

The study of the supercritical water gasification process to solve the biomass waste problem for the alcohol-producing networks

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Abstract

The biomass is the whole organic matter of vegetable or animal origin. This material can be valorised by various ways:

- it can be used by manufacturers (lumber, paper, bio-chemistry);
- it can be used as energy (heat, electricity, fuel);
- it can be used as food or in cosmetics.

The biomass for energy purposes contains plants resulting from cultures and from waste. The dedicated energy cultures are various: oleaginous plants, grasses like corn and sugar cane (carbon rich vegetables), wood... The waste can be solid (industrial, agricultural or domestic) or liquid (waste water, animal dejection...).

Various processes are nowadays used to valorise biomass. This work deals with the evaluation and the optimization of the potentialities of the biomass gasification in supercritical water. The objective is to demonstrate the potential of this process to treat various biomass and residues or organic waste to obtain a syngas with a high hydrogen yield as well as a competitive global energetic balance compared to the other thermal gasification processes.

The chosen bio-resources of this work are the residues of the industrial sector of production of agricultural alcohol (beet and cereal) and wine-producing distilleries. It is thus essentially about marcs of grape, pulps of beets and cereal straws.

In this work, experiments have been carried out at different conversion severities, using a 100mL batch reactor, during 0-60 min, at a pressure of 25 MPa and at temperatures comprised between 400°C and 500°C.

Complete products analyses will be presented. Particularly detailed gas analyses have been performed.

Correlations between the experimental operating conditions and these analyses will be discussed in order to determine optimal experimental conditions to gasify the chosen biomass.

1. Introduction

The conversion of organic waste material to energy can proceed along three main pathways – thermochemical, biochemical and physicochemical. Thermochemical conversion, characterized by higher temperature and conversion rates, is best suited for lower moisture feedstock and is generally less selective for products. Thermochemical conversion includes incineration, pyrolysis and gasification. Bio-chemical conversion processes, which include anaerobic digestion and fermentation, are preferred for wastes having high percentage of organic biodegradable matter and high moisture content. The physicochemical technology involves various processes to improve physical and chemical properties of solid waste. The combustible fraction of the waste is converted into high-energy fuel pellets which may be used in steam generation. Fuel pellets have several distinct advantages over coal and wood because it is cleaner, free from incombustibles, has lower ash and moisture contents, is of uniform size, cost-effective, and eco-friendly.

Gasification is the conversion of biomass to a gaseous fuel. There are many gasification technologies that could potentially be part of the future energy industry. Gasification process converts the intrinsic chemical energy of the carbon in the biomass into a combustible gas.¹

Supercritical biomass gasification process (SCBG) is a suitable gasification process for wet biomass.² It is potentially more efficient than conventional thermal processes which require energy for drying the biomass.

Biochemical processes proceed slowly and lead to unconverted matter. Moreover in the SCBG process water acts as a solvent and as a reactant. Another interesting feature of the SCBG process is its selectivity. Low temperature (200-400°C) favours the production of a methane-rich gas, whereas high temperature (600-800°C) leads to a hydrogen-rich gas.³

In this paper we propose the study of the gasification of real biomass coming from the winery industry. These biomass were treated in supercritical water at various temperatures. We have also turned our attention to physicochemical analyses before and after the reaction in order to better understand the SCBG process. Detailed analyses of the gas phase have been carried out.

2. Experimental instruments and materials

2.1 Batch reactor

Experiments of biomass gasification in supercritical conditions are carried out in a batch reactor in Inconel 625. The experiments have been performed at temperatures above 600°C and a maximal pressure of 350 bars, during 0-60 min. A scheme of the experimental set-up used in this study is shown in the figure 1.

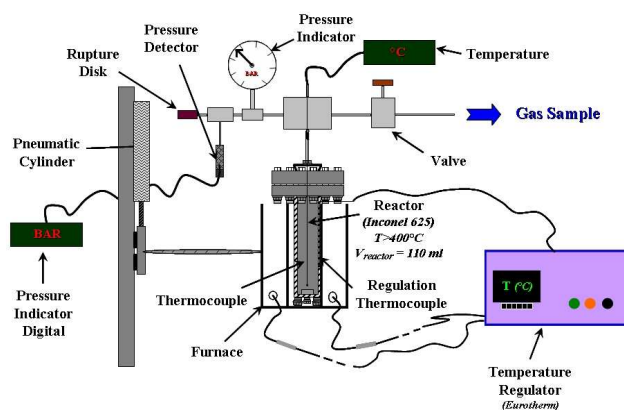


Figure 1. Scheme of the batch reactor used for the supercritical biomass gasification.

The experimental set-up is composed of security parts and control equipments such as a digital pressure indicator connected to a pressure detector, a pressure indicator, a valve for the gas collection, thermocouples (in the batch reactor and in the furnace), a rupture disk (400 ± 10 bars), a temperature regulator (Eurotherm) and a mobile furnace (with a pneumatic cylinder) allowing the interruption of an abrupt temperature increase. Initially the reactor has been purged with nitrogen in order to remove oxygen from it.

The chosen bioresources come from the wine-producing sector. These resources have been selected between all the residues of this industrial sector. The chosen ones are coming from a distillery located near Bordeaux (France). There are the “liquid” resources: the effluent (obtained after the production of ethanol) has less than 5% of particles in suspension in water, two winegrape slurries called the concentrated “vinasse” and the clarified “vinasse”, whose concentrations are different. These slurries present a very viscous aspect, similar to caramel. Figure 2 is a picture of the clarified “vinasse” and of the effluent.



Figure 2. Picture of the clarified “vinasse” (on the left) and of the effluent (on the right)

The reasons of this choice are that the water contained in the biomass is used as a reactant in the supercritical processes, and the supercritical biomass gasification process (SCBG) has the natural capacity to convert the wet biomass.² The experiments have been carried out at the temperatures 400, 450 and 500°C, and at a pressure of 250 bars.

2.2 ICP-OES Analysis in inorganic components

The determination of inorganic elements of the resources is performed by an ICP-OES analysis (Inductively Coupled Plasma Optical Emission Spectrometry). The application of electric tension between two electrodes forms a sparks discharge (plasma). The electric energy is converted in heat-energy who is strongly concentrated on the sample and it permits to vaporize, to atomize, to ionize and to excite this sample. The inorganic elements contained in the analysed sample are excited in the plasma to form atoms or ions. The desexcitation of this atom or ions generate the photon emission.

Nowadays, the ICP-OES analysis is used for the analysis of the major inorganic components and the traces contained in different types of resources. However, the difficulty of this analysis is the mineralization of the sample. It needs a mineralization step with microwaves

after the previous addition of concentrated nitric acid the addition of water and of hydrogen peroxide. This method is very efficient in terms of detection and yields in comparison with the more common methods.

The inorganic elements we have detected and quantified in the chosen bioresources are: Al, As, Ba, Ca, Cr, Fe, K, Mg, Na, P, Si and Zn.

2.3 Gas analysis (GPC)

The gas chromatography is used generally for the separation, the identification and quantifications of gas sample. The chromatography principle lies on the species distribution or solutes between two phases, a stationary phase and a mobile phase. While the mobile phase drives the species to separate molecules, the stationary phase tends to delay them. Interactions between stationary phase and each solute in the sample define different speeds movement according to the interactions intensity, inducing the possibility of solutes separation. The mobile phase is an inert gas called vector gas and the sample analysed is a gas. The peak area gives the solute concentration thanks to an external calibration.

The first instrument used is a “micro-chromatograph” Varian CP-4900 (called “micro-{GC}”). It is a mobile analysis instrument conceived for plugged on-line on an installation thanks to its small size. The instrument has two columns for the separation of different gases. Each column is bound to a catharometer TCD (« Thermal Conductivity Detector »). The principle is the measure of a difference of thermal conductivity deducted of the filament resistance variation, during the passage of the gas. The detector sensibility is 50 ppm. This instrument is used for the detection of H₂, O₂, N₂, CH₄ and CO.

The second instrument used is a gas chromatography Varian (GC-3600) for the analysis of CO₂. Two detectors are present: TCD and FID (Ionization Flame Detector). The detector sensibility is of a few ppm. A capillary column is connected to FID (Carbowax for polar compounds and particularly flighty hydrocarbons). Two columns are connected and are on-line to TCD (a column Porapaq for the separation of CO₂ one others gas, and a molecular sieve separating the others gas). A system of valves separates CO₂ from the molecular sieve.

3. Results and Discussion

3.1 Analytical strategy

During the process, the aqueous biomass has been treated at supercritical operating conditions. It results that at the end of the reaction four different phases have been collected: a gas phase, an organic solid phase, an organic liquid phase, and an aqueous phase. According to the

operating conditions, the yields of the different phases will be different, as well as their physicochemical properties. It is the reason why several analyses have been or will be carried out in order to follow the behaviour of the biomass during the process. These analyses will allow us to understand the key parameters to optimise the gasification process. The following scheme (Figure 3) shows the different analyses which are or will be performed later.

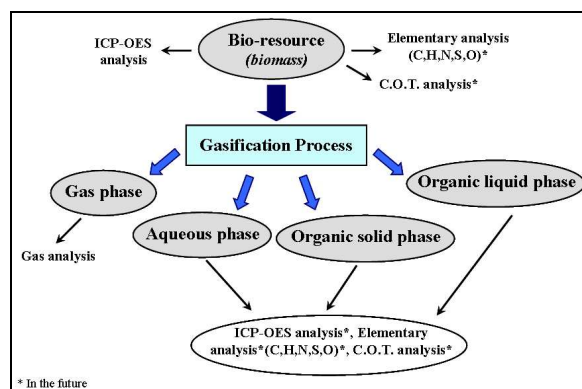


Figure 3. Scheme of the analytical strategy used in this work.

3.2 Analysis ICP-OES of bio-ressources

Various methods have been used to determine the amount of the inorganic elements.⁴ We have chosen ICP-OES method as described in the experimental session. It must be pointed out that the total inorganic elements amount counts for 5% w/w maximum of the total elements of the biomass. But the ICP-OES analyses have been carried out with the objective to study the hypothetic influence of the inorganic elements of the biomass on the thermal conversion. It is well known that metals catalyse the SCBG process, as alkali metals and alkaline earth metals do.⁵ At the moment, the ICP-OES analyses have been performed only on the initial biomass. The results obtained by the ICP-OES analysis (Figure 4) show that the major element contained in the effluent, in the concentrated “vinasse” and in the clarified “vinasse” is potassium. The amount of potassium is between 66.70% and 71.76% molar of the total inorganic elements of the samples. For the concentrated “vinasse” and the clarified “vinasse”, the analyses show a relative important amount of sodium. It is between 22.20% and 24.86% molar of the total inorganic elements of the samples. The effluent is a biomass which contains more phosphorus than the concentrated “vinasse” and the clarified one: 12.03% molar of the total inorganic elements of the sample *versus* less than 4% for the others. Further analyses will be conducted in order to evaluate the quantity of the inorganic elements in the different phases obtained at the

end of the process. The aim will be to understand if necessary the role of each one as a catalyst during the process.

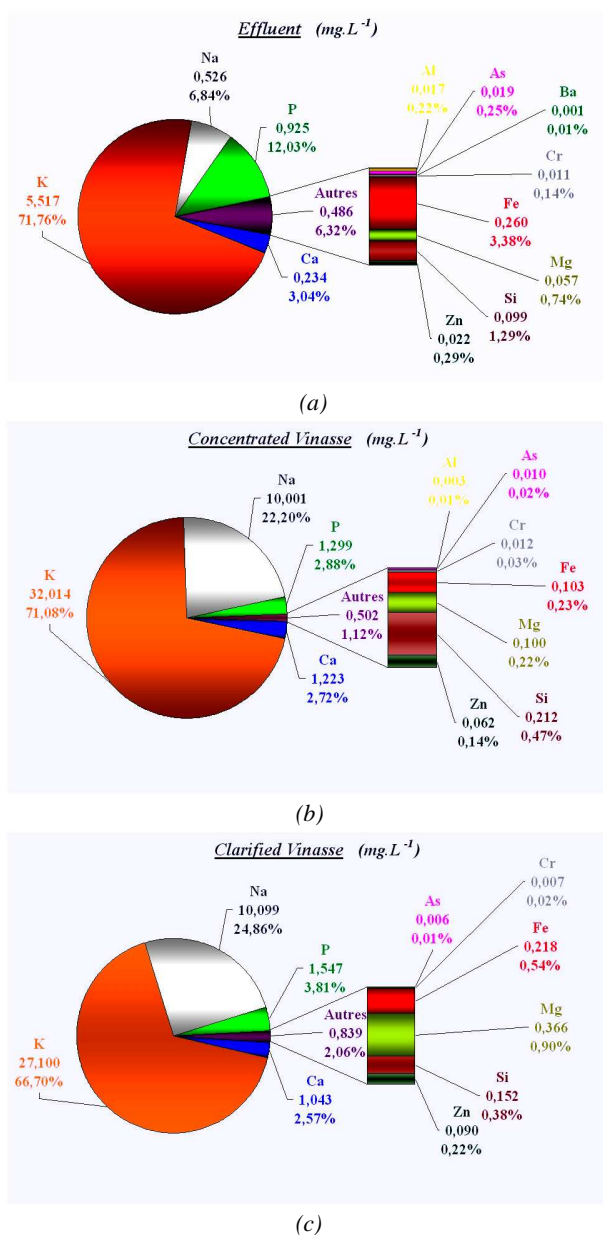


Figure 4. Composition in inorganic element (mg.L⁻¹) of the effluent (a), of the concentrated "vinasse" (b) and of the clarified "vinasse" (c).

3.3 Yields of the process

The results obtained during the gasification process are presented in this part. Table 1, table 2 and table 3 show the yields of the different phases at the end of the supercritical reactions. The yield of the organic solid phase is counted after an efficient drying. And the yield of the aqueous phase is the sum of the recovered water

and the water of the drying of the organic solid phase. The last column is the total yield. It allows to know the efficiency of the process in term of mass balance.

The process has a suitable total yield. No striking trend has been appeared regarding the yields of the different phases. But no organic liquid phase has been obtained for the effluent whereas about one third of the resulted mass is an organic liquid phase for the winegrape slurries. The amount of the organic solid phase keeps a relative low value whatever is the treated biomass.

T (°C)	yield aqueous phase (%)	yield organic solid phase (%)	yield gas phase (%)	mass balance (%)
500	97,21	0,27	0,58	98,06
400	98,03	0,34	0,30	98,67

Table 1. Yields (%w/w) of the different phases collected at the end of the gasification reaction of the effluent (400°C and 500°C).

T (°C)	yield aqueous phase (%)	yield organic solid phase (%)	yield organic liquid phase (%)	yield gas phase (%)	mass balance (%)
500	54,67	2,90	33,47	4,65	95,69
450	56,16	2,40	30,27	4,28	93,11
400	49,89	3,50	39,39	3,63	96,41

Table 2. Yields (%w/w) of the different phases collected at the end of the gasification reaction of the concentrated "vinasse", (400°C < T < 500°C).

T (°C)	yield aqueous phase (%)	yield organic solid phase (%)	yield organic liquid phase (%)	yield gas phase (%)	mass balance (%)
500	52,71	2,67	33,13	3,82	92,33
450	60,88	2,82	23,24	2,91	89,85
400	62,79	2,55	26,91	2,32	94,57

Table 3. Yields (%w/w) of the different phases collected at the end of the gasification reaction of the clarified "vinasse", (400°C < T < 500°C).

The amount of the gas produced during the reaction increases when the temperature increases from 400°C and 500°C. This result has been observed for the effluent and for the "vinasse" also (Table 1, Table 2 and Table 3). But the evolution is not so clear with the figure of the yields. Table 4 shows therefore the volumes really produced during the gasification process. According to the quantity of organic matter initially in the biomass the volumes are very different. The effluent is very poor in organic matter. The volume of the produced gas is relatively small. The two samples of "vinasse" are very rich in organic matter. The volumes of the produced gas

are at least twelve times as big as for the effluent. The effect of the increase of the temperature is the same for the three samples: an increase of the temperature increases the volumes of the gas.

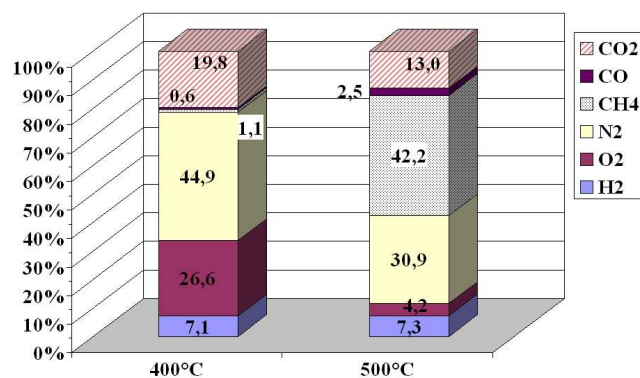
T (°C)	400	450	500
effluent	190	-	270
concentrated "vinasse"	3630	4015	4060
clarified "vinasse"	2650	3095	3210

Table 4. Volumes of the produced gas (mL) for the three biomasses, ($400^{\circ}\text{C} < T < 500^{\circ}\text{C}$).

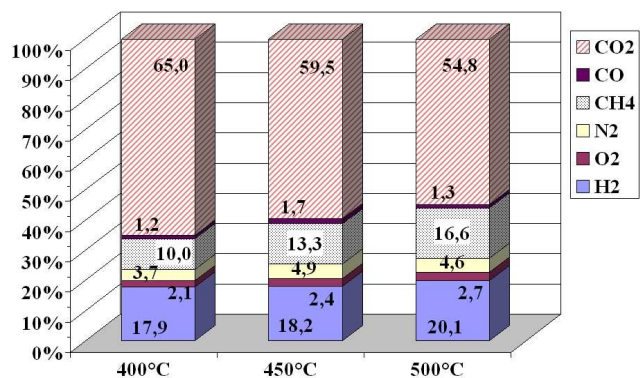
The next part shows that the composition of the gas phase has also been changed according to the operating conditions.

3.4 Gas Analysis

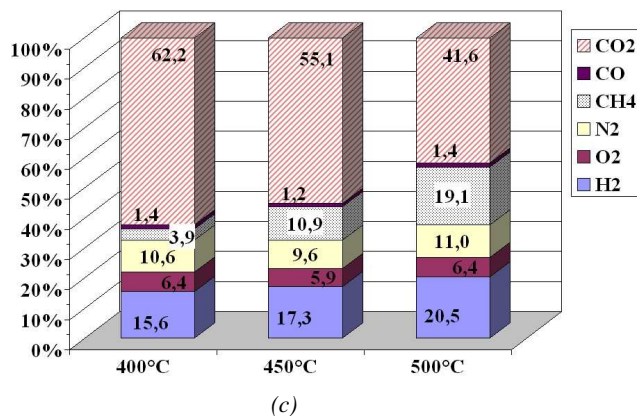
The results of the gas analyses are shown in the figure 5.



(a)



(b)



(c)

Figure 5. Composition (molar percentage) of the gas collected from a sample issued from the effluent (a), from the concentrated "vinasse" (b) and from the clarified "vinasse" (c) treatment, ($400^{\circ}\text{C} < T < 500^{\circ}\text{C}$). N_2 comes from the initial purge of the reactor and from the air inevitably present. O_2 comes also from the air.

All the experiments show that a temperature increase leads to a decrease of the molar proportion of carbon dioxide. This decrease is between 16% for the concentrated "vinasse" and 33-34% for the others. The effect of the temperature on the molar percentage of methane is also noteworthy. This is particularly true for gasification of the effluent where methane is practically absent at 400°C and becomes the major component of the gas mixture when the experiments has been carried out at 500°C . A less clear tendency is also outlined for the hydrogen. Its molar percentage increases also with the temperature but the extent is much lower than for the methane. The amount of carbon monoxide is nearly stable. The same trends were noted by Lee *et al.* on a glucose feed.⁶

An increase of pressure will lead normally to an even bigger preference for the methane with regard to the hydrogen.⁷ It will be studied in the future.

4. Conclusion

The gasification in supercritical water of three selected bio-resources was conducted at a pressure of 250 bar and temperatures of 400, 450 and 500°C . For all the experiments, the yields of the process were determined. The results are in agreement with the literature. But we have to increase the temperature above 500°C in order to favour much more the yield of the gas phase.

The nature of the gases produced during the reaction was also determined. Some trends are emerging:

- The amount of gas produced during the reaction increases when the temperature increases between 400 and 500°C;

- The amount of carbon dioxide decreases when the temperature increases while the concentration of hydrogen and methane increases.

The future works will consist in finishing the physicochemical analyses. These analyses will allow to quantify the total carbon conversion during the gasification reaction in supercritical water (COT and C,H,O,N,S analyses). These analyses will allow also to link the initial concentration of the organic matter contained in the biomass and its nature to the yield of the gasification and the nature of the produced gases. Moreover ICP-OES analyses in all the phases obtained after the reaction will allow us to understand the behaviour of the metals during the biomass gasification and perhaps their catalytic effect on the reaction.

Finally, we want to optimise the process particularly in thinking the use of catalysts to favour one gas relatively to another, and the optimisation of the operating conditions over.

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