

## PRIMARY CHARACTERIZATION OF WINE MAKING AND OIL REFINING INDUSTRY WASTES

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*În această lucrare se prezintă rezultatele studiului privind potențialul energetic al unor deșeuri din industria viti – vinicola și cea alimentară (extracția uleiului), în vederea folosirii acestora ca o potențială sursă de energie regenerabilă.*

*Studiul se axează pe determinarea unor proprietăți fizice și chimice ale produselor printr-o abordare experimentală: analiza primară și analiza elementară, precum și determinarea potențialului energetic al fiecarui deșeu în parte. Produsele analizate sunt: tescovina din struguri roșii și struguri albi, precum și resturile (semințe presate) de floarea soarelui rămase în urma procesului de fabricare a uleiului.*

*The aim of this paper is to present the energetic potential of wastes from wine making industry and from oil refineries in order to be used as a potential source of renewable energy.*

*The study focuses on the determination of physical and chemical properties of products through an experimental approach: the primary and elemental analysis and determination of energetic potential of each waste separately.*

*The products analyzed are the grape marc produced by pressing red and white grapes and also the residues (pressed seeds) left after the sunflower oil manufacturing process.*

**Keywords:** grape marc, sunflower, biomass, renewable sources

### 1. Introduction

The nationwide availability of the grape and sunflower production is presented in the following. It aims to determine national availabilities of materials to be processed in the two separate industries and also to quantify the remaining amount of residues after treatment (extraction).

Cultivation of vines is performed in Romania, almost on the entire territory from the Danube in the south to the counties of Botoșani and Maramureș

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in the North. In Romania there are a total of 37 vineyards, which include 123 centers vines, to which are added 40 independent wine centers, located outside the vineyards.

Vine is cultivated in specific areas dedicated to viticulture, usually located on hills.

Among the 14,700,000 hectares of agricultural surface, 189,000 hectares are cultivated with vines (1.3%) [1].

Total production of grapes may be analyzed taking into account the areas cultivated with vineyards and the grapes' yields. This production is presented in Fig. 1.

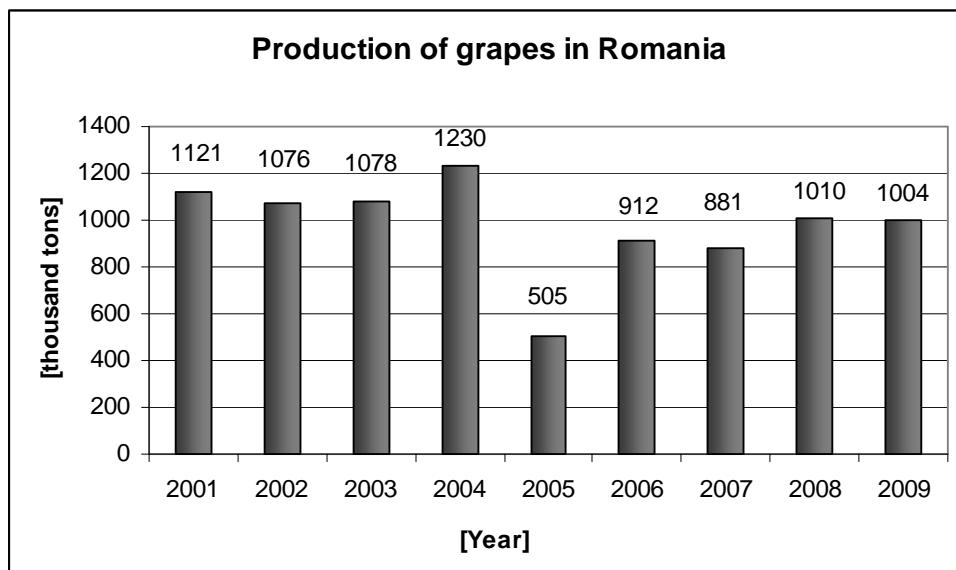


Fig.1. Production of grapes in Romania

The area with bearing vineyards has been reduced since 2001 to 2007 from 244,000 ha to 189,000 ha. In a structural approach, the areas with grafted bearing vineyards are only 7000 hectares higher than hybrid ones.

Low level of grapes' yields shows low level of using natural resources for vine in Romania. Using old technologies, especially in small size exploitations, where mechanical means do not exist, determines low production. The main reasons of obtaining low levels of production are: natural factors that manifest excessively: droughts, floods, spring and fall frosts, and pests' attacks and diseases. In 2005, many of these factors manifested and produced calamities for vine. Hail, shower and storms caused losses of 50% of the production, at national level.

In 2007, the grapes production decreased with 3.4%, and the yields decreased with 2.4% compared to 2006, which was considered a normal year for grapes production. The average in the last few years is about 930 thousand tons of grapes.

The wine production is, on average, 5.5-6 millions of hectoliters. Wine processing is concentrated in large companies, which use modern technologies. The main strengths of wine chain consist in large investments realized by large units, their value accounts for 73 million Euros from 2002 to present, renewing the technologies of wine processing, large availability of wine processing points, closed to vineyards [2].

By utilizing 1 kilogram of grapes, about 0.8 liters of wine are produced and the solid leftover - grape marc - is about 0.2 kg. So we can conclude that significant amounts of grape marc are produced at a national level.

Regarding the sunflower production, sunflower is among the traditional crops in Romania. From the viewpoint of cultivated are in 2009, Romania held the second place among Member States, after Spain.

For this research it was chosen among different oil plants, which are mainly used for bio - fuel production, sunflower that is highly propagated on the Romanian territory.

Production achieved in 2009 classified our country on the forth place after France, Bulgaria and Hungary due to the output by 20% lower than average output of European Union.

The variation of the sunflower production in the last years is presented in Fig. 2 [3].

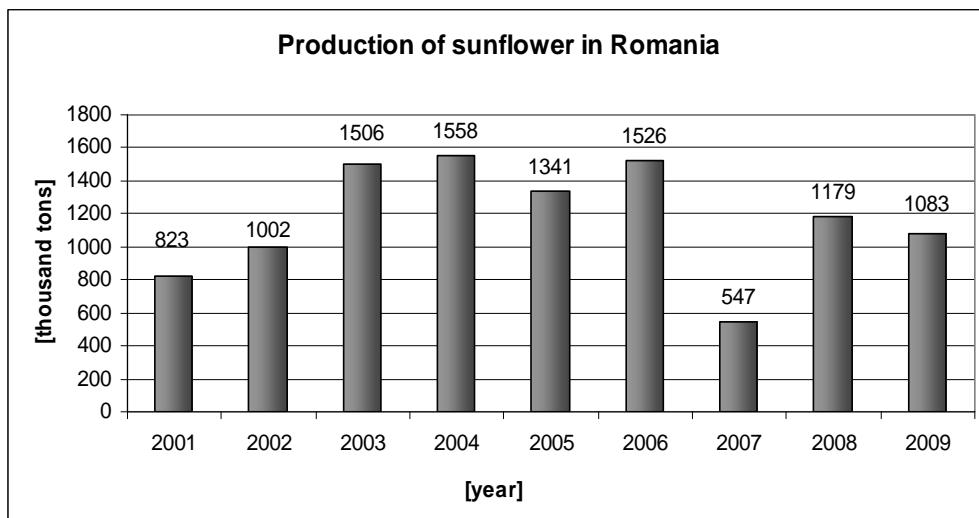


Fig.2. Production of sunflower in Romania

The fruits from the sunflower (achenes) contain about 50% oil with exceptional food quality, which is used in human food (refined) and food industry (margarine, canned food, soap, lecithin, phosphatides, etc.).

Cooking oil is produced by cold pressing process. The line is composed of five machines, which covers the entire process, from seeds selection to oil filter.

The material studied in this paper is represented by sunflower oil cake which results of sunflower seeds cold press.

### 1.1. Nationwide uses of products

In Romania the grape marc is treated in different manners. These modes are presented in the following paragraphs.

Recovery of grape seed can harness in order to obtain oil. Oil from grape seeds is edible, high-quality, dietary advisable for people prone to arterial diseases. In addition to food consumption, may be used in industry for paints and varnishes, in perfumery, in the pharmaceutical industry or in the manufacture of soap with a very good foaming.

By its structure and content of different nutrients, grape marc is a good feed, which can be used fresh, salted, sweetened or dried. Dry pomace has the advantage of being easy to store, like any coarse dry fodder (straw, hay). Drying is done after it has been exhausted of sugar, alcohol and pressed. It turns into something less compact very well and it is placed to dry in the sun in a thin layer of 3-4 cm. Grape seed separated and dried can be used as feed in feeding pigs and poultry. It is given, usually along with grain cereal.

A better destination for grape marc is that it can be used as organic fertilizer. For this purpose it is necessary composting it with some mineral constituents (ash, lime) and mineral fertilizers (phosphates), droppings, scraps of organic farm, for turning into nutrients more available for plants.

Within the European renewable energy policy we can take the example of other countries that have exploited these wastes from the wine industry, reaching to produce electrical and thermal energy.

Like the grape marc's main utilizations, the sunflower oil cake is mainly destined to be processed as livestock feed. It is also used as raw material for protein concentrates in charcuterie.

From the seed hulls artificial fibers are made, like the furfural used in plastics industry. The grinded hulls are used in the manufacture of fodder yeast, about 150 kg/ton product.

These hulls are usually separated from the kernels (seed) before being pressed for oil production at a rate about 80%. The material remained after pressing is called oil cake like it has been mentioned before and except its fodder uses, it can also be transformed into pellets.

In Romania few companies use the sunflower oil cake and sell it as pellets for 0.2 euro/kg.

## **2. Physical, chemical and energetic materials characterization**

The products used in this study are represented by industrially obtained grape marc from both red and white grapes. These materials are derived from a well-known wine institute in Romania, Valea Calugaresca. The institute processes hundreds of grapes every year; after being separated from their stalks in a special machine, the grapes are pressed in automatic presses for high quality wine production.

The fresh grape marc obtained after juice extraction was treated in a drying oven for 24 hours at 105°C. The moisture content of the material as arrived, after pressing, was estimated at about 58% for white grape marc and 70% for red grape marc.

It is mentioned that the separation of stalks in the processing of red grapes had a lower efficiency than in the white grapes. Usually in the consistence of grape marc, we approximated the rate of stalks at about 2%, almost negligible compared with the full amount.

The other materials studied are represented by sunflower oil cake, derived after sunflower seeds pressing. The oil cake was subjected to the same type of drying process, resulting a moisture content of 9%.

## 2.1. Volatile and inert content

For the determination of volatile content, the dried sample (grape marc and oil cake) has undergone a medium temperature pyrolysis process.

For the pyrolysis (as well for the combustion) of the material, it was used an electric furnace, produced by Nabertherm company, type L9/11/SW with the following components: carriage, precision balance, swing gates door and rated operating temperature of 1100°C.

Temperature in the furnace is measured and adjusted with a long life thermocouple from NiCr – Ni, which can work in temperatures up to 1100°C. All operations of command and control are done in a microwave device command and control, type P320MB1, which allows programming the oven temperature variation in time on 5 ramps and 4 levels of temperature and can thus simultaneously set 4 different working temperatures, each one corresponding to a stationary time of the oven at that specific temperature; also it can be adjusted the heating times between two different temperatures.

For the determination of volatile content the temperature was set at 800°C and the crucible with material previously graded, stayed in the oven for 40 minutes.

The samples obtained in the first stage are subjected to a combustion process in order to determinate the total content of the combustible materials, respectively the one of inert (non-combustible). This process took place at a temperature of 1000°C, for about an hour. The combustible fraction (Fixed Carbon and Volatiles) and inert content resulted is presented in Table 1.

Table 1

Proximate analysis of dried material

Material (dry)	Volatile + FC [%]	Inert [%]
White grape marc	97.82	2.18
Red grape marc	96.54	3.46
Sunflower oil cake	96.78	3.22

## 2.2. Elemental analysis

An elemental analyzer was used to establish the composition of the product. We used three types of samples: white grape marc, red grape marc and sunflower oil cake.

The EA 3000 Series used analyzer uses the principle of dynamic flash combustion followed by gas chromatography separation of the resultant gaseous species (N<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and SO<sub>2</sub>) and TCD detection. Using Callidus the most advanced dedicated software for the Elemental Analysis, the instrument provides

precise analytical results, continuous monitoring of instrument performances, full diagnostic, sample row data archival and retrieval as well as results recalculation.

The method in order to establish the C, H, N, S composition uses 2 types of gases: Helium and Oxygen. The carrier gas (He) is flowing through the combustion reactor where the dynamic combustion obtained with oxygen injection in presence of catalyst takes place. Gases are then flowing in the reducing part of the reactor where the reduction takes place eliminating the excess of oxygen and converting  $N_xO_y$  into  $N_2$  and  $SO_2/SO_3$  into  $SO_2$ . Gases coming out from the single reactor ( $N_2$ ,  $CO_2$ ,  $H_2O$ , and  $SO_2$ ) are entering the GC column for peak separation and TCD detection.

The process indicated above takes place under controlled conditions that are reported in the instrument parameters section. The carrier pressure has been established at 80 kPa, the front furnace temperature at 980 °C and also the weight of the sample varies from 0.8 to 2.5 mg. The results of the analysis are presented as following:

Table 1

**Elemental composition of white grape marc**

White grape marc: Elemental composition [%]					
C	H	O	N	S	Ash
52.970	5.938	34.214	0.539	4.159	2.180

Table 2

**Elemental composition of red grape marc**

Red grape marc: Elemental composition [%]					
C	H	O	N	S	Ash
41.210	5.935	45.496	0.659	3.240	3.46

Table 3

**Elemental composition of sunflower oil cake**

Sunflower oil cake: Elemental composition [%]					
C	H	O	N	S	Ash
49.430	7.185	32.121	4.163	3.881	3.22

### 2.3. Energetic potential

After the primary analysis of the materials, it was calculated the high heating value (HHV) and the low heating value (LHV) in order to establish the energetic potential of the material.

For these calculations it was used two different semi-empirical formulas based on the experimentally determined elementary composition.

The first formula used, no. (1) is the one proposed by Demibras for the determination of the high heating value of biomass [4]:

$$HHV = 0.335[C] + 0.1423[H] - 0.154[O] - 0.145[N] \text{ (MJ/kg)} \quad (1)$$

Lower heating value is obtained by a correction factor, calculated according to the formula:

$$LHV = (HHV - 5.83 \times W) \times 4.1868 \text{ (KJ/kg)} \quad (2)$$

Where:

W – is the material water vapor source

HHV – is given in kcal/kg

$$W = W_t + 9 \times H \text{ (%)}$$

Where:

W<sub>t</sub> – total moisture content

H - hydrogen fraction, dry basis

The second formula (no. 3), used in this work for the calculation of the high heating value is the one proposed by Dulong [5]:

$$HHV = 7831 \cdot C + 35932 \cdot H - O/8 + 1187 \cdot O + 578 \cdot N \text{ (kcal/kg)} \quad (3)$$

The results for the dried three types of materials are shown in the following tables:

Table 4

**Calculation of the calorific value for dried white grape marc**

White grape marc: Calorific value (kJ/kg)			
Demibras		Dulong	
HHV	LHV	HHV	LHV
13 242	13 207	21 575	21 562

Table 5

**Calculation of the calorific value for dried red grape marc**

Red grape marc: Calorific value (kJ/kg)			
Demibras		Dulong	
HHV	LHV	HHV	LHV
7 547	7 512	16 158	16 145

Table 6

**Calculation of the calorific value for dried sunflower oil cake**

Sunflower oil cake: Calorific value (kJ/kg)			
Demibras		Dulong	
HHV	LHV	HHV	LHV
12 031	11 989	22 668	22 651

Furthermore the high heating value of the materials was determined using the calorimeter bomb. The results are presented in Table 7. Lower heating value was obtained by the same correction factor, calculated according to formula no. (2).

Table 7

**Determination of the calorific value for dried products**

Material (dry)	HHV measured [kJ/kg]	LHV calculated [kJ/kg]
White grape marc	20 051	20 016
Red grape marc	20 397	20 362
Sunflower oil cake	21 129	21 087

The results obtained with the calorimeter validate only the results obtained by calculation with the Dulong formula, resulting that Demibras formula is not suitable for these types of biomass. Also the formula of Dulong best suits the white grape marc, and the sunflower oil cake, for the red grape marc further research is in progress.

### 3. Waste to energy conversion

For the power generation we considered the combustion process – Rankine/Hirn cycle due to its large-scale application, the residue biomass like characteristics and low pollutant content (S between 0.2 and 3.7 % - depending on residue type and wine process stage).

For the industrial processes (extraction, distillation, refining etc) important heat energy is required. This could be an advantage for the waste to energy conversion chain by adopting combined heat and power generation that increases the global energy efficiency to more than 80%. That leads to lower costs and lower pollution emissions compared to separated-energy production.

We considered a back-pressure steam cycle (imposed by the thermal level of steam consumption in the industrial process), which is useful for example for a continuous distillation or refining process that needs constant heat production. The option for back-pressure or adjustable steam extraction condensing turbine resides in owner developing strategy and feasibility studies. The situation presented here below is just an example for waste to energy conversion through combustion process. For the two scenarios mass and energetic balance it were taken into account the total amounts of grapes, respective of sunflower produced at a national level in the year 2007.

We assumed for the both types of products that the remaining waste represents 20% of the total amount nationwide produced based on specific data.

The studied integration of such a cycle in the industrial process is schematized in Fig. 3.

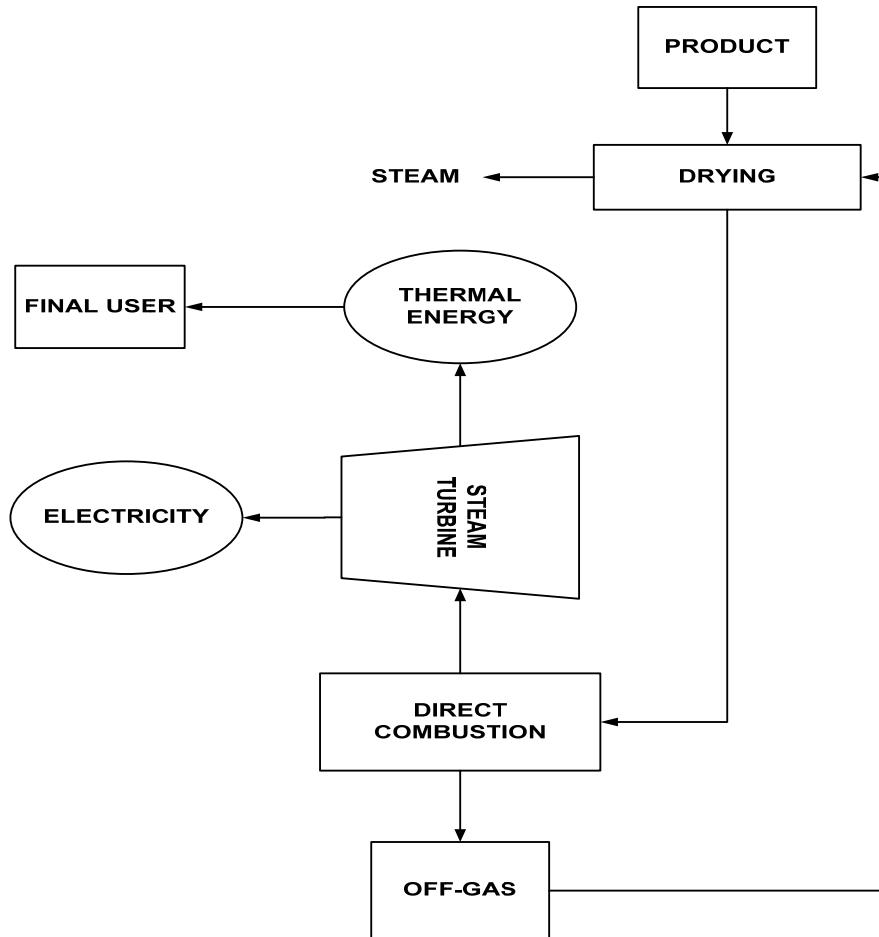


Fig.3. Process scheme for direct combustion with a steam cycle

### 3.1. Centralized energy production from grape marc recovery

In 2007 the amount of grapes produced nationwide was about 880 thousand tons. Estimating that 80% of this quantity is represented by wine, the rest of 170 thousand tons, about 20% is assumed to be grape marc.

Regarding the moisture content, it was assumed that the initial material had a 60% humidity, which was reduced to 8% by thermal drying (process performed by the recirculation of a certain part of the exhausted gases).

Assuming the combustion occurred in a fixed-grid combustor, at a temperature of about 1000°C. With an ingoing grape-pomace stream of 21.25 t/h (for 8000 h/y), it would be possible to obtain about 30.2 MW of thermal energy.

About 4% of that would be wasted in unburned material and combustion residues. Another 1.5% would be wasted in heat losses in different parts of the plant. The recoverable heat would be that in the smoke, so we evaluated the unusable enthalpy of the outgoing smoke, about 12.5%.

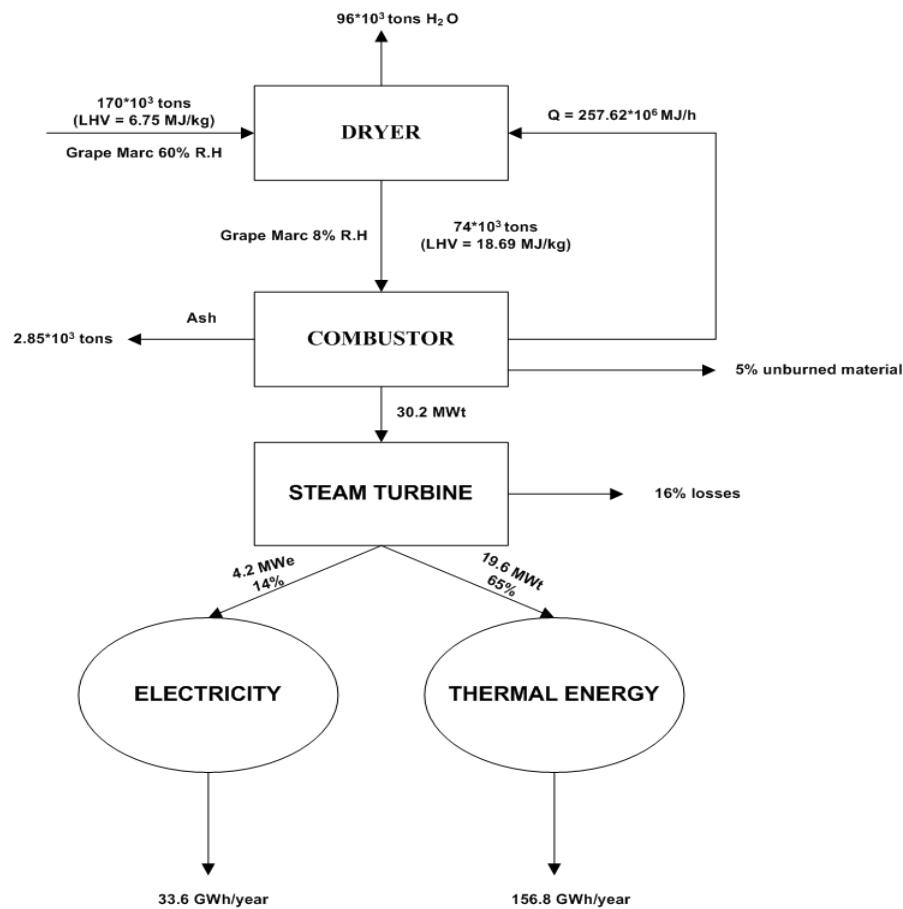


Fig.4. Mass and energetic balance for grape marc

The mass and energetic balance is presented in Fig. 4. The useful thermal power for the thermodynamic cycle would be equal to about 24.7 MW. Considering leaks in the electro-mechanical auxiliaries, equal to about 1% of the total power available at the beginning, we obtain 19.6 MW at the turbine outlet (65% of the initial power). The turbine connected to an alternator, would be able to generate 4.2 MW of electricity (14% of the initial power).

### 3.2. Centralized energy production from sunflower oil cake recovery

In 2007 the amount of sunflower produced nationwide was about 547 thousand tons. We estimated that 20% of this quantity is represented by sunflower oil cake, meaning that 110 thousand tons will be processed in energy recovery. Assuming the combustion occurred in a fixed-grid combustor, at a temperature of about 1000°C. With an ingoing grape-pomace stream of 13.75 t/h (for 8000 h/y), it would be possible to obtain about 64 MW of thermal energy. About 4% of that would be wasted in unburned material and combustion residues. The mass and energetic balance is presented in Fig. 5.

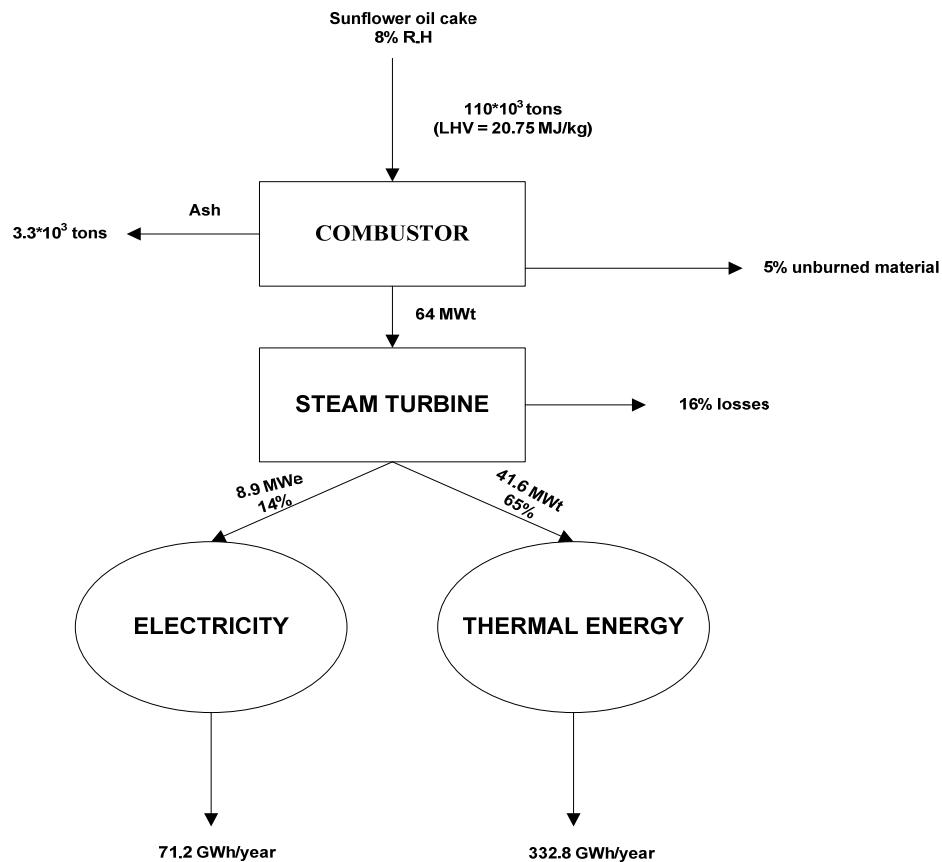


Fig.5. Mass and energetic balance for sunflower oil cake

Another 1.5% would be wasted in heat losses in different parts of the plant. The recoverable heat would be that in the smoke, so we evaluated the unusable enthalpy of the outgoing smoke, about 12.5% [6].

The useful thermal power for the thermodynamic cycle would be equal to about 52.48 MW. Considering leaks in the electro-mechanical auxiliaries, equal to about 1% of the total power available at the beginning, we obtain 41.6 MW at the turbine outlet (65% of the initial power)[7]. The turbine connected to an alternator, would be able to generate 8.9 MW of electricity (14% of the initial power). All the equipments efficiencies were chosen based on their capacity from literature. The solutions presented in this paper are based on overall estimation of the energy conversion chain, advanced studies focused on primary conversion stage being necessary. Further researches are now in progress.

#### 4. Conclusions

For Romania the wine and oil refining industry residues represent an important renewable energy source that was not valorized until now.

Due to a high degree of distribution on the Romanian territory, the uses for these particular wastes could be extended also for power generation.

The experimental study for combustibility properties quantification revealed the possibility of using grape marc and sunflower oil cake for power generation. The low heating value estimated on elemental analysis and directly measured with calorimeter is about 20,000 kJ/kg, over the average Romanian coal for both of the materials. The high volatile content of 72% qualifies these products for direct combustion in grate steam generators, if the water content is higher than 10% (the case of raw product).

For the two energy scenarios the total amounts of grapes respective of sunflower produced at national level for the year 2007, were taken into account. The scenarios presented in the paper is an example for biomass to energy conversion through combustion process using two different types of waste with high availability in Romania.

For advanced electricity production a combined heat and power generation solution can be used with benefits on product drying process and also heat production for wine industry own distilleries.

The option for the thermodynamic cycle type using steam turbine resides in owner developing strategy and feasibility studies.

#### Acknowledgment

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