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# Anaerobic digestion of grape pomace: Biochemical characterization of the fractions and methane production in batch and continuous digesters

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ABSTRACT

In this study, we have estimated the biogas and methane production from grape pomace (variety Cabernet Franc). The physical and chemical characteristics of the raw material were determined, and the structural polysaccharides were identified and analyzed by the Van Soest method. Batch anaerobic digestions were carried out to assess the methane production of the grape pomace, pulp and seeds. The obtained cumulative methane productions are 0.125, 0.165 and 0.052 $Nm^3$ kg $COD^{-1}$ for grape pomace, pulps and seeds, respectively. The effect of grinding on the methane potential of the substrates, as a mechanical pretreatment, was evaluated. We found that it increased the anaerobic biodegradability for grape pomace, pulp and seeds by 13.1%, 4.8% and 22.2%, respectively. On the other hand, the methane potential of the grape pomace was determined in a laboratory pilot plant (12 L) continuously mixed with an organic loading rate of 2.5 kg COD $m^3$ $d^{-1}$ and a hydraulic retention time of 30 days. The corresponding biogas production was $6.43 \times 10^{-3}$ $Nm^3$ $d^{-1}$, with a methane content of 62.3%. Thus, the pilot plant's efficiency compared to that achieved in the batch process was 81.2%. Finally, a significant correlation was found between the biochemical content and methane production.



## 1. Introduction

The significant growth in energy needs has not been adequately followed by renewable energy source development (Rühl et al., 2012). Changing society's dependence on petroleum-based sources to one on renewable biomass-based resources is considered a crucial element for developing a sustainable industrial society and for the effective management of greenhouse gas emissions (Clark et al., 2012).

Anaerobic digestion (AD) is a promising and potent approach for the sustainable valorization of biomass resources in a future biobased economy. It is divided into four phases, hydrolysis, acidogenesis, acetogenesis and methanogenesis (Noykova et al., 2002), which transform the organic matter into mainly a mixture of methane and carbon dioxide called biogas.

The AD of organic waste provides a variety of environmental and public health benefits including the production of a renewable energy platform, greenhouse gas abatement, the possibility of nutrient recycling, reduction of waste volume and odor reduction (Pham et al., 2014). It was reported that 1 $m^3$ of biogas from AD is equivalent to 21 MJ of energy, and it could generate 2 kW h of electricity (Murphy et al., 2004).

The organic fractions of agricultural waste and residues are considered promising renewable energy resources, and their potential can be exploited through an AD process. As French and Lebanese research groups, we have chosen as a starting point to focus on the by-products of winemaking, especially grape pomace (GP), which is the solid residue that remains after the processing of grapes into wine. GP contains skin, pulps and seeds. The grape (*Vitis vinifera*) is one of the most cultivated fruit crops worldwide; in 2012, the world grape production totaled 69.1 million metric tons (Castellucci, 2013). This biomass is available in many countries (as of 2014, 46 states are members of the International Organization of Vine and Wine), and its valorization is a global issue. For example, in France, the annual production of GP is currently approximately 700,000 tons, and its collection is organized for transport from the vineyards to the distilleries. However, these distilleries are energy-intensive. Thus, the electricity and heat produced during the AD of biomass have a direct benefit in highly reducing the dependence on energy imports. The AD of this waste

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also allows the stabilization of organic matter and the reduction of water content. In Lebanon, the GP annual production is estimated to be 1600 tons. This may seem relatively low, but it should be noted that this amount is mainly located in the Bekaa Valley, which facilitates the transport of the sources of biomass to a centralized biogas plant.

Through the decades, the utilization of GP for alternative uses has been minimal, with large portions discarded in landfills. Currently, GP is composted as fertilizer (Ferrer et al., 2001), processed into animal feed (Alipour and Rouzbehan, 2007) or extracted for grape seed oil and polyphenols (Ruberto et al., 2007). However, these applications have limited markets and can absorb only a small portion of the waste generated. As a result, alternative uses are needed to add value to GP (Dwyer et al., 2014); accordingly, its conversion into methane by AD is a promising possibility.

Few studies have been carried out on the AD of grape pomace. In 2010, the biogas potential of some Italian GP was evaluated. Experimental results highlighted their significant energetic potential (Dinuccio et al., 2010). In 2012, research was conducted to develop a thermodynamic equilibrium model of grape pomace anaerobic digestion for predicting the potential production of biogas and its composition. Simulation results showed that it is possible to obtain 94 kW h per ton of GP, covering up to 45% of the energy requirements for the wine-making process (Cáceres et al., 2012). The French Institute of Vine and Wine (IFV) organized a national experimental study from 2010 to 2013 on the reinstatement of these by-products, including the anaerobic digestion of GP. The results showed variability in methane potential depending on many factors such as color, origin and storage method of the grapes (Lempereur, 2014).

Given the aforementioned considerations, this paper focuses on an innovative experimental study carried out to assess and evaluate the methane production by anaerobic digestion for the GP of the Cabernet Franc variety (whole pomace, pulp and seeds). The main objectives were (1) to evaluate the "anaerobic" biodegradability and the maximum methane production of the fractions in batch mode (2) to investigate the effect of the mechanical pretreatment on the GP biodegradability (3) to understand the correlation between methane yield and main biochemical fractions identified by the Van-Soest method, and (4) to determine the biogas and methane production of the whole grape pomace in a scaled-up process using a continuously stirred tank reactor, CSTR. The data obtained are useful to conduct an industrial technical evaluation of the digester.

## 2. Materials and methods

### 2.1. Materials

The grape pomace variety Cabernet Franc was obtained from a winery located in Layon area, France. The grapes were carefully harvested at maturity during the 2013 vintage and the samples were collected immediately after the pressing operation. On arrival, the raw material was stored at −20 °C until utilization. It was ground using a blender (Waring blender 8011EG, Waring Commercial, USA) to avoid clogging the pilot pipes with fibrous materiel in grape pomace. An active inoculum was collected from a local agricultural digester operating under mesophilic conditions. The particulate matter (>1 mm) was removed from the inoculum by passing through sieve. The latter was subjected to a starvation period of 6 days before the start of the experiments, in order to facilitate the evaluation of the biodegradation of the substrate under study. A representative sample of the inoculum was collected and analyzed for total solids (TS), volatile solids (VS) and pH.

### 2.2. Analyses

Total Solids (TS) content were determined by dry weight in oven with forced air circulation at 105 °C until constant weight. Afterwards, Volatile Solids (VS) were determined in a muffle furnace after 4 h at 550 °C and then cooled in a desiccator and weighed. Total Chemical Oxygen Demand (COD) was measured using Merck COD Spectroquant® test, range 500–10,000 mg $L^{-1}$, and by a spectrophotometer NOVA 60 (Merck, Germany). One mL was introduced into the COD cell which is tightly attached to the screw cap and then put into the thermoreactor and heated for 2 h at 150 °C. It is assumed that all organic matter is oxidized with the hot sulfuric solution of potassium dichromate and with silver sulfate as the catalyst. The method is analogous to NFT 90-101. Total nitrogen (N) and total phosphorus (P) were performed using Spectroquant® tests, range 1.0–150 mg N/L and 0.5–25 mg P/L respectively. These methods are analogous to EN ISO 11905-1, DIN 38405-9 and EN ISO 6878.

### 2.3. Van Soest fractionation

The characterization of structural polysaccharides and lignin was carried out by the method of Van Soest, which presents the best compromise between the data obtained on the nature of the structural polysaccharides constituting the lignocellulosic biomass and the time of analysis required to obtain this information (Godin et al., 2011). The method of Van Soest (Mertens, 2002; Soest et al., 1985; Van Soest et al., 1991) can extract nonstructural carbohydrates, pectins, mucilage, soluble tannins to neutral pH, lipids, soluble proteins to neutral detergent and some ash with a neutral detergent solution in excess, acting on the sample for 1 h at 100 °C. This neutral detergent solution is composed of $Na_2HPO_4$, sodium tetraborate, α-amylase, sodium EDTA, sodium lauryl sulfate and sodium sulfite. These products were provided by Merck (Germany). The extracted fraction is separated from the insoluble neutral detergent fibers (NDF) by filtration. Following the action of the neutral detergent, an excess of acid detergent solution (cetyltrimethyl ammonium bromide 2%, $H_2SO_4$ 1 N) acting for 1 h at 100 °C can extract hemicellulose. The extracted fraction is separated from the insoluble acid detergent fiber (ADF) by filtration. Cellulose is extracted by treating the ADF fraction with 72% $H_2SO_4$ for 3 h at ambient temperature. The filtration residue, named ADL, corresponds to the lignin associated with the inorganic material. Hemicelluloses and celluloses were calculated as the differences between NDF and ADF and between ADF and ADL, respectively. The lignin content is equal to the ADL less the ash contained in the ADL (after calcination at 550 °C). Chemical compounds that are not cellulose or hemicellulose, lignin, or ash are called "soluble compounds". For each substrate, four to six samples were analyzed.

The Pearson correlation "r" was determined to evaluate the relationships between methane production and the main chemical parameters of the tested biomasses using SPSS software.

### 2.4. Mechanical pretreatment and particle size analysis

Grape pomace was grinded by means of a blender (Waring blender 8011EG, Waring Commercial, USA) in a total volume of 0.8 L for 10 min and with a speed of 22,000 rpm. It should be noted that every minute of grinding was followed by a minute of pause in order to avoid the increase of the temperature in the solution. The particle size distribution was determined after grinding the GP to reach a concentration of 250 g TS/L in water. Samples were diluted and dispersed in a stirred cell before being analyzed. Particle size was determined by laser light scattering (Mastersizer 2000, Malvern Instruments, UK). The particle size distribution is