

Process Design for Supercritical Water Gasification

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In this paper the layout of pilot plant (100 kg/h) for the supercritical water gasification (SCWG) of biomass is proposed. The proposed layout involves a reactor, units to separate water and hydrogen, a burner and several heat exchangers. This scheme was also simulated by means of the commercial software Aspen Plus[®] (Aspen Tech, Inc.) in order to state the influence of different parameters such as biomass concentration in the feed and biomass typology (glycerol and grape marc). Results show that SCWG process can be energetically self-sustained if minimum feeding concentrations of 15-20% are adopted. The possibility to separate hydrogen and feed it to a fuel cell was analyzed and the electric power production was calculated. The problem of heat recovery and heat dissipation was also analyzed and an evaporative cooling tower was proposed as the most economical solution.

1. INTRODUCTION

In recent years, energy exploitation of biomass residues is gaining an increasing attention for both environmental and economic reasons. Biomass is considered as a renewable energy source which can be beneficial for the global warming issues. Unlike fossil fuels, the usage of biomass is CO₂-neutral, meaning that the amount of carbon dioxide released by its processing is the same amount the plant stored in its tissues during its life, thus giving no net contribution to the atmosphere. From the economic point of view, these types of residues normally have a disposal cost. Their reuse as fuels can thus represent an advantageous profit since they can provide valuable products, such as hydrogen, with an extremely low raw-material cost. In the literature other articles can be found concerning the energy valorization of these residues by means of air or steam gasification [1].

In the present paper, a novel technology is examined: supercritical water gasification (SCWG). This process foresees the usage of supercritical water as the gasifying agent, that is water above its critical point (temperature and pressure above 375°C and 221 bar respectively). Thanks to the unique properties of water at supercritical state, a rapid and tar-free gasification can be achieved, yielding a product gas rich in hydrogen, methane, carbon monoxide and carbon dioxide [2].

Supercritical water gasification seems to be one of the most promising technology to dispose of wet biomass. Other technologies for energy recovery from biomass (like combustion and air gasification) normally need a dry feedstock in order to be energetically sustainable. Since SCWG is a hydrothermal process, a high water content in the biomass does not constitute a problem. It can be thus particularly indicated for the treatment of residual biomass, such as agro-industrial wastes, sewage sludge, etc. [2].

Whilst some experimental work concerning supercritical water gasification has been done, mathematical modeling of SCWG is a relatively less investigated area. Most of the studies in this field have focused on thermodynamic aspects, through the use of models to predict the

equilibrium products of the process [3-4]. Some other works have been devoted to the derivation of a kinetic model [5]. However, all these approaches are concentrated on the description of the reaction itself, thus neglecting all the aspects related to the engineering of the whole SCWG process.

The only attempt to propose a possible process scheme is that of Feng *et al.* [6]. In their article, the authors proposed a process scheme involving a SCWG reactor inside a furnace powered with the gasification gases. Hydrogen was separated by means of a membrane separator and a single heat exchanger between reactor exit and entrance was foreseen. This scheme is very interesting as a concept, but it has not been fully developed for a possible technical application.

In this work a comprehensive process layout for SCWG of residual biomass is proposed. The scheme was implemented by means of the commercial software Aspen Plus[®] (Aspen Tech, Inc.), which was used to perform the simulations. Information about energy sustainability and electric power production was obtained. Two different feedstocks were used for the analysis: glycerol and grape marc.

2. BIOMASS CHARACTERIZATION

The two materials which were chosen for this study are glycerol and grape marc. Glycerol is a well-known compound. A few studies concerning SCWG have been devoted to this material, because it can be a useful model compound for more complex biomass. On the other hand, in the last few years glycerol is gaining an increasing importance, since it is the most abundant by-product of the biodiesel industry.

Grape marc is a residue of the enological industry, that includes all the parts of the grape which remains after wine-making. It consists of a mix of grape stalks, skins and seeds in different amounts.

Table 1 summarizes the most important properties of these two materials, based on the data available in the database Phyllis, powered by ECN [7]. Comparing the marc molecular formula (referring to a ‘pseudo-molecule’ of grape marc) with that of glycerol, it is clear that the two compounds are quite different. Their high heating values are different as well: marc is more “energetic” than glycerol, with a HHV of 21.8 MJ/kg in comparison with the HHV of 18 MJ/kg for glycerol.

Another interesting issue is represented by the H/C and O/C molar ratios in each molecule. As it can be seen in Table 1, both ratios are lower for marc with respect to glycerol, meaning that the former has a higher relative carbon content than the latter. This suggests that a higher hydrogen production can be expected for glycerol.

Table 1. Comparison between glycerol and grape marc. Data taken from [7].

	Glycerol	Grape marc
Formula	$C_3H_8O_3$	$C_{4.57}H_{5.78}O_{2.04}S_{0.01}N_{0.15}$
HHV [MJ/kg]	18	21.8
H/C	2.67	1.26
O/C	1.0	0.44

3.2 Grape marc

The process scheme for the marc, shown in Figure 2, is very similar to that for glycerol (Figure 1). The only relevant difference is represented by the different way the reactor is modeled. As it can be seen inside the dashed area, two reactors are present instead of one. This is due to the particular way Aspen Plus[®] treats real biomass. When a pseudo-compound is used, it is not allowed to feed it directly to a “Gibbs reactor”. It is thus necessary to process first the pseudo-compound in a devolatilizer, that is a reactor that breaks up the molecule in its elementary components (C, O₂, H₂, N₂, S). These products can then be fed to the Gibbs reactor which calculates the equilibrium composition. The two reactors must be connected by a heat stream (Q-IN).

In this case the range of possible gases is wider because of the presence in the biomass of other components, as sulfur and nitrogen. The resulting gaseous species are then H₂O, CO, CO₂, N₂, N₂O, NO, NO₂, SO₂, SO₃, H₂ and CH₄.

Unlike the case of glycerol, here the water has to be cleaned. During the devolatilization process, in fact, the ash initially present in the biomass is released. This ash fraction can be separated from the rest of the gases, but precipitates in the water. In this paper water cleaning is not modeled: the water, exiting from the separation-process, is then reintegrated with the fresh incoming water stream.

Table 2. Flow, temperature and pressure for each stream of Figure 2 (10% wt.).

Stream	Flow [kg/h]	Temperature [°C]	Pressure [bar]
H2O	90	25	1
MARC	10	25	1
MIXED	100	25	1
PUMPED	100	28.11	300
PREHEAT-1	100	275.91	300
PREHEAT-2	100	402.58	300
IN-REACT	100	700	300
SYNGAS	100	700	300
SYNGAS2	100	360	300
WATER	83.36	60	300
GAS-1	16.64	60	300
GAS-2	16.64	312.35	300
GAS-3	16.64	308.19	60
COMB+	15.83	298.35	1
COMB-1	15.83	308.19	60
COMB-2	15.83	298.35	1
CH4	0	-	-
H2STREAM	0.80	308.19	3
AIR (ER=1.2)	49.54	25	1
FLUE	65.38	1554.93	1
FLUE2	65.38	315	1
FLUE3	65.38	190	1

In Table 2 the values of flow, temperature and pressure of each stream of the plant are reported for the simulation with grape marc concentrations in the feed equal to 10%. There are some differences between the values of the streams in the case of the glycerol and those of the marc, depending on the different characteristics of the two chosen fuels.

4. ENERGY ANALYSIS

An interesting issue arising from process modeling is represented by the analysis of the energy requirements.

The two thermal streams, Q-SEPAR and Q-REACTOR, present two different kinds of energy demand. The former results in a cooling request, since the heat arising from separation must be properly dissipated. The latter is the thermal flux arising from the energy balance in the reactor. Two scenarios are then possible, depending on whether Q-REACTOR represents an energy demand or an energy production: see Figure 3.

In the first scenario Q-REACTOR has a negative value, that means the reactor needs to be sustained by an external source of thermal energy. This gap of energy can be covered by supplying the stream “CH₄” to the burner, whose quantity is evaluated knowing “Q-REACTOR” (LHV of methane is equal to 35.83 MJ/Nm³).

In the second scenario Q-REACTOR” is positive. There will be thus a production of thermal energy, meaning that the process is self-sustainable. According to our calculations, process begins to be self-sustainable at about the 22% of concentration of glycerol in the feed stream and, for the case of marc, at around the 17.5% - see Figure 3.

In Tables 3 and 4 is also reported the electric power which can be produced by feeding hydrogen to a molten carbonate fuel cell (MCFC), with an average electric efficiency η of 0.45 [9]. The production of hydrogen as a function of the biomass concentration in the feed is shown in Figure 4.

Table 3 Waste heat, methane consumption and electric power produced for the case of glycerol.

C_{gly} [% wt.]	Q-SEPAR [kW]	Q_{CH4} [Nm ³ /h]	P_{prod} [kW]
5	60.54	6.45	9.05
10	60.25	4.93	11.73
15	57.81	2.84	12.67
20	55.93	0.69	13.04
25	53.87	0.00	13.12

Table 4. Waste heat, methane consumption and electric power produced for the case of marc.

C_{marc} [% wt.]	Q-SEPAR [kW]	Q_{CH4} [Nm ³ /h]	P_{prod} [kW]
5	59.64	6.20	10.10
10	57.30	3.98	12.03
15	54.71	1.42	12.45
17.5	52.91	0.05	12.45
20	51.07	0.00	12.37

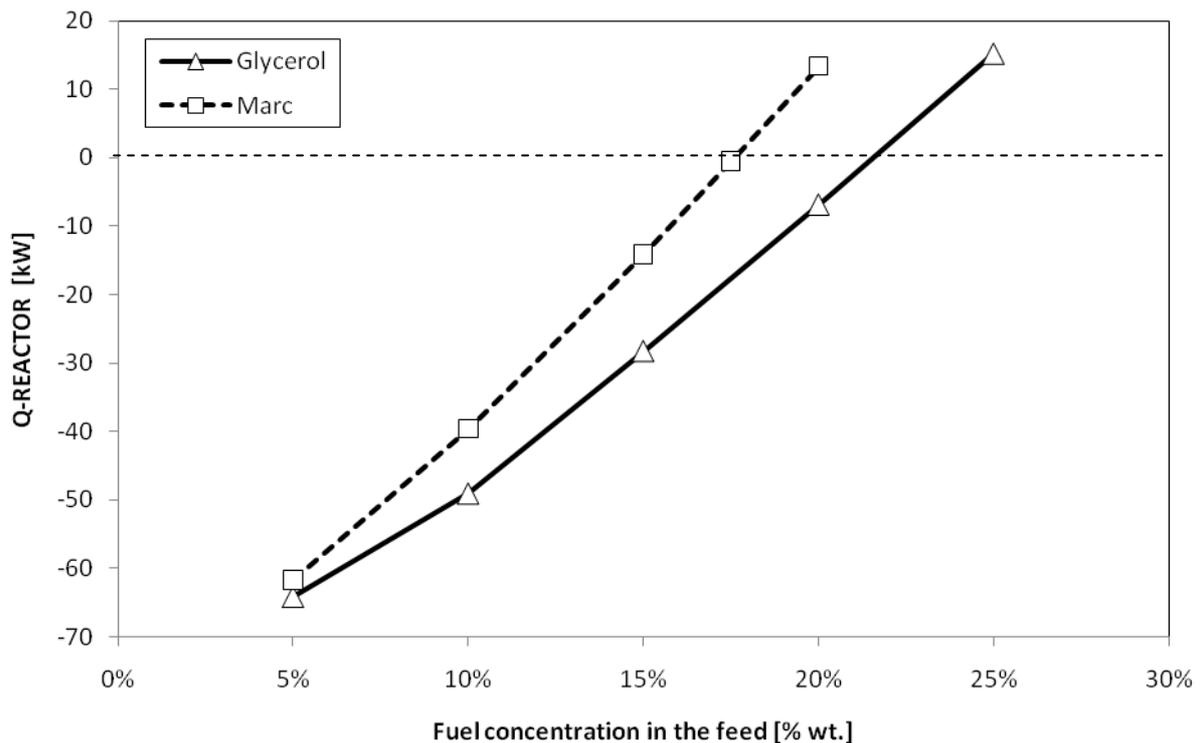


Figure 3. Thermal flux “Q-REACTOR” as a function of biomass concentration in the feed (from simulations where no CH₄ is supplied to the burner).

In Tables 3 and 4 it should be noticed that the decrease of Q-SEPAR is proportional to the increase of the fuel concentration. This can be easily explained. When the quantity of fuel increases, the amount of water decreases; thus, less energy is needed to perform the cooling down. Moreover, the stream SYNGAS2 was imposed to be in vapor phase (see Section 3.1). As the fuel concentration increases, the minimum temperature to obtain a one-phase stream decreases: this is caused by the minor water content. This allows to use a lower temperature for the stream SYNGAS2, thus achieving a larger heat exchange in the block HEATX-1.

In Figure 4 the production of hydrogen is shown. It is possible to observe the presence of a point of maximum for each fuel, where that of glycerol occurs approximately for a 25% wt. feeding stream. Grape marc seems to have a maximum for values around 15-17.5%. The presence of such a maximum point can be interpreted as the combined effect of two contrasting phenomena. Thermodynamic equilibrium, in fact, tends to disfavor hydrogen production as the feeding concentration is increased. On the other hand, if the fuel fraction increases, the absolute production of gas increases too, even though its H₂ percentage is lower. As a result, a maximum point is obtained.

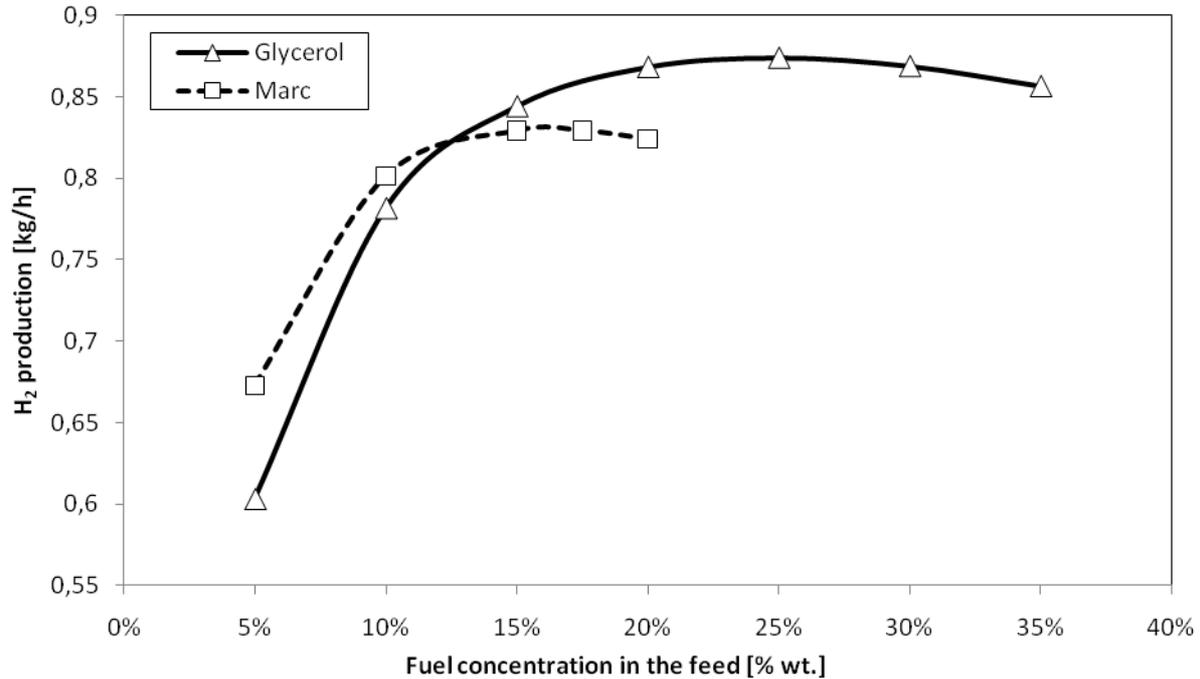


Figure 4. Production of hydrogen as a function of biomass concentration in the feed.

It is also worth of notice the fact the maximum H₂ production occurs more or less in correspondence with the auto-thermal point. Though no theoretical explanation can be found, this fact indicates that working with concentrations around 15-20% is beneficial for both hydrogen production and energy sustainability of the process.

Finally a consideration about the electric power resulting from MCFC. The pumping of the feeding stream needs a power of about 1.5 kW, which holds almost constant as the feeding concentration is varied. The fuel cell can thus produce almost ten times the required pumping power (Tables 3 and 4). On the other hand, the dissipation of the heat deriving from the separation operation results in an energy cost due to the utilization of a cooling cycle. This further energy demand can be evaluated by dividing Q-SEPAR (Tables 3 and 4) by a coefficient of performance (COP ~ 2.5) typical for mechanical refrigeration systems. It is thus noticeable that, though the MCFC produces a remarkable amount of electric power, it would not be sufficient to cover the energy demand of the eventual mechanical refrigeration system. The process would be then unsustainable, unless other solutions are found.

4.1 Evaporative cooling tower

A possible solution to the problem of cooling is represented by the use of an evaporative cooling tower system. Such device is likely to guarantee a minor energy consumption by exploiting the volatilization of water in air. Since the technology is well known, in this paper only a gross sizing is reported (only for the case of the grape marc).

Referring to [10], water can be supplied to the tower at 40°C and recovered at 30°C: the tower works thus with a ΔT of 10°C. Knowing the isobaric heat capacity of water ($c_p \approx 4540$ J/kg K), it is possible to calculate the flow of water necessary to cool down the hot stream in the block SEPAR. The power to dissipate (Q-SEPAR) is reported in Table 5, along with the necessary water mass flow.

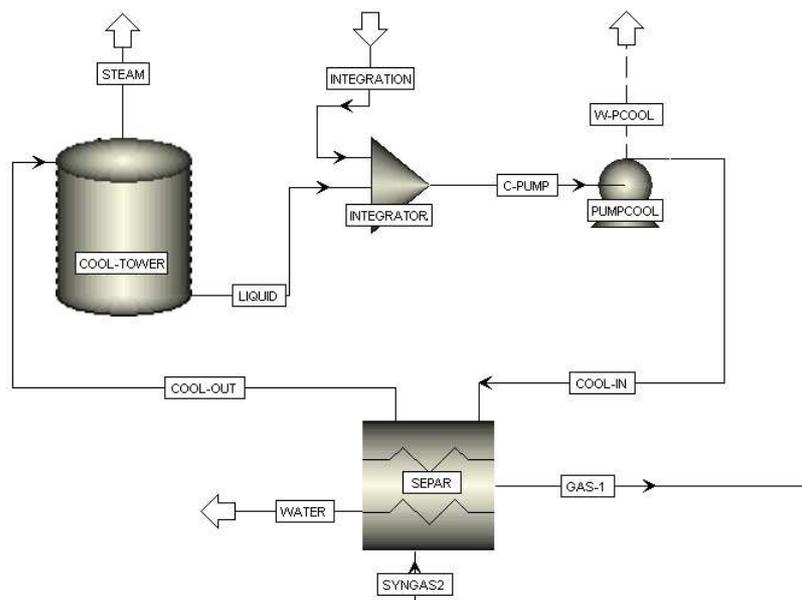


Figure 5. The evaporative cooling tower cycle. The block “SEPAR” is modeled as a heat-exchanger.

The electric consumption (Table 5) of the evaporative cooling tower is given by two machineries: the circulation pump and the fan, which creates the air flow from the bottom to the top of the tower. To evaluate the contribution of the pump, a head loss of 25 m was taken into account and an efficiency η of 0.5 was considered. The power demand of the fan motors is equal to 0.25 kW, which is suitable for cooling towers that present a dissipative power lower than 75 kW [10].

Table 5. Data for the evaporative cooling tower cycle: heat load (Q-SEPAR), total flow of water in the circuit (M_{H_2O}), power request for the pump (P_{PUMP}) and the fan (P_{FAN}), total power request (P_{TOT}), total consumption of water (H_2O_{CONS}).

C_{marc} [%]	Q-SEPAR [kW]	M_{H_2O} [kg/h]	P_{PUMP} [kW]	P_{FAN} [kW]	P_{TOT} [kW]	H_2O_{CONS} [kg/h]
5	59.64	4729.42	0.64	0.25	0.89	88.95
10	57.30	4543.65	0.62	0.25	0.87	85.45
15	54.71	4337.97	0.59	0.25	0.84	81.58
17.5	52.91	4195.12	0.57	0.25	0.82	78.90
20	51.07	4049.73	0.55	0.25	0.80	76.16

As concerns the production of steam, the values are calculated by dividing “Q-SEPAR” by the latent heat of vaporization (2414 kJ/kg, according to [11]). The water to reintegrate in the cycle is the same amount of the evaporative losses. However, a discharge must be foreseen, otherwise evaporation would cause a rise in the salinity of the water in the cooling circuit. Given that, the overall water consumption can be approximately estimated in 200 kg/h.

Comparing the data of the power production in Table 4 with those of power consumption of Table 5, it can be affirmed that the whole process is self-sustainable. For example, for a concentration of marc in the feed stream of about 20% wt., the plant can produce a net power of about 10 kW, accounting also for the power consumption of the first pump (~1.5 kW).

5. CONCLUSIONS

In this paper, a process layout for a SCWG plant was developed. This approach allowed to state which are the conditions to ensure process sustainability, i.e. to guarantee that the energy produced by the plant is at least equal to that required by it. Such analysis is crucial in order to face a possible commercial exploitation of the process.

The study showed that SCWG can be a very effective process to produce hydrogen to feed a fuel cell. This technology would allow an efficient recovery of the energy potential of wet biomass, which could not be treated otherwise without a prior drying process.

Process sustainability can be achieved if biomass concentration in the feed is around 15-20% on a weight basis. Below this threshold, the gasification process is not able to produce enough combustible gas to fulfill the energy needs of the reactor.

A crucial issue that was explored by this work is that of energy recovery. Though the energy needs of the SCWG reaction are inherently small [4], in practice it is not possible to recover the whole amount of process heat, since it is sometimes produced at relatively low temperature. Moreover, this "waste heat" must be dissipated, with a further cost. Here, an evaporative cooling tower was proposed to minimize such expense. Anyway, if a heat-user could be provided (e.g. to warm up pools, greenhouses,...), costs would further decrease.

A possible improvement to this scheme could be represented by the adoption of turbines instead of lamination valves, which is more likely for larger plants. These devices could allow to recover part of the mechanical work to power the pumps, thus increasing the electrical yields. Furthermore, all the units need to be properly sized and designed, in order to perform also a cost analysis and to state the effective convenience and profitability of the SCWG technology.

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