Gasification of winery wastes using hydrothermal diamond anvil cell

P. Escot Bocanegra[*, 1], C. Reverte[2], C. Aymonier[2], A. Loppinet-Serani[2], M.M. Barsan[3], I.S. Butler[3], J.A. Kozinski[4], I. Gökalp[1]

[1]ICARE-CNRS, Orléans, France
[2]ICMCB, Bordeaux, France
[3]McGill University, Montréal, Canada
[4]University of Saskatchewan, Saskatoon, Canada

Abstract

Numerous new projects are today focussed on finding non-polluting energy sources. Interest in the use of biomass for energy purposes has been also revived in this context. Among others, agricultural biomass waste is one of the most promising resources. Its conversion into bio-fuel for further application via combustion increases its economic interest despite its initial low calorific value. In the present study, the conversion process is carried out in supercritical water (SCW), thus improving significantly the energy balance by eliminating the need for drying the biomass. The SCW dissolution, hydrolysis and oxidation of pure substances in a hydrothermal diamond anvil cell (HDAC) have been studied previously, for example, by Sobhy *et al.* [1] and Fang *et al.* [2]. Unique results concerning homogeneous dissolution of naphthalene, cellulose and glucose in SCW were acquired, revealing the possibility of using them as a co-fuel in generating SCW flames. These studies have proved the proposed concept. The current investigation is performed for samples representing real biomass (winery residues) rather than pure substances. Unique visualisations of the gasification process were obtained. Also the products of the decomposition were analyzed. It is expected that this work will contribute in valorizing winery waste by decreasing the cost required for their elimination and, in this way, will also contribute significantly to green house gases mitigation.

1. Introduction

The use of the biomass as a biofuel is a controversial topic because of the competitive use of the same resource as human or animal food. However, organic materials coming from various wastes could be used in place of initial biomass to avoid various ethical problems. Heterogeneous biomass waste of low calorific value (such as agricultural biomass residues) can be converted using SCW processes into biofuels (particularly in hydrogen) for their further application via combustion in burners, engines or gas turbines.

The main goal of the project is to optimize the biomass decomposition process in SCW. Studies of the SCW dissolution, hydrolysis, and oxidation of pure substances in a hydrothermal diamond anvil cell (HDAC) have been completed by Sobhy *et al* (2005) and Fang *et al*. (2008). Unique results concerning homogeneous dissolution of naphthalene, cellulose and glucose in SCW were obtained, revealing the possibility of using pure substances as a co-fuel in generating SCW flames. These studies have proved the proposed concept.

The current investigation has been carried out for samples representing real biomass (effluent and winegrape slurry which are winery residues) rather than pure substances. The variety of molecules composing winery wastes makes it difficult to determine details of the decomposition process. Nevertheless, unique technique applied towards visualization of the process offered initial explanations.

[*] E-mail address: escot@cnrs-orleans.fr
Proceedings of the 9th International Symposium on Supercritical Fluids, 2009

Winery wastes have been decomposed in SCW producing gas and a solid phase residue. The composition of the solid phase depends of the chemical composition of the sample and the level of concentration. Current results indicate that wastes coming from agricultural industries can be converted into fuels (including hydrogen). Thus, the valorization of wastes *via* replacing their disposal by SCW conversion into biofuel/H_2, could become important for selected practical applications.

2. Experimental Techniques

2.1. Material

The winery waste used for this project comes from the distillery called "UCVA distillery cooperative" located near Bordeaux in France. The waste investigated in the study is effluent (Fig. 1-a.) and winegrape slurry (Fig. 1-b.). These two liquids are produced during the ethanol production process.

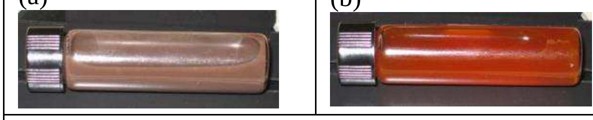
(a) (b)


Fig. 1. Picture of the initial biomass called effluent (a) and winegrape slurry (b).

A huge amount of these liquids have to be treated industrially. To avoid this process and to increase the value of materials, the idea to use them as a fuel source emerged. For this purpose, initial biomass was first characterized. To visualize the two type of biomass by Scanning Electron Microscopy (SEM), samples were dried at ambient temperature (Figs. 2-a and 3-a). It was necessary for effluent visualization to coat this sample by a mixing of gold and palladium to avoid charges on the surface (Fig. 2-a). The analyses of the atomic composition (Fig. 2-b and 3-b) were obtained by Energy Dispersive X-rays Spectroscopy (EDS). The global composition of the analytical sample indicates the presence of carbon, oxygen, phosphorus, potassium, calcium for effluent (Fig. 2-b) and the presence of carbon, oxygen, sulfur, chlorine, potassium for winegrape slurry (Fig. 3-b).

(a) (b)

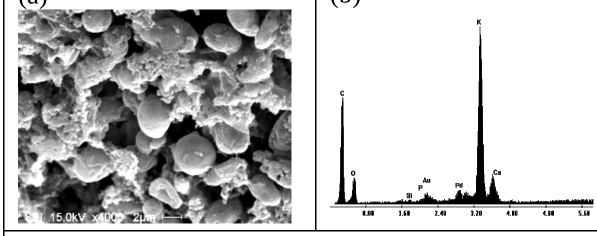


Fig. 2. SEM visualization of the effluent, 4000×mag. (a) with his global EDS analysis (b).

(a) (b)

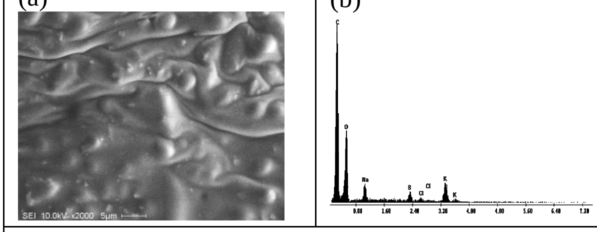


Fig. 3. SEM visualization of the winegrape slurry, 2000×mag. (a) with his global EDS analysis (b).

2.2. Experimental approach

A Hydrothermal Diamond Anvil Cell (HDAC), developed by Basset (1993) was used for phase-change observations of the effluent plus water system up to the supercritical region. The experimental set-up, in which tests can be conducted in fluids at pressures up to 2.5 GPa and temperatures up to 1200°C, is shown in Fig. 4.

Pressure was produced by an anvil composed of two opposing diamond inside the 50 nL reaction hole (inner diameter 500 µm, thickness 250 µm) drilled in an inconel gasket. The winery waste was loaded by placing a sample droplet onto the gasket hole with a microsyringe. An air bubble is created in the reaction hole to follow the increasing pressure (Fang *et al.*, 2008). The screw nuts of the HDAC were tightened alternatively in 5-degree increments per turn, during which the sample was examined by a stereomicroscope (Olympus SZ11) to check the loading.

The sample was heated by two individual microheaters that transferred heat to the diamonds. Nitrogen was introduced into the cell to prevent the diamond from oxidation and to increase the cooling at the end of the experiment. Temperature was measured by two K-type thermocouples attached on each diamonds by ceramic cement and recording were made every 1s. The sample was first heated, then the temperature was stabilized and finally the system was cooled to room temperature. The fast heating rate was set at about 10°C/s up to 500 °C to avoid the sample decomposition before dissolution.

Phase transitions were observed at 110× magnification, and the images were recorded by a Panasonic 3 CCD camera (AW-E300). After heating and stabilizing, the sample was rapidly cooled by cutting power to the heaters while maintaining the nitrogen gas flow.

After the experiment was completed, the HDAC was disassembled, and the residues, remaining on the diamond anvil faces and inside the chamber, were examined by SEM and analyzed by EDS.

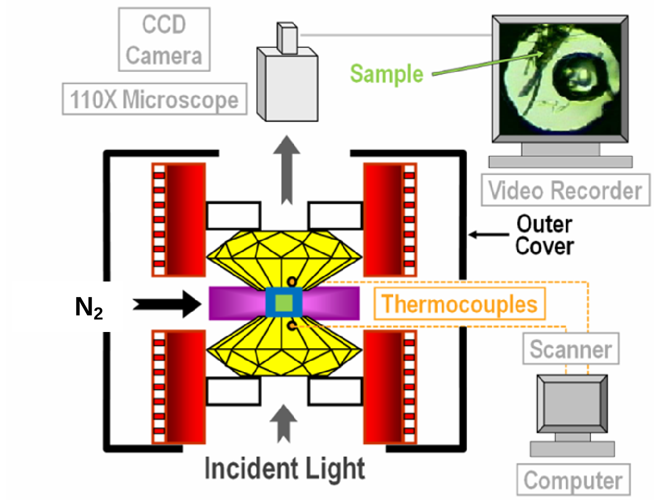


Fig. 4. Schematic diagram of experimental set-up of the HDAC system.

A batch reactor reaction is used to study the nature of the gas released during the decomposition of effluent and winegrape slurry. The total reactor volume is 110 mL. The effluent volume used for the reaction is 16.5 mL, and the reactor volume is completed by air (93.5 mL). The filling ratio obtained is 15 % vol. The winegrape slurry volume used for the reaction is 20.9 mL, and the reactor volume is completed by air (89.1 mL). The filling ratio obtained is 19% vol. The micro gas chromatography is used to analyze the concentration of the produced gases. The quantity of CO_2 is obtained by subtraction.

3. Results and Discussion

3.1. Visualization of the process

The experiments were performed for two different amounts (small and large quantity) of two different compounds (effluent and winegrape slurry) in the reaction hole. The process was recorded and sequences of pictures representing the main stages of the process were extracted (Tables 1-4).

Visual observation of the decomposition process of the small amount of effluent (Table 1) showed various phase changes. First, the air bubble disappears; later homogenization occurs until the supercritical state together with a color change; decomposition begins in the supercritical state and cooling produces residual gas bubbles. Different stages are also observed when the diamond anvil cell is filled with a large amount of effluent (Table 2). The air bubble disappears like in the small amount filling; homogenization occurs until the supercritical state with a color change followed by decomposition in the supercritical state; finally and solid phase formation and cooling. The transformation phases correspond to large variations in the opacity of the solution.

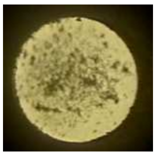
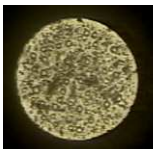
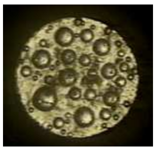
Visualization of the reaction hole	Time from the beginning of the heating (s)	Medium Temperature (°C)
	0	28
	7	125
	21	288
	30	374
	94	496
	118	85
	280	31

Table 1: Sequence of images extracted from the recorded decomposition of a small amount of effluent.

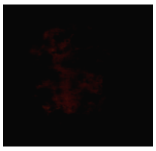
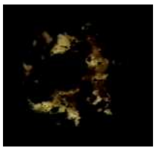
Visualization of the reaction hole	Time from the beginning of the heating (s)	Medium Temperature (°C)
	0	28
	8	77
	19	193
	37	382
	41	414
	53	495
	280	30

Table 2: Sequence of images extracted from the recorded decomposition of a large amount of effluent.

The different stages show the transformation of the initial state to the final residue. The decomposition appears after reaching the supercritical temperature, above 374°C. The decomposition of the effluent was almost complete in the case of small initial amount. When the initial amount of effluent is large some residue left on the diamond faces after the main decomposition of the sample.

When the hole of the HDAC is filled by the winegrape slurry (Table 3-4), also various phase changes are observed. The process of decomposition of small amount of winegrape slurry (Table 3) is the same as for small amount of effluent, the air bubble disappear; homogenization occurred until the supercritical state together with a strong color change;

beginning of the decomposition in the supercritical state; cooling and formation of residual gas bubbles on the side of the hole.

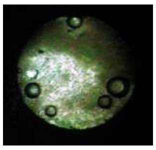
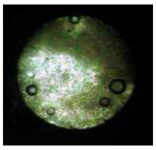
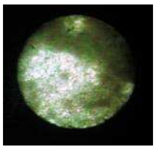
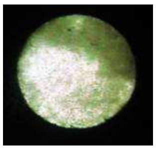
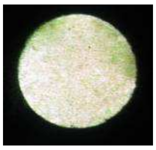
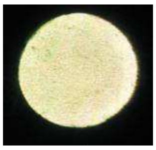
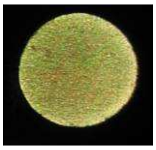
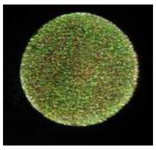
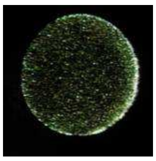
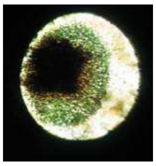
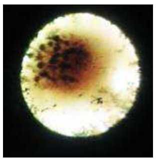
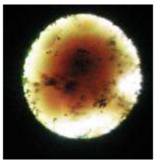
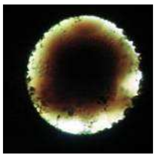
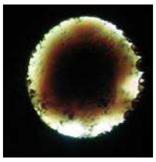
Visualization of the reaction hole	Time from the beginning of the heating (s)	Medium Temperature (°C)
	0	25
	6	25.5
	10	31
	15	84
	19	130
	29	244
	33	311
	38	350
	43	398
	46	451
	51	475
	56	496
	73	503
	111	479
	120	382
	150	38

Table 3: Sequence of images extracted from the recorded decomposition of a small amount of winegrape slurry.

When the diamond anvil cell is filled with a large amount of winegrape slurry (Table 4), different stages are also observed. The air bubble disappear; homogenization, color change, dark phase until the supercritical state; violent and fast decomposition in the supercritical state; solid phase separation and carbonization; after cooling. The transformation phases are link with a large variation in the color of the solution. The decomposition appears after reaching the supercritical temperature. Carbon sphere creation can be observed after the main decomposition of the sample. Then the carbon is coming on the face of each diamonds and the visualization is not possible anymore. From this time to the cooling, the crystallization appears and at the end just water, two different solid phases and a probable gas phase (as the decomposition with few amount of winegrape slurry) are created.

New experiments are in progress to increase the understanding of the process. Raman measurements of the solid/liquid phase and gas analyses during the gasification will permit to follow the decomposition of the initial sample.

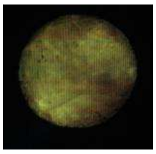
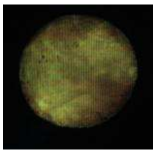
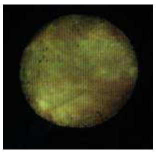
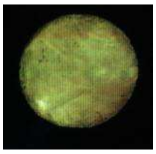
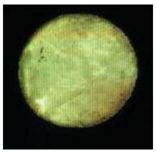
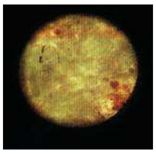
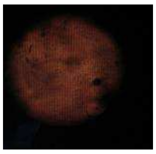
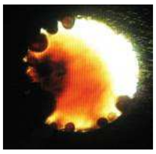
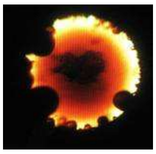
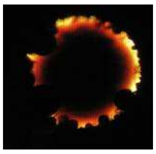
Visualization of the reaction hole	Time from the beginning of the heating (s)	Medium Temperature (°C)
	0	30
	4	31
	9	35
	13	80
	17	166
	21	257
	22	276
	25	324
	31	400
	32	413
	33	427
	34	440
	43	531
	49	539
	55	536
	167	33

Table 4: Sequence of images extracted from the recorded decomposition of a large amount of winegrape slurry.

3.2. Analysis of the gases and residues

The batch reactor studies of the effluent are made at 500°C and 250 bars to be comparable with the HDAC experiments (Table 1-4). The gases produced are H_2, O_2, N_2, CH_4, CO and CO_2. The quantity of each one is analyzed by micro gas chromatography and given in Table 5. The CO_2 mole fraction is obtained by subtraction.

Compound	H_2	O_2	N_2	CH_4	CO	CO_2
Effluent Mole fraction %	33.94	4.69	22.34	8.64	0.14	30.25
Winegrape slurry Mole fraction %	21.08	3.35	6.87	14.57	1.1	53.03

Table 5: Nature and quantity of the produced gases, batch reactor experiments run with effluent and winegrape slurry.

The analyses of the solid residue collected after experiments with effluent (Fig. 6) or with winegrape slurry (Fig. 7-8) give interesting information on the formation of different kind of materials produced during the decomposition of the effluent under supercritical condition. These analyses reveal that some structures are made of $CaCO_3$ (fig. 6a-b). Various quality of structures with a large amount of carbon are found, dry (fig. 6c-d) or with a very high viscosity (fig. 6e-f).

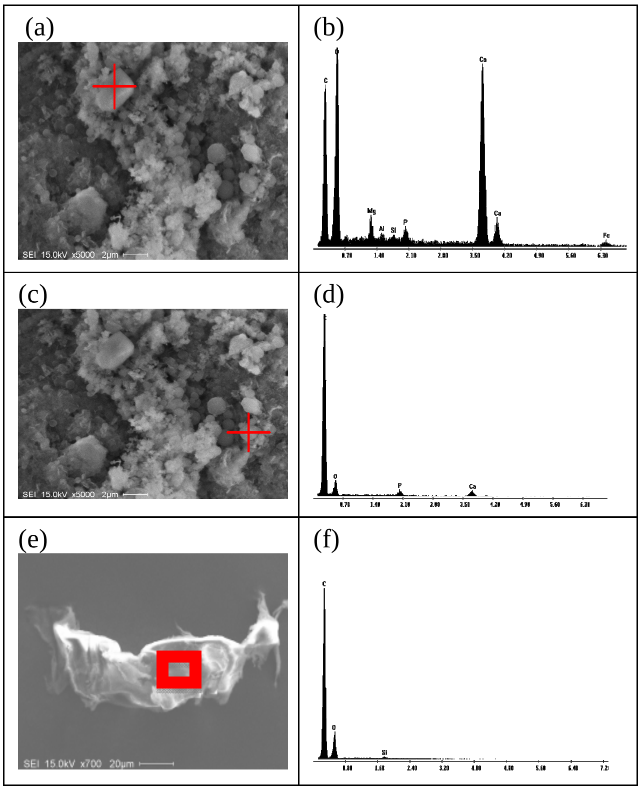


Fig. 6: SEM visualization (a, c, e) and local (geometric shape) (b, d) and global (f) EDS analysis.

The residues of the experiment with a large amount of winegrape slurry were collected inside the hole (Fig. 7) and on each face of the diamonds (Fig. 8).

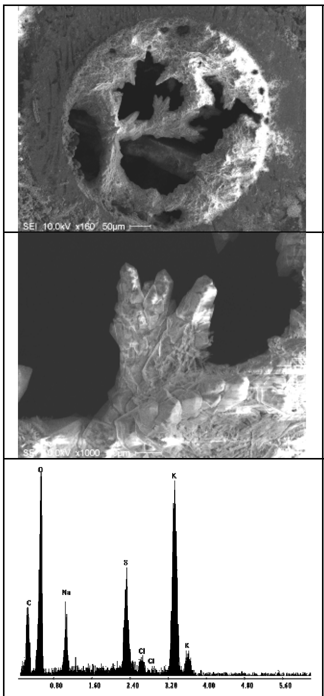


Fig. 7: SEM visualizations (mag. ×160, ×1000) and EDS analysis of the residue localized inside the hole.

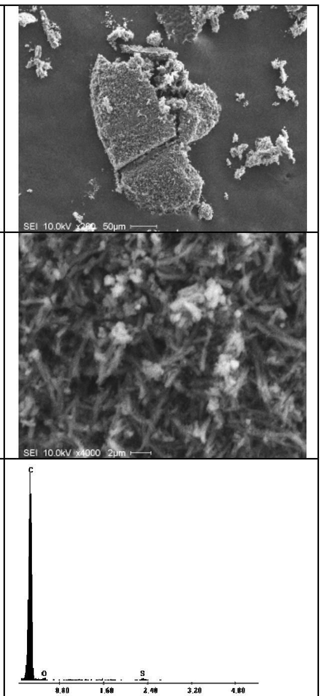


Fig. 8: SEM visualizations (mag. ×280, ×4000) and EDS analysis of the residue localized on each side of the diamonds.

The SEM observations show beautiful crystallization (Fig. 7) on the side and in the middle of the hole. The EDS analysis (Fig. 7) shows that the composition is the same as initial sample, but the relative amount of carbon is much less. The residue left on each side of the diamonds was observed under SEM (Fig. 8). Under high magnification, some needles could be observed (Fig. 8). The EDS analysis reveals that the needles are only made of carbon (Fig. 8).

The residue observations show a separation of the solid phase. Pure carbon appears on each face of the diamonds and all the others compounds crystallize.

4. Conclusions

The decomposition of effluent and winegrape slurry has been examined under supercritical conditions. The optical visualization studies led to very interesting results on the processes. New results on dissolution, homogenization and carbonization are presented. Two different samples have been studied and dissolution process is similar in both cases. The decomposition of samples begins after the critical temperature. It is shown that for low concentration levels the decomposition is almost complete. However, the concentration of sample in water is important in the process. The next goal is to investigate the initial, intermediate and final composition of the materials to get a better idea of the chemical crystallization process of the various elements.

5. Acknowledgements

The authors acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada and the “Agence National pour la Recherche” through individual, strategic, and equipment grants. Thanks are due to H. Campbell (McGill University) for the SEM visualizations.

6. References

Bassett W.A., Shen H.A., and Bucknum M. (1993). Rev. Sci. Instrum., Vol. 64, 2340-2345.

Fang Z., Minowa T., Fang C., Smith R.L., Inomata H., Kozinski J.A. (2008). Catalytic hydrothermal gasification of cellulose and glucose. Int. J. Hyd. Energ., Vol. 33, 981-990.

Sobhy A., Barsan M.M., Fang Z., Assaaoudi H., Butler I.S., Kozinski J.A. (2005). Flames in Water: Destruction of Organics. Proc. Comb. Inst./Can. Sect., 297-302.