

# Vinasse as a Potential for Renewable Energy and Chemicals Recovery

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## INTRODUCTION

Vinasse, also known as stillage, still bottoms, spent wash, slops, vinhaca, vinhoto, dunder, or mosto, is a dilute effluent from the integrated sugar-ethanol industry. Typically, the dry solids content of vinasse is only 5-10 wt.%. On a dry basis, vinasse contains 60-70 wt.% organics with the balance being inorganics, and it has a heating value in the range of 10-15 MJ/kg [1]. Production of 1 m<sup>3</sup> ethanol generates on average 10-15 m<sup>3</sup> of wet vinasse [2]. In Brazil alone, the annual generation of vinasse is approximately 370.10<sup>6</sup> m<sup>3</sup> [3] which is equivalent to an average annual thermal energy supply of about 125 TWh. Nevertheless, compared to other by-products, such as straw and bagasse, from the integrated sugar-ethanol process, the vinasse constitutes only about 3% of the energy in the cane. This energy share of the vinasse is, however, for a sugar mill which produces ethanol only from molasses, the final residue from sugar production. In case when the cane juice, in addition to the molasses, is used to produce ethanol, the energy share of the vinasse increases significantly.

Typical ash content, elemental composition, and heating values of vinasse from our previous work [4,5] are given in Table 1. In addition, analysis of the vinasse using solution state NMR shows that the water-soluble organic components of vinasse are mainly glycerols, lactic acid, acetic acid, carbohydrates, proteins, and aromatic groups.

**Table 1:** Ash content (wt.%), elemental composition (wt.%), and heating values (MJ/kg) of vinasse (db, dry basis).

Ash	Elemental composition													Heating value	
	C	H	N	O	K	Na	Ca	Mg	Si	Fe	P	S	Cl	HHV	LHV
34.1	32.9	4.5	1.0	36.4	14.1	0.4	3.2	0.6	0.6	0.1	0.1	2.7	6.2	14.0	13.0

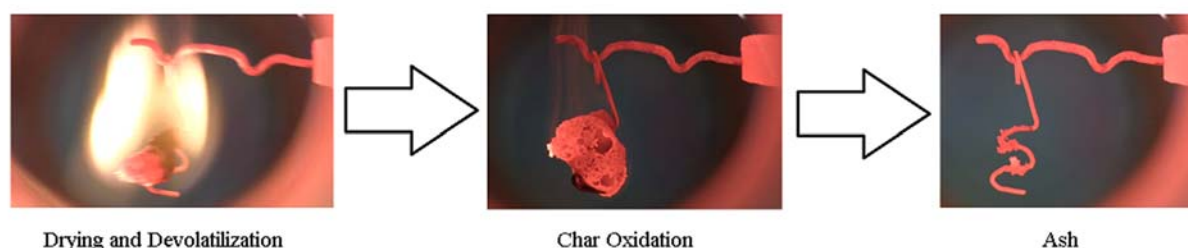
Today, vinasse is mainly used for fertirrigation, providing the soil with water and at the same time fertilizing the soil for sugarcane plants. In some cases, the amount of vinasse produced is greater than the amount of vinasse that can economically be used as a fertilizer. This is because of the cost of transporting it to farmlands farther away from the mill. Thus, there is a need for the development of alternative utilization options.

Thermochemical conversion processes, such as combustion, gasification, and pyrolysis, besides alleviating the environmental problems, have the advantage of recovering the organic fractions of vinasse as energy and chemicals. Also, the ash from these processes can be returned to the soil as fertilizer.

The purpose of this paper is to provide a summary of vinasse pyrolysis, combustion, and gasification results based on our recent studies and literature data. The paper also points out some potential challenges of vinasse thermochemical conversion processes.

## COMBUSTION

It has been shown that vinasse burns in a similar fashion as black liquor and other biomass fuels: the vinasse undergoes drying, devolatilization, and char oxidation, and it swells significantly during the devolatilization stage. Figure 1 shows the stages of vinasse combustion, with the drying and devolatilization stages overlapping, from experiments carried out in a quartz glass reactor, also known as single particle reactor (SPR), at Åbo Akademi. However, Patel [6] and Cortez et al. [2] were unable to obtain stable or sustained flame during combustion of concentrated vinasse in lab-scale setups without auxiliary fuel as input. Also, a recent study by Akram et al. [7] shows that co-combustion of vinasse with coal in a 25 kW fluidized-bed reactor caused agglomeration problems. Although, vinasse combustion has not yet been successfully carried out industrially, boiler suppliers [8] have recently embarked on the design and development of special boilers for burning concentrated vinasse.



**Figure 1.** Vinasse combustion stages (10 mg droplets having 67.4 wt.% dry solids in 10%O<sub>2</sub>/90% N<sub>2</sub> at 900 °C).

## PYROLYSIS

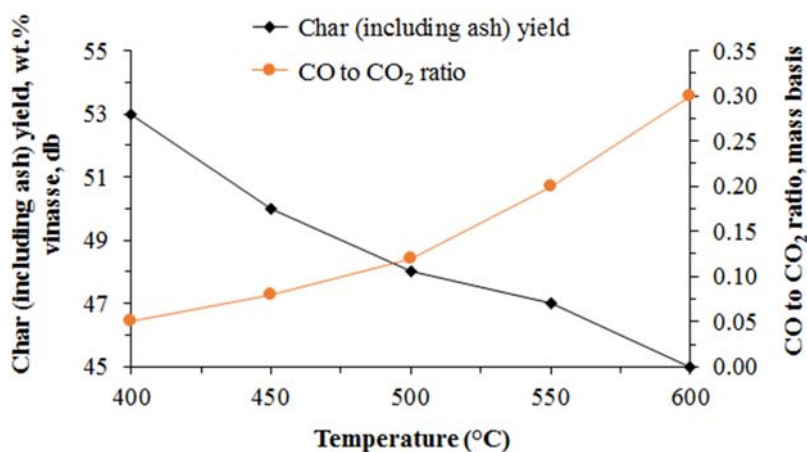
Recently, we have investigated fast pyrolysis of dried sugarcane vinasse in a drop-tube type reactor at 400 and 500 °C. The objective was to determine pyrolysis product distribution and yield. The char (including ash) was in the range of 48-52 on a wt.% dry vinasse basis, whereas the liquid (including water) and gas yields were in the range of 17-20 wt.%.

Analysis of the chars from the pyrolysis experiments using an ICP-OES revealed that most of the potassium in the vinasse was retained in the chars. The retention of most of the potassium in the chars has an important practical implication: pyrolysis may be an interesting option for the recovery of potassium from vinasse for fertilizer. Moreover, further analysis of the chars with a CHNS(O) elemental analyzer showed that, on average, 50% of the carbon in the vinasse was retained in the chars. Therefore, returning the chars to the soil, apart from recovering the potassium for fertilizer, could sequester approximately 50% of the carbon in the vinasse that would otherwise contribute to GHG emission.

The liquid pyrolysis product yield was low compared to the typical 30-70% [9] yields reported in the literature for other biomasses. The high ash content of the vinasse, especially alkali metals, may be the cause for the low oil yield results. Alkali metals in biomass fuels are known to catalyze secondary reactions in the vapor-phase of the pyrolysis product thereby reducing the organic liquid yield and increasing the gas and water yields. Analysis of the pyrolysis oils using a GC-MS indicated that the oils are composed of mainly butanediols, cyclopentenones, cyclopentanones, phenols, and methylated pyridine. These compounds are most likely from the sugars and proteins present in the vinasse.

Analysis of the gaseous pyrolysis product using an online CO and CO<sub>2</sub> gas analyzers showed that the gaseous product is mainly composed of CO<sub>2</sub> at both 400 and 500 °C. Additional data for char yields and CO and CO<sub>2</sub> release during fast pyrolysis of the vinasse in the temperature range of 400-600 °C were obtained using the SPR, which is a simpler setup than the drop-tube type reactor. Figure 2 shows the char yield and CO to CO<sub>2</sub> ratio results from the SPR. As seen in the figure, the

CO to CO<sub>2</sub> ratio increased as the temperature was raised. This is an advantage from the perspective of improving the energy content of the pyrolysis gas, which could be burned in a boiler to produce heat and power. However, from potassium recovery aspect, increasing the temperature has two main drawbacks. Firstly, the char yield decreases with temperature prompting release of potassium into the pyrolysis liquids and gases. Secondly, alkalis in the liquid and gaseous pyrolysis products will have adverse effects on downstream equipment that utilizes the pyrolysis liquids and gases. Therefore, the choice of the optimum temperature for the vinasse pyrolysis requires trade-offs between the contradicting outcomes: potassium recovery vis-à-vis energy content of the gaseous product.



**Figure 2.** Results of vinasse char yield and CO to CO<sub>2</sub> ratio from the SPR.

## GASIFICATION

Dirbeba et al. [4] have investigated CO<sub>2</sub> gasification of vinasse chars and the release of ash-forming matters in CO<sub>2</sub> and N<sub>2</sub> gas atmospheres using a DSC-TGA at temperatures between 600 and 800 °C. The vinasse chars were produced in the SPR at 800 °C in N<sub>2</sub>. The study has shown that, in addition to gasification by CO<sub>2</sub>, several other mechanisms were contributing to the char weight losses in the DSC-TGA. The mechanisms contributing to the char weight losses include reduction of alkali carbonates and vaporization of the alkali metals, sulfate reduction, autogasification, and evaporation of alkali metal salts. Also, the study has revealed that pyrolysis is the main mechanism for the release of organics from vinasse.

Patel [6] studied gasification of vinasse concentrated to 70-75% solids in a lab-scale setup under sub-stoichiometric air conditions. His report shows that 95-96 % carbon conversion was achieved, and the composition of the gaseous product was CO<sub>2</sub> = 10.0-11.5%, CO = 10.0-12.0%, H<sub>2</sub> = 6.7-8.0%, CH<sub>4</sub> = 1.75%, H<sub>2</sub>S = 0.2-0.4%, and about 2% of water vapor. Patel, concludes that concentration of vinasse to high solids content followed by introduction into a furnace with air at sub-stoichiometric conditions in a countercurrent provides the basis for the design of a process for vinasse gasification.

## CHALLENGES

There are two main potential challenges for thermochemical conversion of vinasse for heat and power production and recovery of chemicals. First, the high energy required to concentrate the dilute vinasse to high solids content. Nevertheless, there are some options that can potentially address this problem, including heat and materials integration in the sugar, ethanol, and energy production processes [10,11] and improving the energy efficiency of the integrated process through technology upgrading [12].

The second and most serious challenge is the release of alkali and alkali chlorides during vinasse thermochemical conversion. It has been shown that high levels of alkali, together with high ash content, in biomass fuels are the main cause for ash-related problems in boilers and gasifiers. These problems include ash deposition, fouling, slagging, sintering, agglomeration, and corrosion. We have observed in our previous work [4] that the K+Cl release from vinasse in N<sub>2</sub> and CO<sub>2</sub> gas atmospheres increased almost linearly with temperature with the release level being more in N<sub>2</sub> than in CO<sub>2</sub>. At 600 °C, about 15-30% of the K+Cl in the vinasse was released, while the K+Cl release increased to 70-85% at 800 °C.

Form the point of view of addressing the second challenge and recovering the inorganic fraction of vinasse, pyrolysis of the vinasse at temperatures below 600 °C seems to be an interesting option. This option also provides the opportunity for the liquid and gaseous products to be utilized for heat and power production.

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