# BIOCOPAC, a lacquer from tomato

## Introduction

The European vegetable and fruit processing industry comprises more than 20000 companies and has an important share within the European agro-alimentary industry, which is by far the most important industry in Europe. Of these, over 3000 are tomatoes processing firms. The cultivation and processing of tomatoes is the largest agricultural business in Southern European countries. Every year millions of tons of tomatoes are used and large amounts of tomato by-products are treated as waste. The food industry produces large quantities of by-products, waste and effluent (about 300 million tons / year in the EU), which are, on average, 2 / 3% of the volume of products "dry" and 7 / 10% of products "wet."

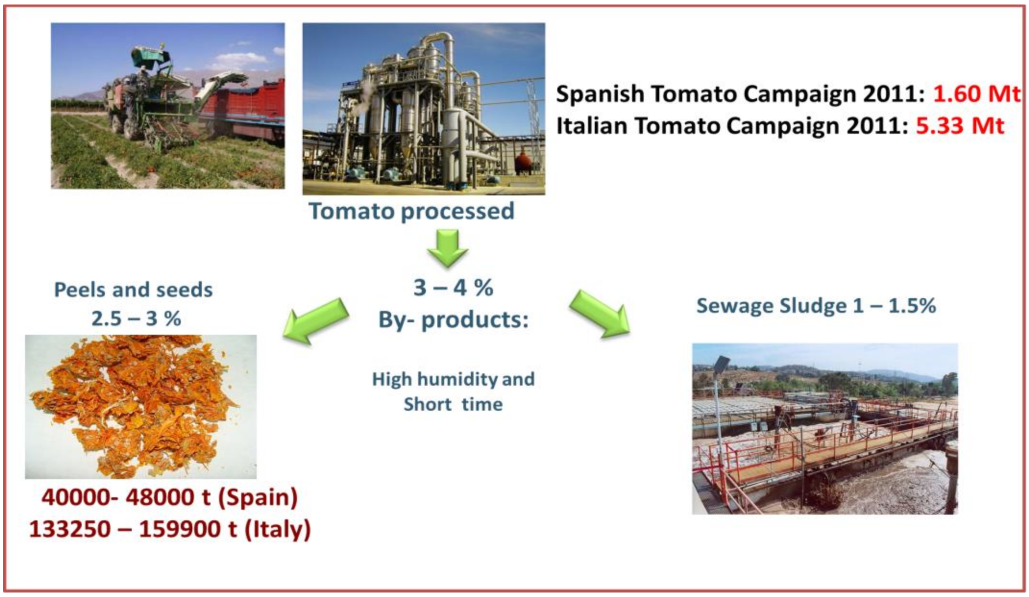


Fig.1: By-products from tomato industrial transformation 2011 based on ISTAT data

Tomato waste consists essentially of the fibrous parts of fruits, seeds and skins, and can constitute as much as 2,2% of the weight of the processed tomato. The cost of disposing of these wastes is over 4 € /tonne. These numbers give an idea of the consequence in terms of costs for a firm and of the impact on the environment, hence it makes sense to make valuable use of the wastes arising from tomato processing.

At the present time tomato waste is used mainly in the zootechnical sector for animal feed or, once it is dried, as the substrate for the production of fertiliser and lately for the production of biogas.

No work has examined the possibility of using tomato by-product in the production of biolacquer. In fact the goal of the project BIOCOPAC, funded by the EU with 800000,00 Euros under the 7 European Framework, is to develop a bio-based lacquer for the protection of metal food packaging, using a natural biopolymer, cutin, extracted from peels and skins of industrial tomato by-products. The idea for the project is based on an old patent developed by SSICA in the 1940.

## Lacquers for metal packaging

The lacquers currently used are based on synthetic resins and among all the epoxy resins are the most utilized in the coatings formulation for the metal packaging, thank to their excellent properties of chemical resistance and adherence. However in the last 10 years, with the advent of ever more sensitive analytical techniques and the greater attention paid to problems of a hygiene/health and environment, the synthetic lacquers have been the subject of several cases of alert. The problem of the migration of residues of polymerisation, monomers and oligomers, plasticizers added to the lacquering system or other additives has given rise to press campaigns and has created doubt and uncertainty among consumers, with consequent damage to the image of the canmaker industry and the firms producing canned foods. The object of the BIOCOPAC project is to develop a natural based lacquer from the tomato skins. In this way BIOCOPAC will meet the demand for sustainable production and for the safeguarding of consumer health, increasing at the same time the competitiveness of the metal can industry, valorising waste produced by the food industry, reducing refuse and obtaining a product with high added value.

**Experimental work**

The experimental work of the project is composed by different phases :

- Analysis of tomato skins;
- Set-up of the extraction's method;
- Analysis of the raw cutin extracted;
- Resin's production;
- Development and application of the BIOCOPAC lacquer
- Production of cans and caps

**Analysis of tomato skins**

The tomato samples, collected in the two tomato factories, partners of the project, that are Conservas Martinete (samples indicated as Spain samples) and Chiesa-Rodolfi Mansueto (samples indicated as Italian samples) have been subjected to chemical and microbiological analysis. The two companies took tomato waste, composed solely of peels skins, at three different times during the production campaign – mid-July, mid-August and mid-September – so as to obtain a sample representative of the entire processing period.
The nutritional composition of the tomato waste has been analysed and the results are reported in the graph below:

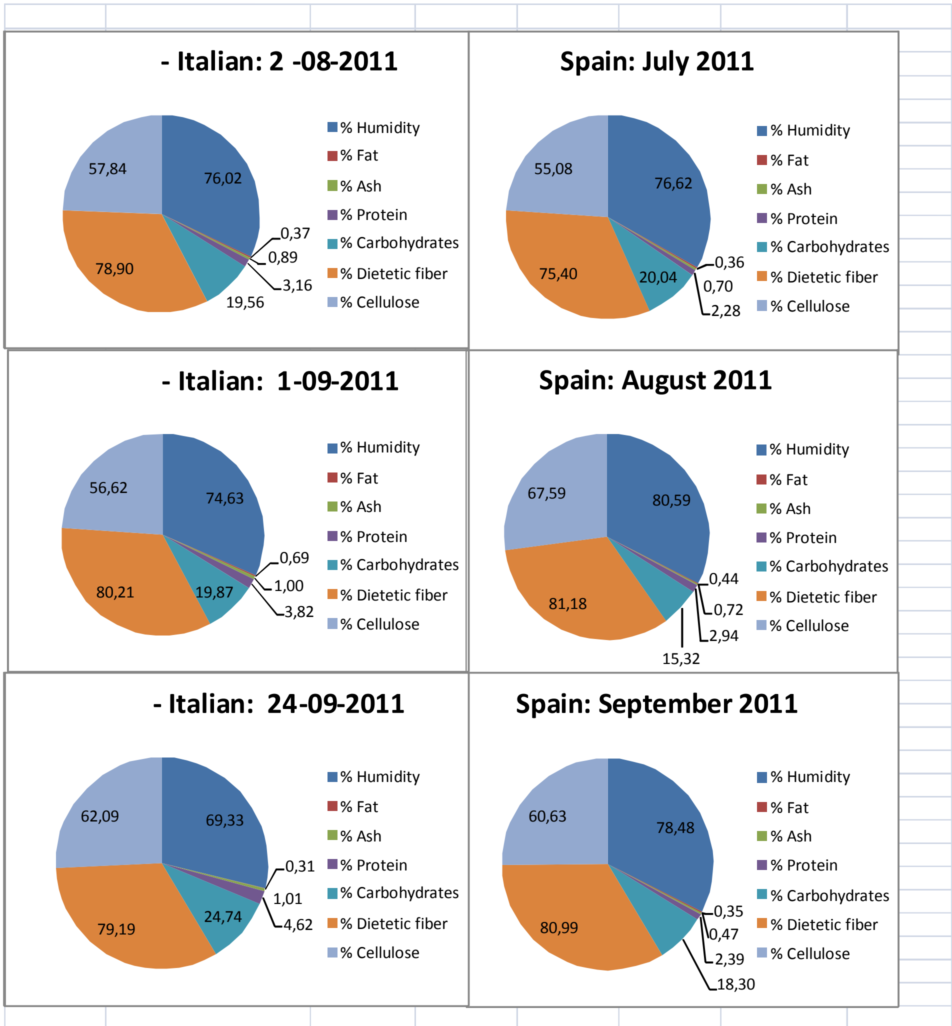


Fig.2: Nutritional composition

As the lacquer will be in contact with food products, the concentration of heavy metals and pesticides have been analysed. The heavy metals analyzed in the products (seed and peels from tomato processing) showed the following values:

| | ppb Sn | ppb Cu | Cd | Ni | Cr | Hg | Pb |
|---|---|---|---|---|---|---|---|
| **Italian samples: 2-08-2011** | 79.26 | 9.25 | < 10 ppb | | | | |
| **Italian samples: 1-09-2011** | 78.89 | 9.70 | | | | | |
| **Italian samples: 24-09-2011** | 78.93 | 7.60 | | | | | |
| **Spain samples: July 2011** | 81.93 | 3.32 | | | | | |
| **Spain samples: August 2011** | 71.96 | 11,85 | | | | | |
| **Spain samples: September 2011** | 88.25 | 4,.90 | | | | | |

Table n. 1: Heavy metals concentration

Only tin and copper have been quantified. Some little differences between the tomato waste samples can be appreciated in relation to copper's concentration. The other heavy metal studied have proved to be a value below the quantification limit of the measuring equipment.


Fig. 3: ICP equipment

As regarding the pesticide analysis, in all the samples analysed the active principles of the pesticide residues always presented values below the significance's limit, as it can be seen in the table below:

| Dried | Permetrine | Fluvalinate – tau(I+II) | Cipermetrine | Chlorpirifos | Methyl Chlorpirifos |
|---|---|---|---|---|---|
| Italian samples: 2-08-2011 | 0.01 | - | - | - | - |
| Italian samples: 1-09-2011 | - | - | - | - | - |
| Italian samples: 24-09-2011 | - | 0.05 | - | - | - |
| Spain samples: July 2011 | - | - | 0.32 | 0.27 | - |
| Spain samples: August 2011 | - | - | 0.08 | 0.26 | - |
| Spain samples: September 2011 | - | - | 0.16 | 1.19 | 0.01 |

Table n.2: Pesticides residues found in tomato waste

All the analysis carried out didn't show significant differences between the samples of tomato residues from Spain and Italy. The behavior is similar in all samples so it is decided to proceed with all of them, homogenizing samples from each country for further activities planned in the project.

**Set-up of the extraction's method**

The following phase of the experimental work has foreseen the set-up of the extraction's method. The procedure of extraction of raw cutin from tomato peels consists in a treatment of skins with an alkaline solution and then cutin is separated through precipitation for successive centrifugation after a treatment with an acid solution.

Fig. 4**:** Separation of tomato peels and seeds from tomato waste

Fig. 5: Dried tomato peels

Fig. 6: Raw cutin

This procedure has showed very good results, as regarding the final product obtained, the yield and the reproducibility of the method as well as the applicability of the method even on an industrial scale.

From our tests experimented both in Italy and in Spain we can say that any kind of tomato residue can be subjected to this extraction procedure, obtaining always raw cutin. This indicates a strong and solid reproducibility of the method.

The final bioresin obtained with the extraction procedure showed a good ability to form a new bio-lack that is the target of BIOCOPAC project.

The method has run not only in laboratory but also in a pilot plant with large quantities and high volumes. This is an important result for the project, as regarding a future application of the patent to industries. Naturally some improvements and modifications can be even studied and applied to obtain a continuous process.

**Analysis of the cutin extracted**

The composition of **tomato skins' cutin** has just been extensively studied in relation to the plant's botany. Recently Garca provided a tomato cutin consisting of **n,16-dihydroxyhexadecanoic** acids where the 10-isomer is largely dominant. The tomato cutin is a **polyester biopolymer interesterificated.** The significant proportion of secondary esters (esterification in the C-10 secondary hydroxyl) shows that the polyester structure is significantly **branched.**

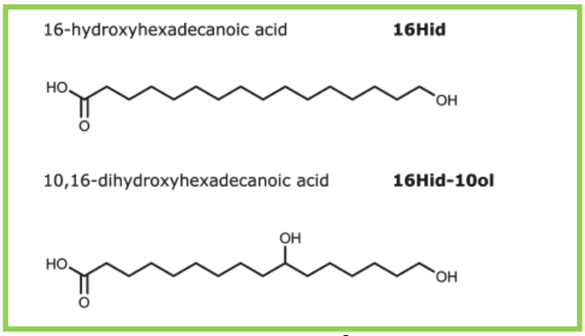

Fig. 7: Composition of tomato cutin

The raw cutin extracted both in laboratory's test and in pilot plant's trial has been characterized by means of FT-IR and GC-MS analysis. The IR and GC-MS spectra obtained (figures n. 8-9) presented always the same aspect with the same dominant peaks, in particular all chromatograms of samples of raw cutin always showed a principal peak, which corresponded to the 10,16 – bishydroxyesadecanoic acid at a retention time of 22 minutes. This compound is the principal unit of tomato cutin, as reported in literature. In fact the principal peak of the chromatograph has produced the following MS spectrum, which the NIST library has identified, with a good probability and other good parameters, as 10,16 – esadecanoic metil sylilate :

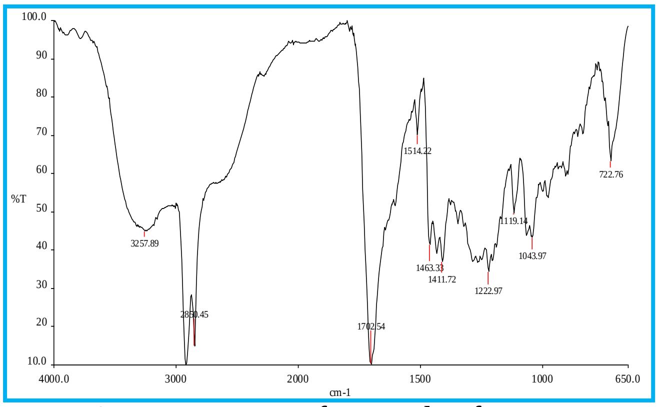

Fig. 8 : IR spectrum of a sample of raw cutin

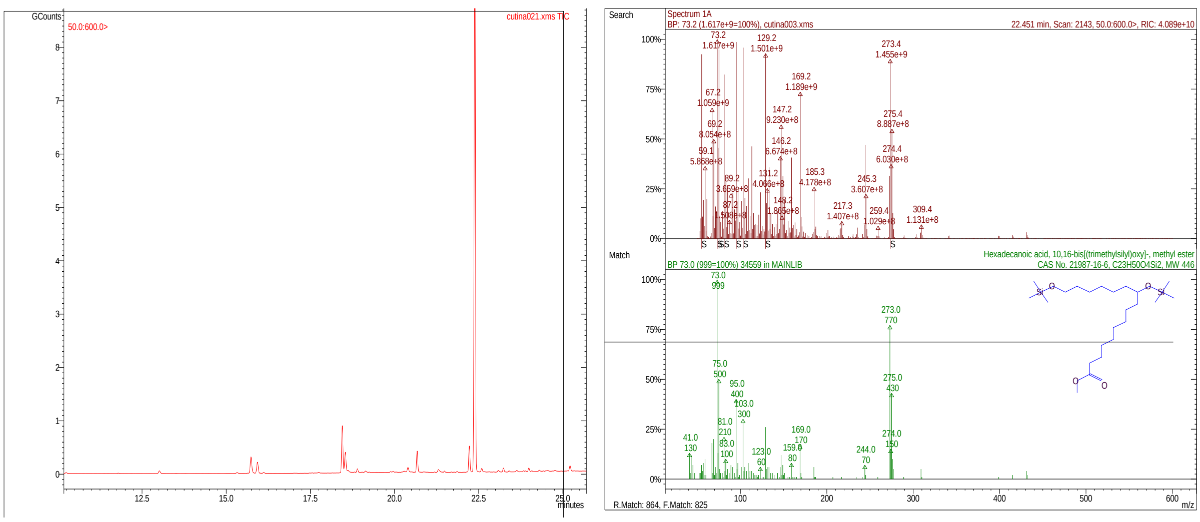

Fig. 9: GC-MS spectra of a sample of raw cutin

**Resin's production**

The experimental work, in the consecutive phase, still in progress, has examined the production of the resin.

For the production of the cutin-based resin two alternative methods are currently underway:

- Homopolymerization of the extracted raw cutin

  With the homopolymerization the cutin-based resin has been obtained from extracted cutin applying particular experimental conditions of polymerization; in this method the cutin polymerizes with itself to get a higher molecular weight resin. In the table below the characterisation of different resin's formulations obtained changing the experimental conditions is reported

| Bulk resin | Units | Resin n.1 | Resin n.2 | Resin n.3 |
|---|---|---|---|---|
| Solids content | [wt. %] | 98.8 | 98.8 | 98.2 |
| Solution in organic solvent | | | | |
| Solids content | [wt. %] | 60.9 | 58.3 | 59,0 |
| A.V. | [mg KOH/g] | 104.7 | 105.9 | 102,4 |
| $H_2O$ | [wt. %] | 0.51 | 0.40 | 0.42 |
| Viscosity | [mPas.s] | n.a. | 605 | 593 |

Table n. 3: Characterisation of different homopolymerized resin's formulations

- Copolymerization of the extracted cutin with selected petrochemicals raw materials

  With the copolymerization some standard polyester resins (indicated in the table below as P-1 and P-2) have been copolimerized with the extracted raw cutin (10% and 20%) and the resultant resins have been characterized, as reported in the table below:

| | Units | P-1 | P-2 |
|---|---|---|---|
| Cutin | [wt%] | 10.1 | 20.0 |
| Formulations Parameters | | | |
| eOH/eCOOH | [-] | 1.6 | 1.5 |
| OH excess | [mmol/g] | 1.1 | 1.1 |
| Alkyd constant | [-] | 1.1 | 1.1 |
| OH# at A.V. = 0 | [mg KOH/g] | 60.6 | 60.0 |
| Bulk resin | | | |
| OH# | [mg KOH/g] | 49 | n.a. |
| A.V. | [mg KOH/g] | 6.7 | n.a. |
| Viscosity | [Pa.s] | 3.2 | n.a. |
| Mn | [g/mol] | 2400 | n.a. |
| Mw/Mn | [-] | 7.5 | n.a. |

Table n. 4: Characterisation of different copolymerized resin's formulations

**Development and application of the BIOCOPAC lacquer**

The first tests about the formulation of a lacquer starting from a cutin based resin have given good results.

Different formulations of lacquer containing from 10 to 100% of cutin have been prepared and characterized in order to find the best formulations for the final bio-lacquer. The more promising formulations have been applied on different metallic substrates (tinplate, tin free steel and aluminium) and some properties such as degree of curing, appearance, sterilization's resistance were measured.

The first results obtained with at least 2 formulations, showed good values of chemical resistance (MEK test), good adherence (tape test), good mechanical properties and a good resistance to thermal sterilization in water. Some problems with the appearance of the lacquers on tinplate substrates were found. However the investigation and the research are still in progress in order to overcame this problem and to study the behaviour of the lacquer in contact with foodstuffs and the compliance with European regulations.

**Production of cans and caps**

On the base of the first best formulations, sheets of tinplate and aluminium have been lacquered. From these lacquered sheets it has been possible to produce 2 piece cans, crown cork, caps. In all cases the lacquer didn't show adherence's loss, rather it has showed a good behaviour in all the products obtained as it can be seen in the photo below:

Fig. 11: Samples of cans and caps lacquered with BIOCOPAC varnish.

**Conclusions**

We consider all these first results very satisfactory and from these first results we are optimistic about the possibility of realize a natural lacquer and, from our point of view, chances of getting a polymeric film obtained from tomatoes are becoming a reality

These first results will be exposed and showed in Bruxelles , on 4/05/13 at EU Open Doors, during the Festival of Europe.

**Bibliographic references**

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European patent application EP 2 371 805 A1 “Method for the application of oligo- and polyesters from a mixture of carboxylic acids obtained from suberin and/or cutin and their use thereof” published by VTT Technical Research Centre of Finland on the 5th November 2011.

*“The project – said D.ssa Angela Montanari, coordinator of BIOCOPAC project –“ will constitute a starting point for further developments in the same direction (other types of natural lacquers), or of metallic and non metallic support. The RTDs will obtain advantages of cultural type, as they will be able to acquire knowledge and experience in a field of research on biolacquers.”*

This innovation not only affect the food industry and the lacquer manufacturers, but will also involve the whole supply chain, as the partners of the consortium are to indicate.
BIOCOPAC Consortium is a private-public partnerships including 4 leading Research Centres, 4 SMEs and 3 large enterprises from 6 different EU countries. It is a European task force where each partner is specialised in a single step of the chain but all linked in one goal. The partnership encompasses the whole agri-food chain, from the tomato transformation and waste treatment industries, up to the lacquers and metal cans manufacturers. The project partners include Stazione Sperimentale per l’Industria delle Conserve Alimentari (IT – RTD Performer) along with Centro Tecnologico Agroalimentario Extremadura (ES – RTD Performer), Fundacion TECNALIA Research & Innovation (ES – RTD Performer), SYNPO A.S. (CZ – RTD Performer), Salchi Metalcoat S.r.l. (IT – lacquer manufacturer), Chiesa Virginio Azienda Agricola (IT – livestock & biogas producer), Conservas Martinete S.A. (ES – manufacturer of canned tomato), National Can Hellas S.A. (GR – metal packing), Rodolfi Mansueto S.p.A. (IT – transformation of tomatoes), Schekolin AG (LI – manufacturer of lacquers) and Saupiquet S.A.S. (FR – canned seafood producer).