

# Energy integration for pressurised processes converting biomass: the case of the supercritical water gasification and liquefaction

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## ABSTRACT

Biomass conversion to fuel will become one of the route to sustainability. Some biomasses are available with strong water content. In order to valorise and to avoid drying, it is meaningful to use “hot water” processes. Two technologies, direct liquefaction performed below the critical point of water and supercritical gasification performed above the critical point are compared. The efficiency of conversions is presented on a matter point of view and in an exergetic point of view. The different routes for the use of biomass, consistent with their initial state are the generation of products such as bio-fuels or combustible gases or electricity.

## INTRODUCTION

The use of biomass is a key feature in numerous scenarios for 2050. In the field of biomass conversion a key point is the efficiency of the conversion. Biomass conversion in “hot water processes” includes a broad range of technology. Classification can be made in regards to the operative conditions such as pressure and temperature. In this case, the position to the critical point of water is considered. Below critical point (subcritical), a biphasic reacting media is generally observed while above critical point (supercritical) a monophasic case is considered. Another classification is to consider the oxygen stoichiometry. Regarding total oxidation of initial compounds, *ie* the case of a combustion, reaction can be performed either in subcritical (generally called wet air oxidation) or supercritical (generally called hydrothermal oxidation). In this case, products are CO<sub>2</sub> and H<sub>2</sub>O. For long those processes have been devoted to effluent treatment [1,2].

Non-oxidative technologies aim to direct conversion in designed bio-products such as oil, combustible gases or designed polymers. In subcritical condition, the process is called liquefaction and the conversion results in three phases (gas, liquid, solid). In supercritical condition the process is called Super Critical Water Gasification and the conversion of the biomass should result in gases even if some by-products are generally encountered [3]. Those processes are very promising for aqueous biomass because those processes could overcome the need of drying before use in equivalent dry route, pyrolysis and gasification. Energy

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integration is an important step stone to make those routes more attractive [4]. Indeed pressurised processes have to prove that inherent advantages can overcome the matter of the required energy for shaft work and heaters. Some preliminary studies are provided but most of them are based on a theoretical conversion assuming that thermodynamic equilibrium is reached [5, 6]. This is particularly true for supercritical processes because the main products being gases, equilibrium calculations are accurate and easier to calculate. In the case of subcritical processes, there still exists a need for such studies based on real conversion such as in [7] for wet air oxidation. In this study, energy integrations based on simulation are presented for non-oxidative processes. The conversion is here modelled in non-equilibrium condition based on experimental results.

## **MATERIALS AND METHODS**

To perform simulation, the data used are based on the experimental work of Doassans [8] for liquefaction and Ondze [9] for SCWG. Many data can be found there and those both works can not be easily summarized here. In those studies extensive parametric experiments have been performed with analytical data on the main products. Main parameters are temperature, residence time, initial concentration of the effluent and pressure.

In the case of the liquefaction the conversion of beech sawdust is considered. Three phases are considered for products. For the three phases, correlations closing atom balance on carbon, oxygen and hydrogen are available. In facts the correlations concern products representative of analysed products following experiments. By example, the liquid phase is represented by 14 compounds. In the case of SCWG, compound model (glucose) and a real waste (distillation beet residue) are experimented. Once again for several temperatures experimental correlations are used to represent a closed mass balance on gases. Along with the gas phase composition a residual effluent with still carbon content is modelled

The detailed correlations are not the aim of this presentation. It is emphasised here that mass balance are closed thanks products consideration on atom balances. Thus mass balance is not filled with water to get 100% of recovery as in [10] by example.

Processes are simulated with commercial software that provide mass balances and enthalpic data for each flows. The heat integration is done with the pinch method. This method gives the theoretical Minimum Energy Required (MER) by the process to be achieved. Extensive presentation of the method is in [11]. Coupled with heat integration, an exergetic analysis is performed. The exergy concept is here useful because shaft work is required to run the conversion. Thus taking into account the second principle of thermodynamic is necessary to keep the correct ratio between heat and work. A complete introduction to the exergy concept can be found in [12]. In biomass process conversion, three exergies are calculated:

- exergy of heat available at a certain temperature
- exergy associated to mechanical work
- chemical exergy calculated with Szargut correlation calculated from the Higher Heating Value (HHV). As products are combustible, chemical exergies from reactant to products are sufficient. Corrections due to a desired chemical pathway such as presented in [13] are not necessary.

Once the MER and all exergies are calculated, those data are gathered to calculate the exergetic efficiency. Thus the efficiency can simply be calculated by eq 1:

$$\eta_{Ex} = \frac{Ex_{USED}}{Ex_{IN}} \quad (1)$$

where  $\eta_{Ex}$  is the exergetic efficiency,  $Ex_{IN}$  is the sum of all exergies entering the system and  $Ex_{USED}$  the useful quantities of exergies at the outlet.

As the end product is not the same, the use of the route is not the same. In the case of liquefaction, the end product is a diesel obtained from oils. After liquefaction, an HDO (Hydro-DesOxygenation) step is simulated following data from [14]. Main assumption resides in the non-conversion of acids and moreover acid's valorisation is not taken into account; while hydrogen is directly supplied in the process with an exergetic debt of twice its HHV.

In the case of SCWG, combustible gases are obtained. Three cases are studied according to main composition of gases:

- hydrogen production. After gasification, a train of reactor performs reforming for light hydrocarbons followed by a second one for the CO reforming and a last reforming for the remaining methane in classical two steps reactor is performed. At least a PSA (Pressure Swing Adsorption) achieves physical separation of hydrogen.

- methane production by using reforming and classical methanation. In this case, the pressure and temperature are suitable with processes conditions, thus no back compressions are used.

- electricity generation with use of the heat contained in the combustion fume only. The syngas is used as generator in a Brayton cycle, again quite suitable with the high pressure encountered in SCWG. Complete combustion of syngas is assumed in the gas turbine.

In the case of liquefaction, entering exergies come from biomass, hydrogen, work for grinder, pumps, compressors and the MER if it is needed to supply some at the hottest temperature of the process. The useful exergy is contained by the diesel produced and by the heat of combustion of gases and solids if some remains. In this case the delivery temperature is 1473 K.

In the case of SCWG, entering come from biomass, work for pumps and compressors, and the MER (that is always needed in this case). The useful exergy is contained in hydrogen for the first case, methane for the second and electrical power plus heat released from the fume in the last case.

In both processes, phases that are not under consideration such as solid and gases in liquefaction are burnt to provide a part or the whole heat for the process. An example of complete scheme for liquefaction is given in figure 1. It is noticeable that liquefaction is the central point but the route is completed by all others utilities in order to perform the whole biomass to fuel route, such as oil recovery by solvent and the HDO step.

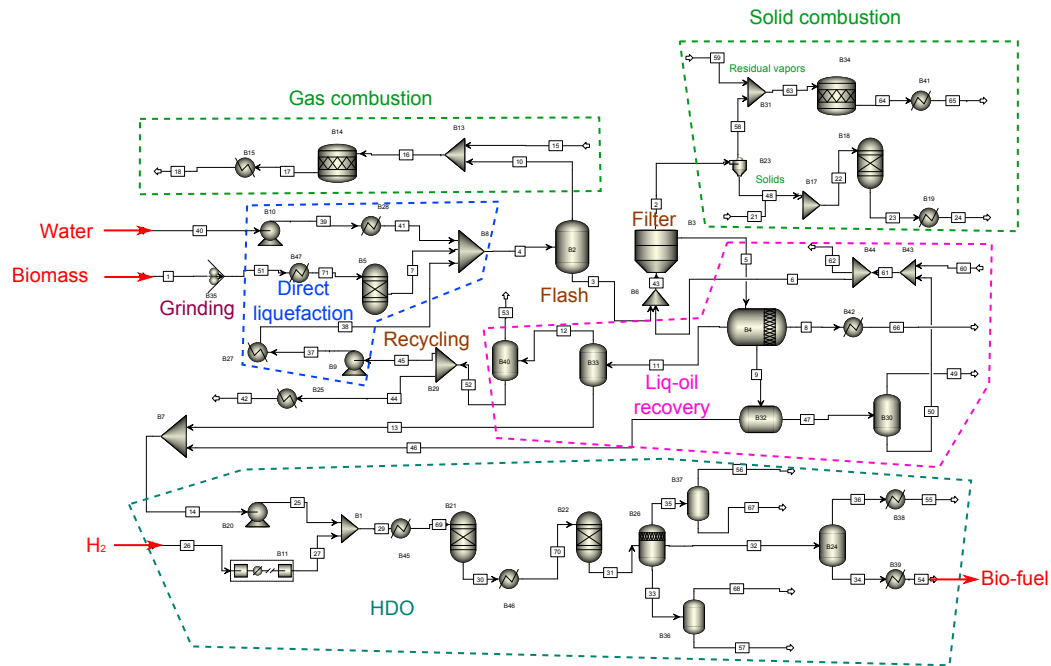


Figure 1: Liquefaction route from solid biomass to biodiesel.

At least optimisation of the process is done in the boundary of the experimental condition. Fitted functions (polynomials or exponential) are used to describe the whole domain from simulated points. Thanks those continuous functions, a Pareto projection is realised by finding the mathematical optimum. An example of the continuous projection of the exergetic efficiency for SCWG and electricity generation is presented in figure 2.

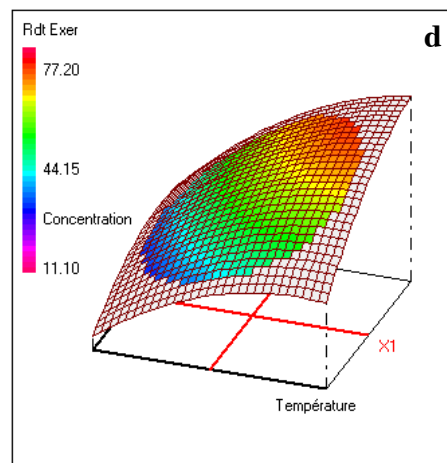


Figure 2: Exergetic efficiency plotted with polynomials versus temperature and initial concentration of the waste

## RESULTS

The simulations are based on some technologies features (turbine... ) that do not necessarily exist in the current time due to the unconventional operating domain. This remark is also true for the reactor for liquefaction and SCWG even if the feasibility seems acquired.

The main influent parameter for both processes is the temperature. In the case of SCWG, the highest studied temperature (873K) gives the best efficiency (figure 3) while the initial concentration has less influence, even if higher concentration increases the efficiency. This is directly linked to the raw conversion of biomass into valuable combustible gas that reaches a maximum with temperature.

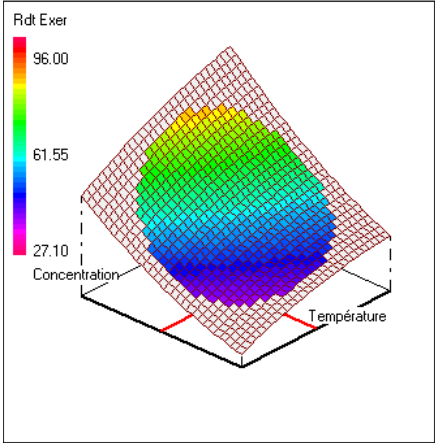


Figure 3: Exergetic efficiency for methane production by SCWG versus temperature and initial concentration of the effluent

For liquefaction, the optimal temperature lies in a plateau in the range from 550 to 590K (the studied range is 510 to 600 K). This optimal zone tallies with the optimal liquid phase production. But the main influent parameter is the humidity. From 80%, the efficiency marks a sharp decrease. Due to strong dilution of biomass into water, the diesel production does not compensate the needs of the process.

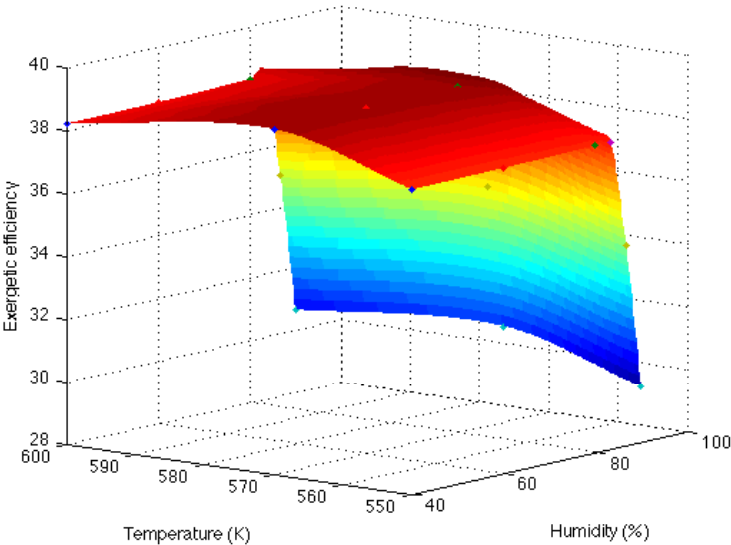


Figure 4: Exergetic efficiency for diesel production by liquefaction versus temperature and initial concentration of the effluent

Maximal simulated exergetic efficiencies are gathered in table 1.

Tableau 1: Exergetic efficiency for each route

	<b>Liquefaction</b>	<b>SCWG-Hydrogen</b>	<b>SCWG-Methane</b>	<b>SCWG-Electricity</b>
$h_{Ex}$	<b>38%</b>	<b>80%</b>	<b>80%</b>	<b>73%</b>

In liquefaction, low efficiency can be explained by the non-use of acids compounds and by the recovery method with solvent. For SCWG, the efficiency being better for the highest temperature, material improvement should be considered to be able to run long time conversion.

## CONCLUSION

The mentioned efficiency proved that improvement of each route could be achieved, mainly for liquefaction. Regarding comparison with dry routes such as pyrolysis or gasification for dry products, those wet routes can compete. Technological improvement and better knowledge on conversion are then encouraged.

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