



# Effect of leaching pretreatment on the gasification of wine and vine (residue) biomass



Siim Link<sup>b,\*</sup>, Stelios Arvelakis<sup>a</sup>, Aadu Paist<sup>b</sup>, Truls Liliedahl<sup>c</sup>, Christer Rosén<sup>c</sup>

<sup>a</sup> Bioresource Technology Unit, Laboratory of Organic and Environment Technologies, Department of Chemical Engineering, National Technical University of Athens, Zografou Campus, GR-15700, Athens, Greece

<sup>b</sup> Department of Energy Technology, School of Engineering, Tallinn University of Technology, Ehitajate tee 5, 19086, Tallinn, Estonia

<sup>c</sup> Division of Chemical Technology, KTH Royal Institute of Technology, Teknikringen 42, SE-100 44, Stockholm, Sweden

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## ABSTRACT

Utilization of biomass residues for energetic purposes increases the share of renewables in the total energy balance. Gasification is one of the thermochemical processes that converts solid biomass to valuable gaseous products. Prior to the gasification process, biomass material could be treated to improve the quality or composition of the product gas. Our focus is on fluidized bed gasification of untreated vine and pretreated vine residue and pretreated wine residue. Natural and artificial leaching were used as pretreatment methods. Our results showed that CO and H<sub>2</sub> content in the product gas are higher in leached (16.9 and 10.0% respectively) vine residue than in untreated material (14.5 and 7.7% respectively). The naturally leached wine residue was found to have the highest CO content (18.1%) and relatively high H<sub>2</sub> content (9.7%) in the product gas, but lower CH<sub>4</sub> (1.0%) and CO<sub>2</sub> content (5.6%). The results of tar measurements indicated that the leaching pre-treatment lowers the tar content in the evolved product gas, e.g. by 36% in the case of vine residues. As a result, the controlled leaching pretreatment is recommended as an effective way of upgrading the composition of agricultural biomass.

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## 1. Introduction

In order to save fossil fuels and prevent global warming, biomass fuels have been given increased attention [1]. Fossil fuels are the primary feedstock for energy/fuels production in the world, but the use of biomass for energetic purposes will decrease the consumption of fossil fuels, and also helps to reduce the greenhouse gas (GHG) emissions. Bioenergy is expected to become one of the major energy resources in the future [2]. Among all thermochemical conversion processes, gasification is one of the most promising routes for the conversion of biomass to energy and fuels. Compared to combustion, gasification exhibits improved energy efficiency in combined cycle plants, reduced emissions, and lower operating temperatures. The conversion of solid biomass to gaseous fuel provides opportunities for retrofitting coal-fired boilers, replacing natural gas in process heating, and developing distributed power systems using biomass that are based on internal combustion engines, gas turbines, or fuel cells [3]. The main reactor types used for

biomass gasification are the fixed bed and the fluidized bed reactors. Fluidized beds exhibit excellent heat and mass transfer between the gas and the solid phase as well as temperature distribution, high specific capacity and fast heat-up. They can tolerate wide variations in fuel quality as well as a broad particle size distribution. However, high dust content in the gas phase as well as arising agglomeration/defluidization behaviour in the case of biomass materials with low melting point ash (due to the presence of the constituents such as alkali metals and chlorine) pose a serious problem for the fluidized bed reactors [4–7]. The distribution of the gasification products could be influenced by different kinds of biomasses and their mixtures under gasification conditions and it is important to study the behaviour of different biomass materials and their mixtures under gasification conditions in terms of the optimization of process parameters and reactor design [8,9].

Many biomass feedstocks benefit from pretreatment to improve physical and chemical properties for downstream energy conversion, both thermochemical and biochemical [10]. One of them is a leaching pretreatment method targeted on the removal of alkali metals, sulphur and chlorine from the biomass material prior to thermochemical conversion [11].

Wine and vine residue are the by-products of the wine industry

\* Corresponding author.

E-mail address: [siim.link@ttu.ee](mailto:siim.link@ttu.ee) (S. Link).

in many countries in the Mediterranean region and their potential as a source for energy production requires investigation. For instance, in Greece, approximately 200 thousand tons of wine residues and 560 thousand tons of vine residues are produced per year [12].

This work studies the fluidized bed gasification of the untreated as well as the pretreated (leached) vine residue, the naturally leached wine residue, and the mixture of the naturally leached wine and the untreated vine residue. Our analysis focuses on the effect of the leaching pretreatment process under controlled as well as under natural conditions on the product gas composition and tar components on the wine and vine residue materials.

## 2. Materials and methods

### 2.1. Materials

We selected two parent fuel biomass materials, such as wine and vine residues, for our study. Both of them originate from Greece and come from Sitia prefecture in Crete. The used materials were prepared and characterized in accordance with American Society for Testing and Materials (ASTM) methods, such as D 2013-86 (Reapproved 1994), D 1102-84, D 3175-89a, D 5142-90, D 5373-93, D 4208-88, D 2015-95 - proximate and ultimate analysis, gross calorific value and ash analysis.

In gasification tests, next parent fuels and blends were used: a) untreated vine residue (UVR), b) leached vine residue (LVR), c) naturally leached wine residue (NLWR), and d) the blend of 50% of untreated vine residue and 50% of naturally leached wine residue (50UVR/50NLWR).

### 2.2. Leaching

The artificial leaching pretreatment procedure was applied on the vine residue. Artificial leaching of the vine residue was carried out according to the method developed by Arvelakis and Koukios [13]. During the leaching process, the sample was put in a 200-mesh plastic grid, tied up and submerged into tap water in a plastic 75 l volume barrel. The used mass/water ratio was 88.8 g/l and the retention time was 12 h. At the end of the process, the sample was left to air dry until constant weight under the sun of the Mediterranean summer for a period of 5 days. During the drying process, the bed thickness of the drying sample was kept below 15 cm to guarantee the fast drying process without material loss due to mold.

Wine residue was exposed to the natural leaching during the winter period of 2006–2007. However, we were unaware of the amount of precipitation received during that time.

### 2.3. Gasification set-up

The atmospheric fluidized bed gasifier was used in this study. The gasification set-up coupled with a schema is described in detail elsewhere [14]. However, we present here some essential data regarding the experiment: the feeding rate of the screw feeder was 4 g/min; the gasification agent used: nitrogen with a flow rate of 9.5 l/min and oxygen with a flow rate of 0.85 l/min; the gasification tests were performed with a reactor temperature of 800 °C.

### 2.4. Evolved gas analysis

The components of the evolved product gas (CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>) were determined by gas chromatography (Shimadzu GC-9AM), which comprises a thermal conductivity detector (TCD) and a flame ionization detector (FID), as described elsewhere [14].

### 2.5. Tar sampling

The tar content of the evolved product gas was measured by the solid-phase adsorption (SPA) method developed by Brage et al. [15], as described in Ref. [14]. The advantages and disadvantages of this method are discussed in Ref. [14].

### 2.6. Brief description of the gasification test procedure

The reactor was heated up to the desired temperature (800 °C) using external electrical heaters. After the reactor temperature was stabilized, the fuel was fed in. The evolved product gas was led only through the ceramic filter and the tar sampling was carried out. During the experiment, the gas composition was determined after every 10 min by the gas chromatograph. The tar sampling was carried out right after the moment the gas chromatograph finished the suction of the product gas for the analysis.

## 3. Results and discussion

### 3.1. Fuel characterization and composition

The leaching pretreatment decreases the ash content of the vine residue (Table 1). The relatively high ash content of the naturally leached wine residue is attributed to the occurrence of the soil material in the sample due to its long stay outdoors during the natural leaching process. In general, it was observed that the amount of ash is reduced via the leaching pretreatment. In addition, due to leaching, the chlorine content was reduced, but the volatile matter content was increased. Previous research results from Arvelakis [12] regarding wine residue verify these assumptions. Also, previous studies have indicated increased volatile matter content after leaching [14,16]. It is clear, that the naturally leached wine residue exhibits extremely low gross calorific value for the biofuel due to the high content of mineral matter, as discussed above. The effect of the leaching pretreatment on the increase of the gross calorific value of vine residue is low, amounting to 5%.

It can be seen from Table 2 that the naturally leached wine sample has relatively high SiO<sub>2</sub> content of 36.8% in ash, which corresponds to 5.4% of Si content of the parent material. This amount is assumed to be much higher than that in the untreated wine residue (0.8% is Si content in the parent fuel), which is attributed to the soil pollution of the leached material. At the same time, the alkali metals (except Mg) and the chlorine content of the leached wine residue were reduced moderately compared to the untreated wine residue. The content of alkali and alkali earth metals and chlorine is lower in the leached vine residue under the controlled leaching conditions compared to the uncontrolled natural leaching of wine residue. This leads to the result that the controlled leaching process produces better results than the natural leaching process. The Si content of the parent material for the untreated and pretreated vine residue is 0.24%. The K<sub>2</sub>O content calculated on the basis of the parent material is 8.3% or the K content of 6.9% for the naturally leached wine residue. The K content of the untreated vine residue in the parent material is 0.38% compared to that of 0.24% in the leached material. The Na content of the untreated vine residue in the parent material is 0.078% compared to that of 0.041% in the leached material. The reduction of potassium is 37% after leaching and for sodium 47%. The chlorine content is reduced after leaching from 0.0042% down to 0.00062% (decreased by 85%), and the sulphur content is reduced after leaching from 0.020% down to 0.014% (decrease by 30%) calculated on the basis of the parent material in the case of the vine residue. The CaO content in the naturally leached wine residue ash is quite moderate, but due to the high ash content, the total amount of Ca

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