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A thermodynamic equilibrium study of Supercritical Water Gasification of Glucose

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Introduction

In order to overcome the lack of fossil fuel, solutions must be found. An environment-friendly process is to produce bio-energies (syngas or synfuels) from biomass. Biomass is considered as a environment-friendly energy resource because, contrarily to fossil fuel, it takes carbon out of the atmosphere while it is growing and returns it when it is burnt [*Loppinet-Serani et al., 2008*]. Moreover, the supply potential is considerable. Schmieder et al. (2000) provide some example of biomass resources for the Netherlands and estimated an energy potential of 6.1 billion m^3 natural gas, corresponding to about 15% of the natural gas consumption of the Netherlands. From this point of view, biomass has an important potential to become a major renewable energy resource. A rising problem of the biomass use is its water content which impose in the case of the classical gasification process a drying step. In the case of Super-Critical Water Gasification (SCWG), water is used not only as a solvent but also as a reactant, avoiding dehydration which is an energetically (and thus financially) expensive step.

The work presented here deals with supercritical water gasification of glucose which is considered as a model compound for cellulose [*Sinag et al., 2003*]. Fig. 1 shows the process considered in this study as well as notations used. In a first part, we expose the thermodynamic models applied to the gasification reactor and the flash separator. In a second part, we show some results concerning the glucose SCWG. More precisely, influence of operative parameters as reactor pressure and temperature and feed concentration on dry gas composition (z_i and y_i) and supplied power (Q) are discussed.
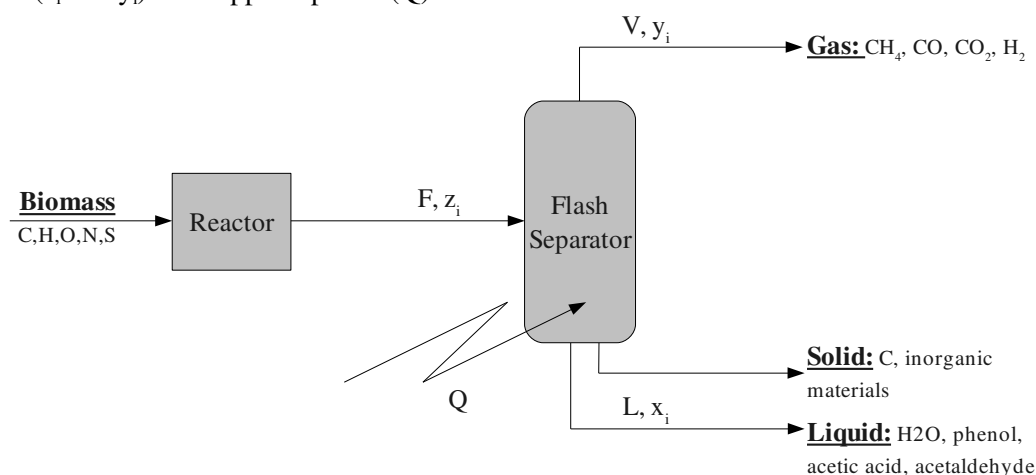

Fig. 1: Principle scheme of the process considered in this study.

Thermodynamic model

Gasification reactor, in this study, is thermodynamically described on the basis of the free Gibbs energy minimization, namely:

$$\Delta_r G_i^0 + RT \ln(K_i) = 0 \tag{1}$$

where $\Delta_r G_i^0$ is the reaction free Gibbs energy of reaction i [J.mol^{-1}], R the perfect gas constant [8.314

J.mol^{-1}.K^{-1}], T the temperature [K] and K_i the reaction equilibrium constant of reaction i [-]. To determine the reaction equilibrium constant (K_i), the law of action mass is written for each reaction and leads to:

$$\ln(K_i)=\sum_{j=1}^{NS} \nu_{ij}\ln a_{Cj} \tag{2}$$

with ν_{ij} represents the stoichiometric coefficient of species j in reaction i and a_{cj} its activity in this reaction, given by:

$$a_{Cj}=\frac{x_j \phi_j P}{P^0} \tag{3}$$

In this last relationship, a fugacity coefficient (ϕ_j) intervene and must be determined. This thermodynamic parameter then needs the use of an Equation of State (EoS). To describe the thermodynamic behavior of each compound, we adopt the Peng-Robinson EoS for its wide application in the field of supercritical fluids [*Tang and Kitagawa, 2005*]. Its function form is written as:

$$P=\frac{RT}{v-b_i}+\frac{a_i(T)}{v^2+2vb_i-b_i{}^2} \tag{4}$$

In this function, v corresponds to the molar volume (m^3.mol^{-1}), b_i is a temperature-independent repulsion parameter and $a_i(T)$ a temperature-dependent attraction parameter. This EoS is extended to mixtures using the classical mixing rules (or van der Waals theory) in first assumption. Mixing parameters are thus given by:

$$a_m(T)=\sum_i \sum_j x_i x_j a_{ij}(T) \quad and \quad b_m=\sum_i x_i b_i \tag{5}$$

where

$$a_{ij}(T)=(1-k_{ij})\sqrt{(a_i(T)a_j(T))} \tag{6}$$

An interaction parameter (k_{ij}) is involved in Eq.(6) and determined, following the Barragan et al. (*2002*) and Tang and Kitagawa (*2005*) recommendations, using critical volume of each species according to:

$$k_{ij}=1-8\frac{\sqrt{(V_{ci}V_{cj})}}{(V_{ci}^{\frac{1}{3}}+V_{cj}^{\frac{1}{3}})^3} \tag{7}$$

Introducing a compressibility factor (Z) and dimensionless parameters A and B, fugacity coefficient in the mixture can be estimated by:

$$\ln(\phi_i)=\frac{b_i}{b_m}(Z-1)-\ln(Z-B)-\frac{A}{2B\sqrt{2}}\left(\frac{2\sum_j(x_j a_{ij})}{a_m}-\frac{b_i}{b_m}\right)\ln\left(\frac{Z+(1+\sqrt{2}).B}{Z+(1-\sqrt{2})B}\right) \tag{8}$$

The aim of this study is to develop a numerical tool supplying compositions of each phase obtained at the downstream of the gasification process. Following the gasification reactor, we then place a flash separator. This multiphase separator is assume to work at ambient temperature and pressure (T=25°C and P=1 atm). MESH equations (Eqs. (9) to (12)) are thus applied.

$$Mass\ Balance: \quad \omega.y_i+(1-\omega).x_i-z_i=0 \tag{9}$$

$$Equilibrium \quad y_i-mK_i(T,P,x,y).x_i=0 \tag{10}$$

$$Sommation: \quad \sum_{i=1}^{NS}(x_i-y_i)=0 \tag{11}$$

where ω (=V/F) represents the vaporized feed fraction and q (=Q/F) the energy supplied to the flash.

Results

We present here results obtained in the case of the Supercritical Water Gasification of glucose. This molecule is considered as a model compound of cellulose [*Lee et al., 2002*], one of the main material of vegetable biomass. In this study, 7 equilibria ((EQ1) to (EQ7)) are considered.

$C_{(s)} + CO_2 \rightleftharpoons 2CO$ (EQ1)

$CO + H_2O \rightleftharpoons CO_2 + H_2$ (EQ2)

$C_{(s)} + 2H_2 \rightleftharpoons CH_4$ (EQ3)

$C_{(s)} + O_2 \rightleftharpoons CO_2$ (EQ4)

$$C_6H_5OH + 5H_2O \rightleftharpoons 6CO + 8H_2 \qquad\qquad (EQ5)$$
$$CH_3COOH \rightleftharpoons 2CO + 2H_2 \qquad\qquad (EQ6)$$
$$CH_3CHO + H_2O \rightleftharpoons 2CO + 3H_2 \qquad\qquad (EQ7)$$
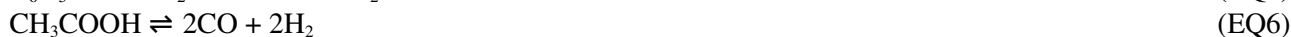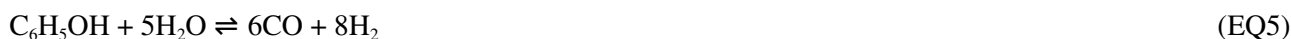
As explicited by aforementioned reactions, we take into account of compounds like phenol, acetic acid and acetaldehyde in addition to classical gas products (CO, CO_2, H_2 and CH_4). These compounds being identified by Kruse and Gawlik (*2003*) as key compounds in the biomass supercritical water gasification, we consider as useful to integrate them in the reaction scheme.

$$C_6H_{12}O_6 \rightarrow 6H_2 + 6CO \qquad\qquad (EQ8)$$
$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad\qquad (EQ9)$$

According to the classical reaction pathway described by reaction (EQ8) and (EQ9), the gas produced can contain, theoretically, up to 66,7 mol% of Hydrogen (H_2) [*Fang et al., 2008*]. This percentage, because we work at thermodynamic equilibrium, is reached for all parameters studied here, as attested by Figs. 1 to 3. From these Figures, one can see that CH_4 percentage is for all cases close to zero, indicating that methanation reaction (EQ3) is very slow compared to other ones and thus is not the prevailing reaction. Calculations predict that a variation of temperature has nearly no consequence on the composition of the dry gas. This result can be extrapolated saying that only the amount of organic material is necessary to predict composition of the gas. In other words, in reality, only the time to obtain thermodynamic equilibrium values is more or less short. The comparison with experimental results provided by Lee *et al.* (2002) seems to confirm this explanation.
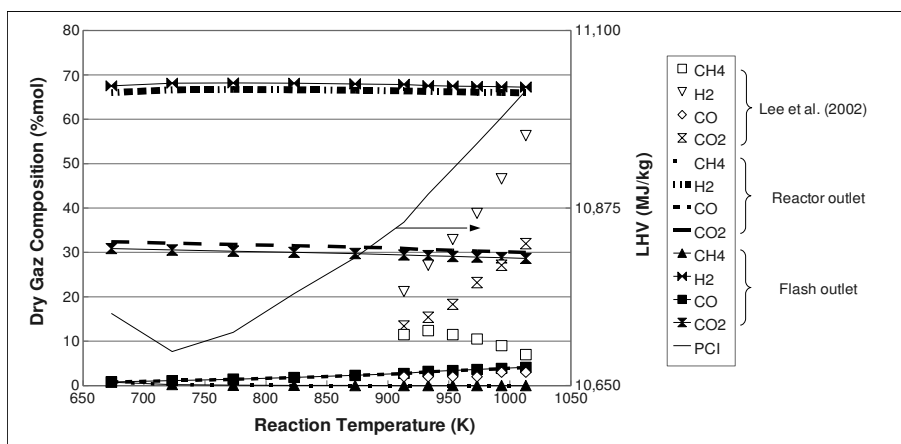

Fig. 1: Effect of temperature on the dry gas composition.
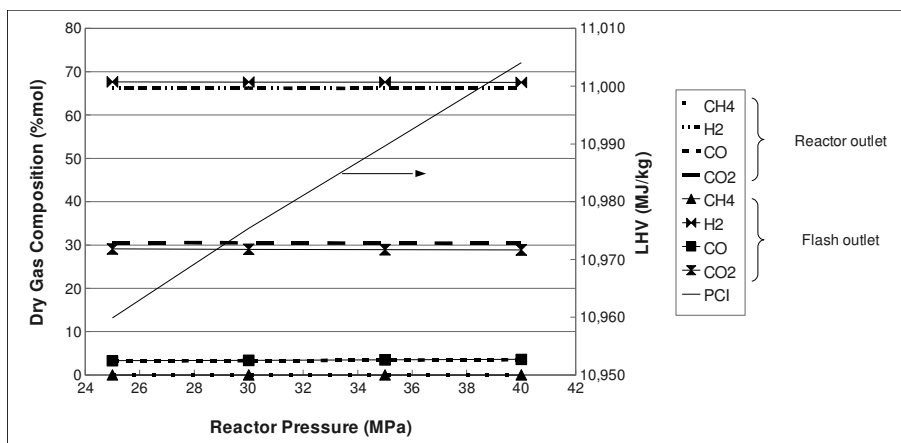*P=28MPa, Feed Concentration: 0,6M.*

Fig. 2: Effect of reactor pressure on the dry gas composition.
T=973.15K, Feed Concentration: 0,6M.

Concerning the feed concentration influence (Fig. 3), H_2 molar fraction value decreases with feed concentration. This means that, because amount of CH_4 stays negligible, H_2 is consumed by CO_2 in order to form CO and water via the WGS reaction (EQ2).
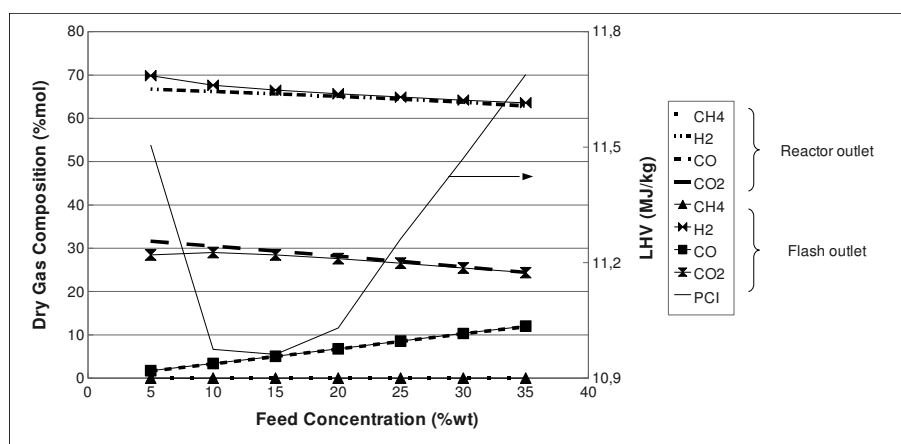
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Fig. 3: Effect of feed concentration on the dry gas composition.
T=973.15K, P=28MPa.

On previous figures, we also plot the Low Heat Value (LHV) of the syngas produced. Figure 1 shows that when reaction temperature is lower than 773.15 K, increasing it will reduced syngas LHV. Beyond this temperature, LHV is increasing. A similar trend is shown when LHV is plot as a function of the feed concentration (Fig. 3). The minimum value is reached when feed concentration is around of 15%wt, but the stays relatively high compared to other parameters (nearly 11 MJ/kg). Contrarily to these parameters, increasing reactor pressure (Fig. 2) always increases syngas LHV. However, as observed for the syngas dry composition, feed concentration stays the mainly influencing parameter. So in order to obtain a syngas usable by a burner, a high reaction temperature (higher than 773.15 K) would be applied, jointly with reactor pressure and feed concentration as high as possible.

Last, concerning phases available at process outflow, one can already write that solid mass flow rate is negligible (about 10^{-9} kg.h^{-1}, and only composed of solid carbon). The liquid phase contains almost exclusively water (more than 99%), the other main compound being CO_2 (less than 1%), indicating that. all organic material is gasified. So, mass flow rates of liquid and gas phases are respectively equal to water and organic material flow rates at the inlet of the process.

Conclusion

This work deals with the supercritical water gasification of glucose. The process considered here consists of a gasification reactor and a flash separator. This last unit provides us some informations about the reusable energy. Thermodynamic equilibrium analysis of glucose gasification in supercritical water gives us some informations concerning the operative conditions. Dry syngas composition is mainly influenced by the feed concentration, reaction temperature having a significant influence but less marked. Reactor pressure seems to have no or a very slight role on the composition. In the objective to produce a syngas that has the higher LHV value, results show that the inflow loading in organic materials, the reactor pressure and reaction temperature must be as high as possible.

The present model will be improved introducing the resolution of the energy balance what will allow to quantify power to supply at the gasification reactor along with the outflow temperature if inflow is introduced with a temperature different form the reactor's one. Another future work will be the analysis of an oxidant role on the gas composition.

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