extensive grazing is considered vital for maintaining many biodiversity-rich habitats and high nature value farmland in Europe.

Habitat loss and fragmentation negatively affects biodiversity on all levels: genetic, species and ecosystem.

Moreover, sheep are currently used to exploit poor carbon footprint lands, which are unsuitable for other agricultural purposes, such as unprofitable uplands constrained by soil type and environment from growing crops for direct consumption. Many breeds are adapted to living in harsh conditions and to feeding on coarser grasses, so they can often be found in poorer and more rural parts of the EU.

They play an important role in the subsistence mixed farming systems and are vital in landscape management, maintaining open vistas and reducing wildfire risk [16]. On the other hand, wool contains elements such as carbon (50 %), nitrogen (16-17 %) and sulphur (3-4 %) which play an essential role in plant nutrition [4]. Literature shows that wool, when used as a fertiliser, increased the dry matter yield of grass grown by between 24 and 82%. The grass grown on plots fertilised with wool appeared a darker shade of green than the grass on the control plots (suggesting a healthier state), with elevated levels of essential elements such as nitrogen (19%), sulphur (19%) and magnesium (7%). The increase in nitrogen in the fertilised grass showed that the nitrogen in the decomposing wool, which is an essential element for grass growth, was being taken up by the grass. The increased sulphur in the fertilised grass would be valuable for wool growth on the sheep, as sulphur is a major component of wool, representing about 3% by weight [5].

7.2. Environment results – Green Houses Gases decrease

Recent literature [17] reports that emissions per kilogram of carcass of meat from ruminants cause highest GHG emissions (Green Houses Gases, including CH_4, N_2O, CO_2, NH_3, NO_X and N_2 - 22 kg CO_2-eq/kg meat for beef and 20 kg CO_2-eq/kg sheep and goat meat on EU average), while the production of pork and poultry meat have a lower carbon footprint with 7.5 CO_2-eq/kg meat and 5 kg CO_2-eq/kg meat, respectively, due to a more efficient digestion process and the absence of enteric fermentation.

However, three main factors are important to have low emission intensities in the livestock sector: high productivity, low dependency of imported feed products, and a high share of pasture in the animal feed diet.

Productivity and share of pasture in the animal feed diet may be increased with increasing management yield and extension of the pasture lands; moreover, in many regions sheep are used to exploit lands which are unsuitable for other purposes. The environmental soundness of using wool derived amendment-fertiliser for the management of grasslands relies of the following considerations:

- grazing animals increases soil carbon sequestration on grasslands;
- carbon sequestration in natural grasslands has no saturation effect, but is continually accumulating carbon in grassland soils;
- fertilisation of grassland, if not over-used, can enhance the carbon sequestration rate;
-fertilisation via the closed-loop cycle grass-wool-grass is an efficient form of recycling because the wool-grass step is solar powered.

The EU produced in 2011 about 1 million tonnes of sheep meat (81 % self-sufficient) and imported 233,000 tonnes, mostly from New Zealand and Australia (EU Single CMO Management Committee, EU SHEEP and GOATS Meat Market Situation, 21 June 2012).

Emissions of 33 kg CO_2-eq/kg are estimated for sheep meat imported from New Zealand, even if emissions from imported animal products were calculated with a different methodology, and are, therefore, not directly comparable with other results of the study.

7.3. Economical results

As final results, increasing management yield and extension of the pasture lands may contribute to employment and profit of sheep farming, increase EU sheep population, and reduce dependency of imported meat which is forecast to rise in the next years.

In fact, as regards import of sheep meat from Overseas, we have to consider that, according to the EU's December sheep census, Europe's sheep population fell by 4% in 2011.

Nevertheless, slaughter is forecast to rise despite the decline of the Europe's sheep population, (http://www.globalmeatnews.com/Industry-Markets/Europe-s-sheep-population-declines). The rate of decline varied greatly, the highest being registered in Italy. Profit increase of sheep farming may contribute to increase Europe's sheep population, thus reducing dependency and emissions of imported feed products.

Finally, even if the number of sheep holdings is important, farm herd sizes are generally small, the output levels low and statistics and studies describing EU small ruminant production systems very scarce. They play an important role in the subsistence mixed farming systems of the countries from Central Eastern Europe, but here information is very limited and often unreliable (Evaluation of the livestock sector's contribution to the EU greenhouse gas emissions (GGELS), final report, Administrative Arrangements AGRI-2008-0245 and AGRI-2009-0296). The project actions will also contribute to a better knowledge of the EU small ruminant production system.

8. Conclusions

The project Life+ Green WoolF aims to demonstrate the viability of converting waste wool into amendment fertilisers using small-scale, local hydrolysis plants, thus reducing transportation costs of both fertilisers and wool wastes, and eliminating scouring and disposal of coarse wools. Tuning of the process will tailor the release speed of nutrients and bio-stimulants and the water storage capacity, which will be specifically tested.

Obtained nitrogen fertilizers are raw materials admitted in organic agriculture as protein hydrolysates made from wool. In addition to increase nitrogen amount in the soil with high nitrogen use efficiency and low impact in eco-agricultural ecosystem, these fertilizers may be used in organic horticulture for their fast or slow nitrogen release in relation to the hydrolysis degree.

Obtained fertilizers could also be used as bio-stimulants of soil microbial activity throught fertirrigation and as stimulants of plant growth by applying as a foliar spray, or as chelating/complexing agents for trace elements (i.e. Fe, Cu, Zn) as a valid alternative to the use of other chemicals.

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