

# Optimal Process Design of Hydrothermal SNG Production from Waste Biomass

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**Abstract:** Hydrothermal gasification of biomass in supercritical water is one of the rare pathways that potentially allows for a complete conversion of wet waste biomass into Synthetic Natural Gas (SNG). This paper summarises an extensive process design study and discusses some key aspects of the process integration and, in particular, the influence of the feedstock on the optimal process design and its performances. It thereby demonstrates that the process design and performance is not only influenced by available technology, catalyst deactivation issues and scale, but also the characteristics of the processed substrate.

**Keywords:** biofuels, hydrothermal gasification, process design, process integration, optimisation

## 1. Introduction

Conventional biomass conversion technologies for the production of fuel and power require relatively dry and clean feedstock and thus suffer from increasing competition for a relatively scarce resource. Hydrothermal gasification of biomass in supercritical water is a promising process alternative to produce synthetic natural gas (SNG) since it relaxes this requirement and grants access to a large range of low quality feedstocks such as wet lignocellulosic biomass and biomass wastes that are difficult to valorise by other means and thus relatively cheap.

Several authors, for example [1–3], have reviewed process fundamentals, chemistry and catalysis for hydrothermal gasification while mainly focussing on the pathway to hydrogen. The production of methane has been experimentally demonstrated in a batch reactor from wood substrate [4, 5], and technology and process development for a continuous process is under way [6, 7]. Most of these studies discuss general process principles, present laboratory and pilot units or focus on detailed experimental investigations. To our knowledge, only Luterbacher et al. [6] has presented a process design model that quantitatively takes energy integration and recovery into account. At the time of their developments, only limited insight into some process steps was yet available. Energy integration has been performed on a scenario basis without optimi-

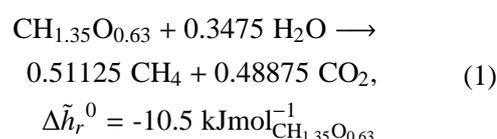
sation, and the synergies between the reaction and separation subsystems through process integration have been disregarded. For this reason, the conceptual process design of hydrothermal gasification for the cogeneration of SNG and power from wet lignocellulosic biomass and biomass wastes has been systematically investigated in [8]. The model of [6] has been improved with both more general and detailed technology models that are reconciled and validated with data from experimental investigations. A general superstructure for integrated product separation, power recovery and heat supply for the process is developed, and multi-objective optimisation is applied to explore the design alternatives and performances for selected candidate substrates.

This paper summarises some key aspects of the process integration and discusses the influence of the feedstock on the optimal process design and its performances.

## 2. Process description

### 2.1. Thermodynamic considerations

The conversion of biomass into methane and carbon dioxide is based on the conceptual overall net reaction, which can be written for a typical composition of lignocellulosic matter:



Technically, the conversion requires a heterogeneous catalyst and is thus impossible to perform directly with the solid biomass feed since the big macromolecules cannot access the active sites. The most envisaged conventional route is thus to first decompose the solid feedstock by gasification and then catalytically synthesise the obtained  $H_2/CO$ -rich producer gas into  $CH_4$  and  $CO_2$  [9]. The conversion of (1) therefore splits up in an endothermic gasification step above  $800^\circ C$  and an exothermic synthesis step at  $350-450^\circ C$  at which  $CH_4$  is thermodynamically favoured. This limits the product yield since a considerable part of the energy content of the feed is required to form intermediate  $H_2/CO$  and is then converted into excess heat in its highly exothermic methanation.

The hydrothermal route omits the endothermic step at high temperature and targets a direct conversion at  $350-450^\circ C$  into  $CH_4$  and  $CO_2$ . Instead of forming an intermediate gas, the biomass is hydrolysed and gasified in a supercritical aqueous environment at around 300 bar, which allows for an efficient contact with the catalyst [4]. The thoroughly fluid processing thereby requires a feed in form of a pumpable slurry with a minimum total solid contents of approximately 20%wt depending on the type of substrate [4, 5]. Although this makes the process suitable for wet biomass since the heat requirement up to the gasification temperature is reduced by high pressure and drying is not required, the design must take care of the high amount of water that accompanies the reacting species throughout the process. As this represents the major share of the heat transfer requirements, the overall performance gets sensitive to the energy integration of the plant.

## 2.2. Technical process layout

Depending on the humidity and type of biomass that is processed, the first step in the block flow diagram of Fig. 1 is to mechanically dry or grind and dilute the feed. The slurry is then compressed to 300 bar and heated close to pseudo-critical conditions, during which hydrolysis and other reactions occur [4]. When passing the pseudo-critical point, inorganics present in the feedstock will precipitate as salts and risk to plug the equipment and deactivate the catalyst if they are not efficiently removed. To do so, the subcritical slurry is injected through a dip-tube into a heated vessel, in which the salts precipitate at supercritical conditions [7]. The hydrolysate then passes through a fixed bed of nickel- or ruthenium-



Figure 1: Block flow diagram.

based catalyst, which converts, at ideal conditions, more than 99.9% of the organic matter into  $CH_4$ ,  $CO_2$ , some residual  $H_2$  and only traces of  $CO$  [5].

In order to inject the produced methane at the required purity of 96%mol into the natural gas grid, it must be separated from water, carbon dioxide and possibly hydrogen. For a typical lignocellulosic feedstock (1) diluted to 20%wt total solids, the crude product contains approximately 84%mol of  $H_2O$  and 8%mol of each  $CH_4$  and  $CO_2$  in a near- or supercritical mixture at  $350-450^\circ C$  and around 300 bar. As indicated in Fig. 1, the process furthermore requires additional heat for the salt separator. The design of the product separation should therefore not only consider the grid quality specifications for SNG, but also the recovery of the exergy potential of the crude and the supply of required heat for the plant. For a similar separation problem in conventional SNG production, it has been shown that the overall process benefits from a tight integration of the reactive and separation systems [10], and similar effects can be expected for a hydrothermal plant.

## 3. Process design

### 3.1. Methodology

Following the developed methodology for the conceptual design of thermochemical production of fuels from biomass, a decomposed modelling approach is adopted to develop and evaluate candidate flowsheets [11]. The material conversion in the process units and their energy requirements are computed in energy-flow models, which are assembled in a process superstructure of all relevant technological options. The material flows defined by this superstructure act as constraints in the energy-integration model that is formulated as a mixed integer linear programming problem in which the heat exchanger network is represented by the heat cascade. Considering waste and intermediate product streams as fuel to supply the required heat, the combined SNG and power production is optimised with respect to operating cost. For the so-determined flowsheet, design heuristics and pilot plant data are used for rating and costing the equipment required to meet the thermodynamic design target.

### 3.2. Combined crude product separation and energy recovery options

While no major technology alternatives for feed pre-treatment, hydrolysis, salt separation and gasification exist, several distinct strategies for the separation and expansion of the crude product are conceivable and might influence the process performance markedly. The crude product from gasification contains more than 80% H<sub>2</sub>O, approximately equal amounts of CH<sub>4</sub> and CO<sub>2</sub>, and some marginal H<sub>2</sub> and CO. Due to the supercritical conditions, its upgrade and expansion to grid conditions potentially allows for recovering mechanical energy, which however competes with the supply of thermal energy required for hydrolysis and salt separation. Another important aspect of the separation system design is the quality of the depleted stream, which may be used to supply the required heat and thus relax the need for a high methane recovery in the separation. The given boundary conditions thereby suggest different strategies for combined product separation and expansion that are outlined in the general superstructure of Fig. 2. Apart from conventional absorptive separation at grid pressure with a dedicated physical solvent followed by a membrane stage to remove residual hydrogen [9], the better solubility of CO<sub>2</sub> compared to CH<sub>4</sub> in water may become technically relevant at the prevailing process pressure. As discussed in [8], a trade-off between selectivity and good absolute solubility might thereby occur with respect to pressure. In any case, the separation is best at low temperature, and additional water is required for absorbing the bulk CO<sub>2</sub> to reach grid quality.

In order to recover mechanical energy from the crude product at high pressure, the separated vapour phase – or the entire supercritical bulk, if no high pressure separation is applied – may be expanded through turbines. It might thereby be advantageous or even necessary to preheat the stream, which increases the thermal efficiency of the recovery and prevents an expansion to far into the two-phase region. Compared to an isenthalpic expansion through valves, this causes less heat to be available from the crude product stream since energy is withdrawn at high temperature. For the liquid phase obtained from the separation at high pressure, the available exergy can be recovered by liquid expanders [12]. As an alternative, the liquid phase could also be reheated and expanded into the vapour domain,

which would allow for extracting more mechanical energy from the available potential, but also requires a considerable amount of heat to be supplied.

If the product is not upgraded to grid quality at high pressure, the liquid vapour and gas separation need to be carried out after the expansion of the crude product and similar technology as in the conventional route applies [9]. For the complete gas separation at grid pressure, a Selexol column seems appropriate. The combination of both high pressure and grid pressure separation is also conceivable. In order to reduce the amount of required additional water and thus pump power, the gas could only be pre-separated at high pressure and a single polymeric membrane stage at grid pressure could be used.

### 3.3. Minimum energy requirements

Fig. 3 shows the minimum energy requirements (MER) of the principal flowsheeting options for wood at the default operating conditions reported in [8]. The composite curves that identify the contributions of the process sections highlight that the layout of the product separation and expansion section determines the pinch point and influences the energy demand markedly. If no power recovery from the crude product is performed (Fig. 3(a)), the process pinch is situated at the salt separator where  $186 \text{ kW MW}_{biomass}^{-1}$  are required at 440°C. Below, the specific and latent heat of the crude product is sufficient for preheating and hydrolysis of the feed, and an excess of about  $150 \text{ kW MW}_{biomass}^{-1}$  can be recovered between 250 and 400°C. Limited power recovery by liquid expansion of the high pressure condensate and/or expansion of the incondensable mixture with previous reheating to the process pinch does not change the MER and only marginally influences the amount of excess heat.

If no separation at high pressure is applied and the crude product including the bulk water vapour is expanded in a turbine, the energy withdrawn as mechanical work is not available anymore at the gasification outlet temperature. As a consequence, the pinch point shifts to the turbine outlet temperature and results in an increased MER at lower temperature (Fig. 3(b)). Reheating the crude might thereby be required to avoid condensation in the final turbine stages and enhances the thermodynamic conversion efficiency, which leads not only to an increased power output but also heat demand.

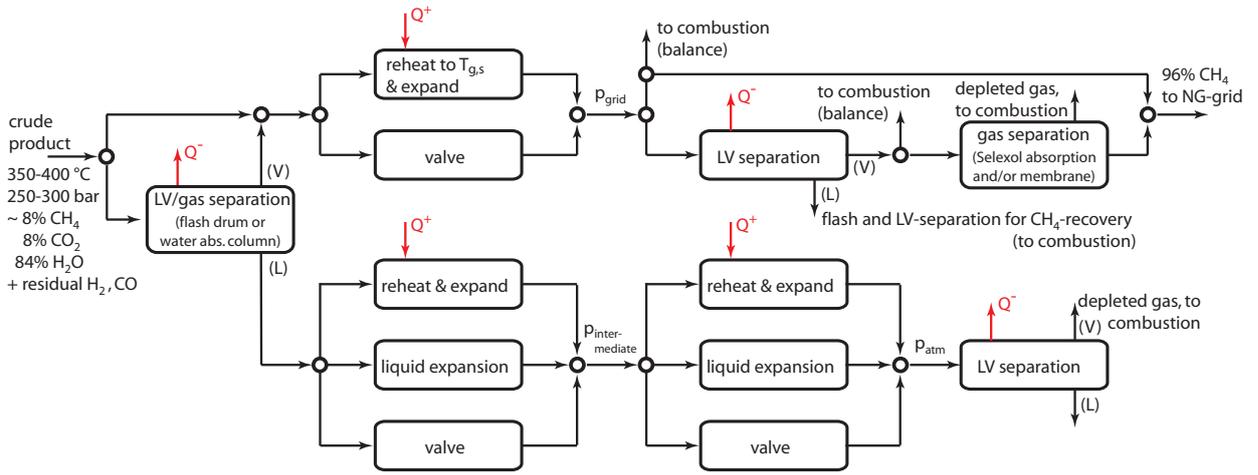
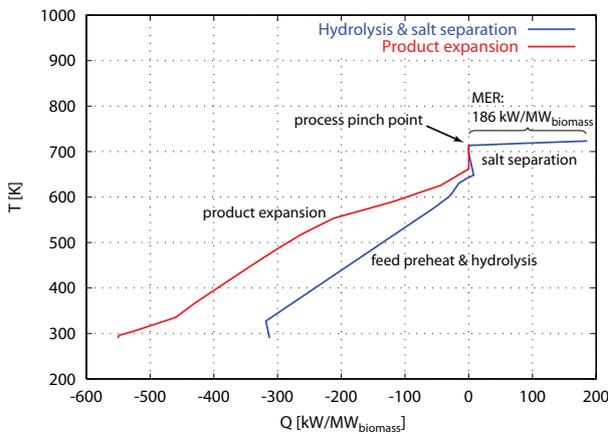
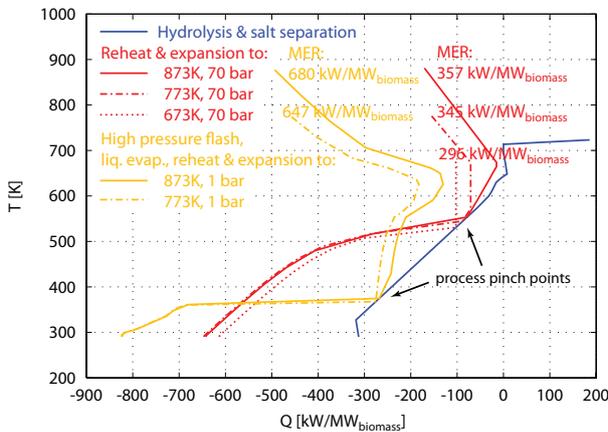


Figure 2: Superstructure including all possibilities for combined crude product separation and expansion.



(a) Product expansion without power recovery.



(b) Power recovery by reheating the entire crude product.

Figure 3: Minimum energy requirements.

If the condensable phase from separation at high pressure is evaporated, reheated and expanded to atmospheric pressure, the characteristics of the process integration change drastically. For such a configuration, the pinch point would shift to the satura-

tion temperature of the mixture at atmospheric pressure and the MER increases to 64–68% of the raw material's heating value. This would require to burn a large part of the produced gas and turn the generation of electrical power to the plant's main purpose.

## 4. Process performance for selected substrates

### 4.1. Candidate substrates

Tab. 1 provides the relevant properties of a selection of candidate feedstocks for hydrothermal gasification. Among the potential substrates, manure and sewage sludge are abundant biomass wastes with a large potential. Coffee grounds and lignin slurry represent typical energetically exploitable by-products. While the former is a residue from the food industry, large amounts of biomass are retrieved as slurries with high lignin content in the pulp and paper industry or in a future production of fuel ethanol from lignocellulosic biomass. In case of the latter, excess heat from the SNG production might thereby also satisfy the requirement for biomass pretreatment and ethanol distillation, and favourable effects might emerge from process integration [13]. Finally, microalgae are considered as a photosynthetically efficient energy crop that are cultivable in photobioreactors on marginal land [14], from which a reduced environmental impact is expected.

Compared to wood, all these substrates offer a higher hydrogen fraction and thus an increased theoretical methane yield from the dry, ash-free substance according to (1). Except coffee grounds and lignin slurry, they yet suffer from a higher ash con-

| Substrate                  | Ref.     | Proximate analysis |                           |  | Ultimate analysis |     |      |     |                | St. coeff. in (1) |                 |
|----------------------------|----------|--------------------|---------------------------|--|-------------------|-----|------|-----|----------------|-------------------|-----------------|
|                            |          | $\Phi$<br>%wt      | ash<br>%wt <sub>dry</sub> | $\Delta h^0$<br>MJ kg <sub>daf</sub> <sup>-1</sup> | C                 | H   | O    | N   | S <sup>a</sup> | CH <sub>4</sub>   | CO <sub>2</sub> |
| Wood                       | [9]      | 50                 | 0.6                       | 18.6   | 51.1              | 5.8 | 42.9 | 0.2 | n/a            | 0.51              | 0.49            |
| Manure (pig)               | [4]      | 97                 | 24.9                      | 21.2   | 48.0              | 8.3 | 36.1 | 7.0 | 0.6            | 0.62              | 0.38            |
| Sewage sludge <sup>b</sup> | [15, 16] | 73                 | 47.8                      | 19.2   | 49.2              | 6.0 | 37.6 | 7.2 | n/a            | 0.54              | 0.46            |
| Coffee grounds             | [16]     | 50                 | 0.3                       | 26.0   | 60.1              | 8.5 | 29.6 | 1.6 | 0.2            | 0.62              | 0.38            |
| Lignin slurry              | [13]     | 75                 | 0.6                       | 23.4   | 55.8              | 8.2 | 36.0 | n/a | n/a            | 0.60              | 0.40            |
| Microalgae                 | [14]     | 87                 | 12.5                      | 25.3   | 57.7              | 7.6 | 25.3 | 8.1 | 1.3            | 0.61              | 0.39            |

<sup>a</sup> n/a: not available in database. All substrates yet contain enough sulphur to assume equilibrium concentration in the supercritical phase after salt separation in order to quantify catalyst deactivation [8].

<sup>b</sup> internal data [15] for a mixture of conventionally digested primary and secondary sludges, ash content and humidity from [16]

Table 1: Properties of the candidate feedstock.

tent which reduces the effective biomass content if diluted to the same dry solids content. Among the substrates, manure suffers from a particular low solids content on an as-received basis and is the only substrate for which water purification by reverse osmosis is considered necessary.

## 4.2. Process optimisation

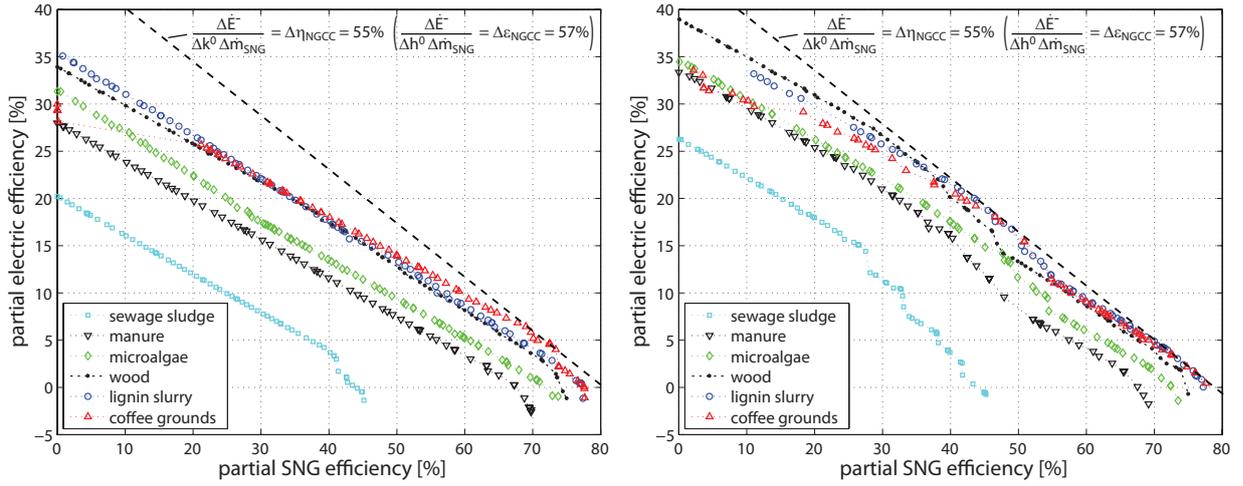
The process design for hydrothermal conversion is particularly flexible with respect to the co-production of fuel and power. In order to explore this particular trade-off, the cogeneration potential is addressed in a first optimisation step that considers the partial SNG and electric efficiencies defined by the ratios of the SNG and electricity yields to the biomass input, respectively, as objectives. In a second step, thermo-economic optimisations of the process design are carried out with and without considering the catalyst cost to investigate the importance of catalyst deactivation in the design. The chemical efficiency, defined as the equivalent SNG yield if electricity is substituted by the amount of gas consumed for its generation in a combined cycle at an exergy efficiency of 55%, is thereby used as an aggregated thermodynamic objective. As economic objective, the specific investment cost per installed capacity is used, including also the total catalyst cost over the entire plant lifetime if catalyst deactivation is considered. Mathematically detailed definitions of these objectives, economic assumptions, and the process design variables to be optimised are reported in [8].

Fig. 4 provides the Pareto fronts of the overall best configurations for all substrates in the different optimisation steps. The maximum partial efficiencies in (a) assess a nearly equal cogeneration potential for coffee grounds and lignin slurry, which are per-

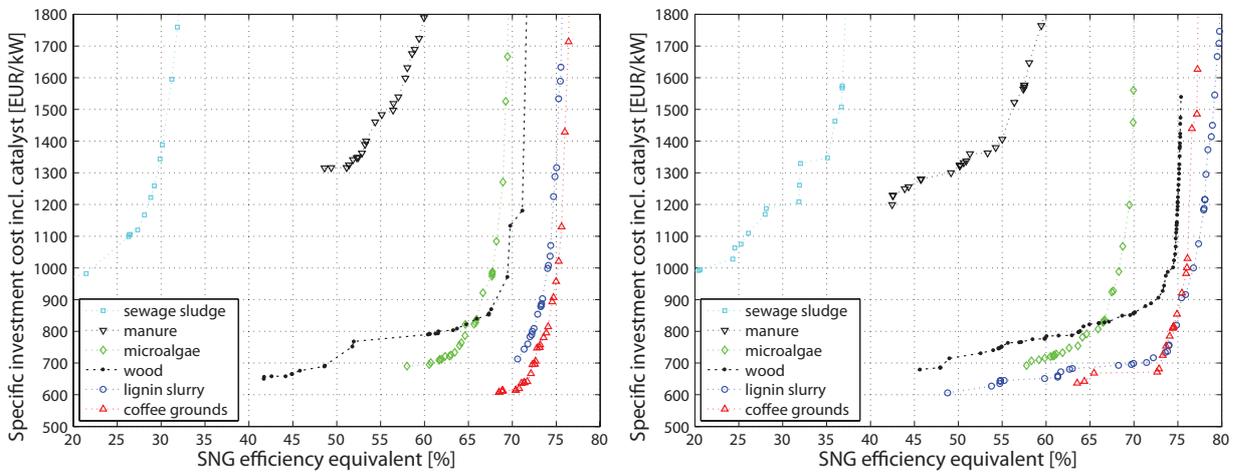
forming slightly better than wood. Microalgae, manure and sewage sludge are consecutively worse. In comparison with Tab. 1, this order mainly follows the ash content of the substrates. With an equal total solids content of 20%, the net dilution of the reactive biomass in water almost doubles in the worst case of sewage sludge and has a fatal impact on process efficiency since the amount of water to be entrained is doubled as well. In addition to the maximum combined efficiency situated close to the maximum SNG yield, power recovery from the high pressure vapour phase allows for a high marginal efficiency in substituting the SNG by electrical power generation. This leads to a second peak with respect to the combined efficiency at net SNG yields below roughly 50%, which is particularly beneficial for low quality substrates like sewage sludge.

The efficiency considerations have a big impact on the thermo-economic performance of the conversion. Compared to coffee grounds and lignin slurry which are dominating the common Pareto domain of (b) and (c), the conversion of wood is slightly less efficient and more expensive due to the higher CO<sub>2</sub> share in the crude product that requires more effort for separation. It is thus competing with microalgae whose conversion is disfavoured by a slightly higher ash content. The waste substrates are clearly worst. While sewage sludge is seriously penalised by its low thermodynamic performance, manure suffers from high investment cost for dewatering and especially wastewater treatment by reverse osmosis.

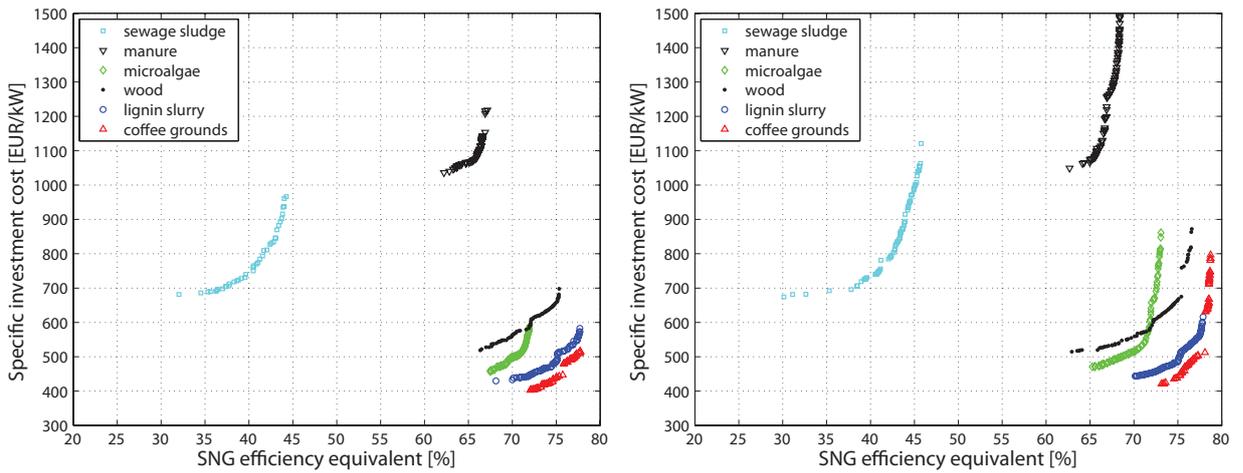
Fig. 5 illustrates the evolution of the process configuration on the thermo-economic Pareto fronts and clearly highlights that the optimal choice depends not only on the availability of energy recovery technology, catalyst deactivation and plant scale, but



(a) Maximum partial efficiencies.

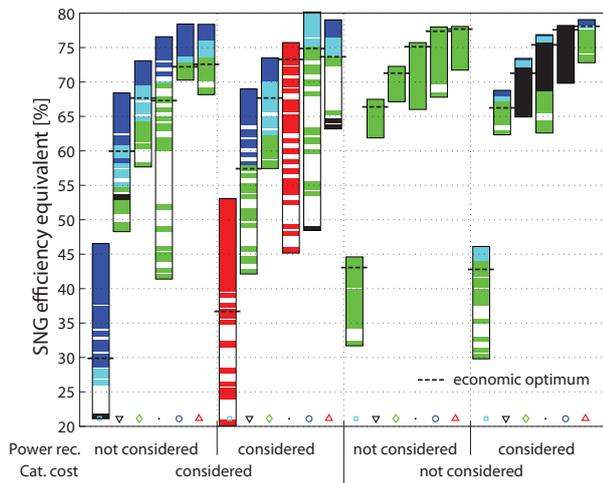


(b) Full consideration of catalyst cost.

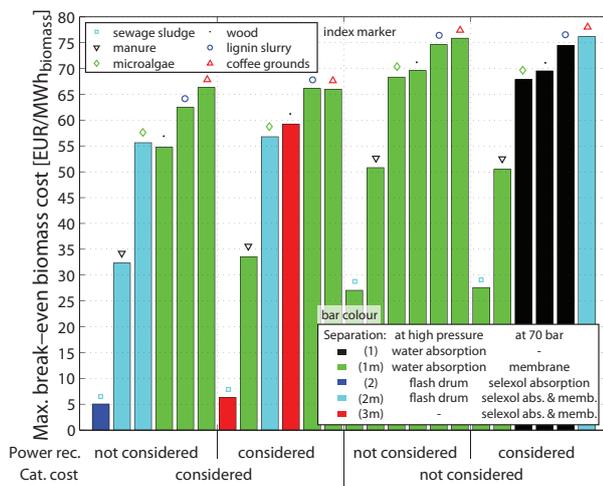


(c) Without catalyst deactivation.

Figure 4: Optimal thermodynamic and thermo-economic trade-off at  $20 \text{ MW}_{th, biomass}$  without (left) and with power recovery from the high pressure vapour phase.



(a) Evolution of the optimal process layout on the Pareto front.



(b) Break-even costs for the most economic solutions.

Figure 5: Optimal process configurations at  $20 \text{ MW}_{th, biomass}$  depending on substrate.

also on substrate properties. Although the use of a single separation technology is more efficient, its combination with a membrane is less costly since the purification requirement is relaxed. The flow-sheets with absorption of  $\text{CO}_2$  in water thereby require less investment than Selexol, but are disfavoured at higher efficiency. An exception is observed if power recovery from high pressure vapour is excluded and catalyst cost can be disregarded, for which water absorption is the unconditionally best technology for all substrates. If catalyst cost is considered and power recovery feasible, superheating and expansion of the bulk crude product emerges as an interesting alternative since its efficiency is less sensible to the design constraints imposed to avoid excessive deactivation. For the economically best configurations, an almost neutral power balance at

high SNG yield seems best if catalyst deactivation does not need to be considered. Otherwise, a yield distribution in which up to 10% of the biomass input is converted into power is more advantageous. The assessed break-even costs for coffee waste, lignin slurry and microalgae are similar or higher to those of wood, which results in considerably higher plant profitability if lower substrate prices apply. Although manure conversion suffers from high investment cost, such plants might yet be profitable since also low compensations for the feedstock can be expected. The conversion of sewage sludge increases the energy efficiency of wastewater treatment, but economical benefits should principally emerge from avoiding another type of waste treatment.

## 5. Conclusions

This paper has summarised a systematic analysis of the process design alternatives for hydrothermal production of SNG from wet biomass and biomass waste. Based on a general superstructure for combined product separation and internal energy recovery from the supercritical conditions, the possibilities for an efficient cogeneration of SNG and power have been explored.

Even with conservative hypothesis on practical design limitations, a sound process integration and energy recovery allows for an energetically and economically viable process design. Thermo-economic optimisations have revealed that the hydrothermal conversion should thereby be regarded as a polygeneration system in which SNG and electricity yields are to a large extent on a par. It is demonstrated that the process design and performance is not only influenced by available technology and catalyst deactivation, but also the characteristics of the processed substrate. Wet but energetically valuable industrial by-products with a high hydrogen and low ash content such as lignin slurries or coffee grounds have been identified as a particularly well suited feedstock that allow for greater efficiencies than wood. Biomass wastes with high ash content such as manure and digested sewage sludge are less advantageous since their effective biomass content is severely reduced if processing is limited to slurries containing no more than 20% total solids. From the perspective of waste treatment with disposal as principal objective, also marginal profit from a complete energy recovery from wastes might yet be valuable.

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## Nomenclature

$\dot{E}$  Electricity, MW

$\dot{m}$  Mass flow, kg s<sup>-1</sup>

### Greek Letters

$\Delta h^0$  Lower heating value, MJ kg<sub>daf</sub><sup>-1</sup>

$\Delta k^0$  Exergy value, MJ kg<sub>daf</sub><sup>-1</sup>

$\epsilon$  Energy efficiency, %

$\eta$  Exergy efficiency, %

$\Phi$  Biomass humidity, %wt

### Subscripts

*daf* dry, ash free

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