International Scholars Journals

African Journal of Food Science Research ISSN 2375-0723 Vol. 3 (9), pp. 208-216, September, 2015. Available online at www.internationalscholarsjournals.org © International Scholars Journals

Full Length Research Paper

A study of solid-liquid extractive techniques and an innovative solid-liquid extraction technology using the Naviglio Extractor®

Daniele Naviglio[1*], Fabiana Pizzolongo[1], Raffaele Romano[1] and Lydia Ferrara[2]

[1]Dipartimento di Scienza degli Alimenti, Università degli Studi di Napoli "Federico II" Via Università 100 - 80055 Portici - Napoli – Italy.

[2]Dipartimento di Chimica Farmaceutica e Tossicologica, Università degli Studi di Napoli "Federico II", Via Domenico Montesano 49 - 80131 Napoli – Italy.

Accepted 29 March, 2015

This document is a review on solid-liquid extractive techniques and describes an innovative solid-liquid extraction technology using the Naviglio Extractor®. Also explained is an application for the production of alcoholic extract from lemon peel. The alcoholic extract, mixed with a sugar and water solution in the right proportions is used to make a well known Italian lemon liquor commonly named "limoncello". Lemon liquor is obtained utilizing the Naviglio Extractor®; the procedure used is fast and efficient and uses about half the weight of lemon peel per volume of ethyl alcohol used for the extraction of the odorous and taste responsible compounds, compared to the commonly used extraction procedures. To test the consumer's preference and compare the taste of the liquor obtained with that obtained by peel maceration from the same lot of lemons and obtained using the traditional recipe, a consumer test has been carried out. One hundred people, chosen from among frequent consumers of limoncello, tasted the two lemon liquors, and evaluated intensity of aroma, colour, alcohol taste and sweetness. In about 81% of the preferences, the liquor obtained using the Naviglio Extractor® was preferred. The extraction process used allows the ethanol from used up lemon peel to be totally recovered so that these can be disposed of as non toxic waste or used in agriculture or as cattle feed.

Key words: Lemon liquor, lemon peels, Naviglio Extractor, maceration, solid-liquid extraction, limoncello.

INTRODUCTION

The most important and delicate phase in the preparation of alcoholic drinks deriving from blending an alcoholic extract with water and sugar is represented by the maceration in ethyl alcohol of matrixes of a vegetable nature, like flowers, leaves, berries, roots, fruits rind etc. The maceration is a very slow process of solid-liquid extraction that occurs at room temperature; it is realized by soaking the solid to extract with an opportune liquid, in a container called a macerator with the aim to extract soluble compounds responsible for odour and taste. The extractable compounds are extracted from the solid matrix of the extracting solvent through diffusion and because of osmosis due to prolonged contact. The solution must be desultorily remixed, during the whole period of extraction, with the purpose of allowing the diffusion of the drawn out substances and avoiding the phenomenon of super saturation in proximity of the solid surface; this event has two negative effects: the extraction process can be blocked and some oxidative processes can be permitted (Nota et al., 2001; Dugo et al., 1998).

The lemon liquor commonly called "limoncello" is produced in Italy mainly in the Campania Region from the alcoholic extract of the external yellow part of the lemon peel which is known as "flavedo". In recent years the production of this alcoholic beverage has exponentially grown (Douglas, 2000) and so many researchers have begun to study the chemical and physics characteristics

* Corresponding author. E-mail: naviglio@unina.it.

of "limoncello" (Bocco et al., 1998; Bonomi et al., 2001; Dugo et al., 2000; Moio et al., 2000; Nota et al., 2001; Naviglio et al., 2002; Versari et al., 2003; Crupi et al., 2007).

Experimental taste-testing has shown that, maintaining a peel/alcohol ratio of 30% (w/v) at least two days of maceration are required to produce liquor that can be considered appreciable, this is because the smaller components (Compounds present under 2% in weight with respect to the total weight of the extractable compounds in ethyl alcohol) of the peel of the lemon are released more slowly in comparison to the larger components (limonene, beta-pinene and gamma-terpinene); the presence of the smaller components is essential to confer the liquor the organoleptic characteristics necessary to make it appreciable to frequent consumers of lemon liquor (Nota et al., 1999; Nota et al., 2001). In these conditions it is inevitable that the alcoholic extract becomes full of water; all the water contained in the flavedo rapidly diffuses in to the solution during the extractive process so that the alcoholic content is lowered from 96% (v/v) to about 80% (v/v), in the case in which the peel/alcohol ratio is 30% (w/v) as quoted above; this is in accordance with the measured water content of the flavedo that is equal to 70% (w/w) (Nota et al., 1999; Nota et al., 2001).

The process of dissolution of water in ethyl alcohol is rapid and it is completed in the first three hours of maceration; because in the maceration the mixing is irregular, during the long phase of stasis of the solution, strong gradients of concentration of water are generated in proximity of the surface of the peels, which in turn lower the alcoholic content locally, favouring hydrolysis reactions of the essential oil compounds (Mazza, 1987; Verzera et al., 1992 a, b). Everything leads to the conclusion that during the maceration of the lemon peel in ethyl alcohol, with the purpose of obtaining an extract containing the whole component of the essential oils, a lowering in the initial alcoholic content is inevitable and this fact causes the collateral reactions of hydrolysis in the essential oils. Finally, it must be noted that maceration is not an exhaustive extractive procedure with regard to the lemon peels; in fact, even extending the maceration long-er, over a month, the peels still preserve part of the essential oils that are no longer extracted because the concentration of the essential oils becomes so high that it reaches an equilibrium between the molecules that enter the solid and those that are released from it (Steady state).

Maceration is an extractive process that is based on two fundamental effects, diffusion and the osmosis; actually, it is the most economical process among all known extractive techniques due to a simple apparatus required: a sealable container. Currently, no other existing technique of solid-liquid extraction is applicable to the extraction of essential oils from lemon peel at room temperature for the production of lemon liquor; maceration is carried out industrially in the same manner as it is done at artisan or family level. This is one of the main reasons for which the "limoncello" is loved by a great number of consumers of alcoholic drinks and the public; the naturalness of the product fully preserves the lemon's beneficial properties (Bocco et al., 1998; Grandi et al., 1994; Horowitz and Gentili, 1997; Middleton and Kandaswami, 1994) and grants the drink strong digestive power, in fact its consumption is preferred especially consumed after meals.

This paper has two aims: firstly as an innovative technology of solid- liquid extraction, the Naviglio Extractor (Naviglio, 2000; Naviglio, 2003) is briefly introduced and compared to the current techniques of extraction, as far as extraction times are concerned, the extractive efficiency and quality of the extracts, particularly with maceration; the other to compare the lemon liquor produced in the traditional manner with that produced using the Naviglio Extractor, which allows the total recovery of ethanol from the used up lemon peels.

Experimental

Materials

The lemons used for the experimentation were taken from the same production stock as the "Ovale of Sorrento" cultivation. Ethyl alcohol at 95% (v/v) is the one commercially used and commonly used for the preparation of alcoholic drinks and it was purchased at the market. The sugar and the water with a low mineral content (Fixed residue<200 mg/L) were purchased at the local market.

Traditional procedure for the preparation of the alcoholic extract of the lemon peels

Lemons (About 7 kg) were washed and dried; only the most external part of the lemon rind (Flavedo) was recovered using a proper utensil; 600 g of lemon peel were transferred to a bowl (Macerator) and covered with two litres of ethanol (Peel/ethanol ratio: 30 g/100mL). The system was left to soak for 48 h and it was occasionally shaken. The alcoholic extract was recovered and paper filtered to eliminate any solid impurity. A sugary solution was prepared by dissolving 2 kg of sucrose in 4 l of water (Sugar/water ratio: 50% (w/v)). Two litres of this solution were added with one litre of alcoholic extract and the resulting mixture was gently stirred for 15 min to obtain the complete homogenisation. The exhausted lemon peels were undergone to the distillation in vapour stream for the gravimetric measure of the residue ethyl alcohol by means of hydrostatic balance.

Innovative procedure for the preparation of the alcoholic extract of lemon peels

Lemons (About 3.5 kg) were washed and dried; only the most external part of the lemon peel (Flavedo) was recovered using a proper utensil; 300 g of peel were put in a porous bag and then it was introduced in the extraction chamber of the Naviglio Extractor (Mod. 2 litres capacity, Nuova Estrazione S.a.s., Naples, Italy) and 2 l of ethyl alcohol were added (Peel/ethanol ratio: 15 g/100mL). To allow the total recovery of the essential oils, 30 extractive cycles of 4 min each for a total of 2 h (2 min in static phase and 2 min in dynamic phase) were performed obtaining at the end the alcoholic extract to be used for the preparation of the liquor. As a side pro-

product used up peels were obtained and treated as follow.

Recovery of ethanol and essential oils from exhausted peels with water

To recovery additional ethanol and essential oils from the used up peels the Naviglio Extractor was filled with two litres of water; two washing extractive cycles (8 min each) were performed to obtain water enriched in ethanol and essential oils. The enriched water was collected and the exhausted lemon peels were undergone to the distillation in vapour stream for the gravimetric measure of the residue ethyl alcohol by means of hydrostatic balance.

Preparation of the lemon liquor

To prepare the lemon liquor a solution containing 1.5 kg of sugar completely dissolved in 3 l of the enriched water was prepared. The alcoholic extract (About 1.9 L) was mixed with a double volume of the aqueous sugar solution enriched in alcohol and essential oils.

Consumer test

One hundred people, 65 males and 35 females from eighteen to forty years old, frequent consumers of lemon liquor, were chosen to carry out the organoleptic test of the comparison of two liquors. The test consisted of blind smelling and tasting of the two lemon liqueurs obtained, one produced following the traditional recipe and one made with the innovative technique. After tasting each sample, consumers were asked to rate the intensity of aroma, colour, alcohol taste and sweetness on a six-point scale. Consumers were also asked to express their global preference. The subjects were advised to use water to rinse their mouths between samples. The samples were presented coded by three-digit numbers and in a randomised order. They were evaluated at room temperature following the indications as reported in literature (Meilgaard et al., 1999). A t-test was used to determine significant differences between products at $p< 0.05$ level, using XLSTAT – PRO 7.5.2 (Microsoft, USA) for statistical analysis of data.

RESULTS AND DISCUSSION Solid-

liquid extraction: an overview

In many industrial processes, the initial phase of the preparation of a product requires the application of a solid-liquid extraction technique to isolate the extractable material contained in the most varied vegetable-type matrixes. The most important example is the medicinal plant sector, from which the active principles with pharmacological properties for the treatment of several human pathologies and illnesses are obtained; similar fields are herbalist, cosmetics and the perfume industry; even in these cases the principal ingredients of theirs products are obtained by submitting parts of plants such as flowers, leaves, roots etc. to solid-liquid extraction. Also in other industrial sectors like the beverage industry, a solid-liquid extraction is used to get alcoholic extracts from the peel of citrus fruit, flowers, leaves etc. that are then mixed to water and sugar to obtain the finished product. The list could continue mentioning many other industrial applications.

At the of solid-liquid extraction there is, without doubt, an experimental observation which anyone can verify: if, a solid matrix containing extractable material is simply dipped in a liquid, this begins to enrich with certain chemically similar substances ("Similia similibus solvuntur") in the phenomena of diffusion and osmosis. This technique of extraction, maceration, is the most simple and most economic and therefore it is widely used. Unfortunately, it is not always applicable because it requires a long period of contact between the solid and the liquid; for example vegetables cannot be left to soak in water due to rapid fermentation processes that lead to putrefa-ction of the extract. The productive demands of the Industry, which impose the production of large quantities of extracts in short times, have found an application in the extraction for percolation; in this case it is possible to treat large quantities of solid material with large volumes of liquid and obtain the extractable substances in a short times, but this process sacrifices the efficiency of the extraction that is kept low because of the limited contact between the solid and the extracting liquid.

The current techniques of solid-liquid extraction use diffusion and osmosis as principles with which it is possible to manage the processes to reduce the time and to increase the yield of extraction. In fact, the actual trend is that of increasing the temperature of the extractive system or extending the contact of the extracting solvent with the solid to achieve better results.

Maceration

Maceration is the extractive technique largely used in limoncello production (Dugo et al., 2000; Moio et al., 2000; Nota et al., 2001; Naviglio et al., 2002; Versari et al., 2003; Crupi et al., 2007) that consists in covering the solid to extract with the liquid and to leave the system in this condition for a prolonged time. The extraction occurs at room temperature and accordingly there is not alteration of the thermo labile compounds; on the other hand the time of extraction is on average quite long given that extraction occurs mainly by diffusive effect, in that it is necessary to occasionally shake the system to favour the diffusion of the extracted components and to avoid super saturation in the immediate proximity of the surface of the solid to be extracted, it leads to a deceleration of the global extractive process. In this way it is possible to obtain lemon liquor and many other very similar alcoholic beverages. Maceration is also a technique widely used in many official methods of analysis (See AOAC methods).

A last effect, ultrasounds or microwave assisted extraction, was introduced recently to enhance maceration , but the related techniques are nowadays under investigations (Stanisavljevi et al., 2007).

Percolation

Percolation reduces times by treating big quantities of solid matrix, but it is not used in limoncello production; this technique requires the realization of a column of solid material packed in the percolators that are big steel cylinders capable of containing tons of material with volumes ranging from 0.5 to 5 cubic metres. In the percolators the extracting liquid flows from the top to the bottom; since in only one passage the yield is not high, it is necessary to recycle the liquid different times to enrich it more than possible in extractable compounds. To increase the efficiency of the process it is possible to heat the percolator and in this case the thermo labile substances are subject to thermal degradation. Gene-rally, the efficiency of the global process is not high, but due to the large quantities of solid employed, the extract results proves to be sufficiently rich in extractable com-pounds. Also in this case the extractive principle is based essentially on diffusion and on osmosis (Hansen and Hinrichsen, 1992). This technique is widely used for the production of pharmaceuticals.

Supercritical fluid extraction (SFE)

A recent technique that requires a particular extractive system is extraction with supercritical fluids especially with carbon dioxide. The limitation of this technique, that requires contact of the solid with the carbon dioxide at the fluid state, is due to the fact that when carbon dioxide is in the supercritical state it acquires the chemical-physic properties of n-hexane. With this method it is therefore possible to extract non polar compounds from solid matrixes. The advantage of this technique is that at the end of the extraction the solvent, the carbon dioxide, is removed under the form of gas giving the possibility to recuperate the extractable concentrate. In on one side it is difficult to use this technique for laboratory uses, from the other this technique finds some important applications at the industrial level like the extraction of oil from seeds, caffeine from coffee, nicotine from tobacco etc., but it is however very expensive and not universally applicable (Mehr et al., 1996; Ching et al., 1998; Giannuzzo et al., 2003; Rajaei et al., 2005).

Extraction using vapour stream

For particular applications such as the production of essential oils and, generally, compounds with high vapour tension, the technique of distillation in vapour stream can be used.

This technique of solid-liquid extraction is peculiar because it requires the transport of volatile compounds from a vapour stream. In any case, since the extractive system is submitted to strong heating, the thermo labile substances undergo some transformations and they are not entirely recuperated. Some examples include the separation of tocopherols from soya sludge and extraction of citrus essential oils (Bannwart de Moraes et al., 2006; Parshikova, 2006).

Ultrasound or microwave assisted extraction (UAE-MAE)

These examples are to show that the techniques of solid-liquid extraction currently used are not universally applicable because they are limited. Besides, the extractive principle on which they are based is essentially linked to the phenomena of diffusion and osmosis of the substances contained in the solid; these tend to occupy the whole volume of the extracting liquid after they have been extracted. To raise the efficiency of these extractive systems a higher temperature is used, which causes diffusion to increase with the purpose of reducing extraction times and obtaining higher efficiency. This expedient is not applicable to vegetable matrixes because they contain substances that degrade themselves by effect of heating.

The use of ultrasounds or microwaves (Luque-García and Luque de Castro, 2004; Stanisavljevi et al., 2007) for the extraction of active principles from medicinal plants leads to obtaining the same results of extraction by squeezing, or even worse results because the system is heated for the prolonged treatment. In these cases the solid matrix becomes completely shattered and gives a mixture that is impossible to separate in its constituents and therefore renders these techniques inapplicable at industrial level.

Soxhlet method for solid-liquid extraction

Another extractive technique from the laboratory is Soxhlet, which is reported as the official method of extraction for numerous analytical methods in which an initial preparation of the extract of a solid sample is required (See AOAC Methods). The Soxhlet also uses the heating of the system, since it is based on the principles of diffusion and osmosis, for which it cannot be used for the substances that are degraded by the effect of heating. It is a process very similar to maceration; the difference consists in the fact that the extractive solvent in contact with the solid matrix is fresh due to its evaporation. Even if accelerated Soxhlet are on the market, in literature some papers that compare this technique with others are reported with the aim of replacing it for the retrieval of different substances (Crespo and Yusty, 2005; Hawthorne et al., 2002; Bowyer and Pleil, 1997). This technique is mainly performed on a laboratory scale because of the difficulty of constructing very large glass containers.

Accelerated solvent extraction (ASE®)

To raise the yield of extraction and reduce the extraction times it is possible to use the ASE® extractor (Accelerated Solvent Extraction) patented by the American Dionex. The material to extract is inserted in a cylindrical steel container and the extracting solvent is introduced;

Table 1. Comparison of the main features related to the current techniques of solid-liquid extraction.

Extractive technique	Granulation	Solvent	Efficiency	Time	Extract quality	Extract stability
Squeezing	not important	indifferent	complete	minimum	unsatisfactory	poor
Maceration	important	fundamental	complete	long	very good	very good
Percolation	important	fundamental	partial	medium	good	good
Soxhlet	important	fundamental	complete	long	unsatisfactory	poor
Distillation in vapour stream	not important	indifferent	partial	medium	unsatisfactory	poor
Supercritical gas	important	fundamental	partial	medium	very good	very good
Ultrasounds	not important	indifferent	complete	medium	unsatisfactory	poor
Accelerated solid-liquid extraction ASE	important	fundamental	complete	minimum	unsatisfactory	poor
Extractor Naviglio®	not important	indifferent	complete	minimum	very good	very good

the temperature of the system is brought above the boiling point of the solvent, which is maintained in the state of liquid thanks to a contemporary increase in pressure. After a brief contact the solid matrix is completely exhausted. Also for this technique it is not possible employ unstable matrixes to the heat but for many analytical applications, especially when many samples are to be analysed, it is very useful (Zuloaga et al., 1998). As with the Soxhlet extractor, ASE is a laboratory technique and currently it is impossible to set up large plants because of very high pressure requested.

Naviglio extractor or rapid solid-liquid dynamic extractor

This document introduces an innovative technology of solid-liquid extraction, which can be used as valid alternative to the existing ones: the Naviglio Extractor®. It completely changes the philosophy of solid-liquid extraction thanks to the discovery of a new principle of extraction: Naviglio's Principle (Naviglio, 2003) . The extraction happens because of the generation of a negative gradient pressure from the inside toward the outside of the solid matrix, therefore it can be conducted at room temperature or sub room temperature. An extractive cycle is constituted by a static phase and a dynamic one; during the static phase the liquid is put under pressure at about 8 - 10 atm on the solid to extract and it is left for sufficient time to allow the liquid to penetrate the inner solid and to balance the pressure between the inside and the outside of it. After this time, the pressure is immediately removed and falls quickly to the atmospheric pressure; in this moment the Principle of Naviglio causes which appears to be as a suction effect of the liquid from the inside toward the outside of the solid; this rapid movement of the extracting solvent transports the extractable material toward the outside. The cycles can be repeated until the solid is exhausted.

Experimental trials carried out until today on more than two hundred vegetable species showed that, working at a pressure of 9 atm, the greatest part of the solid matrixes, independently from the degree of crumbling, can be extracted using about thirty extractive cycles which occur in about two hours.

Besides, the reproducibility of the extraction has been proved on the same matrix in ponder terms and comparative experiments have been conducted with the other extractive techniques, which have underlined the highest recovery in favour of the Naviglio Extractor®, as well as a superior quality of the extract and in any case an alteration of the thermo labile substances has been induced (Cutillo et al., 2006; Micali et al., 2004; Naviglio et al., 2002; Naviglio et al., 2006). Finally, after the validity of Naviglio's Principle was demonstrated, experiments in the pharmaceutical sector of medicinal plants and experiments for the improvement of herbalist products, cosmetics and perfume industry are in progress at the Faculty of Pharmacy of the Università degli Studi di Napoli "Federico II" while the research in the field of food science at Department Food Science is performed nowadays (Naviglio et al., 2006).

In Table 1 the comparison between the different existing solid-liquid extractive techniques is shown and, as it is possible to observe, the Naviglio Extractor ® offers in one solution everything that the operator would like to receive from a solid-liquid extraction.

The new philosophy of rapid solid-liquid dynamic extraction

The rapid solid-liquid dynamic extractor represents an innovative technology of solid- liquid extraction that allows the solid matrixes containing extractable substances in an organic or inorganic solvent and in their mixtures to be exhausted in a short time, compared to the other cur-rently existing extractive techniques. The novelty of the extractor is in the fact that it changes the extractive philosophy because it reverses the tendency of the cur-rent methods, which aim to heat the extractive system to raise efficiency and to shorten the extraction times; the Naviglio extractor carries out the extraction at room or sub-room temperature and it uses an increase of pressure of the extracting liquid on the solid matrix to extract. The importance of extracting at low temperatures

Figure 1. The first experiment production of “limoncello” in the two-syringe system.

lies in the fact that thermal stress is avoided on the thermo labile substances in this way. Therefore it is possible, for instance, to faithfully reproduce the composition of the compounds contained in the medicinal plants without inducing transformations of the active principles, which generally are the more “delicate” substances to extract because they are susceptible to the effects of the temperature. Moreover, extraction is independent from chemical features of the extractive liquid and it makes possible to extract in heterogeneous phase compounds that do not dissolve themselves like essential oils in water (Naviglio et al., 2003).

Naviglio’s principle

The extractor works by alternating a static phase with a dynamic phase; during the static phase the extracting solvent is brought to a pressure of about 9 atm and it is kept in this state for sufficient time to reach an equilibrium between the pressure of the liquid to the outside of the solid matrix and the liquid within it; at the end of the static phase a dynamic phase begins, which is produced by a sudden movement of the pistons; it contributes to a rapid decrease of pressure of the system to lower values. In this moment the extraction of the solid matrix is realized. It becomes possible because a delta of negative pressure is generated from the inside toward the outside of the solid matrix, due to the sudden fall of the pressure of the liquid to the outside of the solid, that is at the base of the new extractive principle (Naviglio’s principle): the extractable substances of the solid are dragged out for an absolute suction effect, in every cycle of extraction constituted by a static phase and dynamic. The last phase allows, at the same time, a rapid and complete remixing of the solid matrix and an immediate diffusion of the drawn out substances in the whole mass of the liquid avoiding the phenomenon of local super saturation or others unpleasant effects (Naviglio et al., 2005).

The Naviglio Extractor® represents a valid alternative in comparison to existing extractives techniques and it mainly finds application in the extraction of the active principles medicinal plants, in the extraction of essential oils of citrus fruit, in the extraction of essences and perfumes, in the extraction of fats etc. It can be dimensioned according to the demands starting from a bench apparatus size for analytical uses up to an industrial dimension for the production of large quantities of extract.

From the principle to the realization of the machine: evolution of the Naviglio extractor®

The functioning of the Naviglio extractor, the statement of Naviglio’s principle and the related considerations are discussed elsewhere (Naviglio, 2003). In this paragraph we briefly want to resume the history of the production of the final Naviglio Extractor machines.

The intuition of the principle explained above came to Dr. D. Naviglio in 1993, when like a vision a movement of pistons similar to that which happens in a car engine appeared in his mind. If a suction effect was achieved this movement could allow the extraction of extractable compounds from solids. To verify the efficiency of extraction, elementary trials were performed connecting two syringes through a duct and producing pressure only using the force of hands (Figure 1); in this way it was possible to have the initial approach in demonstrating the validity of the Principle in the production of a minimum quantity of “limoncello”. These first results gave the possibility to obtain the patent of both the new extractive process and the extractor (Naviglio, 2000).

In Figure 2 the bench-top prototype of Naviglio Extractor® is shown with which it was possible to scient-ifically verify the validity of Naviglio’s principle. It is composed of two cylinders (syringes) that act as extrac-tive chambers, in which two pistons moved by compress-ed air run. This prototype works as elsewhere reported (Naviglio, 2003) and it allows the production of about 50 ml of extract.

In Figure 3 the industrial prototype is shown; it allows the treatment of about 1 - 5 kg of solid (This quantity depending on the value of density of the solid) and obtains about 40 l of extract. The optimization of variables and the necessity of limiting encumbrance to a minimum have been resolved at the same time leading to the construction of the final version of the Naviglio Extractor model of nominal capacity ranging from 0.5 to 2 l (Figure 4). Currently there are models of Naviglio extractor market ranging from a capacity of 0.5 to 400 l. Moreover,

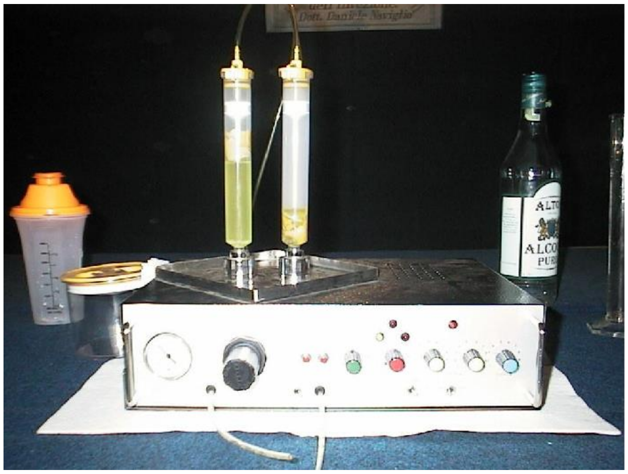

Figure 2. Bench-top Naviglio Extractor® prototype.

Figure 4. Last model of bench-to 0.5 (In the figure), 1 and 2 litre Naviglio Extractor®.

Figure 3. Industrial 50 litre Naviglio Extractor® prototype.

it is possible to realize the same above mentioned principle using solely one extracting chamber and one cylinder lowering the efficiency of the extractive process in respect of a two cylinders-two pistons system with the aim of reducing the production costs.

Finally, the initial working pressure was of about 6 atm but new models of Naviglio extractor® working at higher pressures (9 - 10 atm) have already been built; higher pressures allow a reduction in extraction times contemporarily obtaining an exhaustive process of extraction.

Alcoholic content of the extract

At the end of the maceration process, since the lemon peels contain about 70% (w/w) of water, the alcoholic content of the extract has been lowered in an appreciable manner from 96% (v/v) to about 80% (v/v) and in this case the ratio of dilution to achieve a final liquor to the thirty percent in alcohol is 2.67; in the case of the extract obtained with the Naviglio Extractor® the alcohol content is lowered to about 90% (v/v) and accordingly the ratio of dilution is 3.00. This is due to the fact that the quantity of peel is smaller and, because of washing the peels with water, ethanol and essential oil are totally recovered.

In this way it is possible to get about 12% (v/v) more lemon liquor which represents a source of profit considering the cycle of total production performed in one year.

Disposing of used lemon peels

At the end of the process of maceration, used lemon peels, submitted to the analysis of alcoholic content by distillation in vapour stream, showed a ethanol content of about 15% (v/v) and then they were not disposable as a manure; while the peels deriving from the process of production of lemon liquor using the Naviglio Extractor were lacking in ethanol and then they can be disposed as manure or employed as feed after a drying process at room temperature or in hot air.

Evaluation of the results of the consumer test

Results of consumer test are reported in Figure 5 as a histogram. The two liquors were significantly different ($p<0.05$) for aroma, colour, alcohol taste and sweetness. Naviglio's liquor exhibited a more intense aroma, colour and sweetness than the other one. This shows that by means of this innovative extraction technology it is possible to extract more compounds that increase aroma and colour; moreover, the brief contact of lemon peel with ethanol avoids hydrolysis phenomena of some extracted compounds and in this way the aroma is closer to the fresh lemon aroma. These features result in a preference for Naviglio's liquor; in fact the results of the preference test showed that 81% of the judges clearly preferred the lemon

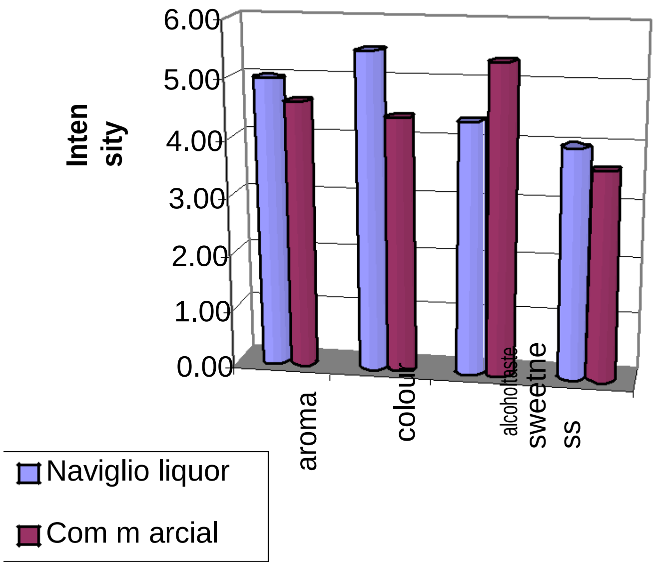

Figure 5. Histogram of data obtained from the consumer test with regard of colour, sweetness, aroma and alcohol for the compared lemon liquors.

lemon liquor produced with the Naviglio extractor®, while the remaining part found the two liquors equivalent.

Conclusions

The Naviglio Extractor introduces some notable advantages in the production of lemon liquor. First of all it reduces the times of extraction of the essential oils from the lemon peel bringing the extractive time from a minimum of 48 h to about two hours; besides the peels are completely exhausted from the essential oils in this period of time, which does not happen in maceration but extends the phase to a long extractive time. Using half the peels that are normally used, in the same way a pleasant drink is obtained similar to that produced according to traditional recipes that require one or two weeks of extraction time. Using a smaller quantity of peels the alcoholic content is not excessively lowered; finally, ethyl alcohol, which is normally lost during the maceration phase (About 10 - 15% v/v), is completely recovered using two rapid washing cycles (16 min.) with potable water that subsequently is used for the preparation of the sugary solution. The total recovery of ethanol in the extractive cycle allows the production of a major quantity of lemon liquor and brings the dilution ratio of 2.67 in the maceration to a value of 3.00.

The current research in finding a best extraction technique did not at the end prove to be as widely reported in recent literature; in this context the Naviglio extractor is giving the best results being a solid-liquid extractive technique that is simple to use and widely used for a great number of applications giving the best results in reducing extraction times, raising the efficiency of the entire process and obtaining high quality extracts.

REFERENCES

Bannwart de Moraes E, Martins PF, Batistella CB, Alvarez ME, Maciel Filho R, Maciel MR (2006a). Molecular distillation: a powerful technology for obtaining tocopherols from soya sludge. Appl. Biochem. Biotechnol. pp. 129-132.

Bannwart de Moraes E, Martins PF, Batistella CB, Alvarez ME, Maciel Filho R, Maciel MR (2006b). Molecular distillation: a powerful technology for obtaining tocopherols from soya sludge. App. Biochem. Biotechnol. pp. 1066-1076

Bocco A, Cuvelier ME, Richard H, Berset C (1998). Antioxidant activity and phenolic composition of Citrus peel and seed extracts. J. Agric. Food Chem. 46: 2123-2129.

Bonomi M, Lubian E, Puleo L, Tateo F, Fasan S (2001). Criterio di caratterizzazione PCA di liquori “limoncello”. Ind. Bevande 30: 371-374.

Bowyer JR, Pleil JD (1997). Comparison of supercritical fluid extraction and Soxhlet extraction for the analysis of organic compounds from carpet samples. J. Chromatogr. 787(1-2): 171-179.

Ching W, Siems WF, Hill HH, Rich HM (1998). Analytical determination of nicotine in tobacco by supercritical fluid chromatography–ion mobility detection. J. Chromatogr. 811: 157-161.

Crupi ML, Costa R, Dugo P, Dugo G, Mondello L (2007). A comprehensive study on the chemical composition and aromatic characteristics of lemon liquor. Food Chem. 105: 771-783.

Cutillo F, D’Abrosca B, Della Greca M, Fiorentino A, Zarrelli A (2006). Terpenoids and phenol derivatives from Malva silvetris. Phytochemistry 67: 481-485.

Douglas D (2000). L’exploit del limoncello. Linea Diretta. 5:9-12.

Dugo P, Mondello L, Cogliandro E, Cavazza A, Dugo G (1998). On the genuineness of citrus oils. Part LIII. Determination of the composition of the oxygen heterocyclic fraction of lemon essential oils (*Citrus limon* (L.) Burm, f.) by normal-phase high performance liquid chromatography. Flavour Fragrance J. 13: 329-334.

Dugo P, Russo M, Mondello L, Dugo G, Pastorino S, Carnacini A (2000). Chemical and physico-chemical parameters and composition of the aromatic fraction of limoncello. Ital. J. Food Sci. 12: 343-351.

Giannuzzo AN, Boggetti HJ, Nazareno MA, Mishima HT (2003). Supercritical fluid extraction of naringin from the peel of Citrus paradisi. Phytochem. Anal. 14(4): 221-223.

Grandi R, Trifiro` A, Gherardi S, Calza M, Saccani G (1994). Characterization of lemon juice on the basis of flavonoid content. Fruit Process. 11: 355-359.

Hansen A, Hinrichsen EL (1992). Some remarks on percolation. Physica Scripta 44: 55-61

Hawthorne SB, Grabanski CB, Martin E, Miller DJ (2002). Comparison of Soxhlet extraction, pressurized liquid extraction, supercritical fluid extraction, and subcritical water extraction for environmental solids: recovery, selectivity, and effects on sample matrix. J. Chromatogr. 892(1-2): 421-433.

Horowitz RM Gentili B (1997). Flavonoid constituents of Citrus. In Citrus Science and Technology; Nagy S, Shaw PE, Veldhuis MK, Eds. AVI Publisher: Westport, CT. p. 397.

Luque-García JL, Luque de Castro MD (2004). Ultrasound-assisted Soxhlet extraction: an expeditive approach for solid sample treatment. Application to the extraction of total fat from oleaginous seeds. J. Chromatogr. 1034(1-2): 237-242.

Mazza G (1987). Studio sulle ossidazioni dei monoterpeni negli oli essenziali. Ess. Deriv. Agrumari. 57: 5-18.

Meilgaard M, Civille GV, Carr BT (1999). Sensory evaluation techniques. 3° ed. CRC Press, London.

Mehr CB, Biswal RN, Collins JL, Cochran HD (1996). Supercritical carbon dioxide extraction of caffeine from guaraná. The Journal of Supercritical Fluids. 3:185-191.

Micali G, Cappellano G, Lo Coco F, Mondello F, Lanuzza F (2004). Nuova tecnologia di estrazione di principi attivi da piante medicinali. XXI Congresso Nazionale di Merceologia, Foggia 9: 22-24.

Middleton E, Kandaswami C (1994). Potential health-promoting properties of Citrus flavonoids. Food Technol. 11: 115-119.
Moio L, Piombino P, Di Marzio L, Incoronato C, Addeo F (2000). L'aroma del liquore di limoni (limoncello). Industrie delle Bevande 29: 499-506.
Naviglio D (2000). Rapid and dynamic solid–liquid extractor working at high pressures and low temperatures for obtaining in short times solutions containing substances that initially were in solid matrixes insoluble in extracting liquid. Italian Patent n. 1,303,417.
Naviglio D, Raia C, Naviglio B, Tomaselli M, Bolognese A, Correale G, Manfra M, Saggiomo S (2002). Confronto organolettico di liquori di limone provenienti da agricoltura biologica. Industrie delle Bevande. 31: 448-455.
Naviglio D (2003). Naviglio's principle and presentation of an innovative solid-liquid extraction technology: Extractor Naviglio. Anal.Lett. 36(8): 1647-1659.
Naviglio D, Raia C, Russo M, Aceto C, Somma A, Ferrarla L, Montesano D, Manfra M, Correale G, Bolognese A (2003). Estrazione dell'olio essenziale di bergamotto. Ingredienti Alimentari. 2(5): 13-18.
Naviglio D, Pizzolongo F, Mazza A, Montuori P, Triassi M (2005). Individuazione di carica microbica responsabile della torpidità del limoncello. Industrie delle Bevande 34(199): 424-430.
Naviglio D, Conte P, Pizzolongo F, Piccolo A (2006). Estrazione di inquinanti da suolo contaminato. Laboratorio 2: 54-58.
Naviglio D, Calabrese F, Pizzolongo F, Di Rubbo L, Mascolo N, Ludovici S, Polcaro A (2006). Produzione di amari ed elisir con
impiego del Naviglio Estrattore in alternativa alla macerazione. Industrie delle Bevande 35: 561-572.
Nota G, Naviglio D, Romano R, Sabia V, Attanasio G, Spagna Musso S (1999). Correlazione tra le caratteristiche organolettiche e le risposte analitico-strumentali di liquori di limoni. Industrie delle Bevande 28: 239-242.
Nota G, Naviglio D, Romano R, Sabia V, Attanasio G, Spagna Musso S (2001). Examination of the lemon peel maceration step in the preparation of lemon liquor. Ital. Food Beverage Technol. 24: 5-9.
Parshikova VI, Krasnoyarskii Gos, Torgovo-Ekon Inst. Krasnoyarsk, Russia. Izvestiya Vysshikh Uchebnykh Zavedenii, Pishchevaya Tekhnologiya (2006), Formation of quality of citrus essential oils obtained by steam distillation. (2-3): 33-36. Publisher: Kubanskii Gosudarstvennyi Tekhnologicheskii Universitet.
Punín Crespo MO, Lage Yusty MA (2005). Comparison of supercritical fluid extraction and Soxhlet extraction for the determination of PCBs in seaweed samples. Chemosphere 59(10): 1407-1413.
Rajaei A, Barzegar M, Yamini Y (2005). Supercritical fluid extraction of tea seed oil and its comparison with solvent extraction. European Food Res. Technol. 3: 401-405.
Stanisavljevi IT, Lazi ML, Velikovi VB (2007). Ultrasonic extraction of oil from tobacco (Nicotiana tabacum L.) seeds. Ultrason. Sonochem. 14(5): 646-652.
Versari A, Natali N, Russo MT, Antonelli A (2003). Analysis of some Italian lemon liquors (limoncello). J. Agric. Food Chem. 51: 4978-4983.
Verzera A, Del Duce R, Stagno d'Alcontrones I, Trazzi A, Daghetta A (1992a). Trasformazioni dei componenti degli aromi solubili agrumari in ambiente acido acquoso. Nota I: Monoterpeni aciclici e monociclici. Industrie delle Bevande 21: 217-222.
Verzera A, Stagno d'Alcontrones I, Donato MG, Del Duce R, Gigliotti C (1992b). Trasformazioni dei componenti degli aromi solubili agrumari in ambiente acido acquoso. Nota II: Monoterpeni biciclici. Industrie delle Bevande 21: 379-386.
Zuloaga O, Etxebarria N, Fernández LA, Madariaga JM (1998). Comparison of accelerated solvent extraction with microwave-assisted extraction and Soxhlet for the extraction of chlorinated biphenyls in soil samples. Trends in Anal. Chem. 17(10): 642-647.